THE HYDROGEOCHEMISTRY OF
THE WASTE AND LOW GRADE
ORE STOCKPILES OF RANGER
URANIUM MINE
– A SYSTEM APPROACH

by

Gregory J. Shirtliff
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Declaration

I, Gregory James Shirtliff, hereby declare that all research in this thesis is my own, unless stated otherwise.

G. Shirtliff.
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Maybe I will give up coffee now too...(thanks Nescafe).
The waste and low grade ore stockpile system at Ranger Uranium Mine (RUM) can be summarised as being made up of 3 different repeating structural fabrics, each having very different hydrological properties. The layers have been termed, Platform/ramp Horizons, Lift Mound Layers and Extension Lens Layers, the terms purposefully chosen to have clear separation from the colloquial language often applied to them and their methods of construction by engineers and sometimes confused by non-engineering mining personal and so that the terminology specifically refers to 'structural/geological' units within a stockpile. Overprinting this fabric and its hydrological characteristics is the location of clay rich weathered material and potential decreases in pore spacing with depth due to consolidation and compaction processes. Whilst water will tend to find preferred flow paths through Lift Mound and Extension Lens Layers, Platform/Ramp Horizons act to slow, halt or divert the flow of water. Both Platform Horizons and layers of weathered material (and potentially the deepest sections of the stockpiles) are zones of higher field capacity and potential zones where saturated conditions may prevail for long periods (perched water tables). These fundamental structural properties can be extended to any free-standing rock stockpile built with similar techniques to those at RUM.

Internal stockpile mapping of the entire RUM waste and low grade ore (LGO) stockpile system shows that the Central Waste rock Stockpile (CWP) should be treated hydrologically in a manner similar to that of a stratified soil as it has multiple Platform Horizons at depth, with a significant concentration of these down the western and northern slopes into the lower western centre and extending towards the Southern Central Waste rock Stockpile (SCWP). In contrast, the southern waste rock pile (SWP) is essentially one single Extension Lens Layer where water infiltrates more readily, residence times through the stockpile are shorter and water flow through the stockpile is governed by parameters such as the connectivity of large pore spaces and the tortuosity of
developed channels. The angle-of-repose slopes (or batter slopes) are also proposed here to be important places of water-rock interaction in the RUM stockpiles, their proximity to the atmosphere and thus a ready supply of oxygen for oxidation reactions enhancing this.

Bulk stockpile composition studies show that primary quartz-chlorite ± mica schist is presently the most abundant rock type in the stockpile system, but this has not always been the case, for prior to the year 2000 weathered material was in greater quantity. This change in dominance from weathered material to primary chloritised schist around the year 2000 may be largely responsible for increases in the concentrations of ions in RUM mine waters since around that same time because weathered material is depleted in most ions and fresh sulfides compared to the primary schist. Since two orebodies have been mined at RUM, this change around the year 2000 is probably the second time that there has been a major change in the geological composition of the stockpiles from a weathered material to a primary rock. Geological mapping shows that the most prominent geological difference between stockpiles, apart form localisations of weathered material, is that the SWP is rich in carbonate, massive chlorite rock, dolerite and footwall sequences (FWS) rocks compared to other parts of the stockpile system, consistent with the geology being mined from the pit during its time of construction.

Scanning electron microscope (SEM) and electron micro-probe analysis (EMPA) studies reveal that the quartz-chlorite ± mica schist consists of quartz and chloritised mica set in a cryptocrystalline chloritic matrix that includes illite/sericite in regions. The resulting major element geochemistry is therefore dominated by the interplay between the proportion of Si (quartz content) and the proportion of Al, Mg and Fe (chlorite content). Two chemistries of chlorites are evident; a Mg-Fe chlorite mostly associated with altered biotite, altered amphibole and feldspar, massive chlorite and some parts of the ubiquitous matrix and a Mg-Al chlorite mostly associated with the ubiquitous matrix and chlorite veins. Zircon, Fe-oxides, apatite and a Ti-oxide phase are prominent accessory minerals in the chloritised schists and are responsible for many of the minor elements in the rocks. Uranium minerals in the waste seem to be the result of dissolution-re-precipitation reactions and are intimately associated with P-species, although the uraninite is the
primary U-bearing phase. Although chalcopyrite is noticeably concentrated in some parts of the deposits (such as with carbonate veining or chert), pyrite is the most abundant sulfide mineral and it shows some positive relationship to increasing ore grade.

Bulk stockpile composition studies, mineralogical and geochemical analysis of individual rock types, the analysis of internal stockpile water, as well as an investigation into the historical mine water database all lead to a conclusion that the oxidation of pyrite and the subsequent generation of acidity (whether at the mineral-water interface or on a larger scale), the dissolution dynamics of chlorite and its ability to buffer such acidity, and the dissolution dynamics of secondary salts and hydroxides are the fundamental processes involved in determining the dominant chemistry of the RUM stockpile drainage.

A stagnant air mass trapped by an atmospheric inversion over RUM during the transition period accumulates particulates and gases from regional burning practices which are ultimately washed out by the start of wet season rains. This results in the early convective rain storm events being acidic (pH 3.6-4.2) and comparatively rich in SO$_4^{2-}$, NO$_3^-$, Na$^+$ and Cl$^-$ compared to the more regular, higher volume rains of the monsoon. In some areas of the stockpiles dust suppression is a far more significant contributor of Mg$^{2+}$, SO$_4^{2-}$ and Ca$^{2+}$ to the stockpiles than rainfall, and just as significant as rainfall for supplying K$^+$ and Na$^+$. It is also a recycle chain in the stockpile system, since the accumulation of precipitates, in particular hexahydrite [MgSO$_4$.6H$_2$O] and U-hydroxides and oxyhydroxides such as Lanthinite (U$_6$O$_7$(OH)$_5$O), from the dust suppression water over the dry season are a contributor to the start of wet season ‘first flush’ of related ions (Mg$^{2+}$, SO$_4^{2-}$ and U$^{6+}$), which ultimately flows back into Retention Pond No. 2 from where the dust suppression water is sourced.

Rainwater that has passed though or over the RUM stockpiles is significantly enriched in Mg$^{2+}$, SO$_4^{2-}$, Ca$^{2+}$, and HCO$_3^-$, compared to rainfall, although the enrichment of Mg$^{2+}$ and SO$_4^{2-}$ is up to two orders of magnitude greater than the others (some 1000 times that of rainfall). Those waters with direct influence from stockpiles are close to and above 90% MgSO$_4$ (MgSO$_4$ to all major ions) with a Mg/ SO$_4$ ratio of 1 (eq/L), away from the
stockpile influence this ratio increases. U$^{6+}$ and Mn$^{2+}$ are the consistently dominant trace metals throughout stockpile derived drainage, U concentrations being as much as two orders of magnitude greater than Mn concentrations (97mg/L U). Cu$^{2+}$, Co$^{2+}$ and Ni become significant trace elements in more acidic water (<pH5.3). Limited speciation modelling suggests that most major ions as well as U, exist in solution either as individual ions or with SO$_4$ as a salt, but as the waters become less influenced by the interaction with RUM's mineral waste, carbonate anions take over as the most common anion partner for cations.

This work demonstrates that the particular hydrological consequence of stockpiles constructed in the manner of those at RUM needs to be considered for work on long term stockpile leachate predictions and site-wide hydrological studies. Particularly, the effect of weathering sulfides on the chemistry of waters emanating from the stockpiles should be taken into account by the Environmental Research Institute of the Supervising Scientist (ERISS).
GLOSSARY

RUM  Ranger Uranium Mine
ERA  Energy Resources of Australia Pty. Ltd.
CWP  Central Waste Rock Pile
SCWP  South Central Waste Rock Pile
NCWP  North Central Waste Rock Pile
SWP  Southern Waste Rock Pile
NWP  Northern Waste Rock Pile
WWP  Western Waste Rock Pile
SOWS  Start of Wet Season
EOWS  End of Wet Season
LGO  Low Grade Ore
ERISS  Environmental Research Institute of the Supervising Scientist
CSIRO  Commonwealth Science and Industry Research Organisation
MEND  Mine Environment Neutral Drainage
ARD  Acid Rock Drainage
AMD  Acid Mine Drainage
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CHAPTER 1

INTRODUCTION

1.1 SETTING

Ranger Uranium Mine (RUM) operates within the large Unconformity-related uranium field (Athabascan type deposits) in the Alligator Rivers region, Northern Territory, Australia (Guilbert and Park, 1996). This thesis reports an investigation into the waste rock piles of RUM; their structure, petrology, mineralogy, geochemistry and critically, their influence on water chemistry.

Discovered in 1969 by airborne radiometric surveys, two orebodies, R1 No.1 and R1 No.3, have been utilised via open cut methods within the Ranger Project Area (Kendall, 1990). Currently production is fuelled by ore from No.3 with the No.1 pit (P#1), where production began in 1981, being utilised for tailings. Waste rock and low-grade material (grade 1 to 3) at RUM are stored predominantly around P#1, west of Pit No. 3 (P#3) and north of the tailings dam (see Figure 1.1) in controlled stockpiles according to grade (Table 1.1). The stockpiles of waste grade rock will eventually be utilised in the construction of final landforms at RUM after mine decommission. However, recent sharp increases in the market price for uranium oxide ($\text{U}_3\text{O}_8$) since the start of this research mean that the waste and low grade ore stockpiles may remain where they are for some time to come with their footprint and volume continually growing due to mine expansion. Energy Resource of Australia Pty Ltd (ERA) announced a significant expansion of Pit#3 to the market, and feasibility studies continue on the prospect of future expansions.
Table 1.1. Ore grade classification according to percent of $\text{U}_3\text{O}_8$ during the course of this study.

<table>
<thead>
<tr>
<th>Grade nomenclature</th>
<th>% $\text{U}_3\text{O}_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Waste rock</td>
<td>&lt; 0.02</td>
</tr>
<tr>
<td>2. Very low grade</td>
<td>0.02 - 0.08</td>
</tr>
<tr>
<td>3. Low grade</td>
<td>0.08 - 0.12</td>
</tr>
<tr>
<td>4. Medium grade</td>
<td>0.12 - 0.25</td>
</tr>
<tr>
<td>5. Medium-High grade</td>
<td>0.25 - 0.35</td>
</tr>
<tr>
<td>6. High grade</td>
<td>0.35 - 0.5</td>
</tr>
<tr>
<td>7. Very High grade</td>
<td>&gt; 0.5</td>
</tr>
</tbody>
</table>

The Ranger lease is surrounded by Kakadu National Park, a World Heritage listed tropical savannah and wetlands area. Mount Brockman, a small piece of an extensive sandstone escarpment running just to the east of the Ranger lease and wrapping around it to the south, overlooks RUM from the south and is probably the most significant aboriginal cultural site in the region. From the base of this escarpment runs a relatively large ephemeral stream, Magela Creek, which sweeps past the eastern side of RUM, reaching it closest towards the north east corner of P#3, and continuing on to the north into Kakadu National Park. Three small tributaries of Magela, now dammed and bunded or completely removed, once drained the area now incorporating the mine. Two of these creeks, Djukmara and Coonjimba, once drained the small local high now occupied by the RUM waste and low grade ore (LGO) stockpiles.

Just downstream of RUM, on Magela Creek near the eastern end of the Jabiru East airport runway, lies a government water monitoring station commonly referred to as 009. The purpose of the monitoring station is to monitor and protect the Magela Creek environs from RUM influence by using a series of normal, action and limit concentrations of various ions associated with RUM mine water. The action level placed on uranium (U) is only 0.9µg/L. The mine is required to stop operating immediately if 009 reaches the limit of 6µg/L U, approximately one quarter of the Australian and New Zealand drinking water standard for U. This is important to consider when viewing U concentrations in RUM’s central retention pond of well over 3000µg/L in the dry season (Ranger Uranium Mine water monitoring database).
Figure 1.1: Location of Ranger Uranium Mine in the 'top end' of the Northern Territory Australia. Note that the bottom image is oblique, looking towards the north to show the flow of the creeks and streams to the East Alligator River and wetlands system and the Arafura Sea in the NE corner of the image. Note, all images from Google Earth (c).
Thus, a full understanding of the hydro-geochemical behaviour of the RUM waste and LGO stockpiles is important because along with tailings, they are probably the greatest environmental and financial risk to the area and company respectively. That risk exists now as fresh unweathered rock is brought up from the mine to weather along side the rock that has been weathering in the stockpiles since 1981, and this risk will exist in the long term future when the waste eventually becomes the permanent final landform of the rehabilitated mine site.

**1.2 PREVIOUS INVESTIGATIONS INTO THE RUM WASTE AND LOW GRADE ORE STOCKPILES**

**1.2.1 Company Reports**

There have been a number of studies, mostly in the form of consultant’s reports or in-house company reports, investigating various aspects of the RUM waste and LGO stockpiles. However, most of these studies have been focused on specific details or have been in the form of limited investigations into certain events, and some of them have been instigated after this research had already begun relaying findings to the company. The studies pertinent to this research include work by Fitzpatrick (1986), Milnes et al. (1986), Milnes (1988), Fitzpatrick and Milnes (1989) Riley et al. (1993) and Klessa et al. (2002) on the composition of the waste rock stockpiles and their weathering characteristics. However, these studies are not extensive; none can be applied to all of the stockpiles as a whole, with most in fact simply focusing on the upper exposed layers only. These studies have been used where appropriate in this research.

The most successful attempt to date to monitor a full wet season of run-off and leachate from a stockpile was undertaken by Puhalovich et al. (2002), who described the chemistry of the mid-late 2001/2002 wet season waters emanating from a grade 2 dump and attempted to estimate infiltration and run-off (although it was admitted in the report that not all of the wet season was monitored). The Puhalovich et al. (2002) study found
concentrations of solutes in stockpile derived waters far exceeding those expected and some of the lowest pH values so far recorded in RUM mine waters. No petrological investigation was undertaken, nor was the general geology of the stockpile investigated, rather it was suggested that the differences in chemistry from that of older measurements may have been due to a difference in geology from Pit#1 to Pit#3, the latter being more endowed in sulfides. However on investigating this claim, it was unsubstantiated, no study, internal or external, had examined this or contained evidence to suggest this.

LeGras and Klessa (1997b, 2001) attempted to model sulphate (SO$_4$) generation from a waste rock (grade 1) stockpile over time using RUM water monitoring chemistry data for a single retention pond. Based on their observations, LeGras and Klessa (2001) argued that SO$_4$ concentrations in a receiving retention pond could be modelled with a relatively simple model, where concentrations peaked some six years after decommission before exponentially decreasing (explained in more detail later). However, the work was completed external to the mine, and it was clear that detailed knowledge of the water body in question and influences on that water body were not known at the time, including potential inputs from other mine water sources due to ‘on the spot’ mine water management practices (pers. com. Klessa, 2005). No further work has been carried out on the LeGras and Klessa (2001) model since.

Much earlier, Nisbett (1990) monitored water quality from the central part of the waste and low grade ore stockpiles (refer to Figure 1.1) for a limited wet season. There are also some discussions on water quality that apparently weren’t completed, such as that of Levy et al. (2001-2005) who used previous findings from separate studies as well as data from mine water monitoring stations to begin to develop an idea of water quality evolution from the stockpiles. Although they could not create a model due to a lack of appropriate data, they did make a different conclusion to LeGras and Klessa (2001) using the same data. Of particular relevance to this research was their conclusion that “improvements to the modelling of run-off and seepage from the WRDs [waste rock dumps] can be achieved only through improvements in the knowledge of the composition...of their constituent rock”. Although no particular internal study has so far
been focused on it, regular and ongoing monitoring of the chemistry of the mine’s central retention pond shows a marked increase in salinity and in particular a marked increase in the concentration of $\text{U}^{6+}$ (see later).

The only genuine attempt to study the hydrology of the stockpiles came from Kuo (1996) however, the data are ambiguous with experimental set-up probably setting a bias to the data (pers. com. Kuo, 2002). A general stockpile hydrology model has been established by a consulting group at EWL Sciences Pty. Ltd. (consultants to ERA), although this is unpublished and simplistic in its approach, with no consideration for variations in composition or structure. The model is based on a consulting engineer’s approach (Coffey International and EWL Sciences), whereby the stockpiles fill with water during the wet season and empty in the dry season, so that stockpile wall stability becomes an issue in the wet season via saturation and then collapse. However, this model was tested via the monitoring of 3 bores drilled into the central stockpile (CWP) during the 2005/2006 wet season and it was proved to be incorrect. The central water bore did not show any significant increase in water levels during the wet season, although it did fluctuate slightly according to individual rainfall events (pers. com. Logan, 2006). In other words, current engineering theory and practices applied to the stockpiles at RUM in regards to stockpile hydrology are incorrect, or at the very least, do not apply at RUM.

This lack of understanding of stockpile hydrology puts mine site water balance models, of crucial importance to the ongoing operation of RUM, at risk of miscalculation. The current model for the stockpiles (as of 2007) diverts water infiltrating the stockpiles according to surface hydrology models beneath the stockpiles (Pillai, 2006). Personal observations in 2006 of the location of an exit point from the stockpiles of a large amount of water that was entering the stockpiles via a pumping exercise meant to supply water to an evaporation pond on top of the stockpiles, clearly demonstrated a diversion of water from the expected flow path through the stockpiles and into a different catchment than planned.
There has also been some experimental work on the composition of the leachate and the potential for acid rock drainage (ARD) of both the waste rock and low grade ore (Jones and Hughes, 1999), although this work was based on a very limited number of non-random bulk samples (different rock types ‘lumped’ together and then pulverised for the experimental sample) and, thus, not representative of the conditions in the stockpiles. The potential for acid generation in only the ore stockpiles was recognised much earlier at RUM by Milnes and Fazey (1988).

1.2.2 Published Material

A large body of work exists on waste rock stockpiles, far more than can be presented here. Most of this work has been due to the rise in awareness of the problem of acid rock drainage (ARD), also referred to as acid mine drainage (AMD). Such international initiatives as the Mine Environment Neutral Drainage Program (MEND) (concentrated in Canada and Australia) instigated much research and succeeded in amalgamating large amounts of unpublished material (see for instance the electronic compilation ‘MEND Reports’, 2001, containing 157 reports, workshop notes and case studies [http://www.nrcan.gc.ca/mms-smm/tect-tech/sat-set/pub-pub-eng.htm#Prediction]) . The majority of this work, however, is focused directly at understanding and predicting ARD.

Almost all of the published material relating to the waste and low grade ore stockpiles of RUM has been related to ongoing work by the Environmental Research Institute of the Supervising Scientist (ERISS) involving the development of a long term (greater than 1000 years) computer based erosion model for the final landform at RUM based on SIBERIA, which is a computer based erosion model developed by Willgoose at MIT, Boston, in 1989. Work using and further developing SIBERIA at RUM started in the late 1990s (see Evans et al., 1988, Willgoose and Riley, 1988, Boggs et al., 2001 and Moliere et al., 2002). The main problem for this work is the changing state of the final landform design, which is now changing annually as the changing price of U₃O₈ continues to change the cut-off between low grade ore and ore (see table 1.1).
Unaffected by the changing design and related to this research is more focused work on the long term erosional stability of the final landform. Wells et al. (2001, 2005, 2006) focus on the physical weathering characteristics of rocks at the surface. These studies use experiments to attempt to simulate long term time periods, such as a full wet season, with very short experiments using cyclical wetting and drying techniques or simple leach studies. Temperatures seem to correlate well with actual temperatures measured in this research, but these studies still suffer from the fact that weathering rates under experimental conditions rarely match those in the ‘real world’, and that much of the work has focused on rock fragments biased towards a very fine grain size, a single rock type based on very few samples without any variation in mineralogy, like a lack of sulfides.

1.3 HYPOTHESIS AND GOALS

It is obvious from the above that the current understanding of the RUM stockpiles, largely based on current engineering practices and applied theory, is incorrect. Field measurements have proven that the hydrological model used for the stockpiles does not apply, and mine water chemistry from the stockpiles has mostly been difficult to predict, even from first year exposure to the wet season rains.

It is believed here that the hydrological and hydro-geochemical models used and still being used at RUM are far too simplistic, and too uni-dimensional in their approach. Studies completed so far at RUM, both internal and external, have been too focused on a single process or too far removed from what is actually happening on site in the operational mine environment. The result of such studies has not only achieved limited success but also have lead to a confusing array of isolated information that is difficult to interrelate and that cannot be applied to all the stockpiles as a whole. Whilst previous studies have identified main rock types in the waste and LGO stockpiles at RUM, and then focused in on them for experimentation (see above), the geology of the stockpiles as a whole and the potential variation between the different individual stockpiles and regions within each stockpile, is still unknown.
The hypothesis of this thesis is that the hydro-geochemistry of waste rock stockpiles can only be understood and predicted by treating the stockpiles as a complete ‘system’, an intricate interplay of processes, not unlike the natural weathering of any other geological phenomena on earth. They are a landform consisting of a package of rock, recently exposed to the atmosphere under a certain climatic regime which will directly impact the way in which they weather. They are the result of certain formational processes (construction methods), which just like any geological sequence, will affect the way they interact with the atmosphere and the way water moves through them. Stockpiles in metal mines have a geology that will not be homogenous throughout and as such they will have different mineralogical and hence geochemical ‘regions’ within them. This means that waters emanating from them will differ depending upon which region of the stockpile system they have interacted with. Even the nature of the original geological processes that formed the rocks and their particular mineral composition has an influence on the way in which the atmosphere and water interacts with the stockpiles in present day.

So the goal of this research is to understand the stockpile ‘system’ at RUM and in doing so understand what is governing the chemistry of the waters that have interacted with them so that future modelling of mine water hydro-geochemistry can be more realistic and more accurate, both during mine operations and for the eventual final landforms. To understand the stockpile system one must understand the mineralogy and geochemistry of the rocks that make up the stockpiles, the external environment within which the stockpiles exist, the chemistry and supply of input water to the stockpiles, how water will pass though them, how oxygen will infiltrate them, and the chemistry of waters already emanating from the stockpiles. Wider than this, this research also aims to increase awareness of the waste rock stockpile as a hydro-geochemical ‘system’ so that future research, wherever it is, focuses more on observations of ‘the real thing’ in situ, within its own specific climatic and anthropogenic regime, rather than inferring from unrealistic lab based experiments, stockpiles manufactured for specific study or large scale burial of instrumentation which is often plagued with bias due to the methods used to bury them (as in the case of Kuo, 1996).
It is the hypothesis of this thesis that large scale and expensive experimentation with stockpiles can largely be avoided; simple and direct observations will give key insight to the complexities of a stockpile hydro-geochemical ‘system’ and explain much of the phenomena that is seen in the chemistry of mine waters influenced by them and water balance models that include them. This thesis will attempt to prove that it is possible to understand an operational stockpile ‘system’, there is no need to wait until mine closure when stockpiles can be systematically de-constructed.

To test this hypothesis this research specifically aims to do the following:

1. Establish and define the structure of the stockpiles and in doing so be able to gain an understanding of the potential hydrological regime that may exist within them and hence an understanding of how and where water may interact with the waste rock.
2. Determine the geology of the stockpiles, including identifying which rocks from the mine make up the waste rock and based on where they have been placed within the piles, if the waste rock piles are geologically similar or markedly different.
3. Identify and characterise the mineralogical and geochemical composition of the individual rock types within the stockpiles but with emphasis on the most important types or type.
4. Gain a complete understanding of the chemistry of the rainfall contacting or entering and reacting with the waste rock in the stockpiles, including the main determinants of rainfall chemistry, natural or anthropogenic (eg, mining contributions).
5. Assess the contribution of both dust suppression water and rainfall to ion contribution to the stockpile system.
6. Examine the chemistry of dust suppression water, the other major input into the stockpiles, ascertain how its chemistry is derived and assess if it is important to the hydro-geochemistry of mine water.
7. Characterise the chemistry of the drainage emanating from the stockpiles.
8. Using the evidence accumulated in the above studies, conceptualise the weathering environment occurring on and within the waste rock stockpiles and ascertain how this is affecting the chemistry of the waters emanating from them, including the identification of the contribution the stockpiles make to mine water chemistry and the dominant mineral-water interactions occurring in the stockpiles.

9. Bring all of the various findings from above together into a general synthesis for the waste rock stockpile system.

The thesis is structured so that each chapter deals with a single component of the stockpile system. Chapter 3 will be dedicated to stockpile structure and hydrology, chapter 4 to geology, mineralogy and geochemistry; chapter 5 to rainfall; chapter 6 to dust suppression waters; and chapter 7 to stockpile drainage. Chapter 8 will discuss the weathering of the stockpiles and their contribution to the system, and the final chapter, chapter 9, will act as a general synthesis and conclusion on the overall hypothesis. All methods are described in Chapter 2.
CHAPTER 2

METHODS

2.1 FIELD WORK LOGISTICS

A total of five expeditions to Ranger Uranium Mine were undertaken for this research. This culminated in some 118 days in the field, although a large percentage of these were spent in travel and in Darwin. Activities in Darwin included the gathering of supplies, undertaking research at the library of the Northern Australian Research Unit (NARU) of the Australian National University (ANU) and the Northern Territory Geological Survey (NTGS), organising sample courier delivery and communicating with sponsors and potential sponsors. Table 2.1 outlines each expedition along with its major focus.

Table 2.1. Field Work to date

<table>
<thead>
<tr>
<th>No.</th>
<th>Expedition Date</th>
<th>Focus</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21/11/1999-9/12/1999</td>
<td>Collection of start of wet season rains. Familiarisation with mine site and waste rock piles. Set up communications with associated staff at mine. Develop water sampling technique.</td>
</tr>
<tr>
<td>5</td>
<td>April/May 2002</td>
<td>Final rock sampling. Leachate sampling. Final research and collaboration with staff at EWL Sciences.</td>
</tr>
</tbody>
</table>
2.2 SAMPLE COLLECTION

2.2.1 Surface Mine Water

Some 64 water samples were collected for this research. This included 15 blanks, 12 groundwater samples (see below), 32 surface water samples (including 1 leachate), 4 duplicates and 1 sample of the Ranger process water. Using the procedure specified below each water sample took approximately 2 hours to collect. Given the logistics in the mine, this amounted to a maximum of three water samples per day but usually less, and so it took some 25 full working days in the field to sample just the 45 surface and groundwater samples here (and not including rain water sample collection).

Table 2.2 is a list of the water samples collected during this research, except for rainfall (see later) in order of the field number and expedition sequence. Each sample’s exact date of collection is also given in the table, along with a brief description of the exact site of location for each sample and a site code. The site code can be used to find the exact location of each collection site within the mine on the aerial photograph of RUM that is presented in Figure 2.1. In Figure 2.1, site locations are colour coded according to whether the site is a surface water sample site, a groundwater sample site or a definitive leachate sample site.
Figure 2.1: Map of the location of sampling sites for surface and ground water samples collected during this research. Sample site codes presented on this map correspond to those in table 2.2, where all samples are listed according to their sample number and date that they were collected. It should be noted that this map shows all samples collected during this research, regardless if they were actually used in the research or not. See text for further details.
Table 2.2. List of all surface waters and ground waters collected from Ranger Uranium Mine during the period of this research. Date of collection, site location code and brief location description are included. Site location code is to be used in conjunction with sample location map in Figure 2.1. Further detail on sample sites can be found in the appropriate chapter dealing with the chemistry of the water samples.

<table>
<thead>
<tr>
<th>Expedition No.</th>
<th>Field No.</th>
<th>Date Sampled</th>
<th>Site Location Code</th>
<th>Site Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>W1</td>
<td>2/12/1999</td>
<td>SWP</td>
<td>Bottom of waste rock pile</td>
</tr>
<tr>
<td></td>
<td>W2a</td>
<td>2/12/1999</td>
<td>Ore</td>
<td>Direct drainage from Ore stock pile</td>
</tr>
<tr>
<td></td>
<td>W2b</td>
<td>2/12/1999</td>
<td>Ore</td>
<td>Drainage downstream of W2a</td>
</tr>
<tr>
<td></td>
<td>W3</td>
<td>4/12/1999</td>
<td>LGO Sump 1</td>
<td>Up-welling water near stockpile in stockpile sump</td>
</tr>
<tr>
<td></td>
<td>W4</td>
<td>4/12/1999</td>
<td>LGO Sump 2</td>
<td>Creek running into RP2 from LGO Sump</td>
</tr>
<tr>
<td>2</td>
<td>R102</td>
<td>12/04/2000</td>
<td>RP1</td>
<td>Retention Pond No. 1, near spillway, near road</td>
</tr>
<tr>
<td></td>
<td>R105</td>
<td>13/04/2000</td>
<td>CCMBL</td>
<td>Bund on Corridor Creek</td>
</tr>
<tr>
<td></td>
<td>R108</td>
<td>14/04/2000</td>
<td>CC</td>
<td>Corridor Creek Sampling station</td>
</tr>
<tr>
<td></td>
<td>R110</td>
<td>17/04/2000</td>
<td>RP2</td>
<td>Retention Pond 2 sampling station</td>
</tr>
<tr>
<td></td>
<td>R114</td>
<td>19/04/2000</td>
<td>SWP</td>
<td>Top of waste rock</td>
</tr>
<tr>
<td></td>
<td>R115</td>
<td>19/04/2000</td>
<td>SWP</td>
<td>Bottom of waste rock</td>
</tr>
<tr>
<td></td>
<td>R118</td>
<td>21/04/2000</td>
<td>DW3A</td>
<td>DW3A, Dewatering bore between RP2 and P3</td>
</tr>
<tr>
<td>3</td>
<td>RW205</td>
<td>5/08/2000</td>
<td>CCMBL</td>
<td>Bund on Corridor Creek.</td>
</tr>
<tr>
<td></td>
<td>RW207</td>
<td>5/08/2000</td>
<td>RP2</td>
<td>As above, not from station</td>
</tr>
<tr>
<td></td>
<td>RW208</td>
<td>6/08/2000</td>
<td>Sump98</td>
<td>NW corner of Sump98</td>
</tr>
<tr>
<td></td>
<td>RW209</td>
<td>6/08/2000</td>
<td>DW3A</td>
<td>DW3A, Dewatering bore between RP2 and P3</td>
</tr>
<tr>
<td></td>
<td>RW210</td>
<td>6/08/2000</td>
<td>DW3A</td>
<td>Duplicate of RW209</td>
</tr>
<tr>
<td></td>
<td>RW212</td>
<td>6/08/2000</td>
<td>LGO Sump</td>
<td>Near to the pile</td>
</tr>
<tr>
<td></td>
<td>RW213</td>
<td>7/08/2000</td>
<td>P1DWB</td>
<td>Dewatering bore for P1 near CC</td>
</tr>
<tr>
<td></td>
<td>RW215</td>
<td>13/08/2000</td>
<td>AMDseep</td>
<td>Seep from excavation wall in WWP</td>
</tr>
<tr>
<td></td>
<td>RW217</td>
<td>13/08/2000</td>
<td>RP2</td>
<td>RP2 after fill from pumping from Pit3</td>
</tr>
<tr>
<td></td>
<td>RW218</td>
<td></td>
<td>Process Water</td>
<td>Process Water</td>
</tr>
<tr>
<td>4</td>
<td>RW303</td>
<td>22/11/2000</td>
<td>OB23</td>
<td>OB23, observation bore WWP influence</td>
</tr>
<tr>
<td></td>
<td>RW308</td>
<td>25/11/2000</td>
<td>LGO Sump</td>
<td>LGO sump away from stockpile</td>
</tr>
<tr>
<td></td>
<td>RW310</td>
<td>22/11/2000</td>
<td>OB24</td>
<td>OB24, observation bore, WWP influence</td>
</tr>
<tr>
<td></td>
<td>RW312</td>
<td>25/11/2000</td>
<td>RP2</td>
<td>As above</td>
</tr>
<tr>
<td></td>
<td>RW313</td>
<td>25/11/2000</td>
<td>DW3A</td>
<td>As above</td>
</tr>
<tr>
<td></td>
<td>RW314</td>
<td>25/11/2000</td>
<td>DW3A</td>
<td>DW3a Duplicate of RW313</td>
</tr>
<tr>
<td></td>
<td>RW315</td>
<td>25/11/2000</td>
<td>WWP 1</td>
<td>Water from bottom of WWP</td>
</tr>
<tr>
<td></td>
<td>RW316</td>
<td>25/11/2000</td>
<td>WWP 1</td>
<td>15-20m from RW315, same water</td>
</tr>
<tr>
<td></td>
<td>RW319</td>
<td>26/11/2000</td>
<td>Bore23552</td>
<td>23552bore WWP influence</td>
</tr>
<tr>
<td></td>
<td>RW320</td>
<td>26/11/2000</td>
<td>OB44</td>
<td>OB44 WWP waste rock influence</td>
</tr>
<tr>
<td></td>
<td>RW323</td>
<td>28/11/2000</td>
<td>WWP 2</td>
<td>WWP run-off channel</td>
</tr>
<tr>
<td></td>
<td>RW324</td>
<td>28/11/2000</td>
<td>OBWWP</td>
<td>Unused observation bore WWP</td>
</tr>
<tr>
<td></td>
<td>RW325</td>
<td>29/11/2000</td>
<td>GC</td>
<td>Grand Canyon, CWP influence</td>
</tr>
<tr>
<td></td>
<td>RW326</td>
<td>1/11/2000</td>
<td>MB</td>
<td>ERA sample of main bore on WWP</td>
</tr>
<tr>
<td>5</td>
<td>RW401</td>
<td>28/04/2002</td>
<td>OB44</td>
<td>OB44 WWP influence</td>
</tr>
<tr>
<td></td>
<td>RW402</td>
<td>30/04/2002</td>
<td>EWF</td>
<td>First bund on the new wetland filter</td>
</tr>
<tr>
<td>ID</td>
<td>Date</td>
<td>Location</td>
<td>Notes</td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>------------</td>
<td>----------</td>
<td>------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>RW403</td>
<td>1/05/2002</td>
<td>MB</td>
<td>Direct sample from tanker (not mapped in Figure 2.1)</td>
<td></td>
</tr>
<tr>
<td>RW404</td>
<td>5/05/2002</td>
<td>Dust suppression water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RW405</td>
<td>5/05/2002</td>
<td>NWP</td>
<td>New NWP stockpile pond – leachate?</td>
<td></td>
</tr>
<tr>
<td>RW406</td>
<td>9/05/2002</td>
<td>r2sed</td>
<td>r2sed near sump 98</td>
<td></td>
</tr>
<tr>
<td>RW407</td>
<td>16/05/2002</td>
<td>GC</td>
<td>As above</td>
<td></td>
</tr>
<tr>
<td>RW408</td>
<td>16/05/2002</td>
<td>RP4</td>
<td>Old RP4</td>
<td></td>
</tr>
</tbody>
</table>

All surface waters were collected by submerging 1-litre high-density polyethylene (HDPE) bottles into the target water body until they were completely full. These bottles were then used to transport the water directly back to the prepared filtering station (see later). All sample bottles were cleaned according to the cleaning procedures detailed below. At all times during sampling water, powder free sterilised surgical gloves were used as an anti-contamination precaution.

Most samples were collected using an extendable aluminium sampling pole with a screw adjustable, plastic coated tri-claw clasp. Where direct access to the water body was possible and the water body was small enough for a representative sample could sample to taken at ‘arms length’, then the sample was taken by hand.

### 2.2.2 Mine Groundwater

A variety of techniques were used to sample the groundwater collected for this research. Groundwater pumping stations were available for the bores, DW3A, MB and P1DWB (refer to Figure 2.1 and Table 2.2). Sampling from these stations entailed purging the bore for at least 10 minutes before beginning sample collection procedures. Samples were taken by hand in 1L HDPE bottles using powder free sterilised surgical gloves and sample bottles as described previously. An example of these pumping stations is shown in Figure 2.2.
Figure 2.2: Pumping station for bore at location MB. Tap has been left open to purge water from pipes whilst in-field parameter instrumentation is prepared before use. Location MB is on the WWP, the bore being used to monitor water beneath stockpile and downstream of tailings dam No.1.

When available, the RUM Environmental Department’s bore sampling vehicle was used to sample bores without pumping stations. This vehicle incorporated a reeled plastic hose with submersible pump powered by a diesel driven generator (Figure 2.3). Bore-water data sourced from the ERA Environmental Department in 2002 was used to calculate bore volume and the bore was purged by 2.5 times the volume before sampling. Where this was not possible the bore was pumped dry twice before sampling.

In the earlier expeditions, a polyvinyl chlorate (PVC) bailer with steel ball-bearing stopping weight attached to a 30-metre nylon rope was loaned from the ERA Environmental Department to sample bores manually. Before any samples were taken, a sufficient amount of water (approximately 20 bails in this case) was taken out of the bore to ensure true groundwater representation.
Figure 2.3: Photograph showing the sampling of an observation bore near the WWP using the water bore vehicle. To the left of the photograph the bore pump and hose has been placed down the bore hole. The generator is connected to the pump via a cable which can be seen as a thin line connected to the hose. The bore water is being pumped from the outlet at the centre of the hose reel (centre photograph). After the bore is purged adequately, the sample is taken from this water.

To collect bore water manually and via the vehicle pump, the sample water was poured into a large plastic beaker before being poured into the sample bottle, which was subsequently filled so that as little air as possible remained in the bottle once closed. Once again, all containers were cleaned according to the cleaning procedures outlined below. At all times during sampling, powder free sterilised surgical gloves were used.

2.2.3 Dust Suppression water

Dust suppression water is the water applied to roads and working areas of the mine by a water tanker vehicle to suppress the creation and movement of dust. The water is sourced from RP2; thus, the samples collected from RP2 can be used to assess the chemistry of the dust suppression water. However, to ensure that there was no significant change in the concentrations of chemical components during the transfer of water from the RP2 reservoir to the dust suppression water storage facility and water tanker, a sample of dust suppression water was collected during the final expedition to Ranger.
The sample was collected whilst the water tanker was idle in an upper level of P3. The sprinklers had been turned off, but water was still running from the sprinkler system. This water was collected by placing a rainfall collector, excluding the supporting post (details of the rainfall collector set-up are given below), beneath the stream of water leaking from the sprinkler system. A photograph of dust suppression water sampling direct from the water tanker is shown in Figure 2.4.

![Image of a water tanker](image.jpg)

**Figure 2.4:** Collecting dust suppression water from the RUM water tanker. See text for details.

### 2.2.4 Internal Stockpile Leachate

Sample RW215 was a sample of leachate found emanating from a wall in an excavation into the eastern section of the WWP. The leachate sampled could be described as a slow leak from a saturated Platform Horizon (see Chapter 3 for explanation) within the wall of an excavation into a section of the western waste rock pile (WWP). No specific preparations had been made for water from such a location and, as it was not known exactly how long such an event would last, a sampling device had to be made from materials available ‘at hand’.

Two samples of the leachate were collected, a small amount for EWL Sciences Pty. Ltd. and a second for this research. The first was taken instantly using an eyedropper to collect small amounts of water that had accumulated in depressions in the clay...
walls (see Figure 2.5a). The depressions were made for this purpose by carefully pressing into the clay with a finger (wearing powder free sterilised surgical gloves). The water was stored in a 125ml HDPE bottle, rinsed as described below, except with limited sample water for flushing. In approximately 30 minutes, 50ml of sample was collected.

Figure 2.5: Internal stockpile leachate sampling at Ranger Uranium Mine. (A) Collection of first sample for EWL Sciences Pty. Ltd., 50ml in 30 minutes by eye dropper method. (B) Diagram of device made to channel water from Platform Horizon into collection vessel. (C) Position of set-up for overnight collection, within the context of the excavation wall. (D) Close-up of set-up for collection of internal stockpile leachate. Note the device from the diagram in (B).
The second sample was collected overnight, being retrieved in the next morning some 14h after set up. Collection was achieved by making a small hole into the clay wall (approximately 80mm long [finger length]) using a gloved finger at a slight upward angle, where the water seemed to be leaking from. A small piece of PVC electrical pipe (approximately 120mm long and 10mm diameter) was inserted into the hole to act as a funnel to direct the water out of the wall. The end of the funnel that was inserted into the wall had been cut in half to a length of approximately 40mm so that it formed an open ended ‘half pipe’ like structure in the hole (refer to Figure 2.5b). The bottom of this ‘half pipe’ structure was placed so that it lay at the same level as the floor of the hole, allowing unimpeded access to the funnel for any water that may pass through the hole. After a very slow drip was attained by the devise, the rest of the pipe (from which the funnel had been made) was inserted vertically into the ground at the leakage sight for a support post (see Figure 2.5). A 125ml HDPE bottle, rinsed as described below, was then strapped to the top of the pipe using PVC tape and positioned so that it caught the drips from the funnel. A full 125ml HDPE bottle of leachate sample was collected overnight. The complete set-up is shown in the photograph of Figure 2.5.

2.2.5 Bulk Precipitation (Rainfall)

Three of the five expeditions to RUM involved the collection of rainfall, the first expedition of December 1999, the second expedition of April/May 2000, and the fourth expedition of November 2000. Such timing was chosen in order to capture the rainfall at the start of the wet season (SOWS) and the end of the wet season (EOWS) at RUM, two periods that had previously been shown to have distinctively different chemistry. The first expedition was used as a preliminary test for collection, temporary storage, transport and analytical procedures. The second expedition was used to collect EOWS rain and the fourth expedition was used to collect SOWS rainfall.

Three primary locations were chosen to collect the rainfall, two sites within the mine that were relatively inactive in regards to mining activity, and one on the Jabiluka access route some 20km from the mine (straight line distance). The geographical locations of these sites are shown in Figure 2.6. The two areas targeted in the mine included the SWP/SCWP area and the NCWP area, however the initial SCWP site
had to be moved to the SWP for the fourth expedition due to mining activity. These three locations allowed comparison of rainfall chemistry within the mine and between the mine and a non-mine site. A fourth location was set up within the mine near Corridor Creek (see Figure 2.6) for the second expedition only; however, only a single sample (R109) of just 3.43mm of rain was collected at this site.

Daily to no longer than weekly, filtered bulk precipitation was chosen as the preferred rainfall sampling method for this study. The main reason for this choice was so that the rainfall chemistry could be compared with the Noller et al. (1990) study of the complete 1982/83 wet season rainfall at Jabiru, only 3.1km from RUM, which also used this method. An explanation of why this comparison needed to be made can be found in the introduction to Chapter 5, dealing with rainfall chemistry at RUM.

An explanation as to exactly what filtered bulk precipitation is in relation to rainfall and, hence, exactly what has been sampled in this study is in important. Bulk precipitation is a method of collecting rainfall whereby the collection vessel is continuously open throughout a given period so that both dry atmospheric fallout (sedimentation of heavy aerosols, including dust and dry impaction of gases and light aerosols) and rainfall is collected. Thus, bulk precipitation samples are representative of total atmospheric input during the time of sample collection. This is in contrast to wet-only precipitation samples, whereby the collection vessel is only open to the atmosphere during the rainfall event, and, hence, dry deposition between rainfall events is avoided.
In this study, the rainfall collectors were set up in the morning and collected the morning after a major rainfall event. If it was not possible logistically to collect the rainfall directly after a rainfall event, or no major rainfall event occurred on the day of set-up, then the collectors were sometimes left for another 24h or until a major rainfall event occurred. At no time were any collectors left in the field for longer than 7 days, as this was the longest amount of time any rainfall collector from the comparison study by Noller et al., (1990) was left in the field. The Noller et al. (1990) study also concluded that there was no significant chemical difference between samples from collectors that had been left in the field for a day and those from collectors that had been left in the field for a week. This was another reason why single rainfall collections did extend up to, but not beyond, a week in the study carried out here.
The lack of chemical difference between daily and weekly rainfall collections may be due to a relatively consistent environment of only slight winds between rainfall events in the vicinity of RUM and Jabiru, as is noted in Chapter 5. Whatever the cause, this fact suggests that the dry deposition supply to bulk precipitation collection vessels in the Jabiru region is minimal and difficult to detect for a collection time of one week or less. Therefore, while the rainfall samples collected here are bulk precipitation and not wet-only precipitation, the actual effect of dry deposition on the chemistry of the sample should be regarded as minimal. The effect should be even less, because the samples were filtered almost directly upon collection (no longer than four hours afterwards—see later). Thus, the dry deposition aerosols had limited time for interaction with the rainwater. Further discussion on this point and an examination of the analytical results from the bulk precipitation samples collected in this study to check for any ‘time-left-in-field’ effect, is given in a later section of this chapter.

The anolyte precipitation sample was collected in a one litre HDPE bottle after passing through a plastic funnel with vertical sidewalls. The funnel was attached to the bottle with PVC adhesive tape. To ensure the funnel was securely held to the storage bottle and in a vertical position, strips of PVC tape were applied lengthways from the sides of the funnel to the side of the storage bottle, then wrapped around each end, effectively wrapping around the funnel and the storage bottle.

This collection vessel was then attached to a timber stake of approximately 1.8m in length, which once hammered into the ground, stood approximately 1.5m high. The vessel was attached to the post with multiple wrappings of PVC tape. Care was taken as to make sure the collection vessel extended well beyond the timber post so as to avoid input and contamination from ‘splash’. However this was not done until posts were securely hammered into the ground. As a result of the heterogeneity of the ground on the waste rock stockpiles, obtaining a vertical position for the collection vessel on the post was easier than trying to obtain the vertical position with the post on insertion into the ground.
To obtain a measure of the amount of rainfall that had fallen during the period of sample collection, the same type of collection vessel as that described above was attached to a steel post (star picket). The steel post was hammered into the ground so that its height from the ground surface was approximately 1.5m, and the vessel was positioned vertically. A steel post was used for the volume collector, rather than the thinner timber posts of the anolyte collectors, for stability purposes to ensure an accurate measure of rainfall volume. Vegetable oil (5mm) was added to the volume collector in the bottom of the storage bottle, in order to avoid loss of volume through evaporation.

The volume collection vessel and the anolyte collection vessel were positioned, so that they were approximately 10m apart to be certain that no cross-contamination from splash could occur. In the preliminary rainfall sampling of the first expedition, cross-contamination was possible in heavy storms at a distance of 2.5m, although only if the collection vessels and funnels were filled.

There were two main differences in the rainfall collection set-up between the two collection expeditions. First, the second expedition set-up consisted of only a single anolyte collection vessel, whereas the fourth expedition consisted of four anolyte collection vessels, as shown in Figure 2.7. The change was made in order to decrease the chance of a contamination event destroying a sample and thus wasting a collection opportunity, particularly considering the limited window of time represented by each expedition.

Second, the funnels of the collection vessels in the second expedition were made from upturned plastic drink bottles with the bottom removed, that had been acid washed (2% \( \text{HNO}_3 \) for 12h) and thoroughly rinsed in de-ionised water (DIW). The funnels from the fourth expedition had been made from upturned HDPE bottles with the bottom removed. Since the rainwater is only in contact with the funnel for a very short period of time before it enters the storage bottle (probably < 1 second), this difference would unlikely affect chemistry. Vertical sidewalls for the funnels was considered important, so as to not loose rainwater through splash, particularly when rain was not falling vertically and particularly in the case of the volume collector.
Figure 2.7: Plan view of the rainfall collection sampling set-up (a) and the location chosen for the Jabiluka non-mine influence site.
To collect the rainfall sample itself the collection vessel was dismantled by cutting the PVC tape connecting the funnel to the storage bottle. The funnel was then removed and the storage bottle cap, which had been kept in a sealable plastic bag, was screwed into place to secure the sample.

Handling of collectors at all times during dismantling and remounting was done using powder free disposable surgical gloves. Storage bottles were discarded after only one use to minimise cross-contamination, but funnels were re-used after thorough rinsing three times each with milli-Q filtered DIW. Cross-contamination through funnels was considered unlikely due to the small amount of time the rain spent actually on the funnel as already discussed above. The volume bottle was closed and stored for accurate measurement back at the laboratory.

2.2.6 Waste rock and LGO Material

Waste rock samples were collected by hand from both in and around the waste and LGO stockpiles of RUM, as well as a limited number of hand specimens from within P3. Unconsolidated material from within stockpile excavation walls was also sampled as were a number of stockpile surface platform horizons. Clay pans both from surface and submerged platform horizons were targeted. A limited number of small hand specimens for mineralogical examination were collected as were a number of precipitates from dried ponds for the same purpose.

The walls of five stockpile excavations have been sampled, these excavations two into the NWP, two into the SWP and one into the WWP. The sampling of the walls was systematic, including sampling vertically through layers of different rock type as well as sampling along sloping layers of different rock type.

To avoid, as much as possible, the effect of more recent weathering directly on the wall from its exposure through excavation, samples were taken from at least 15cm within the wall. However, most exposures of wall were only recent, often being only months old, except for the excavation into the south of the NWP which had been open for a number of years. Unconsolidated material was generally collected in 1 kg samples within plastic sample bags.
2.2.7 Temperature Measurements

A digital TempTec automatic hygrometer/thermometer was used to measure the surface temperature of cobble sized chloritised dolerite on the SWP over 24 hour time periods in April, August and November of 2000; the purpose of which was to get an idea of the temperature flux both seasonally and diurnally on the stockpile surface, and thus the possible initial reaction temperatures for minerals exposed at the surface, including uraninite and uranyl precipitates. The thermometer consisted of a small mobile temperature sensor with an adhesive backing connected by electrical wire to a base unit.

Figure 2.8: Rock surface temperature monitoring on the SWP, Mount Brockman in background. See text for further details of instrument and procedure.
2.3 INVESTIGATIONS INTO STOCKPILE STRUCTURE

Interpretations of the internal structure and fabric of the waste and LGO stockpiles at RUM were made through observations at seven major excavations sites in the stockpiles. These excavation sites have been designated E1 through to E7 and their precise locations can be found in Figure 2.9. E1 (up to 10m in height and 200m long) in the WWP was examined in August 2000, E2 and E3 (both up to 5m in height but E2 approx. 100m long and E3 approx. 200m long) in the NCWP were examined in December 1999 and April 2000 respectively, E4 (up to 10m in height and 200m long) in the CWP was examined in April and August 2000 as well as another excavation in the same area in April/May 2002, E5 (up to 10m in height and 200m long) in the SCWP was examined in November/December 2000, E6 (5m in height, some 200m long) in the SCWP was examined in November/December 2000 and again in April/May 2002, and E7 (up to 5m in height and 200m in length) in the SCWP was examined in April/May 2002. Most of the excavations cut through different structural units in the stockpile and were judged of sufficient height and extent relative to the construction techniques and overall size of the stockpiles to be considered representative of the inside of the entire stockpile system.

Due to confusion with local names given to the various sections of the stockpile (for instance the northern most stockpile is known locally as the western stockpile), the entire waste and LGO stockpile system was sub-divided into the boundaries and names given in Figure 2.9.
Figure 2.9: Location of the major excavations into the RUM waste and LGO stockpile system where observations were made in regard to the internal structure and fabric of the stockpiles. Seven excavations were examined and these have been named E1 through to E7. Note that the waste and LGO stockpile system has also been subdivided into six different sections for the purpose of reference for this study, the Western Waste-rock Pile (WWP), the Northern Waste-rock Pile (NWP), the Southern Waste-rock Pile (SWP), the Central Waste-rock Pile (CWP), the North Central Waste-rock Pile (NCWP) and the South Central Waste-rock Pile (SCWP). Separations are based on stages of stockpile construction. These separations are based on the 1999 aerial photograph, a photo where E5-E7 are yet to exist hence the use of the 2003 aerial photograph for these excavation locations.
2.4 IN-FIELD SAMPLE PREPARATION AND LOGISTICS

2.4.1 Filtering Mine Water and Precipitation Samples

Filtering of all water samples, including precipitation, was accomplished in the field, either straight after collection at the rear of the vehicle (on the swing-down back tray of the vehicle) or after the collection of three to four samples in a clean unused demountable on the mine site no more than 500m away from the furthest sample. The demountable rooms used included the mining office located between the ore stockpile and CWP, and the ERA Environmental Department Office near the main office block of the mine.

A crucial aspect of this research, was the need to filter water samples as soon as possible after collection so that as little time as possible was allowed for solid particles in the sample to react with the sample solution. Filtering of samples is generally done in the laboratory before analysis; however, the analytical laboratories for this research are located in Canberra, and thus samples had to be stored until the end of each field expedition and then transported to Canberra. Thus, some samples had to be stored for up to four weeks before entering the laboratory process which required the need for filtering in the field upon collection.

The focus of this study is on the chemistry of solutions that originate from the stockpiles and, thus, an indication of rock-water interaction within the stockpile 'system'. Whilst solid particles can be a product of such reactions, they can result from processes not of focus here, such as physical weathering and transport processes. Also, residual water chemistry data provided by the ERA Environmental Department and from a recent study of the NWP by EWL Sciences (Puhalovich et al. 2002) clearly show that, apart from Al and Fe, suspended sediment accounts for very little of the concentrations of most ions in waters monitored at RUM, hence eliminating further consideration of suspended particles in this research.
The filtering station was set up over a mat of unused, large plastic garbage bags in an attempt to avoid any contamination from the introduction of foreign material. This was obviously more important when using a vehicle. Heavy items were used to secure the plastic at each corner. During the afternoons in the wet season, a tarp was secured to the back of the vehicle so that it formed a roof and walls around the filtering station leaving one wall free for entry and exit. Along with the correct positioning of the car (as rain rarely fell vertically), this prevented contamination of water by rainfall as well as acting as a barrier to strong storm front winds.

A clear, hardened plastic filter unit manufactured by Geoscience Australia (GA) in Canberra was used to filter all water samples. Filtering was achieved by drawing the sample water through a 0.45μ cellulose nitrate filter (Micropore brand, USA) from the introduction chamber at the top of the filter unit to the bottom holding chamber, by negative pressure produced by a hand pump connected to the holding chamber. Once the introduction chamber was emptied, the filtered sample solution was then poured through the black plastic pump nozzle (after detaching the pump) into HDPE storage bottles.

The procedure was repeated until enough water had been filtered for the desired analyses. For the purposes of this research, three sub-samples of each water sample, including precipitation samples, were collected for storage. This included a 250ml Nalgene HDPE bottle of sample for major anion analysis, a 250ml Nalgene HDPE bottle of sample for major cation analysis, and a 125ml Nalgene HDPE bottle of sample for trace element analysis. Many of the water samples served a dual purpose, being both for this study and that of Kilby (2001). One litre bottles of sample water were also collected only for the Kilby (2001) study, these being for the precipitation of CaSO₄ for S-isotope analysis. Kilby (2001) should be referred to for further details. At all times during the procedure, sterilised surgical gloves were used and changed before proceeding to the next procedural step due to contamination after using the pump.
2.4.2 Water Sample Acidification and In-field Storage

In order to ensure elements in solution stayed in solution the anolyte samples for major cation analysis and trace element analysis were stabilised using 0.4% (1/250ml ratio) analytical grade HNO$_3$ from Aristar (69% sp. gr.). Testing samples with a pH metre revealed that this process lowered the pH of each sample from approximately pH 6-7 to pH 1.6-2.0.

Since NO$_3^-$ and Cl$^-$ were two anions to be analysed in this study, sub-samples for major anion analysis were not stabilised with acid. The main concern with these samples was keeping them sufficiently cool, without freezing, so to minimise or slow down any chemical reactions that may take place, including any biological activity that may have been present.

Sample storage bottles were stored immediately after filtration in the water sample refrigerator at the ERA Environmental Department Office (monitored to be between approximately 3-4°C) or, if this was unavailable, in the refrigerator at the place of accommodation (monitored to approximately 2-6°C). Between the sample collection site and the filtration site and between the filtration site and the place of accommodation, samples were stored in an insulated cooler box (esky) with four one litre ice bricks. Monitoring revealed that temperatures in the esky never exceeded 8°C. At all times during transport and storage, sample storage bottles were housed within snap-lock sealed plastic bags to avoid contamination around the storage bottle.

All samples were transported to Canberra by aircraft in the esky cooled by up to eight one litre ice bricks. On the 2$^{nd}$ field expedition, the samples were personally driven back to Canberra, in which case the same methods of storage were used as those used in the field, with an exchange of fresh ice bricks every 12h where possible. On two occasions, the samples went approximately 36h without an exchange of fresh ice packs in which case a thermometer was used to monitor the temperature inside the esky. The greatest temperature reached for an unknown period of time was 14.1°C. The temperature kept between approximately 3-7°C inside the esky at all times during this road trip. When in Canberra, all samples were kept in a cool room at the
University of Canberra Department of Freshwater Ecology water laboratories, where the temperature thermostatically controlled at 3°C.

2.4.3 Waste and LGO Rock Samples

All rock and earth materials were double bagged in plastic, temporarily stored at the Mine Office and then transported to Sydney in a steel 44 gallon drum via the dangerous goods road transport network. They were then transported to Canberra by aircraft and finally to the laboratory by road.

2.5 CLEANING PROCEDURES FOR WATER SAMPLING EQUIPMENT

2.5.1 Pre-wash Procedures

After an initial trial during the first expedition and after considering evidence from Reimann et al (1999) that suggests there is little to no advantage in washing polyethylene (PE) or HDPE bottles if they are not to be used again, no pre-washing of sample storage vessels was applied during this research. Instead, HDPE bottles were taken directly from their packaging and not opened until needed for use. Before using them for the first time, the HDPE bottles were rinsed three or six times with milli-Q water depending on whether they would be used for storage or sampling respectively. Storage bottles were never recycled and therefore never washed with detergent or acid. The least amount of times the sample bottle was open to the atmosphere was considered better than opening during multiple cleaning and drying phases, since a ‘clean’ working environment was not possible at any stage while in the field.

2.5.2 Sample Collection Vessels

Before sampling, sample collection vessels were rinsed three times with milli-Q filtered DIW before being flushed through three times with sample water. After the filtering process was complete, the bottles were rinsed again three times with milli-Q filtered water. This meant that the sample bottle had been rinsed six times with milli-Q filtered water prior to sampling. All parts of the bottle came in contact with the rinse water every rinse. After every two samples, the sample collection bottles were discarded.
2.5.3 Sample Storage Bottles

Storage bottles were used only once. These bottles were first rinsed three times with milli-Q filtered DIW to discard of any foreign matter inside the bottle. Before the filtered sample water was poured into the bottle, it was used to flush the bottle three times to remove any remaining foreign matter and milli-Q filtered water.

2.5.4 The Filtering Unit

Using milli-Q filtered DIW, all parts of the filter unit were rinsed before and after each sample had been filtered. Each part of the unit was rinsed three times during each wash with particular attention paid to the holding chamber. This meant that all parts of the filter unit were rinsed six times with milli-Q filtered DIW between each sample.

Long term use of the filter unit in a tropical climate meant that the filter unit often did not get time to dry completely between each day’s use. To account for the possibility that organic matter may build up on the sides of the holding chamber because of the lack of drying time, the filter unit was, on occasions, bathed in a 1% HCl solution with DIW and left soaking for two days. After the acid bath, the unit was rinsed liberally and thoroughly with DIW and then wiped out with paper towel before being rinsed again three times with milli-Q. This cleaning procedure was also carried out on one occasion before entering the field because of a visible mark inside the holding chamber.

2.6 ANALYTICAL METHODS FOR AQUEOUS CHEMISTRY

2.6.1 The Chemical Parameters, Redox Potential (eh), Potential of Hydrogen (pH), Electrical Conductivity (EC), Dissolved Oxygen (DO) and Temperature

Where possible, the chemical parameters of eh, pH, EC and DO were measured within the water body of interest before sample collection in the field. In small water bodies or shallow streams, the measurement took place where the sample was collected. In large water bodies the measurement took place in a four litre HDPE beaker as the sample water was being poured into it, once again the water being from
the precise place of sample collection. In such circumstances, the water had passed through the sampling vessel. Bore waters were measured with the same procedure as described above for large water bodies. Rainwater samples were measured for pH only because of contamination concerns and the importance of pH in the chemistry of the rainfall samples.

The eh was measured by an Orion Oxidation Reduction Potential (ORP) Triode Electrode, with model 91-79 set up. The electrode consists of a Pt redox sensor (the sample solution half-cell), a Ag/AgCl internal reference system (the reversible reference half-cell) and a built-in thermister for automatic temperature compensation (ATC). The temperature is measured simultaneously with redox without a separate reference electrode. The 91-79 model is a non-refillable low maintenance gel-filled electrode. The Orion Model 250Aplus Portable pH/mV/ORP/Temperature Meter was used for the voltage measurement.

The Orion Model 210A Hand-held pH Meter was used for the measurement of pH in conjunction with an Orion Low Maintenance Triode pH Electrode. The electrode consists of an epoxy outer body (thus cannot be used with organic samples), housing a pH sensing bulb (the glass electrode) and an internal Ag/AgCl reference electrode system. It should be noted that this reference electrode is incompatible with samples containing Ag complexing or binding agents such as tris, proteins and sulfides. The pH was not measured for a single rainfall sample, R109, for fear of contamination by the probe due to the exceptionally small volume of the sample. EC was measured using the Orion Model 130 Waterproof Conductivity Meter that automatically compensates for temperature variations.

DO was measured by an Orion Model 830 Dissolved Oxygen Meter. This probe consists of an anode/cathode electrode system and an electrolyte separated from the water sample by an oxygen permeable membrane. Automatic compensation for sample and membrane temperatures are achieved through the use of built in thermistors.
Temperature was measured by in-built temperature measuring devices in the eh, pH and DO probes. The temperature was recorded for all three probes separately although the DO oxygen probe measurement was arbitrarily used as the official temperature reading. The variation in measured temperatures between probes was negligible, rarely exceeding a difference of 0.2°C.

All instruments were calibrated regularly according to manufacturing guidelines. The pH and eh meters were calibrated every morning upon the day of use. The pH was calibrated against pH 7 and pH 4 buffer solutions. Little variation was noted between calibrations for all meters. The cell constant of the EC electrode was calibrated less regularly (approximately every third day) after initial testing showed that daily calibration was not needed.

In the week before departure into the field the electrodes were serviced and prepared for measurement according to the manufacturers instructions. The DO probe was serviced only if this was thought necessary after checking for wear and tear of the Teflon membrane, for oxidation products on the gold electrode and for sufficient electrolyte solution behind the membrane. All probes were prepared for storage according to the manufacturers instructions when not in use.

Between the second expedition to Ranger in April 2000 and the third in August 2000, the DO probe membrane was blocked and partially damaged as a result. It was replaced as a consequence. However, after comparing DO results from the April 2000 expedition with all others, it was clear that this blockage existed prior to the second expedition since all of the measurements from this expedition were consistently lower than all others. Obviously this blockage had not been noticed before entering the field. Therefore, a partial blockage of the membrane in the DO probe resulted in a reduced rate of diffusion through it and, thus, lowered the recorded amount of DO for all samples from the April 2000 expedition.
2.6.2 Alkalinity

The total alkalinity of mine waters was found by titrating the samples in the field, using a 0.01M and 0.116M HCl solution titrant to the methyl orange end point pH (approximately pH 4.5). Titrations were performed by hand, with a burette and beakers. Three titrations were performed on each sample, adjusting sample volumes in accordance with alkalinity, volumes were then averaged for the final result. Both HCl solutions were standardized by manual titration using a 0.6023g/L Na₂CO₃ standard solution, burette and a pH metre (see details of pH metre above) in the laboratory.

Total alkalinity is defined here as Acid Neutralising Capacity (ANC) and calculated from the mass balance relationship, concentration (eq/L) times volume (L) of titrant acid (HCl) equals unknown concentration (eq/L) times volume (L) of bases in solution (mine water). Hence, total alkalinity can be calculated from the titration by the following equation:

\[
\text{Total Alkalinity (eq/L) } [\text{HCO}_3^-] = \frac{M \times V_t}{V_s} \tag{1}
\]

where M is the concentration of the acid titrant in eq/L, Vt is the volume of the titrant used and Vs is the corresponding volume of the sample used. In this thesis all major component concentrations are expressed as meq/L, such that equation [1] becomes:

\[
\text{Total Alkalinity (eq/L) } [\text{HCO}_3^-] = \frac{M \times V_t \times 1000}{V_s} \tag{2}
\]

Since the pH of almost all waters analysed in this study place the waters inside the stability field of HCO₃⁻ for the carbonate equilibria system for natural waters (4.5 ≤ pH ≤ 8.3) and Ca has also been analysed, almost all alkalinity in the RUM waters is due to the HCO₃⁻ anion and thus alkalinity in this study is expressed as meq/L HCO₃⁻ or mM/L HCO₃⁻ (see Langmuir, 1997).

Other species also probably contribute to the total alkalinity including the silicates, phosphates and those others not analysed, such as the organic species. However, concentrations of Si and P in the RUM waters found as the result of analysis in this
study suggest that such species will be of negligible significance compared to the carbonate species, as is suggested elsewhere for natural waters (Hem, 1985) and thus, are considered inconsequential and disregarded hereafter.

Where HCO$_3^-$ concentrations have been expressed as mg/L, the meq/L concentration value has been multiplied by the molecular weight of HCO$_3^-$, taken here as being 61.016.

All the titration equipment was rinsed three times before and after use with milli-Q filtered DIW and sample water, the same procedure as that for the sample bottles detailed above. Note that for the burette, this meant the final rinse before the titration was HCl rather than sample water.

2.6.3 Chemical Analysis

A combination of ion chromatography (IC), inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) were used to identify and quantify the ions in solution within the water samples collected for this research.

The major anions of NO$_3^-$, Cl$^-$, SO$_4^{2-}$, Br$^-$ and F$^-$ were analysed by IC. A Dionex 4000i Ion Chromatograph and a Dionex DX120 Ion Chromatograph were used for the analyses, both using an AS 14A column with a carbonate/bicarbonate eluent and both calibrated using EM Science (USA) Certified Standards. The IC instruments were located at Geoscience Australia (GA), Canberra and the standard error for anions on these systems has been calculated as +/-3%. Detection limits for all major anions are given in Appendix 1.

Waters were separated before IC analysis into categories depending on expected concentrations, so that appropriate dilutions could be performed to bring concentrations within range of laboratory standards. Different standards were run for different waters depending on their respective concentrations. In some circumstances where concentrations of various anions were far greater than others, the sample was run twice with two different standards representing the respective concentrations.
Throughout the analysis of samples by IC from the second and third expeditions a problem existed with the calibration for $F^-$, hence $F^-$ concentrations are considered unreliable for these two expeditions and should be treated with caution for all other samples.

The major cations $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{Na}^+$, $\text{K}^+$ and $\text{Si}$ were analysed by ICP-AES. The instrument used was a Varian MPX Radial ICP-AES, housed at GA laboratories with a calculated standard error of +/-5%. The instrument was calibrated using EM Science (USA) certified standards. Detection limits for the major cations on this instrument are given in Appendix 2. Once again different standards were run for different waters depending on their respective concentrations, where large concentrations of few ions existed the sample was analysed twice with different standards representing the respective concentrations.

Trace elements were analysed by ICP-MS. The instrument used was an ELAN 6000 with an AS90 auto-sampler, housed at the Fresh Water Ecology laboratory at the University of Canberra, except for those samples from the final expedition which were analysed using the Dynamic Reaction Cell ICP-MS, also at the Fresh Water Ecology laboratory at the University of Canberra. The instruments were calibrated using internal standard reference solutions. The standard suite of elements analysed by ICPMS included, in order of molecular weight, $\text{P}$, $\text{Sc}$, $\text{V}$, $\text{Cr}$, $\text{Fe}$, $\text{Mn}$, $\text{Co}$, $\text{Ni}$, $\text{Cu}$, $\text{Zn}$, $\text{Ga}$, $\text{As}$, $\text{Se}$, $\text{Rb}$, $\text{Sr}$, $\text{Y}$, $\text{Zr}$, $\text{Nb}$, $\text{Mo}$, $\text{Ag}$, $\text{Cd}$, $\text{Sn}$, $\text{Sb}$, $\text{Cs}$, $\text{Ba}$, $\text{La}$, $\text{Ce}$, $\text{Hf}$, $\text{Au}$, $\text{Hg}$, $\text{Tl}$, $\text{Pb}$, $\text{Bi}$, $\text{Ra}$, $\text{Th}$ and $\text{U}$. All results are given in Appendix 3.

In all cases, samples were analysed twice to check for consistency in analysis. Some samples had high concentrations of only a few elements and in these cases, samples were re-analysed with greater dilutions to take this into account. At consistent intervals throughout the analysis, internal standards were analysed to monitor accuracy. Detection limits were generally regarded to be of two levels, calculations from peaks that resulted in concentrations of less than 0.5$\mu$g/L were considered to be within background and thus, below detection and those less than 1$\mu$g/L but greater than 0.5$\mu$g/L were treated with caution, although above background.
The major ions, Ca, Mg, Na, K, Si and S were also analysed as part of the ICP-MS element suite, however the results from the other analytical techniques were preferred over ICP-MS for these ions.

2.7 ANALYTICAL METHODS FOR GEOCHEMISTRY

2.7.1 Bulk Geochemistry

Selected samples of waste and LGO material were analysed for major and trace element concentrations using a combination of X-ray Fluorescence (XRF) spectrometry and ICP-MS at the GA Laboratories in Canberra.

All samples were crushed with a hand operated hydraulic press to an approximate gravel-size fraction. They were then dried in an oven at 40°C before being ground to approximately 2μm in a tungsten carbide mill at the Australian National University. Approximately half of this material was then ground in a tungsten carbide mill to a coarse powder. A portion of this material (approximately half) was then separated using a traditional splitting method (pouring the powder onto a sheet of paper so that it formed a pyramid and then splitting the pyramid in half). The selected sub-sample was then ground to the recommended 2μm consistency, weighed and then transported to GA in a clear plastic sample vile. The remaining course powder was used for both a reserve and in some cases for mineralogical analysis by X-ray diffraction.

Unconsolidated waste and LGO material from the stockpiles was prepared for analysis using the same method as that described above, although in most cases initial size reduction by hydraulic press was unnecessary, and an initial split was performed before grinding to reduce the sample size by half. Some samples were small, such as mixed clay samples from platform horizons, in which case the entire sample was used for analysis, except for where small amounts were reserved for mineralogical assessment.
At the GA laboratories, a fused LiBO$_2$/Li$_2$B$_4$O$_7$ disk was created with the sample material and analysed using a Phillips PW2402 4kW XRF sequential spectrometer with a Rh-anode X-ray tube as a radiation source. The instrument was calibrated using international standard reference materials. Elements targeted by XRF analysis included the major components (in oxide form) SiO$_2$, Al$_2$O$_3$, Total Fe, MgO, K$_2$O, CaO, MnO, Na$_2$O, P$_2$O$_5$, SO$_3$, TiO$_2$ and the trace elements Cl, Cr, Cu, F, Ni, Sc, V, Zn and Zr. Detection limits for trace elements analysed in the XRF for geochemistry is given in Appendix 4.

Once analysed by XRF, the fused discs were then crushed and ground into a fine powder using an agate mortar, from which a portion from each sample was separated and then dissolved by addition of a 1:5 HF/HNO$_3$ mixture. Each solution was then heated overnight at 110°C in a Teflon beaker. The sample solutions were then analysed by a Perkin-Elmer ELAN 6000 ICP-MS after appropriate dilutions and internal standards were applied. The trace elements analysed by ICP-MS included Ag, As, Ba, Be, Bi, Cd, Ce, Cs, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, La, Lu, Mo, Nb, Nd, Pb, Pr, Rb, Sm, Sn, Sr, Ta, Tb, Th, U, Y and Yb. However, not all of these trace elements were analysed at all times throughout this research. Detection limits for trace elements analysed in the ICPMS for geochemistry is given in Appendix 5.

2.8 ANALYTICAL METHODS FOR MINERALOGY

2.8.1 Bulk Mineral Identification using X-ray Diffraction

Bulk mineral identification of selected rocks and unconsolidated materials was accomplished using X-ray Diffraction (XRD).

Samples were prepared using the same separation and crushing techniques previously outlined until the point of the final grinding step. That is, samples were ground in a tungsten carbide mill to a coarse powder only and no further. Samples were then transferred to an agate mortar, where they were ground with a pestle and addition of acetone or alcohol, to a consistency of a very fine powder (talc-like). After drying at room temperature, sample powders were then carefully packed into frosted glass/aluminium slide holders to prevent preferred orientation, ready for analysis.
Analyses were performed using a Siemens D-5005 X-ray diffractometer using 0/0 radiation from a Co-anode tube radiation source, and parallel beam optics. Standard scans were run over a 2-0 angle of 4-80° at a scan step of 0.02° every 2 seconds. The sample stage was spun during scans at 10rpm to reduce the effect of any preferred orientation still existing in the sample. Mineral identification was accomplished using EVA, a manufacturer supplied computer program that allows the comparison of the sample’s diffraction pattern characteristics (peak shape, peak intensity, peak 2-0 position) to those of mineral reported in the mineral Powder Diffraction File data book (JCPDS-ICDD, 1993).

2.8.2 Clay Mineral Identification using X-Ray Diffraction

Six samples of suspended sediment collected with syringe filters by EWL Sciences from run-off and leachate from the WWP were analysed here by XRD, the results of which are included in this research, and in an unpublished report to EWL Sciences Pty. Ltd. (Shirtliff, 2001).

A preliminary XRD analysis was carried out on each sample without removing the samples from their corresponding filter papers. For this analysis, the filter papers were fixed directly to a glass slide using a light smear of household Vaseline. Where the path of the x-ray beam was to pass over the sample, the exposed edge of the filter paper was carefully removed with a razer blade so that only the sample was analysed.

After the preliminary investigation revealed dominant clay mineralogy, standard XRD clay mineral identification was undertaken using standard pre-treatments (see below). The removal of samples from the filter papers was achieved by first soaking the filter paper, sample side down, in a tub of ethanol for approximately 10 seconds. Then, using tweezers and a small metal spatular, the sample material was gently rubbed away from the filter paper into the tub of ethanol. The material of each sample was then ground to a very fine powder (talc-like) using an agate mortar and pestle. Ethanol was used during the grinding process to insure no loss of mineral structure due to heat.
The samples were then applied to glass slide mounts as a thick suspension using fine glass pipettes; as described by Moore and Reynolds (1989). This method does not achieve the desired perfect orientation of all clay minerals; however, considering the limited sample size and successful preliminary analyses, it was deemed more than sufficient for this case. Before any further analyses the samples were air dried at room temperature for approximately 2.5h.

As suspected, small silicone fibres from the filter papers remained in the samples after separation procedures. These were clearly identified under a plain light microscope. Samples were analysed by XRD before any pre-treatments to establish base trace patterns that had undergone the same initial preparation procedures as the trace patterns that would be received after treatment. An internal standard of the filter paper was also made for comparison with results. This was achieved by carefully cutting away the remaining exposed edges of all the filter papers and combining them into a single standard XRD sample using the same preparation techniques as above.

The three standard pre-treatments for clay mineral identification by XRD are as follows.

1. Glycolation
The glass slides containing the samples were placed into a desiccator where they were solvated by ethylene glycol vapours at a constant 60°C for at least 24h. Once the treatment was completed, the samples were analysed by XRD. Glycol solvation expands the smectite group clays from peaks of 12.5Å (Na rich) and 15Å (Ca rich) to 17Å. This expansion allows them to be distinguished from chlorite and vermiculite which have unit cell thicknesses close to smectites in normal air dried samples.

2. Heating to 350°C
The samples were heated in an oven to 350°C for approximately 1h and left to cool slowly overnight. Once cooled to room temperature the samples were subjected to another XRD analysis. This treatment collapses vermiculite from 14Å to 10Å, thus allowing it to be distinguished from chlorite, which is not effected by such treatment.
3. Heating to 550°C

The final treatment involved heating the samples in an oven to 550°C for 1h and then leaving them to cool slowly overnight. Another XRD analysis was then undertaken on all the samples. This treatment completely destroys kaolinite, so that it is amorphous to x-rays. The major identifying peaks in the XRD trace of kaolinite overlay important chlorite reflections, such that this treatment differentiates them.

All XRD analyses were accomplished using the same diffractometer and software as described above (section 2.8.1), except that scans were run over a shortened 2-θ angle of 2-40°, the area where characteristic clay peaks are concentrated. Also other waste and LGO stockpile samples have been analysed using this pre-treatment technique to identify clay minerals within the samples.

2.8.3 Mineral Identification Relationships using Plain Polarised Transmitted and Reflected Light Microscopy

Plain light and reflected light microscopy was used on thin sections and polished sections of waste and LGO rock samples to identify major mineralogy and characterise mineralogical relationships. The primary reference texts used for this work included Shelley, (1995), MacKenzie et al (1995), MacKenzie and Adams (1994), and Deer et al (1992). A bifocal polarizing light microscope with reflected light capabilities was used for mineral identification and relationship characterisation.

Thin sections were prepared by cutting small blocks from selected areas within rocks with a diamond blade bench saw. Blocks that showed signs of breaking apart were then dried for approximately 12h at 40°C in an oven and then impregnated with an epoxy resin in a vacuum chamber. The impregnated samples were left to solidify (approximately 48h) before being cut to section size with a diamond saw and then glued to the glass section slide. After drying at room temperature the samples were then cut to approximately 50μm and then sanded to this thickness using the birefringence of quartz as a thickness measure. Due to the possibility of using samples under the analysis unit of the Scanning Electron Microscope, no slide covers were applied to the thin sections.
For opaque mineral identification under plain light, (i.e. sulfides etc), selected sections were polished with a 3 and 1μm diamond paste on a Kent Polisher. For those sections that were to be used for plain polarizing microscopy only, sections were further cut-polished to 30μm, the recommended standard thickness for mineral identification with plain transmitted light microscopy (MacKenzie and Adams, 1994).

Some sulfide samples were not made into thin sections, but rather into polished discs. The discs were made by placing the selected sample into a cast (metal disc), filling the cast with epoxy resin and impregnating the sample in a vacuum chamber. The discs were then polished as previously explained.

2.8.4 Mineral Identification and Mineral Chemistry Using Scanning Electron Microscopy and Energy Dispersive X-ray

Scanning Electron Microscopy (SEM) and Electron Microprobe Analysis (EMPA) was used on thin sections and polished sections of waste and LGO rock samples for mineral identification and mineral chemistry. Thin section preparation was as previously described. A GEOL JSM6400 with Oxford ISIS EDXA and ATW window (sensitive down to boron), including quantitative and qualitative element mapping capabilities housed at the Electron Microscopy Facility at the Australian National University’s Research School of Biological Sciences was used for the analysis. The instrument was calibrated before each session specifically for uranium, aside from its regular calibration for major rock forming mineral chemistry. ImageSlave 1024 x 768 slow-scan image acquisition to networked PC was used for all microphotographs.
2.9 CALCULATIONS AND CONVERSIONS

2.9.1 Bicarbonate Calculations for Precipitation Samples

For all rainwater samples bicarbonate (HCO$_3^-$) concentrations were calculated directly from pH using the following equilibrium expression for pure rainwater in equilibrium with the atmosphere (all equations and theory is derived from Stumm and Morgan, 1996);

$$[\text{HCO}_3^-] = \frac{(K_1/\text{[H}^+\text{]}_\text{a})}{\text{[H}_2\text{CO}_3^*]}$$ \[1\]

Considering the equilibrium expression for total dissolved CO$_2$, [H$_2$CO$_3^*$],

$$[\text{H}_2\text{CO}_3^*] = K_H \cdot P_{\text{CO}_2}$$ \[2\]

Equation [1] becomes

$$[\text{HCO}_3^-] = P_{\text{CO}_2} K_H K_1 [\text{H}^+]^{-1}$$ \[3\]

Equation [3] is converted to the logarithmic expression to solve using the measured pH, the logarithm of $K_H$, p$K_H = 1.5$, the logarithm of $K_1$, p$K_1 = 6.3$, the known partial pressure of CO$_2$ in the atmosphere (p$CO_2 = 3.3 \times 10^{-9}$ atm) and a temperature of 30°C, a temperature typical of the wet season at Jabiru. These values are exactly those used by Noller et al (1990) so that the Noller et al (1990) data remains comparable with the data here.

2.9.2 Calculating the Concentration of H$^+$ in Solution Using pH

The concentration of free H$^+$ in all rainfall samples (and other water where necessary) was calculated from the anti-log of pH, so that

$$[\text{H}^+] = 10^{\text{pH}}$$ \[4\]
Rainwaters are not only extremely dilute solutions under standard state conditions, but as was found in this research, in the Northern Territory of Australia free $H^+$ can be one of the dominant components quantitatively (refer to chapter 5). The official unit of concentration for calculations ($H^+$) is moles per cubic decimetre, where 1 cubic decimetre is equal to 1L. Hence the unit of concentration can be interpreted as mol/L.

2.9.3 Rainfall Volume Conversions

All rainfall volumes collected in this research were converted to mm, the standard expression of measure for the amount of rainfall that has fallen over a specified period in a given location (Australian Bureau of Meteorology [ABM]). The mm measurement refers to the perpendicular height in mm for the body of water that would have accumulated on the ground after a rainfall event if the ground were perfectly flat, impervious and able to contain all of the water that had fallen.

2.10 STRUCTURAL MAPPING OF THE RUM STOCKPILE SYSTEM

2.10.1 Platform Horizon Map

The Platform Horizon Map was made by tracing the outline of every surface platform for every stockpile for every year of mining using annual aerial and satellite photographs of the mine and an advanced computer drawing package. Annual photographs were available until 1995 only, when photographs of the mine began being taken less regularly. Available photographs after 1995 were those of 1997, 1999 and 2003.

As each photograph represents a single moment in time, some information may be lost between each photograph. However, the pace of stockpile construction was such that, until 1999, observations of each photograph revealed only small relative increments of change from year to year. After 1999 however, some information was lost due to the three year gap between the 1999 and 2003 photographs.
During construction of the map attention had to be paid to both the construction of stockpiles and the de-construction (removal) of stockpiles. In some areas, for instance the eastern CWP, entire sections of stockpile were dismantled and hence, the platforms polygons that had been created on the map for previous year’s construction had to be deleted or changed to represent their changed outline. Thus, the end result was an accurate representation of exactly what lay beneath the 2003 surface of the RUM waste and LGO stockpile system. The estimated geographical ground error from aerial/satellite photograph to corresponding polygon on the map is 15m for all years until 1999, where it increased to 25m.

2.10.2 Location Map of Highly Weathered Material

The plan view map of the location of highly weathered material within the RUM waste and LGO stockpiles was constructed in almost the same way as the Platform Horizon Map. The difference was that, in this case, aerial and satellite photographic evidence was cross referenced with information regarding the material being mined at the time of the photograph and examination of a limited number of Pit cross-sections showing Pit outlines for certain years. Observations made during the time of this research (November/December 1999 to April/May 2002), were also taken into account and helped to find some of the information missed during that period due to a lack of photography. Geographical errors were the same as those for the Platform Horizon Map.

2.10.3 Ramp Slope Direction Map

The Ramp Slope Direction Map was constructed using exactly the same technique as that used for the Platform Horizon Map except that rather than ramp outlines, only ramp slope directions were recorded by drawing single arrows, the stem of which represented the length of the ramp. Geographical errors were the same as those for the Platform Horizon Map.
2.10.4 Cross-sections

All platform cross-sections were constructed by projecting from the Platform Horizon Map using Adobe Illustrator and then using three dimensional digital elevation models (DEMs) to estimate height. The DEMs were generated after Soole (1998) by the CSIRO Minesite Rehabilitation Research Program in 1998. Aerial and satellite images were used for cross-referencing.

The cross-sections showing the location of highly weathered material were the same as those cross-sections explained above but with the areas occupied by the highly weathered material delineated. Aerial/satellite photographs and personal observations were used for cross-referencing.

2.11 DATA QUALITY

2.11.1 Possible Cl⁻ contamination of 2000 Dry Season Water Samples by re-acidification at the laboratory

ICP-MS results from the August 2000 water samples showed a consistently higher concentration of Cl⁻. The IC results do not show such a contamination, and since the Cl⁻ value from IC has been used here, there is no effect on any Cl⁻ value in this research or in any analysis involving Cl⁻.

ICP-MS analysis of two samples already analysed by IC, and hence, not acidified, did not have any Cl⁻ spike. Two of the ICP-MS samples run on the IC confirmed that the ICP-MS samples had been acidified with HNO₃. The only conceivable explanation for the high Cl⁻ concentrations is that the ICP-MS samples were re-acidified with HCl in the laboratory, possibly because they may have been added to a larger run of samples that had yet to be acidified.

Fortunately Cl⁻ does not have a molecular mass (isotopes 35 and 37) that interferes with any other cations in the ICP-MS that were considered important in this study. Hence, the results were still used in further analyses.
2.11.2 Analysis of Blanks

A series of blanks (milli-Q filtered DIW) were used to test various possibilities of contamination within all water collection, transport and analysis processes. Not all blanks underwent the same procedures as the water and rainfall samples; some blanks were not filtered and some were not filtered or acidified to test the filtering process through the portable filter unit. In the analysis the rainwater was treated separately to the mine water samples. Very little potential contamination was observed in the analysis of the blanks and when contamination was found, it was inconsistent and insignificant in almost all circumstances.

In the major elements (ICP-AES and IC), the most significant potential contamination was a small amount of Na throughout all expeditions except that of the EOWS 1999/2000 samples, and a small amount of K throughout all expeditions. The worst case scenario for Na (i.e. the highest result in the blanks relative to the lowest concentration found in a water sample within the corresponding expedition series) amounted to a potential 7.8% contamination. A similar worst case scenario existed for K (7%). This potential contamination decreased dramatically if other water samples were used for comparison such that worst case scenarios were considered highly unlikely.

A small amount of Ca was found in one blank (RW309), but this represented a worst case scenario of only 0.3%. A small amount of Mg existed in all of the EOWS 1999/2000 samples, but this only amounted to a worst case scenario of 2%. A small amount of SO$_4$ existed in sample RW201, but this represented a worst case scenario of only 1.8% potential contamination.

Although small signs of various trace elements did exist in the blanks (1-2μg/L maximum), only Zn showed consistency. A very small amount of Y (4-7μg/L) seemed to exist in blanks from the SOWS 2000/2001 samples, however the concentrations were insignificant. Fe also was a potential contaminant, however Fe is difficult to analyse (due to its changing oxidation state) and the results were not consistent.
The filtering process definitely contaminated the samples with Zn\(^{2+}\) since only blanks that were filtered contained it. Communication with ECOWISE Pty. Ltd. Laboratories in Canberra, Australia, indicated that the source of this contamination was probably the black rubber seal in the filtration unit. ECOWISE Laboratories no longer use syringes with black rubber seals for this very reason (pers. Comm. ECOWISE Labs, 2002). The magnitude of the contamination ranged from 4-9\(\mu\)g/L, which is small in most rainfall samples, except in sample RW322 (a rainwater sample) where it represented the entire concentration of Zn. A correction of 6.5\(\mu\)g/L (on average) was made to all Zn results in the rainfall analysis. There was no other obvious contamination from the filtering process.

Sample RW317 was contaminated with spurious amounts of U. Results revealed that it contained 90\(\mu\)g/L of U, the next closest concentration being 12\(\mu\)g/L in sample RW321. Analysis of blanks revealed that this contamination was due to a failure of the ICPMS flushing mechanism to adequately flush U from the plasma sample delivery tubes after high U-bearing lead samples had been analysed. Thus, dilute samples analysed after samples containing extremely high amounts of U (19,704\(\mu\)g/L in the case of the lead sample analysed before RW317), were susceptible to U contamination. This sample was corrected by reducing the U concentration to zero, the concentration of the other sample from the same location (i.e. Jabiluka). No adjustment was made to the rainwater samples from the mine due to the possibility that mine site locations may have real contamination from dust.

2.12 NEW ANALYTICAL TECHNIQUES CREATED SPECIFICALLY FOR THIS RESEARCH.

2.12.1 The Total Ion Cumulative Concentration (TICC) Bar

The TICC bar (Figure 5.2a) is a new chart created specifically for this research. It was developed to compare the differences in ion load in rainfall between different parts of the wet season, regardless of how many samples of each part of the season were collected or how much rain each season represented. The calculation was based on the volume weighted mean (VWM) of the sum of total ion concentrations for each sample
within each seasonal group and expressed as a percentage of the VWM for all samples as follows:

\[
\left( \frac{\sum_i [V \times TIC]_A}{\sum_i [V \times TIC]_A + (\sum_i [V \times TIC]_B)} \right) \times 100
\]  

[5]

where \( V = \) volume, \( TIC = \) total ion concentration and \( A \) and \( B \) are simply notations representing respective groups. The bar (chart) is divided into percent, so that a full bar length represents 100%. Equation [5] provides the percentage for group \( A \), such that a simple subtraction from 100 will give the percentage for group \( B \). If more groups were represented (only the SOWS and EOWS rains are the groups used for the TICC bar in Figure 5.2a), then each group calculation would be made by substituting it in the numerator in equation [5] and adding it to the denominator.

The TICC bar can be conceptualised in real terms according to equation [5] as follows; if all of the rainwater samples collected were poured into two containers, one for SOWS rains (group \( A \)) and one for EOWS rains (group \( B \)), and then an equal proportion of solution from each container was poured into another container to make a single sample, the TICC bar shows what proportion of the total ion concentration in that sample is derived from each of the two seasons (or groups \( A \) and \( B \)).

2.12.2 The Diamond Compass Chart

The Diamond Compass charts (Figures 5.2a and 5.2b) were designed and developed specifically for this research to analyse major element rainfall chemistry considering wind direction and speed and thus, the potential source regions for ions constituting the chemistry. They were also used in this study to better highlight the most important differences in major element chemistry between the two groups of rainfall collections, the SOWS rains and the EOWS rains. The traditional ternary diagram that has been used previously in rainfall chemistry for the Northern Territory (see Chapter 5) was thought to be inadequate in representations of such differences. The diamond compass also could be used for other studies other than rainfall chemistry.

In Figures 5.2a and 5.2b the Diamond Compass charts show the relative concentrations of the major cations (\( Na^+ \), \( Ca^{2+} \), \( Mg^{2+} \) and \( K^+ \)), as well as the pH of each bulk precipitation sample. The relative percentage of each of the cations is
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represented by the position of each corresponding side of the central rectangle along the corresponding axis within the circle for each cation. Thus, the relative concentration of the ion labelled on the right hand side of the circle is represented by the position of the right hand side of the rectangle (a vertical line) along the right hand side of the horizontal central axis of the circle (X axis and representing a radius in length).

The centre of the circle represents 0% for each cation and the point at which each radial axis (along the X and Y axis) meets the inner circle represents 50% for each cation, although this value could have been be changed to 100% if needed. Thus, the shape and position of the rectangle within the compass relative to the central anchor (the centre of the circle) represents an accurate visual interpretation of the relative concentrations of the four chemical components. Multiple rectangles could be added to each individual chart so that comparisons could be made within each chart between different rainfall compositions. In the charts constructed for this analysis (Figures 5.2a and 5.2b) average seawater composition rectangles (see Chapter 5 for source of data) were added so that the rainfall could be assessed for a potential oceanic source.

Due to the geometrical and mathematical principles used in the charts, each corner of the rectangle has a position in space relative to the anchor and the two axes defining the quarter of the circle within which it lies. Since each axis represents the relative concentration of the corresponding major cation, the position of each corner of the rectangle represents the concentration ratio of the adjacent cations. It is measured precisely by the point at which a line extending from the anchor, through the rectangle corner, meets the scale on each side of the diamond. So, important ratios such as the Ca/Na ratio used in rainfall studies around the world (see Chapter 5) can be shown in the same graphical space as the relative ion concentrations.

Combined with these chemical parameters, the Diamond Compass charts also show the direction and speed of winds measured during the days responsible for the rainfall collected in each sample. Therefore, the concentric circles in the charts represent a compass. Wind direction and to a lesser extent wind speed, during but particularly directly before a rainfall event, gives an initial indication of meteorological effects and potential direct source regions for the rainfall chemistry observed. The compass
dial is a logarithmic scale running anticlockwise, in this case representing pH, so that the base of the dial is precisely neutral (pH 7) and the top of the dial is pH 3 or pH 11. This dial has been ‘filled’ with a colour according to the measured pH of the solution, red towards the acid side or blue towards the alkaline side. The type of ‘fill’ in a dial (increasing or ‘filling up’ to the top) is meant to give the impression of increasing free H\(^+\) ions on the acidic side or increasing free OH\(^-\) ions on the alkaline side.

2.13 ANALYSIS OF THE HISTORICAL MINE WATER DATABASE AT RANGER URANIUM MINE: DATA ACQUISITION AND DATA SELECTION CRITERIA

All data for the analysis of the historical mine water database at RUM was acquired from the ERA LIMS database for water quality monitoring. Data has been examined from other studies external to this, but are only discussed in context and not added to the fundamental mine database, since there were already far too many potential errors due to differences in analytical and sampling techniques in the mine water monitoring data to allow for additional error from differences in external studies.

The information from the LIMS database that has been used in this study included the measurement of pH and U. Non-chemical parameters that were important included the date of the day that the sample was collected and the sampling location. All data collected from the LIMS database represent samples of mine water collected from the surface.

Since one of the goals of this research was to acquire knowledge of the seepage chemistry of the waste rock stockpiles (see Chapter 1), an effort was made to ensure that the water chemistry under investigation was as closely related to the stockpiles as possible. This meant that not all Ranger Mine water quality monitoring data was included in this study, including the two major retention ponds, Retention Pond No. 1 (RP1) and Retention Pond No. 2 (RP2). RP1 is approximately 1km downstream of the nearest waste and low grade ore stockpile in the Coonjimba Creek catchment. At such a distance, too many other influences could have influenced its chemistry (e.g., Overall, 2002, Overall et al, 2002). Also, the potential dilution factor was the highest of the ponds considered for this study, which is one of the reasons why it is used as a
release pond by the mine. Thus, the chemistry was considered to be far too removed from stockpile seepage to be included in this analysis.

RP2 is Ranger Mine's central retention pond, receiving water from all of site, including as much as possible of all of the seepage and leachate collected from the waste and LGO stockpiles. However, RP2 also receives drainage from a part of the ore stockpiles, a part of the sulfur stockpile, and the general operations area (Speechly, 2006). RP2 is also subject to an intensive water management regime where water is pumped into and out of RP2 from/to Pit#3 and Sump98 (when operational) throughout much of the year (Speechly, 2006). Thus, for the same reason as that of RP1, i.e. too many unknown variables, RP2 water was discarded from the analysis.
CHAPTER 3

DETERMINING THE STRUCTURE OF THE RANGER URANIUM MINE WASTE ROCK AND LOW GRADE ORE STOCKPILES BY FIELD OBSERVATION AND ITS IMPLICATIONS FOR STOCKPILE HYDROLOGY

3.1 INTRODUCTION

Fundamentally, the mineralogical and chemical composition of the material within a stockpile determines the chemical characteristics of the water passing through it (Chapter 4). However, this statement is an oversimplification, because the hydrological properties of the stockpile actually determine which material the water comes in contact with, how much material it comes in contact with, and for how long. Thus, hydrology also influences the chemical composition of water emanating from stockpiles including the concentration of solutes in the water and changes in water chemistry over time.

As with any material, the hydrological properties of a stockpile are controlled by its structure and fabric. However, publicly available information regarding detailed studies of the internal structure and fabric of large scale waste rock stockpile systems is limited. Valuable information can be found in collections of case studies incorporated by Smith et al. (1995) and Morin et al. (1991) but most are associated with coal mine spoils, due to their typical association with acid mine drainage (AMD), and coal mine stockpiles are potentially very different structurally to the RUM stockpiles.

Whiting (1981) was one of the first to attempt to model general waste rock stockpile structures and how they might affect hydrological flow through the piles. Some general structural models can also be found in Morin et al. (1991) and Smith et al. (1995). However, all of these generalised models are conceptualised from a limited number of observations and there has certainly been no published attempt to actually
map in detail the internal structures of a stockpile. One reason for this may be that, once built, it is extremely difficult to access such information from a stockpile short of dismantling it (Smith et al., 1995). Even the insertion of instruments to measure hydrological properties involves changing the hydrological characteristics of the stockpile within the direct vicinity of the instrument and therefore making the data none representative of the stockpile, as occurred previously at RUM (pers. com. Kuo, 2002, Kuo, 1996).

It is extremely difficult to acquire and set up hydrological instrumentation within the stockpiles of a working mine site, particularly if the researchers are not going to be based on site for the full term of the experiment (often several years). Due to changes in planning, changes in cut-off grades and the like, it is not uncommon for such experiments to be either destroyed or at least disturbed so much that the data becomes relatively useless. However, active stockpiles have a distinct advantage; being a source for construction material and changes in plan, mean that waste and low grade ore stockpiles are regularly excavated and redistributed. This allows for direct observation of the internal structures and fabric of the stockpiles, and at times water movement in certain areas of the stockpiles. Importantly, active stockpiles also allow for observations of exactly how the structures and fabric were created as new stockpiles are built and old stockpiles are added to.

It is the general hypothesis of this chapter that simple observations of stockpile construction and excavations into the stockpiles under active stockpile conditions can be used to develop a relatively sophisticated working model of stockpile structure and fabric, and in doing so a conceptual mode of stockpile hydrology. This is despite the fact that complete de-construction of stockpiles and hence complete observations of the internals of a stockpile, is never obtained. This means that there is no need to wait for mine closure, new dam construction, or large scale rehabilitation works that require large sources of rock and hence complete stockpile de-construction. The reason that this is believed to be possible is because construction methods or from a geological perspective, formational processes, are few and are repeated throughout. Thus structure, fabric and hydrological properties seen in a small excavation can be inferred to exist in other regions of the stockpile where the same materials and formational processes (construction methods) exist. In other words, despite their
inherent complexity it is the hypothesis of this thesis that there is pattern in stockpile fabric.

This chapter reports on the findings of these observational investigations and provides a discussion on the implications the findings have for waste and LGO stockpile hydrology at RUM. Data from CSIRO (Soole, 1998) was utilised and combined with the observations above to map and section the major internal structures within RUM stockpile system as of and up until 2000 and 2002, which will be one of the first for an active free-standing stockpile system. All the methodology for this particular study is described in the methods chapter (Chapter 2). A total of seven excavations were examined during this study, these have been named E1 through to E7, and referenced as such throughout this chapter. The locations of these excavation sites are shown in Figure 2.9 (Chapter 2).

3.2 DEFINING AND CHARACTERISING RUM WASTE ROCK STOCKPILE STRUCTURE AND FABRIC

Apart from the prepared stockpile base, sometimes referred to as capping, the waste rock stockpiles of RUM were found to consist of a series of three repeating internal structural formations directly related to the stockpile construction techniques employed at the mine. These formations were superimposed on a less defined and more localised fabric related to geology. Burial related stress and/or age related settling and weathering processes also play a substantial role in the overall stockpile structure at RUM. Figure 3.1 summarises these findings in a single representative cross-section. Figure 3.1 is for display purposes only, and does not represent any actual cross-section through the piles; thus, the vertical order within the stockpiles does not necessarily follow that shown in the cross-section. The cross-section covers at least 2 single lifts and so therefore represents a minimum of approximately 10m in height. Since the repeating structural formations have not been specifically described and named elsewhere as such, they are referred to by nomenclature related to their purpose within stockpile construction methodology, Extension Lens Layers, Lift Mound Layers and Platform/ramp Horizons. All of the structures observed are described separately below.
3.2.1 The Stockpile Base

The clay base or ‘capping’ is a low permeability barrier at the bottom of the stockpile to protect the groundwater from the infiltration of stockpile seepage. At Ranger the base is made from waste-grade clay (grade 1) from around the surface of the deposit (personal communication, Hughes, 2002) and is an extensive feature of the Central Waste Rock Pile (CWP) and Northern Waste Rock Pile (NWP) (see Figure 2.9, Chapter 2), although aerial photography suggests that other stockpile bases may not be of the same quality.

3.2.2 Lift Mound Layers

Lift mounds are mounds of waste material dumped by mine haulage vehicles across the extent of a stockpile platform (see 3.2.4 below) in order to vertically extend or ‘lift’ the stockpile to a higher level. The process is shown in Figure 3.2(c). The actual dumping technique itself is often referred to in mining literature as ‘free dumping’ (Smith et al., 1995), or ‘paddock dumping’ when the technique is used over a large area. Figure 3.2(a) is a classic example of extensive ‘paddock dumping’ on the North Central Waste rock Pile (NCWP) at Ranger, observed in April 2002.

In two dimensions on a cross-sectional view, lift mounds are portrayed as a series of rough half-circles, flat side down, aligned in a single layer. The most ideal example of this observed at Ranger was in August 2000 at E1, captured in the photograph of Figure 3.2(b). Also shown in the photograph of Figure 3.2(b) is the associated infilling structure between each lift mound, completing a full Lift Mound Layer. Again, this is a direct consequence of the construction technique and is shown in Figure 3.2(c). When the extent of the lift is completely filled by the ‘paddock dumping’, a bulldozer proceeds to flatten the tops of the lift mounds to create a surface from which a working platform can be created or from which a further lift can proceed. In this process, in which more material is introduced as needed, material is pushed into the gaps between the mounds. Conceptually, in three dimensions, this not only flattens the tops of the lift mound structures but also creates a corresponding structure, in the approximate form of an inverted pyramid with concave walls, each of which interlock four lift mounds together. When repeated over the entire lift, both the mounds and pyramids form a complete layer of unique fabric.
Recently dumped, less consolidated, less compressed by less load and less weathered material from deeper within the mine

SURFACE PLATFORM HORIZON

LIFT MOUND LAYER

PLATFORM HORIZON

EXTENSION LENS LAYER

'CAPPING' - CLAY BASE

Older, more consolidated, more compressed by greater loads and more pre-weathered material from shallower depths within the mine

YOUNGING DIRECTION

Figure 3.1: Idealised cross-section of the Ranger Uranium Mine waste-rock stockpiles revealing the internal geological structures present within them. Apart from the base capping, there are three major structures, Extension Lens Layers, Lift Mound Layers and Platform/Ramp Horizons. Super-imposed on this are two other general structural features affecting fabric. The first is a greater amount of weathered material towards the base due to the inverse relationship the stockpile construction has with mining the weathered deposit. The second is a greater amount of compacted and consolidated material towards the base due to the younging direction and increased load. Note also the difference between the draping pattern of the Platform Horizon at the surface and the more defined platform at depth. See text for details.
Figure 3.2. Lift Mound Layers: (A) 'Lifting' of the NCWP in April 2002 using 'paddock dumping' technique. (B) 2-D expression of Lift Mound Layer in wall of excavation into temporary pile on the eastern edge of the WWP. Note: Automobile is 1.78m high (C) Cartoon showing how Lift Mound Layers are constructed by first dumping over large areas (1) and then grading and smoothing over the top of the dumped piles (Lift Mounds) to create a surface that is suitable for haulage traffic. Note the interlocked semi-circle/inverted triangle pattern of the layer - compare to excavation wall in B.
A similar structure also occurs even if such ‘flattening’ does not happen, when pre-existing lift mounds are simply covered by extension lenses (see 3.2.3) from stock pile extension processes occurring from an elevated level. The two dimensional observations shown in Figure 3.2(b) confirm that this is the case. Although lift mounds with flattened tops are not actually present in the photograph, lift mounds can be seen interlocked by inverted triangles with two concave sides, the two dimensional equivalent of the pyramid structure described above. Obviously the two-dimension expression of the Lift Mound Layer portrayed in an excavation wall is reliant upon the precise location of the section made by the excavation; that is, whether, it slices through the centre or edge of each inverted triangle.

Observations of fresh lift mounds did not reveal any substantial sorting of material. One would expect some sorting to occur in the truck during haulage, with fines being shaken to the bottom of the load. This then would translate theoretically into some of these fines being concentrated at the end of the dump and thus, on top of the mound. This seems to have occurred to some degree in some of the loads inspected on the NWP; however, its significance and extent is not known.

3.2.3 Extension Lens Layers

Extension lenses are discontinuous, sub-vertical to more gently sloping lenses (30-40 degrees from horizontal) of material observed in stockpile excavations. They are formed by dozers pushing dumped mounds of material over the edges of stockpile platforms in the process of horizontally extending the pile at a particular level. The process responsible for extension lenses is referred to as ‘push dumping’ (Morin et al., 1991). This technique and thus, the extension lenses, are also responsible for the angle of the slope of the external stockpile walls, referred to as the “angle-of-repose slope” (Smith et al., 1995). The cartoon in Figure 3.3(d) demonstrates how these lenses are created in the construction process. Figure 3.3(d) also shows how extension lenses relate spatially to the Lift Mound Layer, and how the Extension Lens Layer structure may have a vertical extent far greater than a single Lift Mound Layer.
Once again, how extension lenses are portrayed in excavation walls depends upon the exact location of the excavation section. If parallel to the direction of stockpile extension, then the two-dimensional portrayal is of sub-vertical layers as was observed in numerous excavations in the RUM waste rock stockpiles shown in Figure 3.3(a-c). However, if the excavation section is perpendicular to the direction of stockpile extension, then the two-dimensional representation seen in the excavation walls will be of stacked horizontal layers. More gently sloped layers will be the result of sections at angles between these two extremes.

In three dimensions the layers do not necessarily have a continuous lithology in any one direction due to ‘event lenses’. In theory, the width of each individual lens is limited by the width of the dozer shovel, which is thus the width of each ‘fall event’ of material over the edge of the stockpile. However, since similar rock types are often piled together near the extension site, a simple consequence of mine geology, the lenses may appear to extend in width until a change in geology is reached. Figure 3.4 shows ‘event lenses’ on the northern side of the CWP.

The thickness and length of the extension lenses should be related. For example, the greater the length of the slope, the more surface area the material has to spread over and hence, the thinner the lens will be (depicted in cartoon No. 2. of Figure 3.3d). However, the thickness and length of extension layers also depends upon the amount of material that is pushed over the edge in each single event.
Figure 3.3: Extension Lenses. (A) 2-D expression of Extension Lenses in a CWP excavation wall, sloping from top right to bottom left of photograph. (B) Extension Lenses in a NCWP excavation (middle layer - top left to bottom right) and (C) a SCWP excavation (sloping from top left to bottom right). Hue and saturation have been altered in both B and C photos to highlight the lenses. (D) How Extension Lense Layers are created during stockpile construction (see text for more detail).

Note: vertical height of excavation wall is approximately 5.5m
Field tests by Nichols (Morin et al., 1991) showed that push dumping sorts the dumped material in the following way:

1. coarse particles are separated to an extent and collect at the bottom of the slope;
2. approximately 40% of the largest particle sizes roll beyond the toe of the slope;
3. fines are not segregated at the top of the slope;
4. most material collects along the upper part of the slope due to friction; and
5. many of the coarse fragments get caught with the fine materials at the top of the slope.

The results of the field tests by Nichols are significant because they show that push dumping results in much less sorting than end dumping, another popular stockpile construction technique where the material is dumped from the truck directly over the edge of the pile. End dumping results in some 75% of the larger material coming to rest beyond the toe of the slope because of the momentum gained by the fall from the truck to the slope. The results of the Nichols field tests also imply there is less large void space availability in the RUM stockpiles in comparison to other case studies around the world (for instance those in Smith et al., 1995); observations of excavation profiles at RUM suggest that this is the case. However, large rocks still congregate to some degree and at least for certain rock types (see 3.2.5), at the toe of extension lenses which may lead to an associated increase in large voids at these locations.
3.2.4 Platform/ramp Horizons

Platform/ramp horizons are thin, somewhat compacted layers of clay to gravel size material formed by dozers, and in rare circumstances, followed by crusher/rollers, smoothing out and compacting material at the surface of the stockpiles. The surfaces have been described previously as stony/gravely pavements with vesicular crusts (Fitzpatrick and Milnes, 1989), a description that matches observations made during this research. However, in areas of heavy vehicle traffic, these platforms have less loose gravel at the surface, particularly in areas where weathered material is being dumped resulting in more clay along the path of the mine vehicles. In most cases, directly beneath the relatively loose gravel, gravel and stone are firmly embedded within a hard fine grained matrix of silt and clay, the amount of the latter largely depending upon the type of material being dumped in the area. Rain splash probably helps to create the fine surface crust (Fitzpatrick and Milnes, 1989).

The purpose of creating the platforms is to create a level working area on, and roads to, the stockpiles that are suitable for mine dump truck traffic and hence, the continuation of waste distribution to the stockpile. Although Figures 3.2(c) and 3.3(d) are primarily showing how Lift Mound Layers and Extension Lenses are created during stockpile construction respectively, they also show how the platforms are formed during these processes.

The compacted surface of the platform generally consists of the existing material beneath it, but at RUM, it is sometimes supplemented by pebble to silt sized crushed rock, specifically made from waste rock for road base purposes. Figure 3.5(a) shows an example of platforms and ramps on the eastern side of the CWP in 2002 and Figure 3.5(b) shows the first platform of an eastern extension of the NCWP, also taken in 2002.

In the wall of excavations the Platform Horizon is almost always a thin continuous, relatively horizontal layer, often only 3 to 10cm thick, separating the more substantial layers of Lift Mounds and Extension Lenses. In some circumstances, the fine-grained material has migrated further down into the more unconsolidated layers beneath the surface in a draping curtain-like pattern, making the effective platform structure much
thicker. This is shown in the surface horizon of the idealised profile in Figure 3.1 and in the upper platform of the excavation shown in the photograph of Figure 3.5(c). This draping platform pattern was only observed at RUM where the underlying layer was relatively porous with an extremely inconsistent size fraction. A logical conclusion is that such a layer is a pre-requisite for the draping platform pattern, since it allows for material being compacted above to be pushed into empty pore spaces.

Figure 3.5(c) shows two types of platform structures in the one excavation wall at site E6 in the SCWP. At the top of the E6 profile is an example of the draping platform structure over a porous layer. Beneath the porous layer is another, older platform structure, sitting on a well compacted/consolidated Extension Lens Layer (see 3.2.3). This older platform represents an abrupt change in structure from relatively porous to relatively non-porous fabric. The actual platform itself is only about 5cm thick and can only just be seen in this photograph. This platform is outlined, along with all of the features of the profile, in Figure 3.5(d) and a closer view can be seen in the image of Figure 3.3(c).

Figure 3.5(e) shows an excavation into the NCWP at site E3 where the platform structure has been thickened by an additional layer of material placed over the original platform. In this case, the additional material is easily distinguished from the original platform since the additional material is highly weathered material from the weathering profile over the Ranger deposit, whereas the material beneath is darker, 'fresher' rock. Figure 3.5(f) shows a similar circumstance of a more recent platform horizon on top of an old one at site E5 in the SCWP.

In three dimensions, the platform horizons obviously cover large areas equivalent to the size of the original working platform for which they represent, such as those shown in Figures 3.5(a) and 3.5(b). Ramp Horizon representation in two dimensions would probably be similar to the Platform Horizons, except Ramp Horizons would vary from horizontal depending on the angle of the excavation section to the sloping ramp structure.
Another significant feature of the platforms at the surface of the Ranger stockpiles is the existence of claypans. These claypans have developed in relatively shallow depressions of various sizes (as small as 30cm and as large as 20m) present on the platform surface by the entrapment of local run-off and the fine particulate matter transported by run-off. Small claypans are evident on the platform in the photograph of Figure 3.5(b). However, a larger example of a claypan on the surface of the WWP in April 2002 is given in Figure 3.6(a).

There is evidence at Ranger that these claypans survive the burial process and thus, become an added feature of Platform Horizons. Figure 3.6(b) depicts part of a claypan that was found in the same excavation as Figures 3.3(c) and 3.5(c) at site E6, Figure 3.6(c) is a close-up image of the claypan surface.

There are two other types of platforms that are only relevant to the current surfaces of the RUM waste and LGO stockpiles, not being present as internal platform horizons. The first of these platforms is the manufactured run-off surfaces of the current working platforms on the CWP and the WWP. In late 2001, the CWP surface (see Figure 3.6d) was crushed to an even finer grade than usual to further reduce the infiltration of rainwater into the stockpile. The WWP surface was also manufactured to increase run-off and direct run-off into a channel built through the centre of the stockpile surface, although this surface is far from being as compacted as that of the CWP. The channel and surrounding WWP platform are shown in the photograph of Figure 3.6(e).

The second alternative platform design can be seen on the current surface of the SWP (see Figure 3.6f). Here the platform has been ripped to form a surface not unlike a ploughed field and for the same purpose, to allow for water to infiltrate more easily and allow plant roots to access water during tree planting exercises. Examination of annual aerial and satellite photography of RUM reveals that this type of platform is rare within the internal structure of the Ranger waste and LGO stockpiles.
Figure 3.5: Platform/Ramp Structures. (A) Platforms and Ramps on the eastern side of the CWP in 2002. (B) Platform on a new extension of the NCWP to the east in 2002. (C) Stockpile profile showing two different platform structures, a draping platform at the surface and a thin platform in the middle of the profile. The various features have been outlined in the trace of the profile presented in (D). See text for further details. (E) Clear platform made from additional material different from the layer beneath, NCWP, March/April 2000. (E) Platform above an extension Lens Layer, SCWP, April 2002.
Figure 3.6: Platform Horizon details
(A) An example of large clay pan on the WWP, 2002. (B) Claypan found on buried Platform Horizon in SCWP (C) Close up of B. (D) The additional crushed surface of the 2002 working platform of the CWP. (E) The purposely constructed drain of the 2002 WWP working platform. (F) Relatively freshly ploughed surface on the western limits of the SWP. See text for details about all photographs.
3.2.5 Geologically Related Structure

Rock type may also play a significant role in internal structures of the stockpile, particularly in regards to pore-space formation and protection, at least in the case of the upper reaches or side slopes of the stockpiles where compression pressures have had less of an effect on structure (see Section 3.2.6). The differences in stockpile structure would occur due to differences in the size, morphology, and physical behaviour under stress, of certain waste rock types.

The most obvious difference, and one clearly observed at RUM, is between fresh rock and weathered material. An examination of freshly dumped Lift Mounds of relatively unweathered schist and dark green pegmatite on the NWP revealed significant cavities beneath the surface of individual mounds. In comparison, an examination of freshly dumped lift mounds of weathered material on the NCWP revealed no significant cavities at all. This is clearly a result of the fact that, after blasting and mining, weathered material tends to disintegrate into a much smaller size fraction than fresh rock. In addition to this, instead of a relatively structured mass of interlocking crystals, the weathered material is dominated by aggregates of micron-sized clay particles. Clay minerals have plastic characteristics in association with water (Deer et al., 1993), and experiments show that clay, as a material, has extremely low compression strength (Davis and Reynolds, 1996, Middleton and Wilcock, 1994). Thus, a reasonable assumption is that both formation and preservation of pore spaces is more likely in regions within the stockpile that are dominated by fresh rock. Observations at RUM during this research support this conclusion. Thus, one can assume with a degree of confidence that in an open-cut pit operation, particularly one associated with a significant profile of weathering such as Ranger, as the pit deepens the stockpile additions become more porous. Considering the prevalence of deep weathering profiles in Australia (Taylor and Shirtliff, 2003), such a stockpile structure may be particularly common in Australian mines.

It is more difficult to ascertain if pore space formation and preservation is different between the different types of fresh rock within the RUM waste rock stockpiles. Significant cavities were found to be present in two of the excavations examined in the stockpiles, site E6 was dominated by dark green pegmatite and schist (captured in
the photograph of Figure 3.5(c) – top layer of profile) and site E7 was dominated by similar rocks as well as massive carbonate. Both sites were distinguished from the other excavations by a significant proportion of boulder-sized and cobble-sized massive rock specimens and the pore spaces were concentrated between these large rocks (for example see Figures 3.6b and 3.6c). Neither of the layers were particularly deep in the stockpiles and thus, were not bearing any significant load. However, as expected observations around the stockpile surfaces at RUM suggest that the large boulder-sized material is dominated by the more massive, less foliated fresh rock. Thus, whilst ascertaining the extent to which different types of rock from the Ranger deposits affect fabric and structure within the stockpiles is difficult, this still seems to be a factor, at least in those areas yet to undergo significant compressional stresses and weathering processes.

Observations also suggest that rock type may play a role in the concentration of boulder sized material beyond the toe of the angle-of-repose slope in extension lens fall events (section 3.2.3 above). Figure 3.5(b) shows a concentration of boulders lying beyond the toe of the angle-of-repose slope, but only in some areas marked by distinct colour changes in the rock, and hence, rock type, of the slopes.

As alluded to earlier, pore spaces created by boulders still need to be able to survive the compressional stresses of load in order to be preserved. Under load bearing conditions, different types of rock should react to induced stresses in different ways. Under low levels of confining pressure, not unlike a rock at the edge of a cavity-like pore space, compression tests of rock at room temperature demonstrate that schist is somewhat weaker than more massive lithologies such as limestone, sandstone and granite (Davis and Reynolds, 1996), although, schist is slightly stronger than marble, a characterisation given to some of the carbonate at Ranger by some authors (Needham, 1988, Nash and Frishman, 1983, Crick and Muir, 1980, Kendall, 1990).

Another difference worth noting between the schists and other rocks at Ranger in regards to structures in the stockpiles is the tendency of schist to form a type of lineament in extension lenses within which they dominate. This was observed at Ranger both on the angle-of-repose slopes and within excavations. This can be seen, in part, in the photograph of Figure 3.3(a), and is obviously a result of a preferred
orientation for the flatter shaped schist rocks when they come to rest on the extension slopes. This same observation was documented by Whiting (1981).

3.2.6 Stress Related Structure

As stockpiles increase in size, so too does the potential vertical load bearing on the material within them. This vertical load applies an axial stress to the unconsolidated stockpile material that works to compress it. The result is a loss of void space and an associated change in the material’s hydrological characteristics. Thus, in stockpiles, populations of larger pore spaces will decrease with depth, because of a parallel intensification of compaction processes.

Identifying this structure in the RUM stockpiles is problematic because there is also the probability that the deeper into the profile one ventures, the more pre-weathered material (that is from the weathering profile over the Ranger deposit) one will find and thus the smaller the number of large pore spaces anyway. Natural consolidation processes (eg. during weathering) also play a part in compaction; however, towards the base of the stockpile, compression stresses are possibly the main contributor.

Simple stress calculations have been made to compare the differences in compression stress that may be experienced by areas at the bottom of each of the waste and LGO stockpiles, and they are presented in Table 3.1. The calculations have been made using the general equation for stress:

\[
\text{Stress (}\sigma\text{)} = \frac{\text{Force (}F\text{)}}{\text{Area (}A\text{)}} \tag{1}
\]

where \( F \) = mass \((m)\) x acceleration \((g)\), and \( g = 9.8m/s^2 \).

No confining pressures have been assumed, or any other stress directions, other than that produced by the vertical load. 1997 stockpile heights have been used for the calculations in Table 3.1 because these were the last known accurate heights available. Two rock densities have been used for the calculation; 2000kg/m\(^3\) is a commonly used density for wet earth in mining and 1800kg/m\(^3\) was the density used...
by Richards (1987) for the unconsolidated ore and waste rock in a previous study on settlement beneath the ore stockpiles at RUM.

Table 3.1: Calculation of stress applied to a horizontal plane of one square metre by vertical load normal to the plane for the bottom of each waste rock stockpile at Ranger Uranium Mine as at 1997.

<table>
<thead>
<tr>
<th>Stockpile</th>
<th>Stockpile Height approx. (m)</th>
<th>Stress (MPa) ( \rho = 2000 \text{kg/m}^3 )</th>
<th>Stress (MPa) ( \rho = 1800 \text{kg/m}^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CWP</td>
<td>45</td>
<td>0.882</td>
<td>0.794</td>
</tr>
<tr>
<td>NCWP</td>
<td>17</td>
<td>0.333</td>
<td>0.300</td>
</tr>
<tr>
<td>SCWP</td>
<td>16</td>
<td>0.314</td>
<td>0.282</td>
</tr>
<tr>
<td>WWP</td>
<td>20</td>
<td>0.392</td>
<td>0.353</td>
</tr>
<tr>
<td>SWP</td>
<td>12</td>
<td>0.235</td>
<td>0.212</td>
</tr>
</tbody>
</table>

As can be seen in Table 3.1, the base of the CWP experiences more than twice as much stress from vertical load than in any other waste or LGO stockpile at Ranger and will hence also have experienced the greatest amount of compression. Differences in compression between the other stockpiles may be negligible due to smaller differences in stress.

3.3 DISCUSSION: ASSESSING THE HYDROLOGICAL CHARACTERISTICS OF OBSERVED STRUCTURES

3.3.1 A Basic Soil Hydrology Approach

Since, in a general sense, waste rock stockpiles can be thought of as masses of unconsolidated material of various grain sizes, the principles of water movement through such a medium can be conceptualised by what is already known about the principles of water movement through soil. At its simplest, water movement through soils can be conceptualised in summary by Darcy’s Law (Singer and Munns, 1999);

\[ Q = A.K.d\psi/dx \]  \[ \text{[2]} \]

where \( Q \) is the volumetric rate of flow (m\(^3\)/s) through cross-sectional area \( A \) perpendicular to the direction of flow, \( K \) is the hydraulic conductivity (m/m\(^2\)/day) and the remaining function is the water potential (\( \psi \)) gradient along the direction of flow. Water potential is an energy measure that describes the potential for water to move. It
is dependant upon the combined effects of a number of components including gravity, pressure, the matric potential (capillary) and the osmotic potential (Singer and Munns, 1999). Whilst water potential is the driving force of water movement, hydraulic conductivity determines the ease with which a porous medium will allow the water to flow through it. Hydraulic conductivity is governed by pore space dynamics, that is, the arrangement of the pores and solids within the material under question and the pore and solid space geometry (Vervoort and Cattle, 2003, Singer and Munns, 1999), although the viscosity and density of water are also factors.

An important consideration, particularly in regards to the climate at RUM, is that both hydraulic conductivity and water potential are dependent on water content (Singer and Munns, 1999). Under conditions of saturation, water potential is at its maximum, all pore spaces are utilised and thus hydraulic conductivity is also at its maximum, and macro-pore dynamics, gravity and pressure tend to govern flow. In unsaturated conditions, matric potential becomes an important parameter restricting total water potential, therefore water tends to be held in tension within smaller pores and larger pore spaces play no part in flow, thus hydraulic conductivity decreases sharply with decreasing degree of water saturation.

3.3.2 Hydrological Properties of Platform/Ramp Horizons

In a study of non-cohesive, sandy gravel mine spoil from British Columbia, Canada, Dawson and Morgenstern (1995) found that low void ratios were reducing saturated hydraulic conductivity values below the expected range for such material. The lowest void ratios were obtained from compacted dump surfaces, where measured values were less than 0.3 and as low as 0.2. The hydraulic conductivity for these values fell to $10^{-4}$ and $10^{-3}$ cm/s. Dawson and Morgenstern (1995) also made in situ and field capacity moisture content measurements for the various mine spoils, where they found a dramatic increase in in-situ moisture content at the compacted surfaces. They also showed that field capacity and void ratio were linearly related (negative relationship), with the compacted surfaces having field capacities in the range of 60-80 percent. In normal stratified soils, if the fine layers are not saturated, the water will not move from the layer until enough pressure head is reached to force it out (Singer and Munns, 1999).
Dawson and Morgenstern’s (1995) work is clear evidence of the increased capability of the Platform Horizons to hold larger amounts of water per equivalent volume for longer periods of time than other structural domains of the stockpiles. At Ranger, this increased water holding capacity is most likely enhanced due to the presence of clays, mostly chlorite, kaolinite and some vermiculite (see Chapter 4), which result in an even lower hydraulic conductivity due to a decrease in pore size (despite an increased void ratio).

The presence of clays, however, will also reduce permeability and thus, enhance the ability of the Platform/ramp Horizon to act as a barrier to water flow through the stockpile. Figure 3.7 is a modified chart showing the results of large scale infiltration tests carried out on mine spoil materials from metal mines in western USA by Vandre (1995). The infiltration rate (in this case hydraulic conductivity at a gradient of 1) is plotted against a value representing the proportion of solid particles below 2.5cm diameter, a value used to highlight the soil-like/rock-like behaviour boundary (see Smith et al., 1995).

General observations at RUM place the Platform Horizons (in bulk) into the upper regions of the chart in terms of average grain size and as a compacted surface, probably have similar hydraulic conductivities to those of the compacted surfaces from Dawson and Morgenstern’s (1995) study (refer to Figure 3.7). However, considering the hydraulic conductivity values for mine spoils with significant clay content, such as those of a clayey basaltic andesite leach heap pile found by Kinard and Schweitzer (1987) of $10^{-7}$cm/s (shown on chart in Figure 3.7), the Ranger Platform Horizons may have infiltration capacities far to the left of the chart in Figure 3.7.
Figure 3.7: A modification of Vandre's (1995) chart showing the results of his study of mine spoil infiltration rates at western USA metal mines. The infiltration capacity is plotted against the percentage of material less than 2.5cm in size, thought to be the earth fill/rock fill behaviour boundary for stockpile hydrology. The original chart has been stretched here to include Dawson and Morgenstern's (1995) lowest hydraulic conductivity measurements on Canadian (BC) coal mine spoil, which represented surface platforms. An arrow points to the direction of where Kinard and Schweitzer's (1987) hydraulic conductivity measurements of clayey basaltic andesite mine spoil would be. These measurements are compared to a range of rainfall application rates that would likely be experienced on the RUM stockpiles based on a total rainfall of 26.4mm over periods from 15 minutes to 8 hours. See text for further details.
3.3.3 Surface Platforms and Run-off at RUM

The effect of Platform Horizons at the surface of the stockpiles is to decrease infiltration into the stockpiles and increase run-off, particularly during high intensity rain. In wet season rainstorms the application rate (the precipitation rate in this case) can often exceed the infiltration rate within the duration of a storm event, and consequently a large proportion of the water is shed as run-off. At Ranger, rainfall not only is limited to a distinct summer wet season, but also is often a daily occurrence, with the majority of rainfall occurring in single events of relatively short duration.

To highlight this, a range of application rates have been calculated for a rainstorm event of 26.4mm, considered here to represent a typical daily amount for February 2002, with a duration of 30min to a maximum of 8 h, and are superimposed on the chart of Figure 3.7. The rainfall amount is a representative figure, derived by calculating the average precipitation for rainy days at Jabiru (10km to the west of RUM) during February 2002 (peak of monsoon period for that wet season), disregarding outlier events (chosen by graphical examination as those below 5mm and one event of 163mm – using Australian Bureau of Meteorology to 9am daily precipitation data). Note that anything below a 44min storm event for this amount of rain equates to an application rate faster than the high-end hydraulic conductivity for compacted non-cohesive sandy gravel mine spoil, comprising the surface platforms as measured by Dawson and Morgenstern (Smith et al., 1995). Even for the eight-hour event, the application rate is some two orders of magnitude greater than Kinard and Schweizer’s (1987) hydraulic conductivity measurements of clayey basaltic andesite spoil and very close to the lowest values measured by Dawson and Morgenstern (1995) for surface platforms. This observation does not even consider the fact that rain will fall at different rates on a single area throughout a storm event, and that there were eight events during February 2002 larger than the 26.4mm used in the calculation, including one of 163mm, six times the application rate of the example used.
Recent investigations (results currently unavailable due to confidentiality clauses) of run-off from the WWP and CWP are not specifically relevant here because the platforms had been prepared differently from those which were present during much of this research (see section 3.2.4). However, run-off calculations were made on the NWP during the 2001/2002 wet season, where the surface had been prepared in a similar way to what can be regarded as normal for Ranger stockpile construction. Puhalovich et al. (2002) concluded that some 30 percent of total rainfall incident to the WWP over the entire 2001/2002 wet season was shed in run-off, although this is probably a conservative figure due to the fact that the platform may not have been completed when rainfall measurements began. This Figure compares reasonably well with run-off coefficients (ROC) calculated by Evans and Riley (1993) for individual rain events in a small-scale experiment carried out on the NCWP platform of 1993. Re-examination of the Evans and Riley (1993) data reveals that, whist ROCs ranged from 0.07 to 0.78 on the 5% slope, the average of 14 events was 0.35.

A ROC of 0.3 is higher than the ROC value of 0.1-0.22 ROC calculated by Daniel et al. (1983) for the stockpiles of the Rum Jungle Mine, also located in the tropical savanna of Australia’s Northern Territory. This difference in ROC values is easily explained if the Ranger platform preparation methods resulted in a surface platform of lower permeability than those of Rum Jungle. This difference in ROC values may also be a result of more accurate measurements by Puhalovich et al., (2002) due to the fact that the surface was specifically pre-designed to focus run-off into the channel where it was measured. It is also not clear if Daniel et al. (1983) included run-off from the angle-of-repose slopes; Puhalovich et al. (2002) do not seem to have done so.

Whatever the case, a ROC of 0.3 still leaves a considerable proportion of water (i.e. 70%) that is potentially entering the stockpiles, even if allowances are made for the maximum evaporation calculations at Rum Jungle of 35%. A few key questions still remain however. For example, how much of the run-off actually exits the stockpile system under normal circumstances (when drainage has not been engineered), and how much of the stockpile material does that water come in contact with before it exits the stockpile system? Observations suggest that it is certainly possible that areas such as angle-of-repose slopes may be in receipt of at least some of this water.
The run-off/infiltration ratio also will vary across a platform. In new areas of the platform, where the stockpile is under extension (on the edges of surface platforms), less compaction will have taken place and so more infiltration will occur.

### 3.3.4 Platform Horizons and Water Retention at Depth at RUM

The accumulation of water around buried platforms occurs in other stockpiles around the world. Significant increases in volumetric water content over depth were found in stockpiles at the Golden Sunlight Mine in Montana, USA (a gold mine), which Smith et al. (1995) interpreted as being caused by variations in grain size and the effect of compaction due to heavy equipment during construction of the stockpile. At the Clarion Coal Mine in Pennsylvania, Diodato and Parizek (1994) found cyclic water content concentrations over depth in accordance with variations in bulk density and porosity. Diodato and Parizek (1994) also concluded that increases in water content were due to areas of compaction of the dump by mine equipment operating at every 1.5m lift.

Morin et al. (1991) argues that areas above such barriers can become saturated resulting in significant perched water tables within stockpiles. Evidence for perched water tables exists at the Myra Falls Mine (Northwest Geochem, 1992 in Smith et al., 1995), the Elkview Mine (Smith et al., 1995), both in British Columbia, Canada and the Rum Jungle Mine in the Northern Territory, Australia (Daniel et al., 1983). At RUM, three of the seven excavation profiles available for observation intercepted a Platform Horizon at depth, only one of these contained direct evidence of a zone of saturation confined in the Platform Horizon (that described previously), however increases in moisture content were observed to be associated with all of them.

The zone of saturation was found at site E1 in what was to be a temporary part of the WWP. On the 13th August 2000, some three months into the dry season, a spring was discovered emanating from a Platform Horizon in a fresh excavation wall (see photographs in Figures 3.8a-b). The spring was oozing from the Platform Horizon itself, a small clay rich layer no more than 10cm thick, its lateral extent was approximately 1.2m. The upper limits of the seep were linear and abrupt except for some evidence of slight capillary movement as is seen in the photographs.
The preserved claypan at site E6 (shown in Figure 3.6b and c) is proof that such structures are not necessarily destroyed during construction processes. And it is evidence that the specific hydrological properties of claypans make them potential sites for small perched zones of saturation confined within the Platform Horizon. The presence of a spring 3 months after the last rainfall event of the previous wet season suggests the presence of a much larger hydrological feature, and proves that the Platform/Ramp horizons are major features of internal stockpile hydrology, acting to inhibit, redirect and contain flow. Increases in water content directly associated with the Platform Horizon at the top of a certain layer, but not in the Platform Horizon itself, was only evident in visual inspections where there was a significant difference in grain size, like the top layer of Figure 3.5(c).
3.3.5 Water Retention in Lift Mounds and Extension Lens Layers

Differences in moisture content were observed to be more a question of the type of material in the Lift Mound or Extension Lens Layers (mostly whether it was fresh rock or weathered rock), or of the degree of consolidation/compaction, than a fundamental difference in structure between the two types of layers. This would suggest that local differences in water retention may not be limited to the Platform Horizons. It may occur within certain areas where weathered material has been dumped, either as Lift Mounds or Extension Lenses, in a layer of predominantly fresh rock. It may also occur between entire layers where a certain lift has been built with fine grained or weathered material on top of or beneath layers of fresher rock of larger average grain sizes. Whiting (1981) also predicts the existence of perched water tables unrelated to platforms.

Thus, a potential hydrological characteristic specific to Extension Lens Layers is that alternating layers of high and low water content may exist parallel to the angle-of-repose slope, depending on grain size and clay content. Alternately in Lift Mound Layers, where paddock dumping of weathered material is followed by an infilling layer of larger grain size less weathered rock, a situation may exist whereby the inverted triangles of the Lift Mound layer work to channel flow between the lift mounds of less permeable material. An example of inverted triangle valley type structures can be seen in Figure 3.8(a) above the spring at E1, although it cannot be known whether this had any role in the development of the saturated zone.

3.3.6 The Base and the Underlying Water Table

Aerial photographs of the early CWP stockpiles (Figure 2.9 Chapter 2) clearly show the capacity of base layers to inhibit any significant amounts of water penetrating through them and the resulting ponding that occurred around the initial stockpiles. Given that the early stockpiles were dominated by more weathered material from the upper regions of the No.1 ore body, the lower regions of the CWP may have a high capacity for water retention although the estimated 0.794MPa of vertical pressure may work to lower total pore volume and force some dewatering. The amount of water retained in the CWP base, and any of the other stockpiles, will depend on the amount of water reaching it, the effectiveness of any redirection, and the amount of water...
escaping through it. The latter depends upon the condition of the capping (if any) i.e. whether it has been compromised and if so how significant this has been.

Richards (1987) predicted with a simple computer model, that sufficient settlement could occur beneath the 1% ore stockpile at RUM, at the time some 14m in height, to allow significant ponding of water in the base of the dump for long periods. This may also be occurring beneath the waste and low-grade ore stockpiles, particularly the CWP, a possibility that Richards (1987) also suggested in the early period of stockpile construction, and so assisting in the establishment of a water table. Considering that the CWP is over 3 times the height of the stockpile in Richards' (1987) model, it is possible that the subsidence occurring beneath the base of the CWP is much greater than that expected for the ore stockpile in 1987.

Ground water infiltrating from below may not be a significant problem at RUM as it is elsewhere (see Smith et al., 1995 and Morin et al., 1991) because the majority of the stockpiles have been placed at one of the highest original elevations in the mine area and thus not within the path of a groundwater discharge zone or directly on top of an underlying water table (see Salama and Foley, 1997). That being said a hydrological study of the entire mine area carried out by CSIRO Land and Water found that a post-mine groundwater mound was developing beneath the area occupied by the SCWP (Salama and Foley, 1997) indicating groundwater recharge from this dump. This may be a result of a less than sufficient capping for that area. Colour differences are suggestive of at least a different proportion of clay in the SCWP base to that of the CWP base. Whether this mound ever breaches the surface and thus penetrates the base of the SCWP is unknown, but it is certainly possible.

The WWP is located across a small catchment drainage zone, down stream and against the northern wall of the original tailings dam, a wall that is known to leak and in fact constructed in the belief that it would do so (Salama and Foley, 1997). Thus it is probable that the base of the WWP at the tailings dam wall contact receives water from an external source, increasing the probability of high water content in that area of the stockpile.
3.3.7 Flow through High Porosity/Large Void Layers

Sites E6 and E7 were the only excavation walls where relatively large voids were discovered. These occurred in unconsolidated material where rocks/boulders were not separated by the finer grained matrix. These areas were at the base of their corresponding layers, which were in turn beneath an existing surface platform at the time. Both of the excavations were in the SCWP and as already described above (3.2.5), rock type also seemed to play a role in the creation of the particular fabric.

Both sites are proof that in the RUM stockpiles, situations exist where layers of generally low permeability are separated by layers of generally high permeability. If the difference in void ratio is high enough, which seems to be the case at sites E6 and E7, it can be envisaged that such layers will act only as a brief path of relatively vertical transport between the layers. This will occur at those times where potentials or pressure head are large enough in the above layer of lower permeability, whether saturated or not, for it to release water, most probably during certain storm event flows. The remainder of the time these layers of large void ratios will stay relatively dry. Infiltration experiments in layered sand columns by Carey et al., (1994) model precisely this behaviour. They conclude that the larger pores of a loamy sand layer act as a capillary break for the finer sand layer above it. Saturation experiments by Walser et al. (1999) aimed at assessing the retention of liquid contaminants in soils also show such behaviour, although their model suggests an extremely small but important steady state flow between the layers.

3.3.8 The Southern Waste Rock Pile (SWP)

Disregarding a limited area where grasses are growing as well as a road extending along the northern section, the SWP has no definitive platform, either at the surface or at depth. This is because it has been constructed by continuous extension (approximately west to east) and the surface platform has been subsequently ripped for tree planting. In effect, it represents a single Extension Lens Layer with no capping platform. Also, observations suggest that the SWP has a higher proportion of non-schist rocks than other parts of the RUM stockpiles (see Chapter 4), a factor which may equate to a larger proportion of large void spaces, particularly at the stockpile’s base where extension lenses may concentrate them (see 3.2.3).
The result is that compared to the CWP, SCWP and NCWP, the SWP will have characteristics of higher void ratios and hydraulic conductivities, as well as infiltration rates closer to those of Vandre’s data of Figure 3.7. In areas where high void ratios exist, the connectivity of these voids will become a major influence on hydrology. For instance in areas where high connectivity exists, tunnelling may occur resulting in both less water-rock contact time and less overall water-rock interaction per application event. A number of case studies examined by Morin et al. (1991) suggest that tunnelling is not uncommon in stockpiles.

Good evidence of tunnelling on the SWP was found in a purpose built drain located along the southern edge of the stockpile. The drain, built to divert water across the SWP and out the SWP culvert, opened up a channel near the culvert entrance point, but on top of the stockpile. Water flux and moisture content measurements at various depths within the SWP made by Kuo (1996) also support claims of extreme heterogeneity and tunnelling within the SWP hydrological structure. However, extreme caution must be taken when considering the Kuo (1996) data because the experimental set up may have influenced the results. The different lysimeter depths and locations were achieved by digging a sloped trench into the stockpile and then infilling this once the instrumentation was in place. A slightly compacted slope surface potentially resulted in a preferential flow path, the effect of compaction on infiltration and water content has already been outlined above (see 3.3.2). Also, the infilling of the trench probably did not result in an Extension Lens Layer structure, again setting up a different structure to the rest of the SWP. Finally, the surface may not have been prepared the same as the surrounding surface.

A number of shallow holes (maximum depth of 30cm) were dug into the SWP surface to examine the fabric, both during the wet season and the dry season. This revealed that although larger rocks tend to dominate the surface of the ripped areas, finer-grained material (clay-sized to sand-sized particles) is prevalent directly beneath, at least to the maximum hole depth examined. During the wet season this material was wet, becoming even wetter during rainstorm events. However during the dry season all of the test holes made were relatively dry suggesting that evaporation processes are effective to at least the maximum hole depth in the SWP. Thus the SWP sub-surface
may be a place of water retention, a layer of relatively consistent fabric and associated water content across the ripped areas sitting above the more heterogenous structure below.

If the SWP has a water flow relatively unhindered by Platform Horizons but influenced by channelling, as it seems to be, then SWP hydrology may be close to fitting a model based on Kinematic Wave Theory (see Germann and Beven, 1985, 1986 and Smith et al., 1995), although more attention would have to be applied to tortuosity parameters (see Vervoort, 2003; Vogel, 1997).

3.3.9 Angle-of-repose Slopes

Most angle-of-repose slopes on the edges of the RUM waste and LGO stockpiles seem to have a similar structure to the SWP surface, where finer particles have been washed to a layer below the surface rocks. An example of this is given in the photograph of Figure 3.9. In areas of highly weathered material, this structure does not seem to occur, most probably due to more consistent gran sizes in the loads of weathered material.

It is difficult to ascertain the infiltration capacity of these surfaces. The absence of induced compaction and their unconsolidated nature would suggest that infiltration rates of angle-of-repose slopes are amongst the highest of all surfaces of the RUM stockpiles, however prominent slopes should severely limit the depth to which water can infiltrate into the stockpile from them due to the influence of gravity. That being said, they may be important regions of water-rock interaction within the stockpile system.
Figure 3.9: An example of the surface fabric of an angle-of-repose slope after a number of wet seasons. Finer grained material has been washed away to beneath the larger rocks. This slope is on the SCWP near a former site of revegetation.

3.4 LOCATION OF THE MAJOR STRUCTURES WITHIN THE RUM STOCKPILE SYSTEM

Once the likely effect of certain structures on stockpile hydrology is known it is important to know where these structures are located. This is difficult without totally deconstructing the piles, as suggested by Smith et al. (1995). However, at Ranger it was considered possible to map both the location of the Platform Horizons and major concentrations of weathered material within the stockpiles, two of the most important structures to the stockpile hydrology at RUM.

3.4.1 Platform Horizons

Figure 3.10(a) is a map of the Platform Horizons. It shows every Platform Horizon within the RUM waste and LGO stockpile as of the year 2003 that could be accounted for by the mapping method used. The method by which the map has been achieved and all associated geographical errors are explained in the methods chapter and will not be repeated here. It should be noted that due to the mapping method a limited
number of platforms may not have been mapped, although these will be concentrated in the more recent years and within the more recently constructed stockpiles, particularly the NWP, see Chapter 2 for further explanation.

Each polygon on the map represents the perimeter, not including the angle-of-repose slope, of a Platform Horizon or major Ramp Horizon that exists within the stockpiles including the current surface platforms. Each colour represents the year a platform was exposed at the surface at its maximum extent. The colour sequence is repeated from 1990 onwards with thicker polygons. The map is complex, almost to the point of unreadable, but this is precisely its point, to show that even if one simply considers the minimum number of platform horizons, the internal structure of a stockpile system is extremely complex and difficult to discern.

Cross-sections of each stockpile have been made and displayed in Figure 3.10(b-e). The locations of these cross-sections are found on the map (Figure 3.10), and labelled accordingly. Note that both the 2003 surface and the 1997 surface have been outlined in the cross-sections. This is because the 1997 surface is the last surface delineated by actual elevation data, whereas the 2003 surface, and all platforms since 1997, have estimated heights based on the examination of satellite images, various photographs of the stockpiles taken during this study and on-site observations. It is for this reason also that no cross-section has been made for the WWP, which wasn’t constructed until after 1997.

The map and cross-sections show that Platform Horizons are prominent internal features of the RUM stockpiles and therefore will be a dominant influence on stockpile hydrology. This is especially the case for the CWP and SCWP where a concentration of Platform Horizons exists. The CWP and SCWP cross-sections reveal a cluster of platforms within the central lower parts of the CWP and extending laterally into the SCWP. The region incorporating this cluster is therefore a potential zone of increased water retention, depending on how much water it receives. A pattern has emerged, particularly within the CWP, whereby Platform Horizons become progressively larger towards the surface creating a type of umbrella effect.
The cross-sections also reveal a large number of Platform Horizons extending to the angle-of-repose slopes of both the 1997 and 2003 surfaces, particularly along the western edge of the CWP (Figure 3.10b). This may work to decrease the possibility that water penetrating the angle-of-repose slopes will advance deep within the stockpile. However it may also work to catch infiltrating water and hold it in a region that probably has access to a continuous supply of oxygen, and thus promoting a zone of increased redox. In some instances, platforms actually form part of the surface and extend inside the pile. This is seen most prominently in the NCWP cross-section (Figure 3.10d), a situation which has the possibility of increasing the potential amount of water entering the stockpile through the corresponding angle-of-repose slope. This depends on the slope of the platform and hence the direction of run-off.

The complexity of the Platform Horizon locations demonstrates that stockpiles constructed from a freestanding position like those of Ranger are not made up of a simple series of laterally extensive lifts. In other words the effectiveness of bore hole monitoring of hydrological properties in establishing reliable information that can be transferred to the stockpile scale will be entirely dependent on the number and spacing of bores unless prior knowledge of structure has been obtained. This will be particularly the case for those stockpiles that have undergone continual change whereby sections are being removed and rebuilt, as has been the case at Ranger.

The cross-sections suggest that there are some large areas in the stockpiles relatively free of Platform Horizons:

- a section of some 20m in height on the middle eastern side of the CWP and extending into the centre (Figure 3.10b);
- a 15m high section in the upper west of the CWP that extends downwards at an angle (45° on cross-section) into a central pocket (Figure 3.10b);
- some 20m in the upper south of the CWP (Figure 3.10b);
- most of the bottom 15m of the north western parts of the NCWP (Figure 3.10d); and,
- almost all of the SWP (Figure 3.10e) and WWP (Figure 3.10a).
Due to the nature of stockpile construction, extension lenses will be dominant in those large sections of the stockpiles that remain relatively free of Platform Horizons. This is particularly the case for the SWP, the hydrology of which has been discussed above (3.3.8).

Mapping also revealed a pattern in the Ramp Horizons within the stockpiles. Figure 3.11 is a map of the direction of slope of all of the major Ramp Horizons within the Ranger waste and LGO stockpiles including the ramps of the current surface (as of 2003). The methodology used to construct the map is similar to that used to construct the Platform Horizon map and is detailed in Chapter 2.

The map shows that deep within the CWP the early ramps sloped south to south easterly before eventually turning into a single ramp much higher in the stockpile that sloped to the northeast, as it still did as of 2003. Another major set of ramps sloping mainly from the SCWP and higher in the CWP but also the SWP, feed into a single major ramp that is positioned between the CWP and SCWP and that slopes to the northeast. Some more current ramps slope from the SCWP to the southwest towards a major drainage structure and major ramps slope from the eastern end of the WWP and the northern end of the NCWP to the northeast.

It should be obvious from the Ramp Horizon slope map that if ramps can possibly redirect internal flow then within the entire central stockpile system (i.e. disregarding the WWP, SWP and NWP) this would occur mostly to the northeast toward the CWP drainage pond and RP2 because the entire ramp system in this area appears to imitate a channel system that drains in that direction. This does not include the current situation where ramps on the SCWP slope towards the drainage to the southwest and hence away from the RP2 catchment.

However whilst Ramp Horizons may direct flow towards RP2 and the CWP drainage pond it may not necessarily mean that the water will actually reach these ponds, it will only go as far as the slope allows. Thus, if the ramps are diverting water, it may accumulate in the central ramp drainage in the SCWP/CWP area.
Figure 3.10(a): Map of Platform Horizon perimeters within and upon the RUM waste and LGO stockpiles. See text for details. See Chapter Two for mapping method.
Figure 3.10(b-c): Cross-sections of the CWP (B) and the SCWP (C) showing the location of Platform Horizons within them. See text for details.
Figure 3.10(d-e): Cross-sections of the NCWP (D) and the SWP (E) showing the location of Platform Horizons within them. See text for details.
Figure 3.11: Map of slope directions for major Ramp Horizons within the RUM waste and LGO stockpiles. Note that the thickness of the arrow stems has no relation to the width of the ramp and the actual slope of each ramp is not included on the map as this information is unavailable.
3.4.2 Concentrations of Highly Weathered Material

Figure 3.12(a) is a plan view of the location of concentrations of highly weathered material within the RUM stockpiles using the Platform Horizon map above. The method used and the colour representations are the same as those used for the Platform Horizon maps and will not be repeated here. The concentrations of highly weathered material have been simply added to the above cross-sections to create the cross-sections in Figures 3.12(b-e).

There is little doubt that the major concentrations of highly weathered material in the RUM stockpiles occur in the complete eastern section of the CWP (Figure 3.12b), the base of the CWP (Figure 3.12b-c) and the complete south eastern section of the NCWP (Figure 3.12d). Another large section of highly weathered material is located on the southern edge of the CWP that extends into the SCWP area, just in from the 2003 angle-of-repose slope, and much of the lower levels of the WWP. These areas represent large potential reservoirs of moisture in the RUM stockpiles, definitely in the wet but perhaps even surviving the dry season although the new CWP and WWP surfaces (discussed above, 3.2.4) may reduce water supply to these areas.

3.4.3 Gas Movement

The presence of large concentrations of material with high clay content combined with a complex network of Platform Horizons not only complicates and hinders water flow, but will do the same for gas flow. Gases move through stockpiles by both gaseous and aqueous diffusion and advection and through convection (Davis and Ritchie, 1986, Morin et al., 1991 and Lefebvre et al., 1992, Bennet et al., 1990 in Lu, 2001). Due to the unconsolidated nature of stockpiles, gaseous advection/convection is often assumed to be the dominant transport mechanism for gases within them (see Morin et al., 1991 and Garvie, 2002). Advection/convection occurs through a number of mechanisms, barometric pumping at the surface (through delays in the pile adjusting to atmospheric pressure changes), wind advection into the pile (caused by higher external pressures developing on the windward side of the pile), and thermal
Figure 3.12(a): Map of Platform Horizon perimeters within and upon the RUM waste and LGO stockpiles with those areas consisting of highly weathered material highlighted. See text for details. See Chapter Two for mapping method.

Platform Horizon and Highly Weathered Material Map of the Ranger Uranium Mine Waste and Low Grade Ore Stockpiles

KEY

1980
1981
1982
1983
1984
1985
1986
1987
1988
1989
1990
1991
1992
1993
1994
1995
1997
1999
2003

Highly weathered material (pen thickness)

Scale 1:5000
Figure 3.12(b-c): Cross-sections of the CWP (B) and the SCWP (C) showing the location of highly weathered material (pre-weathered within the mine sequence) within them. Ramp Horizons are as in figure 3.10(b-e); highly weathered material is shaded brown.
Figure 3.12(d-e): Cross-sections of the NCWP (D) and the SWP (E) showing the location of highly weathered material (pre-weathered within the mine sequence) within them. Note that a layer of highly weathered material between the 1997 and 2003 surface of the NCWP has not been included because it was observed in the field only and exact location is not known.

(D) North Central Waste-rock Pile (NCWP) Cross-section Showing Location of Highly Weathered Material (orange colour)

(E) Southern Waste-rock Pile (SWP) Cross-section Showing Location of Highly Weathered Material (orange colour)
convection (caused by exothermic oxidation reactions, primarily pyrite, lowering pressure through heat). It is the latter of these that tends to be considered the main driving force of air flow into stockpiles (Morin, 1991) despite all three sometimes being observed as was the case at Rum Jungle, Australia (Harries and Ritchie, 1985, 1987). Once thermal convection is established, it effectively maintains itself by supplying oxygen to the site of oxidation.

Just as with water flow, it is not only the gradient (in this case the pressure gradient caused by heating at the oxidation site) that regulates flow but also the permeability of the material for which the flow must pass through. ANSTO suggest that convection is only significant when permeability is \( \geq 10^9 \text{m}^2 \) (Garvie, 2002), others suggest that it needs to be greater than \( 10^{-10} \text{m}^2 \) (Lu and Zhang, 1997 and Bennet et al., 1990 in Lu, 2001). To relate these measurements to the discussion above, a permeability of \( 2 \times 10^{-13} \text{m}^2 \) is approximately equivalent to a hydraulic conductivity of 0.1 cm/s (see Figure 3.7). This is far above the hydraulic conductivities postulated for Platform Horizons as well as fine-grained material with high clay content (in Figure 3.7 and discussed above), as is the highly weathered material at RUM. It can therefore be assumed that airflow through these structures will be governed by diffusion rather than convection, and hence they will probably work to spoil airflow within, and in some places, into the stockpiles. Convective cells may be restricted to areas less congested by such structures, effectively localising oxidation. This in turn may work to reduce stockpile scale oxidation rates and the long term weathering of the RUM stockpiles.

### 3.5 SUMMARY AND CONCLUSIONS

It has been proven here that whilst complexity and heterogeneity exists in free standing waste and low grade ore stockpiles, there is pattern in their fabric; at RUM, this is in the form of 3 distinctive macro-scale structures, Lift Mound Layers, Extension Lens Layers and Platform/Ramp Horizons (named here uniquely to avoid colloquial language such as ‘paddock dumping’). Each one of these structures has its own unique hydrological characteristics.
These individual patterns are the result of formational processes (construction techniques) and they are observed throughout the stockpiles wherever those particular formational processes were active. It is considered here that there should be no reason why any other stockpile in the world constructed with the same techniques as that at RUM should not have the same macro-scale structures.

Due to the direct link between the structure and formational process, this study has also proven that if one has knowledge of how each section of the stockpile system was constructed, then one can also infer the internal structure of that particular section of the stockpile. In other words, there is no need to have a situation where one needs to observe a complete stockpile de-construction to learn about the internal structure of the stockpile and hence there is no need to wait for mine closure, new dam construction, or large scale rehabilitation works that require large sources of rock and the de-construction of a stockpile. More importantly, the technique used here, means that a conceptual hydrology model specific to a particular stockpile system, such as that at RUM, can be made whilst the stockpile is still active when the conceptual hydrology is actually needed, rather than later, after de-construction. However, the more detailed model of the stockpile structure and thus conceptual hydrology could only be made here with the support of annual aerial photographs and regularly compiled mine site elevation data which allowed observations to be made on how each section of the stockpile was constructed.

In terms of the structures observed and their hydrological properties, it is proposed here that it is the type of material that is more important to hydrological characteristics within Extension Lens and Lift Mound Layers rather than the specific structure of the layers themselves. However, because it is not uncommon to have differences of material type within very short distances within these layers, and because the different layers are structurally different, then some hydrological characteristics will be particular to certain layers.

As with other studies elsewhere, due to compaction processes occurring during construction, Platform Horizons are major hydrological features of the mine waste rock stockpile, both internally and at the surface. It is clear that Platform/Ramp Horizons act to slow, halt or divert the flow of water through stockpiles. They are
zones of higher field capacity and zones where saturated conditions prevail for long periods, a feature that is enhanced in localised areas where clay rich claypans have been preserved. At Ranger, one such localisation of saturation was found three months after the last rainfall event of the previous wet season. It is also possible that due to the nature of ramps connecting various stockpiles to central stockpile transport routes, Ramp Horizons may work to direct some of the water they intercept into these central locations, although there is no direct evidence to support this claim. At the surface, there is little doubt that Platform Horizons act to increase the run-off/infiltration ratio.

Most hydrological investigations of waste rock stockpiles around the world rely on measurements from instrumentation such as lysimeters from a limited number of observation points (see Morin et al., 1991 and Smith et al., 1995). This research shows that whilst important generalised hydrological information may be obtained from using such a technique, in regards to free standing stockpiles such as those at Ranger, the technique is flawed in that its success in identifying hydrological features is totally dependant on the number, spacing and depth to which such instruments are placed. This is because the structural features most important to internal stockpile hydrology are by no means uniform in their location or even orientation as has been shown by the structural maps and cross-sections produced in this study.

This study shows that Platform Horizons vary in size, shape, composition, are of slight to negligible slope, are not necessarily equidistantly spaced vertically or horizontally, can be clustered in certain areas, and totally absent from others. The type of material can vary substantially both laterally and vertically, to the point where, like at Ranger, different sections of stockpiles may have completely different hydrological properties.

In terms of waste rock stockpile research internationally, this means that free standing stockpile structures at mine sites cannot necessarily be treated as simple single piles of dumped rock because this is probably far from reality. Thus, column experiments or the large-scale replica experiments such as that currently under way at Cluff Lake Mine in Saskatchewan by staff and students of the University of British Columbia,
Canada, must incorporate such complex structure as outlined here, in order to adequately represent the free standing stockpile.

In terms of understanding the stockpile hydro-geochemical system at RUM, the following has been determined from this study:

1. All evidence presented here suggests that the hydrology of the SWP is different to all waste and LGO stockpiles at Ranger because it represents a single Extension Lens Layer with no internal Platform Horizons or any significant surface platform. As a result, more water will infiltrate the SWP surface than at other stockpiles, residence times through the stockpile will be shorter and water flow through the stockpile will be governed by parameters such as the connectivity of large pore spaces and the tortuosity of developed channels.

2. All other stockpiles at RUM but particularly the CWP will have hydrology complicated by multiple Platform Horizons at depth, hence RUM stockpile hydrology must be treated more like that of a stratified soil than that of a simple porous medium as has been suggested for Rum Jungle stockpiles (Pantelis and Ritchie, 1991). A significant concentration of Platform Horizons exists in the CWP, down the western and northern slopes into the lower western centre and extending towards the SCWP.

3. Large concentrations of material from the Ranger deposit weathering profile will also complicate flow through the RUM stockpile system due to its dramatically different hydrological properties and behaviour under compressional stress. The largest of these concentrations occur at the eastern end of the CWP at its drainage point, in early piles now lying at the base of the CWP, the early eastern section of the NCWP and a large proportion of the lower WWP.

4. A significant proportion of the water incident to the stockpile surfaces at RUM, disregarding those of the SWP, will be shed as run-off, as much as 30 percent according to recent calculations on the NWP. Under normal circumstances where surfaces have not been designed to direct this run-off, some of this water will still enter the stockpiles.
5. Through the direct receiving of rainfall as well as run-off from surface platforms, angle-of-repose slopes will be important areas of entry for water into the stockpiles. The amount of infiltration is unknown, due to slope a significant proportion of water may still move down and away from the face of the slope rather than into the stockpile, although the common occurrence of Platform Horizons extending to the slope surface and even beyond will help to capture some of this water. Whatever the case, the angle-of-repose slopes are important places of water-rock interaction in the RUM stockpiles, their proximity to the atmosphere and thus a ready supply of oxygen for oxidation reactions enhancing this importance.

6. Due to a combination of consolidation and compaction processes as well as an increase in the degree of weathering evident in material entering the stockpiles (that is weathering that has occurred in-situ within the deposit and not in the stockpile) there will be a general decrease in the average pore space size and thus hydraulic conductivity with depth in the stockpiles. The increase in pre-weathered material with depth is due to the inverse relationship stockpiles have with the geology of the deposit and is probably a phenomenon of particular importance to Australian open cut mines and anywhere else in the world where significant weathering profiles are common in the landscape.
CHAPTER 4

A COMPREHENSIVE INVESTIGATION INTO THE GEOLOGICAL COMPOSITION OF THE RANGER URANIUM MINE WASTE ROCK STOCKPILES

4.1 INTRODUCTION

The purpose of this Chapter is simple, to gain a comprehensive understanding of what the Ranger Uranium Mine (RUM) waste and Low Grade Ore (LGO) stockpiles are made of, and where within the stockpiles this material is likely to be located. This will complete the analysis of the stockpiles started in Chapter 3 and provide the basis for understanding the chemistry of waters influenced by the stockpiles.

There have been a number of studies, mostly internal company reports, attempting to comprehend the composition of the stockpiles, at least to the point of single purpose needs, like for instance, estimations of S content (Milnes, 1988; Jones and Hughes, 1999; leGras and Klessa, 2001; leGras et al. 1993; Riley et al. 1993; Noller, 1991). The Riley et al. (1993) study involving the geochemical and mineralogical analysis of Rotary Air Blast (RAB) drilling into the NCWP, CWP and SCWP in 1992 is certainly the best view yet of the composition of the stockpiles, despite problems encountered such as potential cross-contamination from collapsed holes. However, the Riley et al. (1993) study is over ten years old, the stockpiles have grown considerable since this time, and when the study was undertaken in 1992, P3 waste and LGO material had yet to enter the RUM stockpile ‘system’. Despite the Riley et al. (1993) study previous studies are limited in their extent and do not provide a clear and comprehensive overview of what the RUM waste and LGO stockpiles are made of. It is the purpose of this study to fill that gap.

To do this, this study aims to:

- Estimate the bulk stockpile composition and approximate where the different compositions are likely to be within the stockpiles;
- Identify the major rock types within the stockpiles as opposed to that in the mine;
• Geochemically characterise the waste and LGO material in the stockpiles;
• Investigate in detail the mineralogical and mineral-chemistry of the most abundant rock type in the stockpiles, both current and projected, with emphasis on identifying the environmentally important uranium and sulfide mineralogy within this rock type; and,
• In light of the importance of sulfides such as pyrite, for producing acid conditions that may help to leach environmentally significant elements from the stockpiles, to estimate the bulk pyrite and chalcopyrite abundances in waste and LGO material, the two dominating sulfides at RUM.

Before presenting this study however, a background into the rocks of RUM is given. It is important to emphasize the fact that the waste and LGO stockpiles of RUM are a product of not only mining, but also geological processes at work over two billion years before mining began.

4.2 METHODS

Technical details into individual methods used in many of the analyses undertaken in this study are presented in the relevant section. Certain areas of this study utilise the geochemistry results performed on 20 rock specimens sampled from the waste and LGO stockpiles specifically for this research. A combination of XRF and ICPMS using facilities of the rock lab at Geoscience Australia, Canberra, were used to determine major and trace element concentrations in these rocks. Details of these methodologies are presented in the Chapter 2. However much of the geochemistry is derived from a previous study by Nash and Frishman (1983) from some 370 drill core samples from both Ranger No.1 and Ranger No.3 (further details below in the appropriate section).

The mineralogical and mineral-chemistry study of the quartz-chlorite-mica schist was achieved by plain and reflected light microscopy of thin sections made in the thin sectioning laboratory at EMS ANU, as well as SEM and EMPA analysis using the facilities at the microscopy unit at RSBS ANU. Details of these methods are presented in the Chapter 2.
4.3 THE ROCKS OF RUM – PUTTING THE STOCKPILES INTO A GEOLOGICAL CONTEXT

4.3.1 Regional Geological Correlation

The majority of the rocks that make up the waste rock stockpiles at RUM are derived from a sequence of what are largely metasedimentary rocks, known as the Cahill Formation. The Cahill sequence forms a continuous folded belt approximately 5 km, covering an area of some 15,000 km² geographically. The ribbon like, V-shaped occurrence stretches roughly north-south from approximately the entrances of the South Alligator and East Alligator rivers in the north to the escarpment of the Arnhem Land Plateau near Mount Partridge Range in the south (see Figure 4.1).

Regionally the Cahill Formation is situated within the eastern limits of an extensive synclinal geological formation known as the Pine Creek Geosyncline (PCG) of which it is part of. The PCG extends at the surface in an approximate triangle, covering some 66,000 km² south and east of Darwin. The region within its geographic bounds consists of Proterozoic metasediments, dolerite and granite interspersed with minor granitoid Archaean basement domes (Needham et al., 1980). It is surrounded on all sides by sediments of Middle Proterozoic to Mesozoic in age, which overlay it with a marked regional unconformity (see Fig 4.1(top)).

Exposure of the PCG, including the Cahill Formation, is moderate to sparse, as deposition of Cainozoic cover sequences and deep weathering has occurred extensively in the region. Likewise in the vicinity of RUM in situ and reworked weathering products (nodules, pisoliths, Fe concretions and mottled clays), unconsolidated sands, mud, silt and clay of the Tertiary to Quaternary (estimated ages only from Needham, 1988) conceals most of the geology. It is thus not surprising that a large proportion of the weathering profile above RUM is now part of the waste and LGO stockpiles of RUM.
4.3.2 Regional Stratigraphy

At its simplest, the PCG consists of a stack of clastic, organic and chemical sediments with minor volcanics overlaying a granitic basement. Deposition of the PCG pile began some time after 2400Ma (the age of the youngest basement rocks) and finished prior to 1870Ma (the age of pre-metamorphic granadiorites in the northeast) (Needham et al., 1980). It has been suggested by Needham et al. (1988) that the 10 km, maybe 14 km, of supracrustals more likely accumulated in less than 20 million years around 1900Ma.

Both the PCG and basement were significantly metamorphosed around 1800Ma (see Needham, 1988), and then eroded before being overlayed by a large platform cover of shallow marine, fluvial and colluvial sediments, with interspersed volcanics. During deposition the basin was perhaps as large as 100,000 km² (Needham et al., 1980) and as a result equivalent sedimentary units in stratigraphic time can vary in type from one side of the basin to the other, depending upon their relative environment of deposition. Conformity of the sedimentary units with interbedded tuff units across the basin indicates the chronostratigraphic nature of the geosynclinal pile (Needham et al., 1980).

4.3.2.1 Basement Complexes

The granitoids of the PCG can be split into two groups; those emplaced before regional peak metamorphism (approx 1800Ma), thus undergoing deformation, and those emplaced after. Of the five major granitoid complexes emplaced before peak metamorphism, only the Nanambu complex underlying RUM in the east, and the Rum Jungle and Waterhouse complexes in the west are definitive PCG Archaean basement, dated at 2500Ma ± 100m.y. (Page, 1976 in Ferguson et al., 1980; Richards and Rhodes, 1967; Page et al., 1980). Predating even these however, are metasediments, some granitised, banded iron formation, volcanics and metabasics which are contained within and engulfed by these three granitic complexes (Ferguson et al., 1980; Needham et al., 1980; Needham, 1988).
Figure 4.1: Tectonic Setting (above) and the geology of the Alligator Rivers Uranium Field (ARUF) (below)
From Needham, (1988)
Rocks of the Nanambu complex, basement to the RUM orebodies, have been subdivided on the basis of age and lithology into: unmetamorphosed Archaean two-mica granite; metamorphosed Archaean granite (now predominantly augen gneiss); and Early Proterozoic pegmatoid leucogneiss, schist and migmatite. This latter subgrouping is thought to represent a portion of Lower Proterozoic basal arkosic rocks, which were accreted onto the Archaean granitoids during peak metamorphism (Needham et al., 1980; Page et al., 1980).

4.3.2.2 The Cahill Formation and the PCG

Table 4.1 shows the cross basinal stratigraphy of the PCG. The RUM ore bodies occur in the lower member of the Cahill Formation, the second major sequence of sedimentation within the PCG.

<table>
<thead>
<tr>
<th>WEST OF THE SOUTH ALLIGATOR RIVER/JIM JIM CREEK</th>
<th>ALLIGATOR RIVERS URANIUM FIELD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burrell Creek Formation (greywacke, siltstone)</td>
<td>Kapalga Formation</td>
</tr>
<tr>
<td>(chert-banded ferruginous siltstone, ruff, greywacke, minor shale, carbonatic)</td>
<td>Kapalga Formation (chert-banded ferruginous siltstone, greywacke, shale, minor arkose)</td>
</tr>
<tr>
<td>Gerowie Tuff (tuff, conglomerate siltstone, argillite, shale, reet chert nodules, banded iron formation)</td>
<td>Kapalga Formation?</td>
</tr>
<tr>
<td>Koolpis Formation (chert-banded ferruginous siltstone, carbonaceous shale, carbonatic, banded iron formation)</td>
<td>Myra Falls Metamorphics</td>
</tr>
<tr>
<td>Coomalie Dolomite (carbonatic)</td>
<td>Wildman Siltstone (interbanded siltstone and carbonaceous shale, Minor quartzite)</td>
</tr>
<tr>
<td></td>
<td>Nourlangie Schist</td>
</tr>
<tr>
<td>Crazy Formation (conglomerate, sandstone, minor shale)</td>
<td>Mundagine Sandstone (sandstone, conglomerate, silstone, phyllite)</td>
</tr>
<tr>
<td></td>
<td>Cahill Formation (upper member)</td>
</tr>
<tr>
<td>Celia Dolomite (carbonatic)</td>
<td>Mission Formation (carbonaceous shale, calcaire, carbonatic, sandstone)</td>
</tr>
<tr>
<td></td>
<td>Cahill Formation (lower member)</td>
</tr>
<tr>
<td>Beeston Formation (fidiolite sandstone, arkose)</td>
<td>Kalamaz Group</td>
</tr>
</tbody>
</table>

**Table 4.1:** Stratigraphy of the Pine Creek Geosyncline from west to east across the basin. Source (Needham, 1988)
The Cahill Formation has been separated into two groups, a lower carbonaceous sequence and an upper more psammitic member. The lower member, host to RUM, is some 300 to 600 metres thick and consists of carbonaceous schist, marble, calc-silicate rock, para-amphibolite and dolostone, and schist and quartzite. The upper member conformably overlies the lower member and consists of interlayered feldspathic quartz schist, feldspathic schist, feldspathic quartzite, and minor mica schist and quartzofeldspathic gneiss. At Koongarra this member has an apparent thickness of some 2500 metres due to repeated faulting and folding (Needham, 1988). The lower member corresponds to the Masson Formation (part of the Namoona Group) in the Rum Jungle area to the west, together, the lower Cahill Formation and the Masson Formation is host to most of the uranium deposits and other mineralisation of the entire PCG.

A significant interpretation of these rocks is the identification of evaporitic parentage for some of the metamorphic carbonate sequences, indicating a transition from sub-tidal, low energy marine to intertidal and supra-tidal evaporitic facies. Evidence suggests that in the west these evaporites formed in thick continuous stromatolitic algal mats where as in the east, they formed lens shaped masses up to 250 metres thick (now calcitic dolomite to magnesite marble) within the partly carbonaceous and calcareous sediments of the lower Cahill Formation. Importantly the thickest lenses of the latter are adjacent, to or partly within, the major uranium orebodies, although at RUM it has been suggested that this has been replaced by chert. The carbonates have thus been suggested as a possible Mg source for the medium to high Mg-chlorites, which are common to all the major uranium deposits (Needham, 1988).

Close to RUM, interpretation of the Jabiru drill traverse (Needham and Stuart Smith, 1976) revealed that the Upper Cahill Formation appears to be overlain, in some places conformably and in others unconformably, by the Nourlangie Schist. It is thought that this is simply a high grade metamorphic equivalent of the relatively homogenous Wildman Siltstone, which overlays Upper Cahill Formation equivalents elsewhere. In fact east of the Nanambu Complex the stratigraphic succession of the PCG becomes a monotonous combination of schists and gneiss corresponding to an increase in metamorphic grade away from a central PCG trough. Further to the east of RUM, the Nourlangie Schist grades into metamorphically differentiated schist and gneiss of the
Myra Falls Metamorphics. Parent lithologies are mostly unrecognisable in this group however resisters are present, which indicate remnant Kakadu Group and Cahill Formation lithologies. The hosting of the Nabarlek Uranium deposit in these metamorphics further supports the presence of the Cahill formation.

4.3.2.3 Cover Rocks

New light has been shed on the plateau forming cover rocks of the PCG by the Arnhem Land section of the National Geoscience Mapping Accord (NGMA), a combined mapping project between the Australian Geological Survey Organisation (AGSO - now Geoscience Australia [GA]) and the Northern Territory Geological Survey (NTGS). Previous studies (Walpole et al., 1968 and Roberts and Plumb, 1965 in Sweet et al., 1999; Needham and Stuart-Smith, 1985) have separated the massive cover of sandstone with interbedded volcanics known as the Kombolgie Formation and the underlying accumulation of felsic volcanics and associated sediments, known as the El Sherana and Edith River Groups, with a marked regional unconformity. The new evidence from dating and examination of differences within the Kombolgie Formation itself suggests this hiatus may be as short as a few million years and that in fact the sandstones of the lower Kombolgie Formation are of the same tectonic regime as those of the El Sherana and Edith River Groups, which outcrop more extensively to the south.

A major regional unconformity was recognised within the Kombolgie Formation, which effectively separates the lower from the upper sandstone sequences. The Kombolgie Formation has been renamed the Kombolgie Subgroup (as that of the greater Katherine River Group) and is possibly 100 million years older than previously thought (Sweet et al., 1999). If the new dates are correct then the proposition that these rocks are the most north westerly preserved extent of the McArthur Basin, as has been presumed in the past (Needham et al., 1980; Needham, 1988), cannot be true. More importantly for RUM, the new 1822-1720Ma age constraints mean that primary uranium mineralisation of RUM ore at 1737 ± 20 Ma (for Orebody No. 3) (Ludwig et al., 1985, 1987) now fit well within a post-Kombolgie mineralisation model as proposed by Maas and McCulloch (1987) for Jabiluka, Koongarra and Nabarlek. Previous ages for the Kombolgie Sub-group were based on
a basement ridge forming dolerite (Oenpelli Dolerite) being dated at c.1690 Ma and one of the volcanic members within it being dated as 1645 Ma (Page et al., 1980 in Needham, 1988).

Some one billion years separates the depositional stratigraphic record above the Kombolgie Subgroup. In the far north east of Arnhem Land, below the escarpment at Junction Bay, a sequence of Middle Cambrian sandstone and shale (Wessel Group) has been preserved, the basal unit containing the trace fossil Skilithos (Plumb et al., 1976). Also preserved in pockets of Arnhem Land are the Mesozoic Bathurst Island Formation and even more rare, upon the plateau, the Mesozoic Petrel Formation. The former consists of a sequence of fossiliferous paralic sediments palynologically dated from Neocomian to Cenomanian (Early to Late Cretaceous) in age.

4.3.2.4 The RUM Weathering Profile

There have been many suggestions for the age of the weathering profiles in the Northern Territory and northern Australia, including Mesozoic to early Tertiary (Grimes, 1979), Late Mesozoic (Twidale, 1983), Miocene (Twidale, 1994), Early to Mid-Tertiary and Palaeocene (Twidale and Campbell, 1995). Dating of Mn-oxides in weathering profiles on Groote Eylandt in the Gulf of Carpenteria to the east of RUM resulted in ages in the Eocene, Oligocene and Miocene (Dammer et al. 1996).

It has even been suggested that the weathering profile in the Alligators Rivers region had already been formed to an extent before deposition of the Precambrian Kombolgie cover sequences (Needham, 1988). This has been based largely on the Kombolgie-PCG unconformity surface resembling the current landscape surface below the escarpment. In fact it has been claimed that the clays of this weathering profile may have been involved in ore genesis at RUM (see Needham, 1988). It is yet to be established whether this is the case, however it is clear that weathering is still active at the surface (own observations). A recent chronological study (U-series disequilibria) on pisoliths in the pisolitic ferruginous horizon capping the RUM weathering profile by Bernal (2003) suggests there are no preservations of Fe-oxides older than 300 ka.
4.3.2.5 Igneous Intrusions

An extensive combination of sills, dykes, volcanic plugs and granites have intruded the PCG and its cover sequences, the rocks of RUM not isolated from some of these events. These include the Zamu Dolerite sequence at 1914 ± 170 Ma (Page pers. comm. 1984 in Needham, 1988), the Nabarlek Granite at 1780 Ma minimum (Page et al., 1980), the Tin Camp Granite at 1755 ± 15 (Page et al., 1980), the Jim Jim Granite at 1732 ± 11 (Page et al., 1980), the Oenpelli Dolerite at 1688 ± 13 Ma (Page et al., 1980), the Mudginberri and Maningkorrrirr Phonolite dyke swarms at 1316 ± 40 Ma (Page et al. 1980) and far from RUM, the Wurugoij Dolerite plug at 1200 ± 40 Ma (Needham, 1988) and a small vertical porphyritic olivine basalt that cuts the Nungbalgarri Volcanic member of the Kombolgie Formation, dated at 522 Ma (Needham, 1988).

One of the most significant to RUM is the Zamu Dolerite since it has been suggested that amphibolites within the RUM deposits belong to this sequence of intrusives, although alternative origins are possible (Reynolds and Miezitis, 1985). The Zamu Dolerite outcrops as lensoids up to 2 km long which are aligned parallel to the dominant foliation in the surrounding Cahill Formation or Nourlangie Schist, narrow dykes transgressing (apparent) the foliation of paragneiss in the Nanambu Complex and a 167 metre thick sill-like amphibolite intersected by drilling beneath the Jabiluka No. 1 Orebody (Needham, 1988).

Chloritised but unmetamorphosed doleritic dykes within the RUM orebodies have been postulated to be Oenpelli Dolerite however dating of a similar rock adjacent to Orebody No. 1 suggests that they may be unrelated chronologically. The Oenpelli Dolerite occurs as three ellipsoidal lopoliths that crop out as arcuate ridges up to 100 metres high and 1 km wide in the centre and south of the region. It also includes scattered exposures of dolerite north of Oenpelli, rare sub-vertical, possibly stringer dykes around 1 metre wide and as an isolated exposure of dolerite in the west of the Alligator Rivers Uranium Field (Needham, 1988). The altered dolerite intersected by drilling directly east of the RUM No.1 orebody was dated at 1370 ± 30 Ma (Page et
al., 1980), an age similar to the Mudginberri and Maningkorri Phonolite dyke swarms.

4.3.3 Mine Geology

Figure 3.3 shows the simplified geology of the RPA. Figure 3.4 shows cross-sections of both Orebody No.1 and Orebody No. 3 from Kendal (1990). The geological units have been separated according to the stratigraphy and nomenclature used within the mine.

The Footwall Sequence (FWS) is part of the Nanambu Complex, the unit is extremely variable consisting of schist, gneiss, microgneiss and granite, the granitic textures being more dominant away from the ore body both laterally and vertically (Kendall, 1990). These characteristics suggest that the direct basement to the RUM ore bodies is actually that part of the Kakadu Group accreted onto the underlying granite during metamorphism referred to earlier. An apparent conformable contact with the overlying mine sequence, (Colville, 1974 in Reynolds and Miezitis, 1985) is consistent with Kakadu Group/Cahill Group relationships (see regional stratigraphy above). Closer to the ore, the unit has been chloritised and sericitised.

The Lower Mine Sequence (LMS) corresponds with the lower member of the Cahill Formation and basically consists of two carbonate units separated by lenticular schist. The lower carbonate unit is a magnesian marble, having recrystallised during metamorphism, which accounts for the bulk of the LMS. It is believed that some of the lower carbonate has been replaced by massive chlorite (Kendall, 1990). The upper carbonate is an impure carbonate with interbedded chlorite schist and patches of massive chlorite. It is believed that closer to the ore this unit is replaced by chert known locally as Jasperoidal chert (Kendall, 1990).

The prominent lenticular schist is mostly quartz, chlorite and sericite, and can be used as a marker unit throughout most of the RPA (Kendall, 1990). The FWS/LMS contact is often masked by a 10 metre faulted section known as the ‘footwall shear zone’. This section contains shredded fragments of FWS schist and gneiss and LMS schist combined in a chlorite matrix (Kendall, 1990).
Figure 4.2: Geology of the Ranger Project Area (RPA) including the two orebodies exploited at Ranger Uranium Mine, Ranger No.1 and Ranger No. 3. Source: modified from Hein (2002).

The **Upper Mine Sequence (UMS)** is up to 500 metres thick and is also part of the **Lower Cahill Formation**. It consists mainly of quartz-feldspar-biotite schist and microgneiss, altered to a quartz chlorite schist closer to the ore zone. Carbonaceous bands, interpreted to be metamorphosed beds of black shale, occur in some parts of the sequence. The UMS is the main host to uranium mineralisation within the RPA.

The **Hanging Wall Sequence (HWS)** is thought to correspond to the **Upper Cahill Formation**. It is a group of micaceous quartz-feldspar schists with frequent interbeds of amphibolite and localised horizons containing garnets.
Figure 4.3: Geological cross-sections of the Ranger Uranium Mine orebodies. Source (Kendall, 1990)
Olivine dolerite dykes and sills seem to be more common in Ore Body No.1 than anywhere else in the RPA (Kendall, 1990; Reynolds and Meizitis 1985). They have been mapped locally simply as ‘basic dykes’ and have been intruded along faults associated with the primary uranium mineralisation. In the LMS of orebody No.1 the dolerite occurs as steeply dipping bodies up to 70 metres thick whilst in the UMS it occurs as veins mostly less than 40cm thick (Kendall, 1990). The dykes follow faults associated with primary uranium mineralisation but do not host primary mineralisation themselves except for one instance (Kendall, 1990).

According to Kendall (1990) four types of Pegmatite, all barren, can be found within the RPA. Dark green quartz rich and quartz poor pegmatites are usually 50-100 metres in thickness and are thought to be the result of an in situ digestion of LMS rocks rather than intrusives (Kendall, 1990). They are generally confined to the LMS and seem to be conformable with LMS stratigraphy. Light green quartz-rich and quartz-poor pegmatites are found throughout the mine sequence but are more common in the UMS and HWS. Shearing and chilled margin contact relationships with their surrounding rocks indicate that these pegmatites are definitely intrusive (Kendall, 1990). Most are between one and ten metres thick and dip easterly at 20-40° along a NE strike.

A section of the Kombolgie Sandstone has been interpreted in ore body No.3, allegedly a down-faulted block of the once covering sandstones (Reynolds and Meizitis, 1985). However, recent work by Hein (1999) does not support such an interpretation; instead she argues that it is simply part of the PCG sequence. After personal observations of freshly mined boulder sized specimens of this material, made in April 2002, it is argued here that although this material is chloritised, it is relatively un-metamorphosed compared to the metasediments of the PCG in the mine, and thus not part of the same metasedimentary sequence. It is still easily recognised as a sandstone with well preserved, up to cobble sized, well-rounded rock fragments interspersed within it. It may or may not be Kombolgie related, but it is definitely post-peak metamorphism at RUM, and not part of the Cahill formation or Nourlangie schist. It is thus proof that chloritisation and movement of the ore-related fault at RUM has occurred post-cover deposition, an important fact in regards to the timing of
chloritisation, and possibly even uranium mineralisation, at RUM, as well as its relationship with the unconformity.

4.3.4 Ore Genesis

There is yet to be one defining theory that explains unequivocally ore genesis at RUM, or any of the unconformity-related uranium deposits for that matter. It is agreed that in general mineralisation of all unconformity related uranium deposits is associated with the precipitation of chlorite, white mica, and hematite (Komninou and Sverjensky, 1996). At RUM, this is where agreement tends to end. For instance, according to Hein (2002), mineralisation at RUM is largely associated with normal faulting and fault breccias created by brittle deformation during a period of E-W extension that followed emplacement of the dolerite (1690 Ma if Oenpelli dolerite). However, Vanderhor (2001) suggests that mineralisation was associated with an ESE-WNW to E-W shortening event that followed deposition of the Kombolgie sandstone (now 1822-1720Ma, Sweet et al., 1999).

Earlier studies have proposed an Archaean basement (Binns et al., 1980) or the lower Proterozoic sediments (Needham and Roarty, 1980; Ferguson et al., 1980) as sources for the uranium in the ARUF deposits, with deposition occurring via adsorption onto clays (Ferguson et al., 1980) or reduction by graphite-carbonaceous matter (Binns et al., 1980; Donnelly and Ferguson, 1980).

Probably the most generally accepted theory to recent, involves the overlying sandstones and prehnite-pumpellyite facies altered interbedded volcanics as the source of the uranium (Maas, 1989) with large-scale hydrothermal activity involving highly saline diagenetic fluids transporting the uranium (Crick and Muir, 1980; Maas, 1989). This model envisages deposition of the ore by reduction via either mixing with a methane bearing fluid and/or direct interaction with the graphitic and/or ferrous Fe-bearing schist (Wilde et al., 1989) or alternatively changes in more simple chemical parameters, such as pH, temperature and pressure (Komninou and Sverjensky, 1996; Wilde et al., 1989).
Such a model explains the high salinities found for ore forming fluids, the large volume of un-apposed oxidised fluids needed, the 100 - 200°C ore forming temperatures and the unconformity relationship (Maas, 1989). The problem for this theory was the fact that at RUM, the U-Pb 1737 ± 20 Ma (Ludwig et al. 1987) and minimum 1650 Ma ($^{87}$Sr/$^{86}$Sr) (Maas, 1989) age of primary uranium mineralisation meant that ore formation was pre-Kombolgie deposition, unlike the other ARUF deposits (1650 Ma – see in Hein, 2002; Maas 1989). However, the new age of 1822-1720Ma for the Kombolgie sub-group (see above) means that this is a problem no longer. Still, a discrepancy remains between the alleged ages of RUM and other ARUF deposits, a discrepancy that may suggest different processes operating at RUM (Maas, 1989).

4.4 THE MINE TO WASTE TRANSLATION

It should be clear that only the geology that is located within the confines of the actual RUM pits will be extracted from the deposit, and only that geology that is not part of the higher-grade ore, in this case above grade 3 (refer to Table 1.1), will be distributed to the waste and LGO stockpiles. Therefore a translation must be made from what is the geology of the mine, to what is the geology of the waste and LGO stockpiles.

4.4.1 Identification of the Dominant Lithology - An estimation of the Relative Bulk Composition of the RUM Waste and LGO Stockpiles

General observations of the entire surface of the waste and LGO stockpiles as well as some 7 excavations into the stockpiles suggest that schist, of all nomenclature, is by far the dominant lithology of the waste and LGO stockpiles of RUM. Location mapping of weathered material already presented in the previous Chapter (Figure 3.12) also suggest that weathered material is a significant component of the waste and LGO stockpile system.
To test this and to approximate just how dominant schist and weathered material is, a bulk stockpile relative composition estimation has been made here for the 1999/2000 end of financial year (EFY) and the 2002 end of calendar year (ERA changed to calendar year reporting in 2001). These two years have been chosen because the former correlates to the major water sampling expeditions of this study and the latter correlates to the final expedition to RUM and a time of continued changing water chemistry in RP2, the mine’s central retention pond (see Chapter 6). The results of these estimations are presented in Table 4.1 and Figure 4.4 as relative percent of total material stockpiled. Included in Table 4.1 is a direct conversion of this percentage into tonnes of waste and LGO based on the total estimated tonnes of waste and LGO distributed to the stockpiles as of the 1999/2000 FYE (50.94246 million tonnes) and 2002 calendar year (64.56446 million tonnes) (calculated from data presented in annual ERA Company Reports).

It is acknowledged here that the direct conversion from percent to tonnes does not take into account the different densities of the different materials. However, since annual tonnage figures are calculated by mine staff using maximum load constants for each truck, and thus also do not take into account such details, it was considered unnecessary to do so here. It should also be noted that the tonnage figures used above for the total waste and LGO stockpiled, take into consideration all that waste and LGO that has been diverted from the stockpiles and into construction projects.

The estimation basically involves delineating the relative amount of each rock type of nomenclature according to Kendall (1990), that has been mined from each pit at RUM but not classified as high grade ore (above grade 3), which is distributed to the ore stockpiles, and that was not distributed to construction projects.

The proportional calculations were made using the most recently published geological cross-sections of both pits, those of Kendall (1990) (Figure 4.3 above), with approximate pit outlines projected upon them. The pit outlines were approximated using final pit outlines for P1, December 1999, P3 geological cross-sections and observations and photographs of P3 during 2000 and 2002. The depth of surface oxidation and hence proportion of weathered material was taken from the original published cross-sections of Hegge et al. (1980), as was the vertical scale.
Proportions of each rock type used for construction purposes and thus not delivered to the stockpiles were calculated using known P1 depth limitations for certain years along with the recorded tonnage of total waste and LGO diverted to construction projects in EFY Company Reports. Projecting these depths onto the cross-sections meant that potential rock types diverted to construction could be delineated and proportioned according to their relative abundance. However it was also known that only certain schists and chert were physically viable construction materials (ERA Company Reports), although some weathered material was used in the earlier years. It should be noted that the significant diversions of waste to construction projects only occurred during the mining of Orebody No.1, from 1982/83 to 1991/92.

It is believed here that there are more accurate methods for estimating relative bulk stockpile composition, however these were not possible in this case. Further discussion on other possible methods as well as the inherent assumptions involved in the method used here can be found in Chapter 2.

Table 4.2 and Figure 4.4 shows that, based on the estimation, weathered material was by far the most dominant material in the waste and LGO stockpiles in 1999/2000, accounting for some 41% of total stockpiled material. UMS schist was significantly more dominant than any other rock type, accounting for some 18.5% of the stockpiles and some 31.4% of the un-oxidised material. If all schists are grouped together, as has been done in the rock characterisations of this study (see later), then they account for approximately 24.8% of the waste and LGO stockpiles and 42% of the un-oxidised material. In this respect then, the estimation has proved general observations correct, schists and weathered material dominate the waste and LGO stockpiles of RUM. In fact combined, schists and weathered material made up some 65.8% of the waste and LGO stockpile ‘system’ at RUM in the 1999/2000 EFY. In a direct conversion, this equates to some 33.52 million tonnes.

Other significant constituents of the waste and LGO stockpiles at RUM are the LMS Chert and the various forms of pegmatite, accounting for some 11.2% and 10.3% of the stockpiles in 1999/2000 respectively. These figures take into account the fact that approximately 43% of all of the chert mined was used in construction projects, according to the estimation.
### Bulk stockpile relative composition estimation

<table>
<thead>
<tr>
<th>Rock Type</th>
<th>1999/2000</th>
<th>% of total</th>
<th>Million Tonnes</th>
<th>2002</th>
<th>% of total</th>
<th>Million Tonnes</th>
</tr>
</thead>
<tbody>
<tr>
<td>HWS Schist</td>
<td>3.45</td>
<td>1.76</td>
<td>2.85</td>
<td>1.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>UMS Schist</td>
<td>18.46</td>
<td>9.4045</td>
<td>32.72</td>
<td>20.203</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FWS Shear Zone</td>
<td>5.75</td>
<td>2.93</td>
<td>4.75</td>
<td>2.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lenticle Schist</td>
<td>2.77</td>
<td>1.4088</td>
<td>2.28</td>
<td>1.4088</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Schists</td>
<td>30.43</td>
<td>15.5033</td>
<td>42.60</td>
<td>26.3018</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pegmatite</td>
<td>10.34</td>
<td>5.27</td>
<td>8.54</td>
<td>5.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dolerite</td>
<td>4.59</td>
<td>2.34</td>
<td>3.79</td>
<td>2.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbonate</td>
<td>2.3</td>
<td>1.17</td>
<td>1.90</td>
<td>1.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weathered Material</td>
<td>41.14</td>
<td>20.96</td>
<td>33.95</td>
<td>20.96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LMS Chert</td>
<td>11.2</td>
<td>5.7037</td>
<td>9.24</td>
<td>5.7037</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100</strong></td>
<td><strong>50.947</strong></td>
<td><strong>100</strong></td>
<td><strong>61.7455</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 4.2:** Bulk stockpile relative composition estimation for the 1999/2000 end of financial year (EFY) and the 2002 end of calendar year (ERA changed to calendar year reporting in 2001).

**Figure 4.4:** Pie charts showing the results of the bulk stockpile relative composition estimation for the 1999/2000 end of financial year (EFY) and the 2002 end of calendar year. All schists are in shades of blue so that the increase in the total schist proportion can be seen more clearly.
The estimation for the year 2002 shows how the bulk composition of the stockpiles will change as mining of Orebody No. 3 progresses. By 2002, most of the weathered material has already been mined and so its bulk proportional representation in the waste and LGO stockpiles will decrease over time. Most of the waste and LGO material that will be mined to access the ore lens will be UMS schist, HWS schist and Pegmatite, and so these rock types will progressively represent more of the waste and LGO stockpiles. Final pit outlines for P3 suggest that a significant proportion of carbonate will also be mined and added to the waste and LGO stockpiles of RUM. However, this will depend on whether current management and corporate owners of the mine decide to continue to mine the majority of the ore or choose to close the mine early, well before such depths are achieved.

4.4.2 Lithological Distribution Estimation

It is believed here that dominating lithology in the waste rock stockpiles of any mine is not only determined by the abundance of the different rocks, but also how they are distributed throughout the stockpiles. If localised, rocks of small abundance have the potential to dominate hydro-geochemical relationships within certain areas of the stockpiles.

However, as in bulk composition estimations, it is also believed here that the only chance of having a detailed and accurate geological map of the waste rock stockpiles in a mine is if that mine has kept detailed records of waste rock management and distribution. A complete lack of waste rock management record keeping makes this impossible in many mines. However, it is proposed here that at least an estimation of the lithological distribution within a waste rock stockpile system can be made if sufficient information about the avenues for rock type localisation in stockpiles can be obtained through investigation.
It is considered here that there are three main avenues for the localisation of certain rock types in freestanding waste rock stockpiles around the world. These are as follows:

1. The purposeful storage of certain rock types by the mine for various reasons, including for example the engineering properties of certain lithology for use in construction projects like roads and retaining walls etc.

2. Grade control measures whereby certain rock types may be characteristic of a certain grade and thus distributed to certain grade areas of the stockpile system. An example would be a barren intrusive body that is distributed to the lowest grade areas of the stockpiles.

3. The geology of the mine combined with the mining technique being utilised. Specifically, this refers to the situation whereby certain lithology is being mined at a particular time in the life of the mine when a certain part of the stockpile system is being constructed, resulting in all of that particular lithology being localised in that part of the stockpile system.

At RUM the first of these avenues was confirmed and the rock type and its location resolved from discussions with the chief geologist during the second expedition to the mine in April 2000. The mine had purposefully stored a large body of carbonate from P1 in the northwest corner of the SWP (pers. comm. – Hughes, 2000). Observations authenticate this; the carbonate storage can still be found outcropping in the northwestern area of the SWP and is clearly distinguished in aerial photographs (Figure 4.5).

However to obtain a complete estimation of lithological distribution within the RUM waste and LGO stockpiles a full investigation into the other two avenues of localisation was undertaken here. To do this, an investigative technique was developed whereby the mining and stockpile construction histories were in effect, reconstructed as accurately as possible.
A dominant mix of UMS schist, Dark Green Pegmatite and Chloritised Kombolgie Sandstone, all from P3 and all relatively unweathered.

Eastern section dominated by UMS Schists and Dark Green Pegmatite from P3.
SE section at depth dominated by weathered to partly weathered material from P1.
The rest of the pile is a mix, but includes layers of weathered material that are not laterally extensive, upper regions in the central area are from P3.

Mixed pile mainly from P3. Layers of weathered material from P3 are common at the base and towards the south. Schist (mostly UMS) will tend to be dominant.

Mixed pile with weathered material at the base from P1 and a large store of weathered material in the NE corner.
Upper regions dominated by schists (mostly UMS) from P3.

Mixed stockpile.
Massive chlorite rock observed in eastern areas.

Mixed pile, however, Massive Chlorite Rock, Chloritised Dolerite and Carbonates more abundant here than anywhere else (observations and predictions).
Large store of pure carbonates in NW corner.
Concentration of carbonate observed at depth in western area.
The precise methodology and an example of its use can be found in Chapter 2. Basically however, the method involved a first step of approximating the final pit outline (disregarding benches) for P1 and the pit outline for P3 as at August 2000 and May 2002 in relation to the latest published central geological cross-sections of the mine by Kendall (1990). In addition to the pit outlines, the approximate level at which mining had reached in P1 at the end of each financial year, for a limited number of years, was also established using official geological reporting in EFY company reports (these cross-sections are displayed in the related section in Chapter 2). This information could then be used to identify the main lithology being mined at particular times during mining history. A detailed examination of the annual aerial photographic record of the mine was then undertaken to determine which parts of the stockpile system were being constructed at certain times during mine history. Cross-referencing the results of these two studies allowed for an approximation as to what lithology went where, in the stockpiles. At all times, where possible, direct observations of stockpile lithology on the surface and from the 7 excavations investigated was used to cross-examine the results obtained.

Figure 4.5 represents the outcome of the investigations, an estimation of the lithological distribution within the waste and LGO stockpiles of RUM as of May 2002. It should be emphasized that this is an approximation and as such has been confined to a general view.

Figure 4.5 shows that carbonate is not only limited to the north western corner of the SWP, but also probably distributed throughout the SWP and the south eastern areas of the SCWP. It also shows that nowhere else in the stockpiles will carbonate be found in any similar abundance. This is due to the facts that at the time most of the carbonate was being mined (from 1989/1990 financial year to 1994) the SWP was being developed and that most of the carbonate is of waste grade, the grade of the SWP.

Due to the geological distribution of chert in the mine sequence it is probable that chert is located throughout those stockpiles constructed during mining of P1, the CWP, the NCWP, the SCWP and the SWP. Pegmatite should also be located throughout the stockpiles, particularly in the lower areas of the CWP and once again
in similar areas as is carbonate, due to a significant proportion of the pegmatite being sourced from similar lower sections of P1 (refer to Figure 4.3). The pegmatite of P3 should be present in the upper levels of the CWP, the WWP and the NWP, with those of the latter most likely being of the dark green variety (observations in the western wall of P3). FWS shear zone rocks will be spread relatively thinly throughout the CWP, NCWP, SCWP and SWP area due to the nature of its occurrence in P1, a thin band climbing the western wall.

Schist will also exist in all stockpiles. It most likely accounts for most of the NWP and the unweathered rock of the WWP, as well as large proportions of the NCWP and CWP, particularly the lower and upper regions of the CWP. It will be least dominant in the SWP and the southern areas of the SCWP, areas that were constructed when schist was not necessarily the dominant rock type being mined. That being said, most of the lenticle schist that entered the stockpiles during the latter period of mining in P1, is likely to be mostly located in the SWP and SCWP areas.

The location of the weathered material has already been mapped in Chapter 3 due to its importance in the structure of the stockpiles and its potential implications for stockpile hydrology. The maps and cross-sections showing the location of the weathered material are found in Figures 3.12(a-e) and these should be referred to. Basically, weathered material, being more prominent in the early stages of mining, is located in the earlier stages of stockpile construction. It is in the centre and bottom of the CWP, the south eastern section of the NCWP, and forms a large part of the WWP due to the mining of P3. Benches of weathered material also occur sporadically throughout the SCWP and southern areas of the CWP. However, the highest concentration of weathered material occurs on the eastern edge of the CWP directly overlooking the LGO sump (refer to Figure 2.1). Highly weathered material of LGO grade has been purposefully stored in this location from the beginning of mining at RUM; Figure 3.12(b) shows the magnitude of this concentration.

It can be concluded then, that there is indeed a shift in dominant rock type within the stockpiles due to localisation of certain lithology. Hence the geochemistry and mineralogy of the schists and the weathered material may not dominate the hydro-geochemistry of all areas of the stockpiles.
Carbonate and other P1 waste grade rocks, such as chloritised dolerite, dominate the western sections of the SWP and the south eastern area of the SCWP. Weathered material dominates the entire eastern corner of the CWP, but also the base of the CWP and the lower sections of the WWP. The NWP is a relatively lithologically homogenous stockpile (as of May 2002), being dominated by unweathered schist, with dark green pegmatite and potentially very minor amounts of the down-faulted section of Kombolgie Sandstone (see section 4.3.2). Schist will also dominate most of the CWP and the upper parts of the WWP.

The Riley et al. (1993) mineralogical and geochemical analysis of samples from RAB drilling into the NCWP, CWP and SCWP, whilst limited in its extent of stockpile coverage and completed prior to mining of P3, provides some evidence in support of the above distribution estimation, at least in terms of a major difference in rock type in the southern areas of the stockpiles where the SCWP meets the SWP. In the Riley et al. (1993) mineralogical data the NCWP was dominated by quartz, with sub-dominant to minor chlorite, minor mica and trace hematite and rare feldspar and siderite. The CWP was similar, however only three samples were analysed due to the failure of both attempted drill holes to extend further than 4 metres. The SCWP was dominated by quartz, with sub-dominant chlorite and/or magnesite and dolomite and minor chlorite and/or magnesite and dolomite. The Riley et al. (1993) reflected these mineralogical findings.

4.5 IDENTIFICATION OF WASTE ROCK IN THE STOCKPILES

Table 4.3 is a brief summary of the rock types found on the waste and LGO stockpiles of RUM. The table provides a summary of the dominant mineralogy of each rock type for the geochemical analysis that follows as well as to provide a reference for the identification of RUM geology within the stockpiles. It was found during this research, that the lithological identification of individual rock specimens on the stockpiles was difficult without any stratigraphic reference from the mine.
The information is based on observations made during this research on all stockpile surfaces, slopes and excavations as of December 1999 through to November 2000 and minor investigations made during May 2002, including investigations of the south western wall of P3. Information has also been sourced from Ewers and Ferguson (1980), Needham (1988), Kendall (1990) and Von Gunten et al. (1999), as well as from the unpublished reports of Colville (1974), Reynolds and Miezitis (1985) and Milnes (1988). Original drill core descriptions of the deposit were also utilised as were a limited number of original thin section reports, particularly those of Kitto (DDH No.S1/54, 1971), Johnson (DDH No.S1/56, 1971) and Kitto and Eupene (DDH No.S1/55, 1971).

Basic mineralogical investigations by plain light microscopy of thin sections made from a limited number of selected rock samples were used to qualify the information retrieved from the above sources. Note that in Table 4.3 two mineralogical descriptions are given for the weathered material, one from Milnes (1988) and one from Von Gunten et al. (1996). Both are considered here to be applicable to the weathering profile of RUM, Von Gunten et al. (1999) describes the weathering profile of P3 where as Milnes (1988) describes weathered material from P1.

Nomenclature is that used by Nash and Frishman (1983) and Kendall (1990), the same as that used in the mine geology descriptions above. All schists have been grouped together in Table 4.3 due to their relative lack of difference in hand specimen and due to their similar dominating mineralogy of quartz, chlorite and muscovite minerals. This has been noted elsewhere. A recent geological mapping investigation of P3 by Vanderhor (2002) found that distinguishing between the HWS and UMS schists is difficult even within the mine. This is because the original separation of the two lithologies is based on a gradual change from muscovite-chlorite schist to chlorite-muscovite schist (from HWS to UMS respectively). Thus it is a distinction between the degree of chlorite alteration of a single unit rather than any true stratigraphic description that differentiates the two schists (Vanderhor, 2002). Hence distinguishing in hand specimen on the stockpile the precise amount of alteration that determines whether the rock is a HWS or UMS schist would be somewhat arbitrary and considered of no real benefit here. The dominance of the UMS schists in the mine geology will equate to a dominance of this rock in the stockpiles anyway.
### Summary of Ranger Uranium Mine Waste rock Types

<table>
<thead>
<tr>
<th>Lithology</th>
<th>Colour (hand specimen)</th>
<th>Distinguishing features (hand specimen)</th>
<th>Major Minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schist</td>
<td>Grey-deep olive-green- dark green</td>
<td>Schistose foliation and cleavage, segregation banding, thin Qtz veins ± sulfides (carbonate veins reported closer to ore), dark green with soapy surface (chlorite), Secondary Fe-oxides present on foliation plane surfaces.</td>
<td>Quartz, chlorite + sericite ± muscovite ± altered biotite.</td>
</tr>
<tr>
<td>Chert</td>
<td>White to smoky grey with continuous wisps of red, light green and darker grey streaks.</td>
<td>Massive, conchoidal fracturing, voids are common with void walls filled with Calcite + Quartz + Hematite crystals or Quartz + Hematite crystals (most obvious crystals observed with the naked eye).</td>
<td>Quartz</td>
</tr>
<tr>
<td>Carbonates</td>
<td>Light grey coloured surface with a pinkish brown tinge. Freshly exposed surfaces are white, sparry and commonly display layers of red to deep red in colour, some of which also have a yellowish green tinge.</td>
<td>Voids relatively common with euhedral crystals of calcite, quartz and gypsum. Chalcopyrite common in voids, veins and accumulations of small pod-like occurrences. Massive boulders common.</td>
<td>Dolomite, magnesite, calcite, ± tremolite ± chlorite.</td>
</tr>
<tr>
<td>Chloritised Dolerite</td>
<td>Dark to olive green, sometimes spotty (see next).</td>
<td>Massive, homogenous rock with aphanitic textures although it can develop rosettes of light green crystals in a darker groundmass. Red/brown (hematite) crosscutting veinlets are common. Specimens are often seen as exfoliated masses with small egg shaped stones as a result.</td>
<td>Chlorite, remnant plagioclase laths, remnant olivine, pyrite, hematite veinlets common</td>
</tr>
<tr>
<td>Pegmatite – dark green – light green – unchloritised</td>
<td>Deep green – light opaque green - White to slightly grey with black tourmaline</td>
<td>Light green – quartz rich areas that are friable. Unchloritised – kaolinitisation of feldspars well developed on some samples.</td>
<td>Chlorite content varies + microcline feldspar with quartz, muscovite and tourmaline.</td>
</tr>
<tr>
<td>Massive Contorted Chlorite rock</td>
<td>Dark green with purple/red to brown inclusions</td>
<td>Contorted texture, red/purple to brown inclusions of hematite common.</td>
<td>Chlorite, quartz,</td>
</tr>
<tr>
<td>Weathered Material</td>
<td>Pallid white to orange brown and reddish brown in places</td>
<td>Schistosity still evident in some quartz and muscovite rich samples. Generally present in an unconsolidated form.</td>
<td>Fine-grained hematite, goethite, residual quartz, illite, kaolinite and smectite (Milnes, 1988 – Pt 1). Quartz, chlorite/vermiculite, goethite, kaolinite and mica (below 6 metres – P3). Zones of Fe-oxide enrichment and some residual soils containing smectite, montmorillonite and beidellite (above 6 metres – P3 - Von Gunten et al., 1996)</td>
</tr>
</tbody>
</table>

Table 4.3: Descriptive summary of the materials in the waste and LGO stockpiles of RUM.
4.6 A CLOSER LOOK: MINERALOGY AND MINERAL-CHEMISTRY ASSOCIATIONS OF THE MAJOR WASTE ROCK TYPE – THE QUARTZ CHLORITE SCHIST

A limited number of rocks sampled directly from the stockpiles and from P3 during this research were analysed for geochemistry by XRF and ICPMS to use as both a reference check of Nash and Frishman (1983) nomenclature and to provide geochemistry for rock types not catered for by Nash and Frishman (1983) (see section 4.7). Three of these samples, representing the most abundant and most widely distributed primary rock type within the stockpiles (according to calculations above), the quartz chlorite schist, were investigated by Scanning Electron Microscopy (SEM) with Electron Micro-probe Analysis (EMPA) to confirm mineral chemistry relationships in the rock. Waste grade rocks were targeted due to the probability that waste material is commonly used for capping of waste-dumps, and will be used for similar purposes in the final landform preparations at RUM (pers. comm. Jones, 2004).

There were three main aims of this exercise.

1. To ascertain the mineralogical controls on the major element chemistry of the dominant primary waste material residing in the waste and LGO stockpile of RUM;
2. To establish the resident minerals for uranium in the primary waste grade material; and
3. To establish the main S-bearing phases within the primary waste grade material.

In light of these goals the three schist samples chosen for further investigation included a sample of low U content (Sample A5 – 17ppm U), a sample of higher U content (Sample A9 – 112ppm U) and a sample containing sulfides (Sample A4 – 12ppm U and 1.64% SO₃). Plain and reflected light microscopy was also used on
these three samples, as well as a number of other samples, to investigate general mineralogical relationships and structure. For further details in regards to methodology see the appropriate sections in Chapter 2. The results of major element and trace element geochemical analysis for these three samples are displayed in the tables of Appendix 6 and 7 respectively.

4.6.1 General Mineralogy and Fabric

Apart from the sample containing sulfides, all of the schists examined can be summarised as consisting of quartz and chloritised mica set in a fine grained and cryptocrystalline chloritic matrix that includes K bearing regions. The sulfide-bearing sample differed in that it contained only cryptocrystalline chlorite and sulfides as its major mineralogy.

The K rich areas within the chloritic matrix are likely a mixture of chlorite and fined grained mica such as illite and/or sericite (see below). Common accessory phases include Ti-oxides, Fe-oxides, pyrite, apatite and zircon. Chalcopyrite is also abundant in some samples, but according to the limited studies achieved here, is only related to significant quartz veining where it exists within the vein and wall rock.

Segregation into separate quartz rich and chloritised mica rich alternate layers is evident (see Figure 4.6c), although this is weak in some samples. As seen in Figure 4.6(c) there also seems to be some development of segregation into layers rich in oxides. Both the quartz and the chloritised mica show distinct lineation concordant to the major foliation of the rock (Figure 4.6c). A second, less defined foliation seems to be present in many of the chloritised mica crystals, expressed by slight twisting folds in some crystals and second generation lath intergrowths offset to the major foliation and lineation (see Figure 4.6b).

Remnant structures of what were probably feldspar crystals are still evident under crossed polars as patterns within the chloritic matrix, as is the 60-120° cleavage of less common remnant amphibole structure. The chloritic material associated with these structures is of a slightly different texture (not as fine) to the matrix chlorite.
Figure 4.6: (a) Photograph of sample A9 - dark green chlorite quartz schist fitting with descriptions for UMS schist (Drill core logg descriptions and geochemistry of Nash and Frishman, 1983). (b) Thin section photograph showing texture in sample A9. Note the segregation of oxides (top left) quartz and chloritised mica laths as well as positioning of mica lath intergrowths at an angle to foliation. (c) Thin section photograph of chlorite vein in sample A5. (d) SEM photomicrograph of region of sample A5 showing line of dissolution and re-precipitation of chloritised laths within quartz. See text for further details.
Extremely fine-grained chlorite filled (+- quartz +- accessory phases such as apatite) veining is common in some samples, both concordant to, and at angles with, foliation (for example see Figure 4.6c). Often where veining occurs, the adjacent material is disrupted. There is clear evidence in sample A5 of partial dissolution and re-precipitation of minerals along lines at angles to foliation (see Figure 4.6d). This is suggestive of post-peak metamorphism pressure induced alteration along lines of weakness where stresses have been focused.

Relatively rare elongate but rounded quartz grains are conspicuously suggestive of resister grains of detrital origin but this is uncertain since the RUM orebodies has undergone up to upper greenschist to even amphibolite facies grade peak metamorphism. Some of these grains share boundaries that are suggestive of melt-induced suture.

4.6.2 Major Mineralogical Controls on Chemistry

The restricted major mineralogy of only two to three phases, quartz, chlorite and chloritised mica is responsible for the major element geochemistry shown below (section 4.7) whereby it is dominated by the interplay between the proportion of Si (quartz content) and the proportion of Al, Mg and Fe (chlorite content). This is true, not only for the schist, but for most rocks, other than the carbonates, in the two RUM deposits due to the extensive nature of the chloritisation.

In this analysis, six different chloritic materials have been identified by habit and location. These include a ubiquitous matrix chlorite (Figure 4.6b and 4.7a), a matrix chlorite associated with replacement structures (Figure 4.7a and b), an Fe-rich massive chlorite in a sample associated with a chalcopyrite rich area near a quartz vein (Figure 4.7c), vein chlorite (Figure 4.6c and Figure 4.7a), chloritised mica laths (Figure 4.7d and 4.9b) and a K bearing chlorite/fine-grained mica matrix aggregate (Figure 4.7a and c).

The composition of the chloritic material varies significantly, however, there are some general associations with habit and location that are distinguishable. Table 4.4 presents a number of completed EMPA analyses of chloritic material from the three
samples analysed. The chart shows that by composition, the ubiquitous matrix chlorite is mostly Al-Mg-chlorite, although higher Fe content was also found on occasions. In the chloritised mica laths, the chlorite was found to be mostly Fe-Mg chlorite with less Si and Al than other varieties. The massive chlorite from sample A4 are also Fe-Mg chlorites, however the Mg and Fe content varied so that either cation could dominate the octahedral sites. Although few completed analyses are given here the chlorite associated with many of the replacement structures within the chloritic matrix is also an Mg-Fe chlorite where as the vein chlorite was found to be mostly Al-Mg chlorite similar in composition to most of the matrix chlorite.

In general it was found that the chlorite mineral chemistry could be summarised by a decrease in Fe with a corresponding increase Si content so that:

Wt% FeO: lath chlorite > massive chlorite ≥ replacement chlorite > matrix chlorite = vein chlorite
Wt% SiO₂: lath chlorite = replacement chlorite ≤ massive chlorite < matrix chlorite = vein chlorite.

### Chlorite composition

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>FeO</th>
<th>K₂O</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Massive Chlorite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A4a6</td>
<td>34.73</td>
<td>29.54</td>
<td>17.39</td>
<td>1.18</td>
<td>0.4</td>
<td>85.25</td>
</tr>
<tr>
<td>A4a12</td>
<td>34.7</td>
<td>29.01</td>
<td>19.86</td>
<td>0.79</td>
<td>0.22</td>
<td>84.57</td>
</tr>
<tr>
<td>A4a13</td>
<td>33.25</td>
<td>30.71</td>
<td>17.02</td>
<td>1.4</td>
<td>0.27</td>
<td>82.55</td>
</tr>
<tr>
<td>A4a19</td>
<td>32.72</td>
<td>29.21</td>
<td>18.95</td>
<td>1.35</td>
<td>0.25</td>
<td>82.81</td>
</tr>
<tr>
<td>A4a10</td>
<td>30.72</td>
<td>24.43</td>
<td>22.5</td>
<td>1.4</td>
<td>0</td>
<td>79.05</td>
</tr>
<tr>
<td>A4a11</td>
<td>30.94</td>
<td>19.98</td>
<td>29.84</td>
<td>4.29</td>
<td>0</td>
<td>85.03</td>
</tr>
<tr>
<td>A5f5a</td>
<td>34.34</td>
<td>26.34</td>
<td>25.06</td>
<td>2.34</td>
<td>0</td>
<td>87.87</td>
</tr>
<tr>
<td>A5f6a</td>
<td>36.04</td>
<td>28.68</td>
<td>21.02</td>
<td>1.83</td>
<td>0.33</td>
<td>87.87</td>
</tr>
<tr>
<td>A5_3a4</td>
<td>34.54</td>
<td>29.15</td>
<td>20.47</td>
<td>1.38</td>
<td>0</td>
<td>85.65</td>
</tr>
<tr>
<td>A5_3a5</td>
<td>33.32</td>
<td>17.89</td>
<td>29.77</td>
<td>6.35</td>
<td>0</td>
<td>86.94</td>
</tr>
<tr>
<td>A9</td>
<td>33.5</td>
<td>29.61</td>
<td>17.5</td>
<td>1.26</td>
<td>0.31</td>
<td>82.18</td>
</tr>
<tr>
<td>A9_4_fp1</td>
<td>32.1</td>
<td>26.45</td>
<td>24.29</td>
<td>2.24</td>
<td>0</td>
<td>85.05</td>
</tr>
<tr>
<td>A9_4_fp4</td>
<td>30.15</td>
<td>24.03</td>
<td>20.37</td>
<td>10.17</td>
<td>0.38</td>
<td>85.1</td>
</tr>
</tbody>
</table>
Table 4.4: Chlorite composition by Electron-microprobe analysis for three waste samples from the RUM waste and LGO stockpiles. See text for further details.

Table 4.5 displays some other EMPA analyses of chlorite minerals from RUM rocks as well as some examples of more ideal compositions of end-members from Deer et al. (1992). Taking into consideration that Bernal (2003) only separates the Mg-rich from the Fe-rich varieties, the analyses here from samples originating from P1 compare well with Bernal’s (2003) average compositions of chlorite from P3. In terms of the Deer et al. (1992) ideal compositions, the chlorites of RUM can be classified as either Mg-Al Clinochlore (matrix and vein), or Mg-Fe chlorites (laths and massive).
Average chlorite compositions for RUM rocks – Previous studies

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂</th>
<th>Al₂O₅</th>
<th>MgO</th>
<th>FeO</th>
<th>K₂O</th>
<th>Total</th>
<th>Mg/Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ewers et al. (1980) average (all)</td>
<td>33.05</td>
<td>21.542</td>
<td>21.57</td>
<td>7.81</td>
<td>0.17</td>
<td>84.1</td>
<td>2.8</td>
</tr>
<tr>
<td>Bernal (2003) Fe-rich average</td>
<td>30.1</td>
<td>20.9</td>
<td>16.1</td>
<td>16.4</td>
<td>0.44</td>
<td>84.3</td>
<td>1.0</td>
</tr>
<tr>
<td>Bernal (2003) Mg-rich average</td>
<td>34.4</td>
<td>24.8</td>
<td>23.1</td>
<td>4.05</td>
<td>0.66</td>
<td>87.12</td>
<td>5.7</td>
</tr>
<tr>
<td>Deer et al. (1992)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clinochlore (France)</td>
<td>27.12</td>
<td>27.66</td>
<td>30.99</td>
<td>1.44</td>
<td>0</td>
<td>87.17</td>
<td>21.5</td>
</tr>
<tr>
<td>Chamosite (Ireland)</td>
<td>25.07</td>
<td>19.78</td>
<td>1.11</td>
<td>39.3</td>
<td>0.93</td>
<td>88.05</td>
<td>0.028</td>
</tr>
<tr>
<td>Mg-Fe chlorite (UK)</td>
<td>25.62</td>
<td>21.19</td>
<td>15.28</td>
<td>25.43</td>
<td>0</td>
<td>88.94</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Table 4.5: Average chlorite compositions for RUM rocks as given by Ewers et al. (1980) and Bernal (2003) as well as example compositions given by Deer et al. (1992)(pp 336 analyses No.1, 3, and 2 in order in this table) to compare with more ideal compositions for end-members. Ewers et al. (1980) Figures are based on original diamond drill core samples (Ranger No. 1 bias) and Bernal (2003) Figures are based on samples from the northern wall of P3 (year 2000 pit extents).

The K bearing regions of the chloritic matrix, often of slightly lighter tone under the SEM than surrounding material, contain some 4-9% K₂O. Such a K content suggests that these regions are not pure chlorite but a mixture of phyllosilicates, a phenomenon that is not uncommon (see Evarts and Schiffman, 1983, Bettison and Schiffman, 1988 and Shau et al., 1990). The inability to differentiate between the two minerals is probably due to individual mineral grains being smaller than the 4μm EMPA beam width. Rare aggregations of fine-grained muscovite minerals with over 10% K₂O (on analysis - oxides) and no FeO or MgO (on analysis – oxides) were also found within the matrix (Figure 4.7a and Figure 4.9c), suggesting that ultra-fine grained muscovite minerals, such as illite or serricite, mixed with similarly sized chlorite may be responsible for the K bearing chloritic matrix. Ewers and Ferguson (1980) come to a similar conclusion after x-ray diffraction analysis of similar material in the chlorite cement of breccia in the ore zones of the ARUF deposits.

The chloritised mica laths are often only partially chloritised with muscovite still existing within them as alternating layers with chlorite (the composition of the chlorite outlined above). This alternating composition is clearly evident in thin section where it is portrayed by alternate layers of contrasting optical properties (Figure 4.7(e) and (f)). Such distinction is just as clear under the SEM, where the
lighter Fe-bearing chlorite layers are conspicuous against the darker muscovite (Figure 4.8c and d). The chlorite layers do vary in composition from Fe>Mg to Mg>Fe, although the former seems most common. Figure 4.8a and b shows two SEM photomicrographs of muscovite laths along with their composition according to EMPA analysis. These two muscovite minerals are typical of the composition of the muscovite minerals in the two samples analysed. Below these photomicrographs is the average composition of muscovite analysed by Bernal (2003) from the northern wall of P3 (Year 2002 pit extent. Note the composition of the muscovite in Figure 4.8(b) compared to that of Figure 4.8(a), where the muscovite chemistry has deteriorated with increasing Mg and Fe at the expense of all other major components. The less affected muscovite of Figure 4.8(a) is not dissimilar to the average composition of the muscovite from P3 from Bernal (2003). Using recent mica nomenclature by Rieder et al. (1999) and explanations by Spear (1995) and Deer et al. (1992) much of the muscovite analysed in the three samples chosen for this study can be classified as phengite mica with a slight deficiency in interlayer cations.

These interstratifications of Mg-Al chlorite, muscovite and Fe-Mg chlorite compositions within the same crystals may represent remnant parallel intergrowths of muscovite with biotite and their subsequent alterations or resistance to alteration under chloritising fluids. Parallel intergrowths of muscovite and biotite are not uncommon in metamorphic rocks (Deer et al. 1992).

4.6.3 Accessory Phases and Minor Elements

Zircon, Fe-oxides, apatite and a Ti-oxide phase are prominent accessory minerals in the chloritised schists and are responsible for many of the minor elements. Figure 4.7(e) and (f), Figure 4.8(c) and (d) and Figure 4.9(a-e) show the relationships between some of these minerals with each other and the major mineralogy. Two phases of Ti-oxides were discovered, one within the chloritic matrix and one within the cleavage plane of the chloritised mica laths. The Ti-oxides are relatively pure, although a small amount of Fe was found substituting, up to approximately 0.5% FeO (on analysis – oxides). On one occasion, some 1.08% V₂O₅ (on analysis – oxide) was found associated with a matrix zircon. The phase found precipitated along cleavage lines within the chloritised mica laths may contain slightly more Fe, one analysis
suggested as much as 1.32% FeO (on analysis – oxide), however due to the small width of these minerals compared to the EMPA beam, much of this Fe may represent interference from the surrounding chloritised lath. Under reflected light, internal reflections of the Ti-oxides within the chloritised mica are more indicative of anatase. XRD analysis performed on a bulk sample of A9 also favoured anatase.

Fe-oxides are also present within the cleavage and cleavage partings of the chloritised mica laths. In some of the larger cleavage partings hematite can be found as a pseudomorph or part pseudomorph of pyrite (see for example Figure 4.8c and d). Where this is the case, EMPA analysis suggests some S is still present, associated with the hematite. In some instances EMPA analysis suggests a larger proportion of Fe to O in these Fe-oxides that would equate to a composition closer to magnetite, however once again, the possibility of interferences from adjacent minerals mean that no firm conclusion can be made. That being said the abundance of deep red internal reflections under reflected light suggest that most of this material is hematite. Fe-oxides were also found precipitated along small fractures in quartz and associated with U-bearing minerals in quartz.

It is well known from experimental and natural occurrences that Ti uptake by biotite is both a function of metamorphic grade and Mg content, with Ti in biotite increasing with increasing metamorphic grade and Fe/Fe + Mg ratios (Guidotto et al., 1977 and Robinson et al., 1982 in Spear, 1995). Thus the occurrence of the Ti oxide phase along with hematite and pyrite within the cleavage plain of the chloritised mica may be evidence of a retrogressive reaction taking place in a higher temperature biotite phase and/or the effect of the Mg-rich chloritising fluid, whereby a loss of Fe and/or increase in Mg within the mica undergoing chloritisation has expelled the Ti. Chlorite replacing biotite has been noted as an indicative feature of a major retrogressive metamorphic event that took place soon after peak metamorphism at RUM (Ewers and Ferguson, 1980).
Figure 4.7: Different chlorites found in this study (see text for further details). (a) SEM photomicrograph showing a number of chlorites and their relationships to each other. (b) a close up of the left hand corner of A to highlight the replacement chlorite within matrix chlorite. (c) Thin section photograph of the massive chlorite in sample A4. (d) SEM photomicrograph of a completely chloritised mica lath with infilling K-bearing chloritic material in cleavage partings. (e) Plain light thin section view of a chloritised mica lath with alternating layers of chlorite and muscovite. (f) Reflected light thin section view of the same chloritised mica lath as that of E. Note the opaque areas within the cleavages of the mica in E are pyrite and Hematite and much smaller Ti-oxides (anatase).
Average Muscovite Composition from Bernal (2003) - P3 (Ranger No. 3.)

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Figure 4.8: (a) and (b) Two typical muscovite minerals and their composition in the samples analysed for this study. The average muscovite composition from Bernal has been included for comparison purposes. Note that Bernal (2003) muscovite is from samples from P3, whereas the samples in this study most likely originated from P1. (c) and (d) Two photomicrographs of the same region in sample A9. (c) Shows the relationship between different chlorites. Bottom right is a Mg-Al chlorite of what seems to be a completely chloritised mica lath due to remnant Ti-oxide positions, although this cannot be confirmed. Top right is a matrix Mg-Al chlorite. Top left shows Mg-Fe chlorite and Muscovite layers (see text for details). (d) Shows the relationships of minor phases within the context of the major minerals.
Figure 4.9(d) shows evidence that the Ti-oxides in the mica lath cleavage plains have produced zones of weakness or small partings in the mica where fluids seemed to have been allowed to penetrate. Thus surrounding the Ti-oxides are areas of altered mica or where the mica has been completely destroyed and replaced by K bearing chloritic material.

Apatite was found in all samples within the chloritic matrix as well as within chloritic veins. Habit ranged from rounded to irregular resorbed boundaries to relatively euhedral prisms, the latter particularly prominent within the chloritic veins. Two relatively pure phases were found, a flour-apatite (Ca$_5$(PO$_4$)$_3$(F)) (Figure 4.8c and d), and an apatite containing no F, most probably the end member, hydroxyapatite (Ca$_5$(PO$_4$)$_3$OH) (see Figure 4.9d), according to comparisons with apatite chemical analyses from Deer et al. (1992). This apatite phase is responsible for the Ca v P correlation discussed below, the strongest geochemical correlation in the RUM rock suite and one well recognised throughout the ARUF deposits (Frishman et al. 1985).

Zircon was found throughout all samples analysed and its composition and habit varied greatly. Most zircons were found as small rounded crystals (10μm) ‘floating’ in the chloritic matrix and often in close proximity to apatite and Ti-oxides (see Figure 4.8c and d and Figure 4.9d), in fact some were found surrounded by Ti-oxide and some were found on the surface of larger Ti-oxides. In some of the schist samples not analysed by EMPA, zircons were observed as inclusions in chloritised mica, often with pleochroic alteration haloes due to radiation. However euhedral hexagonal crystals were also found and a large prismatic and zoned zircon was found in sample A5 (bottom left of Figure 4.7a), the schist sample with the least amount of U.

Two relatively pure zircons (referring here to those with the highest ZrO$_2$ and SiO$_2$ content on analysis and EMPA totals near to 100%) were identified, a normal zircon containing approximately 0.9-2.0% HfO$_2$ (from EMPA analysis - oxide), and a U-Th zircon with no Hf, but approximately 0.9-1.2% UO$_3$ and 2.8-3.65% ThO$_2$ (on analysis- oxide).
Figure 4.9: Focus on a region in sample A5 showing relationship between major and minor mineral phases. (a) SEM image showing texture of sample sand and aggregation of oxides and other minor phases in certain regions. Note the meandering string of oxides through center of image from bottom left to top right seemingly associated with a dissolution feature. (b) Inset of A showing a chloritised mica lath. Note the light and dark areas in the matrix identified in the insets of C and D. (d) Inset of B showing the relationship between the minor phases and the chloritised mica and matrix materials. Note that the aggregation of zircon, Ti-oxide and phosphate is associated with an area that resembling that of a resorbed section of the chloritised mica. Most of the matrix in this area is K-bearing chloritic material. (e) View of D in thin section under plain light at 40x magnification.
On rare occasions the Hf zircons were found to contain small amounts of P, Ca and Fe, all of which were also found in the U-Th zircons along with small amounts of Al, Mg and on rare occasions some Sc. According to analyses from Deer et al. (1992) all of these elements, except for Sc, have been found in zircon elsewhere. In the only zoned zircon analysed variation between zones was minimal except for a lack of Hf in its centre and the presence of impurities such as Fe, Ca, Al, Sc and P near to the centre.

Although not quantified here, there seemed to be a distinct difference in the zircon chemistry between the samples analysed. In the sample containing the least amount of U (17ppm), there did not seem to be any dominance between the Hf and U-Th zircons, whereas the schist containing the most amount of U (112ppm) seemed to have far fewer Hf zircons compared to U-Th zircons. However, XRF results do not support such a suggestion; both rocks have similar proportions of Hf, Th and Zr. In the chalcopyrite-bearing sample no Hf-bearing zircons were found, and this reflects in the chemistry with a significant increase in the Zr/Hf ratio to 51.3 for the chalcopyrite-bearing sample from 37.8-38.5 for the other samples.

Less pure zircons were abundant. P and Fe were the most common additions to the zircon chemistry, followed by Ca, Al and Ti, and rare Rb and rarer Nd, at the expense of Zr and Si. In some cases Zr and Si decreased to such an extent, and other elements, particularly Th, increased to such an extent that the mineral could no longer be identified as Zircon. One mineral was found with as much as 28.67% PtO2 (on analysis- oxide). In most cases such increased concentrations of ‘foreign’ elements only occurred as concentrations within certain regions of zircon minerals. These regions were small compared with the EMPA beam width and so interferences from the surrounding Zr/Si based mineral may have occurred, resulting in the inclusion of Zr in the analysis of what is actually a completely different mineral. Further work would need to be undertaken to accurately determine the nomenclature of some of these minerals. It should also be noted that native Au was also found as small inclusions in quartz (see Figure 4.10e).
4.6.4 Uranium Bearing Minerals

The above shows that U is found in U-Th zircon in the waste schists. U and Th were also found associated (up to approximately 6 wt% UO₃ for each on analysis) with extremely fine grained (approx 4μm diam.) Zr-P-Si based minerals near Ti-oxides in sample A4, the sulfide sample. However these minerals do not explain the 6 times higher concentrations of U in sample A9 than the other schists, considering that samples A9 and A5 have very similar proportions of Zr. SEM examination and EMPA analysis revealed that the difference in sample A9 is that it contains U-based minerals.

Most of the U-based minerals found in sample A9 occurred as small coliform type structures (10-40μm in length) within quartz grains, an example of which is displayed in Figure 4.10(a) and (b) although other forms were found (Figure 4.10(c-f), and Figure 4.11). Rare U-P minerals were also found intimately associated with elongate Fe-oxides (Hematite) in cleavage partings within chloritised mica laths (Figure 4.10(c-d). Under the SEM these occurred as small (<4μm) bright regions within the Fe-oxides, the regions too small for any accurate EMPA analysis.
Figure 4.10: SEM photomicrographs showing examples of the habit and location of uranium based minerals found in sample A9, the waste grade sample with higher U content. See text for further details. Note Au was also found in the quartz.
Figure 4.11: (a) Skeletal uraninite in quartz, sample A9 (b) Inset of A (c) Inset of B. Note that each number corresponds to the reference number given to each of EMPA analysis of Table 4.6. The lines mark out the precise location of each analysis. See text for further details. (d) SEM photomicrograph of sample A4 showing relationship between quartz, massive chlorite and sulphides. (e) Close-up of sulphides in sample A4 showing relationship between pyrite and chalcopyrite and Ti-oxides, apatite and massive chlorite.
Figure 4.11 (a-c) displays a number of SEM images of a skeletal uraninite specimen in quartz. This was the only sample found where the uraninite form has been preserved. However, due to the nature of the uranium minerals found here it is suggested that most of them have formed from the dissolution-re-precipitation of euhedral uraninite. The core of the skeletal uraninite in Figure 4.11 has been mostly replaced by K-bearing chloritic material (analysis A92-2, Table 4.6), evidence that suggests successive chloritisation events after primary uraninite deposition. Importantly however, EMPA analysis suggests that much of this remobilisation has not necessarily transformed U into more oxidised, and more stable at low P-T conditions, mineral species.

**EMPA analyses results for selected U-minerals**

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Table 4.6: EMPA analyses results for selected U-minerals. The reference number relates to the numbers in Figures 4.10 and 4.11 and show precisely where these analyses were performed on the mineral.
Table 4.6 displays EMPA analyses of four selected U-minerals found in sample A9. Analysis A92-A92-9 are from the same specimen, that of Figure 4.11(a-c). A reference number is given to each analysis that corresponds to the precise location of each analysis in the minerals displayed in Figures 4.10 and 4.11.

In almost all circumstances U was not distributed evenly throughout the uranium minerals, rather being concentrated in certain areas within the minerals or in certain bands towards the mineral edges. Importantly, where U is concentrated (up to 91wt%), U is the dominant element at the molecular level. In the EMPA analysis atomic conversions of the raw analytical results, the ratio of atomic oxygen to all other elements is always somewhere between 3:1 and 2:1. This ratio, combined with the fact that, so long as the analyses are correct, no water seems to be present in the minerals, suggests that these minerals are of the simple oxide uraninite structure type (which are of fluorite structure type) or very similar.

Uraninite can be conceptualised as \((\text{U}^{4+}_{1-x-y-z} \text{U}^{6+}_{x} \text{REE}^{3+}_{z} \text{M}^{2+}_{2+z})\text{O}_{2+x-y-z}\) according to Finch and Murakami (1999). In other words uraninite of nominal composition, \(\text{UO}_2\), does not exist in nature, rather it is always partly oxidised, the consequence of which is additional oxygen. This would explain the variation from a 2:1 oxygen to uranium ratio in the high U minerals in sample A9 towards slightly greater amounts of oxygen. Uraninite also often contains REE and certain favourable divalent cations.

The other significant elements in the high U minerals of sample A9 are P and Fe, although Si is also important in some. Mg, Al, K, Ca, W and Pb were also found in small amounts although it is possible that some of the Mg, Al and K, as well as Si and Fe, may be associated with analytical interferences from the chloritic material in the skeletal uraninite sample. These elements have all been previously reported as impurities in uraninite (Berman, 1957; Frondel, 1958; Finch and Ewing, 1992b; Pearcy, 1994; Janeczek et al. 1996; Foord et al. 1997; in Finch and Murakami, 1999). However it has also been suggested that many of these elements, particularly those that cannot substitute into the uraninite structure to any significant degree, such as Al, Si and P, are probably related to spurious mineral inclusions (Finch and Murakami, 1999). Some of the most common mineral inclusions found in uraninite include coffinite (based on a structure of \(\text{USiO}_4\cdot n\text{H}_2\text{O}\)) and clay minerals, such as kaolinite.
and chlorite. Such inclusions are more common in extremely fine-grained uraninite (Finch and Murakami, 1999), as the uraninite found in sample A9 is. There is a strong argument for the replacement of Pb by Ca during alteration of uraninite, as an important charge balancing reaction, possibly compensating for $U^{6+}$ (Finch and Murakami, 1999).

The absence of Th coupled with the relatively small amounts of Pb, when Pb was actually found to be present, supports a low temperature aqueous environment of formation for these uraninite minerals. This is because Th is relatively immobile in low temperature environments compared to U, resulting in Th being generally only found in uraninite of magmatic origin, and because Pb in uraninite generally destabilizes the mineral, either through structural change from accumulation of Pb from radioactive decay, or auto-oxidation from the instability of Pb$^{4+}$ and its tendency to reduce to Pb$^{2+}$.

Away from the areas of uraninite in the skeletal uraninite mineral, U decreases and most other impurities increase along with a probable increase in H$_2$O (due to a decreasing sum of components). Other trace elements are associated with the skeletal uraninite and these include S, Sr, Ce, Ir, Pb and Rb, in fact in the edges of the coliform texture as much as 10.48% IrO$_2$ (on analysis – oxide) is present in places. A detailed study would be needed to identify these minerals, however it is considered likely here that they are related to increased proportions of $U^{6+}$ via the oxidation of the uraninite. Increased P in some areas may be indicative of phosphate inclusions. The differing concentrations of various trace elements within the U-based minerals may give an indication as to the chemistry of the fluids responsible for their precipitation and formation, something that may be of interest for future study on the RUM deposit.

Whatever the case, the important finding here is not only that U-based minerals are responsible for variations in U in the waste grade RUM waste rock, but also that a significant proportion of this U is in the form of uraninite, a mostly reduced uranium species, and thus if given the opportunity, is readily available for oxidation and to be given up to solution.
4.6.5 Sulfides

Sample A4 was specifically chosen to investigate the nature of chalcopyrite visible in hand specimen within the chloritised schists. Figure 4.11(d) is an SEM photomicrograph of the relationship between the quartz, the chlorite matrix and the sulfides. As can be seen, the sulfides are restricted to the chlorite matrix and the contact between the quartz and the chlorite matrix is a transgressive one, suggesting incomplete crystallisation of both materials upon meeting. It is difficult to ascertain the exact crystallization history in the section, most of the sulfides seem to have crystallized first, pyrite followed by chalcopyrite (see Figure 4.11(e)), however the relationship between some of the quartz and chalcopyrite suggests that at least some of the quartz had already crystallized. In the bottom left hand corner of the photomicrograph of Figure 4.11(d) there is also clear evidence of truncation of quartz by a chlorite vein, possible evidence of remobilisation of chlorite.

Figure 4.11(e) shows that chalcopyrite generally occurs as large anhedral crystals, often encompassing euhedral, but mostly anhedral pyrite. Ti-oxide, apatite and occasional Fe-oxide are also associated with the chalcopyrite.

Chalcopyrite was not found in the other samples studied. However pyrite was found to be relatively common in cleavage partings within the chloritised mica in the sample containing the highest amount of U. Figure 4.8(c-d) is an example of one of the larger specimens of pyrite, in this case partly pseudomorphed by hematite. No pyrite was found in the schist sample containing no U-based minerals. This finding is supported by the fact that the schist containing the U-based minerals has more than double the bulk rock S content than the schist where no U-based minerals were discovered. However a SO\textsubscript{3} content of 0.011% (on analysis – oxide) in this latter sample does not rule out the possibility that pyrite may be present in the rock.
4.7 WASTE AND LOW GRADE ORE GEOCHEMISTRY

4.7.1 Introduction

This geochemical analysis of the RUM waste and LGO rocks is largely a re-analysis of an existing geochemical database found in Nash and Frishman (1983). The Nash and Frishman (1983) database is the largest and most representative multi-element geochemical database of the rocks of the RUM deposits with geochemical analysis of 370 rock samples. It entails samples from drill core from both the Ranger No.1 and Ranger No.3 deposits with 20 samples taken from drill core from unmineralised rocks over 1km from the ore zones. There is however, a bias in the number of samples towards the No. 1. orebody.

The Nash and Frishman study (1983) separates the data into different rock types however in doing so, does not discriminate for ore grade and includes those samples external to the deposit. It includes a comparison of ore rocks to none ore rocks, but this is based on field-measured radioactivity with the cut-off at a 250ppm equivalent (the waste cut-off for RUM is 170ppm equivalent and the LGO/ore cut off is 1000ppm equivalent) and does not separate the different rock types. Therefore, for the purposes of this project, the Nash and Frishman (1983) geochemical database has been re-analysed according to the specific purpose here; to characterise the geochemistry of the different types of waste and LGO material most likely to be found in the RUM waste and LGO stockpiles. Grade separations have been forced on the Nash and Frishman (1983) data according to the percent U equivalent values for the official percent U\textsubscript{3}O\textsubscript{8} grade cut-offs used in the mine for the corresponding grades, that is 0-170ppm U for waste (grade 1), 170-1000ppm U for LGO (grades 2 and 3) and above 1000ppm U for ore (grades 4-7). Therefore, it should be understood, that these are actual grades and not grades based on field-measured radioactivity as is the method used to distinguish grades in the mine.

All Nash and Frishman (1983) data has been visually inspected for abnormal outliers and assessed according to the outlier assessment criteria outlined in the appropriate section of Chapter 2. Only a single sample of LGO grade UMS schist and a single sample of massive chlorite rock were omitted from the analysis as abnormal outliers.
The schist sample had over 221 times the average amount of CaO, over 232 times the average amount of P and only 9.28% SiO₂ compared to the average 65.15% for the rest of the samples. It is considered here that this sample was most probably a concentration of apatite, although limited sample size may also have been of some possible consequence. The chloritic marble outlier contained some 82.8% total Fe₂O₃ compared to the average 3.46% of the rest of the samples.

Rocks classified by Nash and Frishman (1983) but not classified by Kendall (1990) have been included in the analysis. The LMS schist is found interbedded in the upper impure chloritic carbonate of the LMS sequence and so has not been separated by Kendall (1990) whereas Nash and Frishman do make this separation. The FWS schist is interpreted by Kendall (1990) as part of the FWS basement rocks but also as being incorporated in the FWS shear zone. Nash and Frishman (1983) separated the FWS schists from the other rocks, however their significance in the stockpiles will be minimal due to their dispersed distribution. The granitic dyke is somewhat of an unknown. It is thought here that the granitic dyke may actually correspond to the unchloritised pegmatite.

A limited number of geochemical analyses by XRF and ICPMS (for some trace elements) was performed on selected rock samples for this research, however the purpose of most of these were to either align field identification with Nash and Frishman (1983) nomenclature or to qualify the Nash and Frishman (1983) data. Only for the weathered material, the examples of the light green and dark green pegmatite and the sample of the yellow/green weathered granitic rock were these analyses used in the following geochemical study. These latter rocks were included because Nash and Frishman (1983) did not analyse any of the RUM weathering profile, nor differentiate between different varieties of pegmatite.

For the weathered material data is taken from an analysis of a single bulk composite sample of weathered waste material from P3. This sample was derived from a store of samples remaining from a study by Jones and Hughes (1999), and thus subsequently corresponds with sample R3L1 from the Jones and Hughes (1999) study.
The dark green pegmatite geochemistry is taken from an analysis of a single specimen of dark green pegmatite (sample RR770) sampled from the western end of the southern wall of P3 on the May 2002 P3 base. The light green pegmatite geochemistry is taken from the analysis of two rock specimens (samples A14 and A16) sampled from the surface of the SWP, one (sample A11-the waste sample) being more weathered than the other. The weathered yellow/green granitic rock geochemistry is taken from a single specimen (sample RR215(b)) sampled from the south eastern wall of the CWP in November 2000.

4.7.2 Major Element Geochemistry

Figure 4.12 shows the relative major element geochemical composition of all of the waste and LGO materials described in the previous section, based on arithmetic means of data from Nash and Frishman (1983) and geochemical analyses made here. In most cases, three hollow pie charts have been produced for each rock type, representing three grades of uranium mineralisation, waste, LGO and ore grade as outlined above. The number inside each hollow pie chart represents the number of samples represented by each chart. All schists have been grouped together (Figure 4.12(a)), as have those rocks most likely to be concentrated in the SWP (Figure 4.12(b)).

Figure 4.12(a) shows that most of the waste and LGO schists have consistent relative major element compositions, particularly the UMS schists, which do not even seem to change significantly in the ore zone. They tend to portray their high quartz content and have approximately double the amount of Mg to total Fe, consistent with the dominating chlorite composition towards the Mg-Al Pennite/Chlinochlore varieties shown above.
Figure 4.12(a): Hollow pie charts showing the relative major element composition of schists (and gneiss in the case of the FWS) in the RUM waste and LGO stockpiles based on averaged data from Nash and Frishman (1983). The data for each rock type has been separated into waste (0-170ppm), LGO (170-1000ppm) and material that should not be in the waste and LGO stockpiles, ore grade (>1000ppm) for comparison purposes. The number in the middle of the hollow pie charts is the number of samples represented by each individual chart. See text for further details.
Figure 4.12(b): Hollow pie charts showing relative major element composition of carbonates, dolerite, chert and massive chlorite rock, components of the RUM waste and LGO stockpiles. Data has been separated into waste (0-170ppm), LGO (170-1000ppm) and ore material (>1000ppm), except for carbonates where no LGO data existed for chloritic marble and no ore material existed for LMS marble, adn for the massive chlorite rock, for which no LGO material existed. The data is averaged data taken from the Nash and Frishman (1983) database. The number in the middle of the hollow pie charts is the number of samples represented by each individual chart. See text for further details.
Figure 4.12(c): Hollow pie charts showing relative major element composition of weathered material, one of the major components of the RUM waste and LGO stockpiles, as well as that for the Granitic Dyke, Kombolgie Sandstone, Light Green Pegmatite, Dark Green Pegmatite and Weathered yellow/green Quartz rock. Data has been separated into waste (0-170ppm), LGO (170-1000ppm) and ore material (>1000ppm) where possible. The data for the Granitic Dyke and Kombolgie Sandstone is averaged data taken from the Nash and Frishman (1983) database. The data for the weathered material is from an XFR analysis performed for this research of a bulk sample of weathered material from P3 taken by Jones and Hughes (1999). For all other rocks the data is from XRF analysis from selected specimens sampled directly from the RUM waste and LGO stockpiles. The number in the middle of the hollow pie charts is the number of samples represented by each individual chart, C=bulk composite. See text for further details.
However the less abundant FWS and HWS schists have greater amounts of total Fe relative to Mg. The decrease in the Mg/Fe ratio is consistent with decreases in chlorite alteration. A much greater amount of K relative to other elements in these schists is indicative also of a decrease in the amount of chlorite alteration, the K most likely preserved in remnant feldspars and/or mica, consistent with mine descriptions. However it may also relate to the preservation of K in K-bearing chloritic material from an original higher K-feldspar content, despite the ubiquitous chloritisation.

The LMS schist differs markedly from the other schists, having a much larger proportion of chlorite elements, possibly a result of a lack of quartz in this rock. In the mine, this schist is located within the upper carbonate unit, where the massive chlorite is also found in “patches” (Kendall, 1990). The massive chlorite rocks show a similar lack of Si content and hence it is possible that these two rocks are related to each other or have been confused with each other in Nash and Frishman’s (1983) sampling.

The LGO grade LMS schists also have a completely different Mg/Fe relationship to other grades of the same rock, in that they have almost as much total Fe as they do Mg. It is possible that this is caused by a combination of hematite alteration and a small sample number, as also seems to be the case with the single sample of Massive Chlorite ore. A waste grade sample of Massive Contorted Chlorite rock containing a significant amount of pervasive hematite alteration analysed here also had a similar Mg/Fe ratio. Such alteration may be common for the region of mine geology to which these rocks belong. That being said, the mineral chemistry analysis of sample A4 above provides a simpler possible explanation, that the massive chlorite matrix dominates these rocks, which is consistently a Mg-Fe chlorite of varying Mg or Fe dominance.

Ti content corresponds to Ti-oxides, shown above to be common accessory minerals in these rocks. Titanite (referred to as Sphene in Ewers and Ferguson, 1980) has also been recognised as a common accessory mineral in the wall rocks of all the ARUF deposits (Ewers and Ferguson, 1980). The Ti content of the dolerite is consistent with the average chemical composition of dolerites provided by LeMaitre (1976 in Best, 1982) and due to Ti-oxides.
One of the most important features shown in Figure 4.12 is the markedly different chemistry of the rocks that are concentrated in and potentially dominate the SWP and southern SCWP areas of the RUM waste and LGO stockpiles. This difference is even more significant when it is considered that the LMS schists originate from within the upper carbonate unit in the mine, and are thus also probably concentrated in the same area of the stockpiles. The geochemistry of the carbonates differs dramatically from the other rocks, being extremely rich in Mg and Ca and poor in Si, a consequence of the magnesite, calcite, and dolomite mineralogy. The impure chloritic carbonate has increased proportions of Fe, Al and Si at the expense of Mg and Ca in comparison to the more pure marble, consistent with the chloritic nomenclature. The dolerite has higher concentrations of K and a reduced proportion of Si relative to the dominant schists, except for the two ore grade samples where increased chloritisation has come at the expense of K content. Mg dominates the Massive Chlorite Rock. Thus, the SWP and SCWP area has a very different geochemistry than other areas of the RUM waste and LGO stockpiles.

The relative major element composition of the weathered material differs from the schists in that it has more total Fe than Mg. This is a direct consequence of the preferential leaching of Mg during the weathering process. A recent geochemical study of the northern wall of P3 by Bernal (2003) showed a gradual loss of Mg to Fe towards the surface, confirming this.

Finally, Figure 4.12 also clearly shows the progressive increase in chloritisation towards the ore zone of the RUM deposits. Almost all of the rocks shown in Figure 4.12 show an increase in the chlorite components (Fe, Mg and Al) at the expense of Si and on most occasions K, in the more U rich samples.

It is also important to point out here that, disregarding the carbonates, whilst K is lacking in some schist samples, Figure 4.12(b) shows that almost all of the chert and massive chlorite rocks do not contain any significant amounts of K. This is important because if pre-ore or syn-ore fluids were K bearing as has been modelled for the ARUF deposits (Komninou and Sverjenensky, 1996) based on fluid inclusion evidence from Wilde et al. (1989) then either these fluids did not enter the chert and massive chlorite rocks, or they were no longer saturated in regards to white mica.
when they did and thus not precipitate any K-bearing phase. It may also suggest that the K was sourced in situ from the destruction of a K-bearing phase (for example biotite, white mica or K-feldspar), or at least, the destruction of a local K-bearing source caused infiltrating fluids to become saturated in regards to white mica. In thin section, relic feldspar shapes, amongst others, are still evident amongst the K-bearing chloritic groundmass (see later). Ore and alteration fluids of the RUM orebodies are not the subject of this thesis and so this will not be developed further here.

4.7.3 Trace Element Geochemistry

A number of trace elements, particularly the rare earths, were deemed unreliable by Nash and Frishman (1983) in their geochemical study of the RUM deposits due to problems with the analytical method and the potential interference of high U content. Removing the unreliable elements left 22 trace elements for re-analysis here.

Figures 4.13(a) and (b) display the pattern of trace element distribution for each rock type, using arithmetic means of the Nash and Frishman (1983) data, for the 22 elements retained for re-analysis. Each element is represented along the x-axis from chalcophile through siderophile to lithophile and partly atmophile according to a Goldschmidt based element affinity classification by Gill (1996).

The right hand side of the charts in Figure 4.13 show that, apart from small variances, all of the RUM waste and LGO materials have a relatively similar pattern of abundance of the mostly lithophile elements (F through to Cl), except for the more pure carbonate, the LMS marble. This is probably due to associations of the lithophiles with similar dominant silicate mineralogy, even the chloritic carbonate seems to have been effected significantly by the introduction of chlorite when compared to its more pure counterpart. The pattern is one of higher F, Na, Rb, Zr, U and Cl and lower Sc, Sr, Y, Cs and Th with varying amounts of Ba. Although in the strictly waste grade material, Ba is much higher and U lower.
Figure 4.13(a): Trace element geochemistry of the RUM waste grade rocks and materials. Data utilised from Appendix I in Nash and Frishman (1983). Concentrations are log10 of arithmetic means in parts per million (ppm). (N) = analysis by instrumental neutron activation. All others by inductively coupled plasma spectrometry.

Figure 4.13(b): Trace element geochemistry of the RUM LGO grade rocks and materials. Data utilised from Appendix I in Nash and Frishman (1983). Concentrations are log10 of arithmetic means in parts per million (ppm). (N) = analysis by instrumental neutron activation. All others by inductively coupled plasma spectrometry.
The similarities do not hold for the chalcophile and siderophile elements on the left hand side of the chart. This should not be surprising, since many of these are transition elements, their higher valencies allowing them to form a wide range of coordination complexes and therefore to be effected by different geological conditions. Many of these elements will be more associated with minor phases, such as sulfides and oxides, phases that may vary greatly in abundance between different lithology and may have other factors involved in their distribution, like the concentration of fracturing in the rocks. Those waste and LGO materials that seem to show greatest deviation from the trend in the chalcophile and siderophile areas of the chart include both of the carbonates, the granitic pegmatite, the weathered material (waste only sample) and the FWS schist (waste only).

Figures 4.14(a) and (b) repeats the charts of Figure 4.13, but without the logarithmic scale in order to highlight element enrichment that may be characteristic of certain rock types. In the waste materials, both the carbonates are enriched in Mn and Cl compared to the other rocks. The chloritic marble seems also enriched in Ga, however this value has been affected by a single sample of over 4204ppm Ga, the average without this sample being only 15.7ppm. It is important to know, however, that large amounts of Ga are possible in the chloritic marble and thus Ga is a potential indicator element for such lithology. This sample was also associated with high P, F and Al values. Figure 4.13 shows that the LMS marble is also associated with lower amounts of Ni, Ga, V, Cr, Zn, P, Sc. Cs, Zr and Ba compared to all of the other rocks.

Cl is the major anion in seawater and exists in numerous mineral phases within evaporites, mainly halite, kainite (K₄Mg₄Cl[SO₄].11H₂O), sylvite (KCl), carnallite (KMgCl₃.6H₂O), and bischofite (MgCl₂.6H₂O) (Guilbert and Park, 1986; see also Fuge, 1978). Evaporites have been suggested as the precursor for the marble in the Alligators Rivers region (section 4.3) and thus Cl bearing dolomites would fit with this model. It is not uncommon for dolomite rocks to have similar Cl abundances as those quoted here (see Behne, 1963 and Johns and Huang, 1967 in Fuge, 1978). Likewise, Mn is also common constituent in carbonate minerals, for instance it is most often found substituting for Mg in dolomite, but it is also a genuine constituent of ankerite, can substitute for Ca in calcite and Mg in magnesite, although the latter is
Figure 4.14(a): Trace element geochemistry of the RUM waste grade rocks and materials highlighting the dominant elements characteristic of different lithology. Data utilised from Appendix I in Nash and Frishman (1983). Concentrations are arithmetic means in parts per million (ppm). (N) = analysis by instrumental neutron activation. All others by inductively coupled plasma spectrometry.

Figure 4.14(b): Trace element geochemistry of the RUM LGO grade rocks and materials highlighting the dominant elements characteristic of different lithology. Data utilised from Appendix I in Nash and Frishman (1983). Concentrations are arithmetic means in parts per million (ppm). (N) = analysis by instrumental neutron activation. All others by inductively coupled plasma spectrometry.
very rare (Deer et al., 1992). There is also the obvious Mn-carbonate, rhodochrosite, although this mineral was not found in the limited plain light microscopy of carbonate sections carried out during this research. There is also no mention of rhodochrosite in previous descriptions of the RUM carbonates (Colville, 1974; Ewers and Ferguson, 1980; Frishman et al. 1985; Needham, 1988; Kendall, 1990).

Only two other elements are potential indicators for certain waste materials. P is highly enriched in the massive chlorite rock, the LMS schist and the chert and Na is enriched in the FWS schist and to a lesser extent in the UMS schist and the granitic dyke. The Na enrichment is most likely related to the presence of small amounts of remnant feldspar. The P is due to the presence of apatite, since those samples being enriched in P are also enriched in Ca.

The LGO chart (Figure 4.14b) shows similar results for the carbonates, both being identified by high Mn concentrations. The granitic dyke is distinguished by high P, Na, Ba and Mo concentrations but all of these are being affected by a single sample within a sample group size of only 3. Without this sample, P would still be high in the granitic dyke, although more around the levels shown by the Chert, Kombolgie sandstone and the LMS schist. P was an identifying element for the chert and the LMS schist in the waste materials as well. The dolerite and lenticle schist have high Na content although it must be emphasized that LGO grade material for these two lithologies are represented by only a single sample in both cases.

The most important conclusion to be made from both Figure 4.13 and Figure 4.14 is that the lithologies that are most likely to have a dominating influence in the waste and LGO stockpiles of RUM, either through bulk abundance or local concentrations, can be separated according to the trace element geochemistry presented in the four charts. The carbonates of the SWP are characterised by high Mn and in their purest form, the LMS marble waste material, are depleted in Ba, Cs, Zr, Sc, Zn, Cr, V, Ga and Ni. As the LMS marble increases in grade, it moves towards a similar lithophile trend as the other rocks, but the trend of the chalcophiles and siderophiles remains unaligned. The weathered material has higher Y and Cu than the other important rock types but lower F and much lower Mo.
Figure 4.15 is a chart of similar construction to those above, but showing the difference in trace element geochemistry between the ore and the waste and LGO material. The chart reveals a clear increase in Y, Pb and Mo in all lithology towards materials of ore grade. Therefore, these elements may have the potential to be used as hydro-geochemical indicators of ore grade material in the waste and LGO stockpiles. That being said, the Mo relationship cannot be considered certain, its interment relationship with U (see below) and the questions posed by Nash and Frishman about their own data, are considered cause for suspicion of interference from U.

**Figure 4.15:** Comparison of trace element geochemistry between the ore, LGO and waste grade materials of Ranger Uranium Mine. Data utilised from Nash and Frishman (1983) database and XRF analysis from this study.
4.7.4 Major Geochemical Relationships and Their Controls

The windows based JMP software and Datadesk statistical packages were used to perform a graphical based multivariate correlation analysis on the Nash and Frishman (1983) data for unweathered rocks of the RUM suite that had been collated specifically for this research.

Not surprisingly, the results of the analyses suggest that the major element geochemical relationships in the non-carbonate rocks of RUM can be explained by the relative proportion of the three major mineral phases in the suite, specifically the interplay between the proportion of quartz versus chlorite and the presence or absence of muscovite. Figure 4.16 best describes this relationship, where SiO\textsubscript{2} is plotted against Al\textsubscript{2}O\textsubscript{3} (Figure 4.16a) and MgO (Figure 4.16b) and MgO is plotted against Al\textsubscript{2}O\textsubscript{3} (Figure 4.16c). In Figure 4.16(c) both the carbonate and those samples containing no K, and hence no muscovite, are highlighted. As is shown, strong negative correlation exists between both Si and Mg and Si\textsubscript{2} and Al. Yet despite this strong similar behaviour towards Si, Mg and Al are only correlated positively to each other when muscovite is not present. This is because the relationship with Si is due to the dominance of quartz and the fact that geochemical analytical results represent proportions of a whole, as in weight percent, or part of a certain amount, for example ppm, and not an absolute concentration. So, as quartz increases the proportion of all other components, and hence their related elements, in this case Mg and Al, decrease. However, muscovite composition minerals are also a significant component when present, and the lack of Mg in muscovite ensures that Mg and Al only show positive correlation when chlorite is the only other major phase present besides quartz. In other words, the proportion of muscovite is independent of the proportion of quartz and thus there is no induced correlation brought about by the dominance of quartz and the nature of geochemical data in the bulk rock geochemistry between primary muscovite elements and what are essentially non-muscovite elements.
Figure 4.16: Summary of major element geochemical relationships. See text for further details. Note the points in (d) are smaller to reveal detail.
Figure 4.16(d) and (e) show that a similar relationship exists with Ti, whereby Ti correlates with Al throughout the data set yet seems to only correlate with Mg when no muscovite minerals are present. Once again this is because of the independence of muscovite concentrations, and the fact that, as was shown in the mineralogical analysis above, Ti-oxides are not only related to the chloritic matrix but are intimately associated with the chloritised mica, always being found in the cleavage planes of such minerals. Thus Ti is correlated to Al due to induced correlation, being part of the non-quartz or ‘other mineral’ proportion of the rock, but is only correlated with Mg when muscovite is not present due to its ‘real’ correlation with muscovite.

4.7.5 Major Element Relationships in the Carbonates

The obvious geochemical differences between the carbonates and all other rocks at RUM are clearly delineated in the geochemical correlations. This is particularly the case for major element relationships involving Si throughout the entire dataset, whereby in the chlorite dominated rocks increases in Si equate to an increase in quartz and a subsequent decrease in other major components, as outlined above. Contrarily in the carbonates, an increase in Si equates to an increase in impurities in regards to the carbonate mineralogy, silicates such as chlorite and tremolite rather than quartz. Hence, as Si increases in the carbonates so too do the silicate related elements, such as Ti, Al and Total-Fe, and potentially those elements related to the chloritisation events. These three minerals also tend to correlate with each other positively, however the strongest of these, and the strongest correlation of all elements in the carbonate rocks, is that of Ti and Al (Figure 4.17). Such a strong relationship is further evidence that Ti and Ti-oxides are intimately associated with the mica minerals.

Chlorite related Mg does not correspond to this trend, due to the fact that Mg in the carbonates also relates directly to carbonate minerals such as dolomite and magnesite. Although weak, a negative relationship between Mg and Ca found in the carbonates may be an indication of the competition between magnesite and calcite as dominant mineralogy, or competition between the elements themselves within dolomite, another of the dominating minerals in these rocks.
4.7.6 Trace Element Relationships and Their Controls

It is difficult to interpret the relationships amongst the trace elements due to the potential effect of induced correlation. However a number of associations are worth noting.

The abundant apatite noted earlier is well represented in the RUM waste and LGO geochemistry by a close to linear correlation between P and Ca in all non-carbonate rocks (see Figure 4.18). It is the strongest bivariate relationship in all the Nash and Frishman (1983) data and for the data produced from geochemical analysis from this research. This relationship has been discussed in detail by Frishman et al. (1985) and according to them the abundance of apatite in the RUM rocks is the product of a net introduction of P by post Kombolgie and post-ore formation metasomatism. Frishman et al. (1985) conclude that data from the literature (for example Binns et al., 1980; Eupene et al., 1975 and Gustafson and Curtis, 1983) suggests that the same metasomatism events have taken place at Jabiluka, Koongarra and Nabarlek.
A group of elements, Cr, Zn, Ga, V, and Ni all seem to have a similar relationship with Al as did Mg, in that they are positively correlated to Al, but only in those samples that do not contain mica minerals (the relationship is almost identical and so not shown here). The similarity with the Mg and Al relationship suggests a similar control, that all these elements are associated with the non-muscovite mineralogy, and so correlate with the proportion of chlorite, and hence Al in the chlorite, when muscovite is not present. When present, the abundance of the muscovite minerals interfere with the simple quartz-chlorite relationship.

Zn, Ni and Cr are known constituents of chlorite (Deer et al., 1992), substituting in the octahedral sites, and so these elements may be related to chlorite directly, although only Ni has good positive correlation with both Mg and Total-Fe. All of the elements noted above except Ga, are recognised participating ions in octahedral sites of muscovite, according to Reider et al. (1999), however it has been recognised that that the similarities in chemistry between Ga and Al, allow Ga to also be a potential substitute for Al in Al bearing phases (Goldschmidt, 1954). However, the fact that these elements correlate to Al except in K bearing phases, requires that they are not related to muscovite, or if they are, they are more strongly related to other phases that are not related to the proportion of muscovite minerals. All of these elements can be categorised as chalcophile elements with lithophile tendencies, according to the
Goldschmidt based classification by Gill (1996), and so it should not be surprising that these elements are associated with each other.

4.7.7 Uranium Associations and the Differences between Waste, Low Grade Ore and Ore

The LGO and waste database constructed from Nash and Frishman (1983) data for the above analysis of geochemical associations in the RUM rocks was separated into waste and LGO categories to examine the possibility of differences between the two types of material. This was done due to the fact that these two grades are separated to some degree in the stockpiles (see Chapter1). The ore grade data was also examined separately to determine if the geochemical relationships in the stockpiles are significantly different to that of the ore.

In all of the above associations there was no significant difference between waste, LGO and ore geochemistry data. However, this homogeneity of geochemical relationships does not extend to the ore metal itself. In the ore material excellent positive associations occur between U and Th, Mo, Y, Sc, Pb, Mn and Na and some association also seems to occur between U v Ga as well as a very general association between V and U and Total-Fe and U, although these latter two associations are not strong enough to be considered significant. The association with Sc is only evident in the higher concentration ores, greater than approximately 3000ppm U.

The relationships are logarithmic in nature as the data is heavily skewed to the right, although all are clearly evident on a normal numeric scale, just less defined. Figure 4.19 displays these logarithmic relationships across the entire grade scale. As can be seen all U associations except that with Pb, Mo and to some extent Na and Ga break down close to the LGO-ore cut-off of 1000ppm U, so that in the LGO material only these four associations remain. Even the relationships with these four trace elements begin to loosen in the LGO material. By the time U proportions have reached waste grade levels (<170ppm) all clear associations with U have dissipated, although association is still evident between U v Pb, Y and Mo, the latter seen as a tight string of data points through the centre of the waste region of the plotted data. The nature of
Figure 4.19: Significant correlations between uranium and other elements in the Ranger rocks using the Nash and Frishman (1983) database and the relationship those correlations have with ore grade. Note the decrease in correlation with decreasing grade. See text for details.
the U v Mo correlation (absolute straight line and 1:1 correlation when correlated) as well as the warning by Nash and Frishman (1983) that Mo values should be treated with caution is enough to disregard this relationship. That being said, there still may be some association between U and Mo, it just needs to be treated with caution.

This finding means that during periods of ore formation, in regions away from the ore zone, conditions were such that co-precipitation of the ore related elements did not occur, if indeed these are ore related elements. This is not unusual in hydrothermal and metasomatism ore systems where different solubilities, saturations and other chemical conditions (for example interaction with wall rock) can separate different elements out of fluids at different distances from the central ore zone as these fluids progress outwards from that central zone (Guilbert and Park, 1996). The relationship between U and Y shows a similar trend.

Of those elements described above, Pb, Mo, Fe and V are recognised as being commonly associated with Athabasca type unconformity related uranium deposits, which RUM is generally categorized as belonging to (Guilbert and Park, 1996). It should also be pointed out that regression analysis by Nash and Frishman (1983) also found that Th, Y, Pb, Na and Sc had some association with U in the ore samples, although these were categorised by field measurement only and included all samples above 250ppm (according to field measurement).

The lack of, or significant weakening of correlation of elements with U found in the Nash and Frishman (1983) data in the waste is supported by the geochemical data from this research, representing 20 waste grade samples collected directly from the RUM stockpiles. That is except in regards to Pb. Figure 4.20(a) shows that, although outliers exist, U and Pb are associated to some degree in the rocks collected here.
To further test the U v Pb association, analytical data from the early 1973-drilling program of the No. 3 orebody (P3) undertaken by Geopeko Ltd. were collated and analysed here. Pb, Cu and %U₃O₈ were the only chemical values recorded at the time. Figure 4.20(b) displays the log association of %U₃O₈ v Pb of all of the data collected, representing some 914 samples in total from Orebody No.3. The chart shows a similar trend to that of the Nash and Frishman (1983) data whereby a strong well constrained association in higher grades broadens with decreasing U content until finally dissipating to almost no correlation at all around the 0.02 %U₃O₈ value (the waste – LGO cut-off).

Galena has been documented as being associated with the ore as minute inclusions and filling fractures in uraninite (Ewers and Ferguson, 1980), but there is no reference to its association away from the ore zone as such. In the mineralogical analysis of the schists above, no galena was found. However Pb was still found associated with uranium in the skeletal uraninite (see Table 4.6 and Figure 4.11). Rather than being associated with the UO₂ based areas of the crystal, it was found in zones of moderate P content, which still had uranium as the major cation. Pb was not present in those areas where P was in abundance, but correlated to P in the mid-range P concentrations.
(approx. 4-5wt% P₂O₅). Such a relationship, whereby Pb is not associated with every U-based mineral in the waste, and when it is, it is not necessarily associated with the primary uraninite mineral, explains the relationship between these two elements in the entire Nash and Frishman (1983) data set in Figure 4.19. That is, Pb is associated with primary ore minerals in the high grade rocks of RUM as has been observed (Ewers and Ferguson, 1980), but at the low grade – LGO cut-off, an abrupt and distinct disassociation occurs, where Pb is no longer necessarily associated with all U-based minerals. Thus, the U-Pb correlation not only becomes less defined, but the slope of the defining linear equation decreases towards a lower Pb/U ratio. Such an abrupt change in the slope of the U-Pb correlation in the RUM deposits needs to be investigated further as it may be important for ore deposition and deposit evolution models.

In conclusion, the only significant differences between the geochemical associations in the waste and LGO material in the stockpiles, disregarding weathered material, is that in the LGO material Pb, Mo, and to a lesser extent Na, V and Ga seem to be associated with U. However, in the waste material, only Mo and to some extent Pb, maintains any association to U at all. Not surprisingly, the major difference in geochemical relationships between the ore and that material entering the waste and LGO stockpiles is related to those elements associated with the ore metal itself. Thus, the strong log linear correlations between the ore and its related elements should not be present in the waste and LGO stockpiles, although the associations will still be evident in the higher U containing LGO material.
4.8 SULFIDES AND SULFUR IN THE WASTE AND LGO STOCKPILES

4.8.1 Estimating Major Sulfide Mineral Content in the Waste

The mineral chemistry investigations carried out in this study suggest that in the primary waste, although pyrite is difficult to see in hand specimen in rocks in the RUM waste and LGO stockpiles, it does exist in waste grade schist containing around 100ppm U. Thus, although chalcopyrite is clearly evident in the stockpiles, disseminated pyrite, commonly recognised as the main cause of ARD, may be an important environmental consideration.

Although reference has been made to estimations of the bulk S content of the waste rock when discussing sulfides in the waste (for example leGras and Klessa, 2001, leGras et al. 1993), there does not seem to have been any genuine attempt to estimate the amount of any sulfide mineral in the bulk waste; if there has been, the data is not widely available or readily accessible and has not been obtained here. Such estimations are a complex issue with many variables that can cause considerable error, the major one being that estimations of bulk S content vary greatly. However it is believed here that at least an idea of the potential amount of pyrite and chalcopyrite in the bulk primary waste rock, the two major sulfides observed in this research, can be achieved.

Using geochemical data from XRF and ICPMS analysis of 19 samples of primary waste rock from this research and geochemistry data from other studies, an estimation has been made of the maximum average amount in wt% of chalcopyrite, galena and pyrite in bulk waste and LGO material at RUM. Table 4.7 displays the results of the calculations, according to the data’s source. Table 4.8 displays the values for S, Pb, and Cu that have been used for the calculations, according to their source. All values are arithmetic means and accompanying standard deviations of data referenced from databases or directly referenced values from publications and reports. Where necessary S values have been transformed from S03 values. In all cases, databases have been re-analysed to sort samples into waste (<170ppm), LGO (170-<1000ppm) and ore (>1000ppm) categories based on geochemical data.
### Bulk average sulphide estimations

<table>
<thead>
<tr>
<th>Source</th>
<th>Sample Type</th>
<th>Grade</th>
<th>Sample Size</th>
<th>Galena PbS (wt%)</th>
<th>Chalcopyrite CuFeS₂ (wt%)</th>
<th>Pyrite FeS₂ (wt%)</th>
<th>% of total S in Pyrite</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>primary rock</td>
<td>waste</td>
<td>19</td>
<td>0.00064</td>
<td>0.0026</td>
<td>0.0075</td>
<td>70</td>
</tr>
<tr>
<td>This study</td>
<td>NCWP profile</td>
<td>waste</td>
<td>7</td>
<td>0.0012</td>
<td>0.0124</td>
<td>0.0168</td>
<td>56</td>
</tr>
<tr>
<td>Riley et al. (1993)</td>
<td>RAB drill chips from stockpiles</td>
<td>waste</td>
<td>51</td>
<td>0.0024</td>
<td>0.0177</td>
<td>0.0505</td>
<td>71</td>
</tr>
<tr>
<td>Jones and Hughes (1999)</td>
<td>P1 primary rock</td>
<td>waste</td>
<td>NA</td>
<td>0.0024</td>
<td>0.005</td>
<td>0.0355</td>
<td>79</td>
</tr>
<tr>
<td>Jones and Hughes (1999)</td>
<td>P3 primary rock</td>
<td>waste</td>
<td>NA</td>
<td>0.0035</td>
<td>0.005</td>
<td>0.0393</td>
<td>80</td>
</tr>
<tr>
<td>Noller (1991)</td>
<td>primary rock</td>
<td>waste* unknown</td>
<td>0.0023</td>
<td>0.0185</td>
<td>0.1048</td>
<td>86</td>
<td></td>
</tr>
<tr>
<td>Riley et al. (1993)</td>
<td>RAB drill chips from stockpiles</td>
<td>LGO</td>
<td>43</td>
<td>0.0056</td>
<td>0.0221</td>
<td>0.0776</td>
<td>72</td>
</tr>
<tr>
<td>Jones and Hughes (1999)</td>
<td>P1 primary rock</td>
<td>LGO (2)</td>
<td>NA</td>
<td>0.015</td>
<td>0.0972</td>
<td>0.1328</td>
<td>58</td>
</tr>
<tr>
<td>Jones and Hughes (1999)</td>
<td>P3 primary rock</td>
<td>LGO (2)</td>
<td>NA</td>
<td>0.0126</td>
<td>0.0271</td>
<td>0.1179</td>
<td>74</td>
</tr>
<tr>
<td>Jones and Hughes (1999)</td>
<td>P1 primary rock</td>
<td>LGO (3)</td>
<td>NA</td>
<td>0.0281</td>
<td>0.0743</td>
<td>0.1235</td>
<td>60</td>
</tr>
<tr>
<td>Jones and Hughes (1999)</td>
<td>P3 primary rock</td>
<td>LGO (3)</td>
<td>NA</td>
<td>0.0337</td>
<td>0.1950</td>
<td>0.1515</td>
<td>46</td>
</tr>
</tbody>
</table>

Table 4.7: Calculations of the maximum average amount in wt% of chalcopyrite, galena and pyrite in bulk waste and LGO material at RUM based on the data from Table 4.8 below. * = <0.2U rather than U3O8.

Once again, waste and LGO material has been separated. The calculations use mean concentrations of Pb, Cu and S from various databases and published material and the ideal molecular proportions for pyrite, chalcopyrite and galena from Deer et al. (1992). Due to the large amount of Total-Fe being held in minerals other than pyrite, the amount of pyrite is calculated from the amount of left over S, after subtracting the amount of S used to make galena and chalcopyrite from the total S concentration.

Three major assumptions are made for these calculations. Firstly, it is assumed that all Pb is held in galena and all Cu is held in chalcopyrite. This may not be the case, indeed the waste investigations carried out above suggest that galena is not present in the waste grade UMS chloritised schist. Secondly, all S is assumed to be related to
sulfides, this also may not be the case, particularly in geochemistry from within the stockpiles where weathering reactions have begun to transfer S from sulfides to minerals such as sulphates. Thirdly, it is assumed that pyrite, chalcopyrite and galena represent all of the sulfides in the RUM rocks. This will definitely not be the case, however it is clear from Ewers and Ferguson (1980), plain and reflected light microscopy and SEM examination of thin sections of waste material from this study, as well as examination of a limited number of petrography reports to RUM of ore samples (Pontifex and Associates, 1997, 1991; Central Mine Services, 1987, 1987, 1971, 1971), that the main primary sulfides in the RUM rocks are pyrite, chalcopyrite and galena, any others are of only minor significance. All of the above assumptions equate to the calculations of mean abundance for the three sulfides given here as being maximum values. This is particularly the case for pyrite, whereby it is assumed that the entire leftover S after chalcopyrite and galena belongs to pyrite.

Table 4.8 shows how difficult it is to ascertain the amount of sulfides in the waste and LGO stockpiles. In the different studies on waste there is an order of magnitude difference between the lowest estimation of bulk S content from this study, 0.005%, to that of Noller (1991), 0.057%. It should be noted that the estimation from this study does not include sample A4, collected specifically for its abundant vein associated chalcopyrite, considered here to be an outlier with 0.657% S. However, such occurrences exist, and so to this extent it must be considered a minimum value.

The Riley et al. (1993) and Jones and Hughes (1999) data is probably the most representative of the RUM waste rock. The Riley et al. (1993) data is from geochemical analyses performed on drill chip samples from rotary air blast (RAB) drilling into the NCWP, CWP and SCWP. The drilling was limited in its success, only 5 from 13 holes being successfully cased and often very few of the 2m interval sampling being completed in a single hole. However, there is a possibility that internal weathering processes may have already converted S in sulfides into sulphates and lost S to solution that has passed from the stockpiles, or that S values have been influenced by the influx of other sources such as rainfall or dust minimisation application waters (Dust suppression water) (see Chapters 5 and 6). Each value in the Jones and Hughes (1999) data represents a bulk analysis of a 44-gallon drum equivalent volume of primary rock for each waste and LGO grade (grade 1, 2 and 3).
from each pit. These rocks would not have suffered from a great deal of processes from within the stockpiles as they were sampled fresh, from the surface, and external sources would also not have any major influence. So, it is based on these two estimations of S content that it is regarded here that the bulk mean S content of the RUM waste material is likely to be between 0.021 and 0.033 wt\% S.

<table>
<thead>
<tr>
<th>Source</th>
<th>Sample Type</th>
<th>Grade</th>
<th>No. of samples</th>
<th>S Wt%</th>
<th>Pb ppm</th>
<th>Cu ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>primary rock</td>
<td>waste</td>
<td>19</td>
<td>0.005</td>
<td>5.53</td>
<td>8.84</td>
</tr>
<tr>
<td>This study</td>
<td>NCWP profile</td>
<td>waste</td>
<td>7</td>
<td>0.014</td>
<td>10.71</td>
<td>42.86</td>
</tr>
<tr>
<td>Riley et al. (1993)</td>
<td>RAB drill chips from stockpiles</td>
<td>waste</td>
<td>51</td>
<td>0.033</td>
<td>20.45</td>
<td>61.35</td>
</tr>
<tr>
<td>Jones and Hughes (1999)</td>
<td>P1 primary rock</td>
<td>waste</td>
<td>NA</td>
<td>0.021</td>
<td>20.6</td>
<td>17.3</td>
</tr>
<tr>
<td>Jones and Hughes (1999)</td>
<td>P3 primary rock</td>
<td>waste</td>
<td>NA</td>
<td>0.023</td>
<td>30.7</td>
<td>17.3</td>
</tr>
<tr>
<td>Noller (1991)</td>
<td>primary rock</td>
<td>waste* unknown</td>
<td>209</td>
<td>0.057</td>
<td>20</td>
<td>64</td>
</tr>
<tr>
<td>Nash and Frishman (1985)</td>
<td>primary rock</td>
<td>waste</td>
<td>112</td>
<td>NA</td>
<td>75.29</td>
<td>(124.65)</td>
</tr>
<tr>
<td>Geopeko drill core</td>
<td>P3 mostly primary rock</td>
<td>waste</td>
<td>156</td>
<td>NA</td>
<td>18.06</td>
<td>(28.82)</td>
</tr>
<tr>
<td>Nash and Frishman (1985)</td>
<td>P1 primary rock</td>
<td>waste</td>
<td>156</td>
<td>NA</td>
<td>28.72</td>
<td></td>
</tr>
<tr>
<td>Nash and Frishman (1985)</td>
<td>P3 primary rock</td>
<td>waste</td>
<td>53</td>
<td>NA</td>
<td>28.72</td>
<td></td>
</tr>
<tr>
<td>Riley et al. (1993)</td>
<td>RAB drill chips from stockpiles</td>
<td>LGO</td>
<td>43</td>
<td>0.05 (0.062)</td>
<td>48.44 (34.39)</td>
<td>76.6 (47.64)</td>
</tr>
<tr>
<td>Jones and Hughes (1999)</td>
<td>P1 primary rock</td>
<td>LGO (2)</td>
<td>NA</td>
<td>0.1064</td>
<td>114.6</td>
<td>336.6</td>
</tr>
<tr>
<td>Jones and Hughes (1999)</td>
<td>P3 primary rock</td>
<td>LGO (2)</td>
<td>NA</td>
<td>0.0742</td>
<td>109.5</td>
<td>94</td>
</tr>
<tr>
<td>Jones and Hughes (1999)</td>
<td>P1 primary rock</td>
<td>LGO (3)</td>
<td>0.0962</td>
<td>243.3</td>
<td>257.1</td>
<td></td>
</tr>
<tr>
<td>Jones and Hughes (1999)</td>
<td>P3 primary rock</td>
<td>LGO (3)</td>
<td>0.1537</td>
<td>291.4</td>
<td>675.1</td>
<td></td>
</tr>
<tr>
<td>Nash and Frishman (1985)</td>
<td>primary rock</td>
<td>LGO</td>
<td>51</td>
<td>NA</td>
<td>102.59 (118.4)</td>
<td>858.86 (3496.17)</td>
</tr>
<tr>
<td>Geopeko drill core</td>
<td>P3 mostly primary rock</td>
<td>LGO</td>
<td>402</td>
<td>NA</td>
<td>124.20 (170.25)</td>
<td>206.53 (289.73)</td>
</tr>
<tr>
<td>Nash and Frishman (1985)</td>
<td>P1 primary rock</td>
<td>LGO</td>
<td>45</td>
<td>NA</td>
<td>92.98</td>
<td>948.22</td>
</tr>
</tbody>
</table>

Table 4.8: Bulk S, Pb and Cu proportions for RUM rocks of various grades from various sources. Numbers in brackets are standard deviations. Note the large standard deviations, hence the large margin of error in the calculations of Table 4.7. See text for details.
The sulfide abundances calculated from the Riley et al. (1993) and Jones and Hughes (1999) data imply that pyrite accounts for some 71-80% of total S over the other two minerals, and is by far the most abundant sulfide mineral on average. The calculations based on the Jones and Hughes (1999) data suggest that some parts of the stockpiles will contain as much as 0.15wt% pyrite. This is a maximum value, but exactly how close this represents reality will remain unknown for now. Mineralogical investigations carried out here show that pyrite is the most common sulfide mineral in the schists, however concentrations of chalcopyrite are also a common feature of the rocks.

4.9 DISCUSSION

4.9.1 The Significance and Implications of the LGO Material for the Environmental Management of the RUM Waste and LGO ‘System’

There are few areas of the waste rock stockpiles, other than the SWP, that are composed of waste only material. This means that in terms of the hydro-geochemical behaviour of the current stockpiles, the nature of the LGO material may be of greater significance than the waste in most areas of the stockpile ‘system’. The significance may change in the final landform, depending on how the waste is used. The differences between the LGO and waste in terms of the amount of sulfides available for oxidation and the amount of uranium available for leaching is substantial and a very important consideration for future stockpile management and mine closure planning. For example in Table 4.8 the total bulk S increases by more than 50% in the Riley et al. (1993) LGO data compared to the waste grade data and in the grade 3 Jones and Hughes (1999) data S is well over 6 times that of the waste in the LGO material. All of the Jones and Hughes LGO data equate to over 0.1% pyrite based on the calculations in Table 4.7 and there is up to an order of magnitude more galena throughout all of the LGO data compared to what is in the waste. This is consistent with both the geochemical and mineralogical analysis achieved in this study (see sections 4.5 and 4.6).
It is important to point out that the Jones and Hughes (1999) grade 3 material from P1 and P3 are both above the LGO/ore cut-off to some extent and thus are technically not LGO material according to the criteria used throughout this thesis. However, the Geiger counter screening method is similar to the method used to separate material in the mine, and thus the presence of higher grades of material amongst waste or LGO is a reality (see below).

Whatever the case, the important conclusion to be made here, is that LGO material is highly enriched in bulk mean S and sulfides relative to waste. This means that if the grade location information provided by RUM is correct and only the SWP remains a waste only pile, then any estimation of bulk S or sulfide content in the primary rock of the stockpiles based primarily on waste geochemistry and mineralogy will have the potential to be a severe underestimate.

Likewise, the LGO material is important in regards to U, not only because of the amount of the U it contains, but because of the form within which it is proposed here to be in. That is, due to the presence of uraninite type mineral chemistry found here in the higher grades of waste schist, that uraninite type minerals are the main ore mineral in the RUM deposits (Ewers and Ferguson, 1980; Kendall, 1990) and that the geochemical analysis of numerous datasets performed here, shows that a previously observed relationship between galena and uraninite (Ewers and Ferguson, 1980) seems to still exist in much of the LGO grade material. There should be little reason for the LGO material to behave any different during weathering processes than the ore material, apart from the total amount of U released. It is also important to note that this coincides with the probability for pyrite and other sulfides to be far more abundant in the LGO material than in the waste, and thus have the potential for local acid generation, increasing the potential for U release.
4.9.2 Sulfides – The Concentration Effect

Observations made during this research prove that, although pyrite may be well disseminated to some extent within the waste grade schists, this is not always the case; sulfides will be concentrated to some extent in the waste and LGO stockpiles. Jones and Hughes (1999) have previously suggested that this may be possible.

Figure 4.21(a-b) is a photograph of a primary waste grade (Geiger counter reading only) dark green chloritised schist sample (UMS schist) containing large amounts of pyrite. This specimen was sampled from the SW wall of P3 in May 2002 from part of a region of clearly visible pyrite, in pod-like masses (0.2-1cm diameter) and as fine smears on foliation surface, fractures and slippage planes. This material would have been taken to an area of the stockpile being built at the time of extraction from the pit, and subsequently formed a concentration of pyrite in the stockpiles. It remains unknown as to how many regions of pyrite concentration in the mine have formed subsequent concentrations in the waste and LGO stockpiles.

Large concentrations of chalcopyrite were found in excavation E7 in the form lensing veins and crystal masses on void walls within the carbonate as well as cobble sized rocks containing masses of pod like chalcopyrite structures. An example of the latter is shown in Figure 4.21(c). Although the ability of these sulfides to generate acidity is negligible due to their host rock, it is still an example of how sulfides can be concentrated in the stockpiles.
4.9.3 Potential for Concentrations of Ore Grade Material to Occur in the Stockpiles

Nash and Frishman (1983) divide their dataset into ore bearing and non-ore bearing samples for statistical analysis based on field-measured radioactivity. The non-ore bearing samples are supposed to be equivalent to less than 250ppm U, although in their appendix a different figure is given that is equivalent to less than 420ppm U. Figure 4.22 compares the ore-code given to samples by Nash and Frishman (1983) with their equivalent U concentrations from INAA analysis, the non-ore samples correspond to codes 1, 2 and 3. The chart shows that a significant proportion of the non-ore samples from locations near to the ore zone (grade 3) have well over the 250ppm or 420ppm U, with some grade 3 samples containing up to 3000ppm U, and one sample of UMS schist containing 6350ppm U. Figure 4.22 suggests that when close to the ore, if field measured radioactivity measurements (those utilised by Nash and Frishman, 1983) were to be used to determine whether material went to the waste
and LGO or ore stockpiles, it would be possible to have ore material distributed to the waste and LGO stockpiles.

As already highlighted, in some cases the Jones and Hughes geochemical results for U also did not match the field based radioactivity measurements used to screen the samples, although these were by much smaller margins, and not comparable to, the Nash and Frishman (1983) example. The most significant increase was a grade 3 sample (670-1000ppm) from P3, which had equivalent to 1429.79ppm U.

Both these examples give support to the argument that it is possible that radioactivity measurements of rock in the mine (downhole radioactivity probing of blast holes [up to 6m deep]), but particularly up to 120 tonne loads of rock in each truck load as it passes through the discriminator, may be non-precise methods of U quantification in the rocks. It is further argued here, that because of this, it is possible for discrepancies to occur around ore grade boundaries, and therefore near to the ore-LGO cut-off boundary it is possible to have ore grade material classified as grade 3 material and sent to the appropriate part of the LGO stockpiles.

One of the reasons for a potential discrimination problem is the nature of the ore, in that strong structural controls such as fracturing (Needham, 1980; Vanderhor, 2001) seem to have resulted in large differences in grade over short distances in space. Drill hole 97 of the Ranger No. 3 orebody from the Nash and Frishman (1983) database is a perfect example of this (Figure 4.23), where U increases to 17700ppm from 13.2ppm in just over two vertical metres downhole and returns to 216ppm U (lower LGO levels) in the next two vertical metres of depth. Such occurrences are not uncommon in the Nash and Frishman data and not limited to either orebody, for instance drill hole 64 from the Ranger No.1 orebody (P1), where within a metre from 182.5m to 183.4m depths, U concentrations decrease from 5510ppm to 743ppm, beneath the LGO-ore cut-off.
Field measured radioactivity v INAA U analysis

Key

1 = <0.05% U3O8 = < 420ppm U: >100m from ore zone
2 = <0.05% U3O8 = < 420ppm U: 20-99m from ore zone
3 = <0.05% U3O8 = < 420ppm U: 0-19m from ore zone
4 = 0.05 - 0.2% U3O8 = 420 - 1700ppm U
5 = 0.2 - 0.5% U3O8 = 1700 - 4200ppm U
6 = >0.5% U3O8 = > 4200ppm U
7 = ore intercept remote from economic ore

Figure 4.22: A comparison between U content as measured by field radioactivity measurements and Instrumental Neutron Activation Analysis (INAA), both by Nash and Frishman (1983). This shows the potential for ore grade material to enter waste grade classification via field measured radioactivity method when close to the ore zone. Note that two cut-off grades are given for the waste-ore cut-off. This is due to the fact that two were quoted by Nash and Frishman. Appendix is as written here, but in text they qualify grades 1-3 as being below 250ppm.
Such large changes in uranium concentrations over short distances within the mine, particularly when, like that shown in Figure 4.23, small localisations of ore grade are surrounded by large areas of waste and LGO grade, enhance the potential for small localisations of ore to end up in the waste and LGO stockpiles.

![Figure 4.23: Uranium Concentrations in drill hole 97 from Ranger No.3 orebody (P3). Data from Nash and Frishman (1983) database.](image)

**4.10 CONCLUSIONS AND SUMMARY**

This study is the first comprehensive investigation into the composition of the waste and LGO stockpiles of RUM. Combined with the investigations of structure in Chapter 3, it can be used as a fundamental reference and basis for the current and future environmental management of the RUM waste and LGO stockpile 'system'.

Although, as expected and as has always been assumed, the quartz-chlorite-mica schist is the most abundant material in the RUM waste and LGO stockpiles, this has not always been the case, up until very recently (2000-2002), the most abundant material in the waste and LGO stockpiles of RUM was weathered material. The evidence here proves that the most abundant material in working waste rock piles will
change over time as mining progresses through different lithology. This change in geology over time will be especially significant in continents where significant weathering profiles have developed over orebodies, such as Australia. Waste rock stockpiles in continents with significant weathering profiles will undergo a change from initial compositions of heavily leached and oxidised material to primary un-oxidised rock. In some deposits, this may be the difference between moderately acid environments of weathering products, to acid generating weathering environments of fresh sulfide minerals. At RUM, with the utilisation of two orebodies and thus two open pits, there has been a cycle, whereby weathered material dominated early on as P#1 was initiated, then reduced in its relative abundance as P#1 deepened, before becoming more abundant again as P#3 was initiated.

Localisation at RUM has resulted in the dominant waste materials not necessarily being the most important materials when considering hydro-geochemistry of all parts of the stockpiles. The weathered material is concentrated in certain layers of the NCWP, particularly in the SE corner, and SCWP, as well as in the bottom of the WWP and CWP. However due to storage considerations at RUM, the weathered material is the only material present in the entire NE corner of the CWP and thus will be significant for all water bodies influenced by it, specifically the LGO sump. Despite representing only small proportions of the bulk stockpile composition, a combination of storage considerations, grade control and mine geology/mining technique has resulted in carbonate, massive chlorite rock, dolerite and FWS rocks combining to represent a significant and possibly dominating composition for the SWP and eastern SCWP region in the RUM waste and LGO stockpiles.

These concentrations of certain rock types are significant because the geochemistry of both the weathered material and the other mixed composition of the SWP area are vastly different to that of the quartz-chlorite-mica schists. Ca, Mg and CO$_3^{2-}$ chemistry should be significant in the SWP area compared to other areas of the stockpiles, due to the carbonates, as should the trace elements Mn and Cl. Higher relative amounts of Mg will be reinforced by the massive chlorite rock chemistry. The weathered material has lost significant amounts of Mg compared to the primary rocks, and thus is depleted in Mg. It is also significantly depleted in Mo, containing almost none at all, as well as F and Cl, but enriched in Y and the Fe-oxide associated metals,
such as Cu, Ni and Mn. The resistant minerals are also enriched in the weathered material, hence it contains increased proportions of Zr compared to the schists.

It has also been shown here that the practice of organising the stockpiles in accordance with ore grade, introduces geochemical characteristics specific to certain areas dominated by certain grades, although only in relation to the geochemical relationships with U. It has been shown that as the higher grades of uranium are reached, the correlations that U-associated elements have with U become stronger. In the ore Th, Mo, Y, Sc, Pb, Mn and to some extent Na and possibly Ga show good correlation with U, but in the LGO only Pb, Mo and to some extent Na and Ga remain, with a much weakened correlation. In the waste, only the relationship between Pb and U remains, although the relationship is weak. Such relationships may also be important for considering source materials for water chemistry at certain locations within the mine.

Detailed mineralogical investigations undertaken here show that even in waste grade schist, the amount of U is being governed by uraninite type mineralogy. Although the uranium based minerals were not primary euhedral uraninite crystals, they were also not necessarily of the chemistry that would be stable in open oxidative environments. Thus, oxidation of uraninite will still play a significant role in the release of U to solution in the RUM waste rock stockpiles, just as it would in the ore. This will probably become significant in the higher grades of the LGO material, which is after-all, the most abundant grade in the waste and LGO stockpiles of RUM.

However, very different from the ore, where uraninite is associated with chlorite, the U-based minerals in the waste schist were most commonly found within quartz grains. Disregarding the obvious implications this may or may not have for the genesis of such minerals, this will probably hinder oxidation and release of uranium in the stockpiles, due to a lack of access for fluids to the mineral. That being said, small fractures emanating from the U-based mineral housing within the quartz were common. The only other place uranium minerals were found was in the cleavage partings of chloritised mica, associated with Fe-oxides. Due to problems associated with limited grade control techniques and the because of the nature of the ore body, above waste-grade material will end up in the waste and LGO stockpiles.
Pyrite was found to be the most common sulphide mineral, occurring mostly as inclusions within cleavage partings of chloritised mica crystals. However, an already oxidised, haematitic skin surrounded almost every pyrite grain found, a factor which will reduce the initial acid generating ability of each grain upon exposure to oxidative environments. Concentrations of pyrite and other sulfides will occur in the waste and LGO stockpiles. Likewise it is believed that because of the nature of the orebody, which in places seems tightly controlled by structure, that small 'hits' of uranium mineralisation may make it to the waste and LGO stockpiles of RUM. This is particular in regards to regions of the orebody which fluctuate around the LGO-ore cut-off grades.
CHAPTER 5

THE CHEMISTRY OF BULK PRECIPITATION INCIDENT TO THE WASTE ROCK AND LOW GRADE ORE STOCKPILES OF RANGER URANIUM MINE AND ITS SOURCES

5.1 INTRODUCTION

Rainfall is a supplier of additional chemical components to the hydro-geochemistry of the stockpile system. However, more than this, it is also a supplier of fresh oxidants and solvent, as well as a mechanism of transport to flush weathering products and refresh weathering surfaces. This makes it a crucial part of the stockpile system. The northern monsoon climate dumps an annual average of 1498.2mm (ABM data) of rain onto the Jabiru Airport, adjacent to RUM. Approximately 95.6% of this rain falls over an average of 95.2 rainy days and only from November through to April every year, the NT wet season (calculated using ABM data).

A number of studies regarding the chemistry of rain within the tropical savannah of Australia’s NT are represented in published material (Wetselaar and Hutton, 1962, Galloway et al. 1982, and Likens et al. 1987, Ayers et al. 1993, Ayers and Gillett, 1988, 1988a, Noller et al. 1985, 1990, and Gillett et al. 1990, 1994). Two of these studies are particularly relevant to this research due to their location being in close proximity to RUM (Gilett et al. 1990, 1994, Noller et al. 1985, 1990). However, the last chemical analysis of precipitation was performed on nine precipitation samples collected during the 1984/1985 wet season, some 15 years prior to this research. It was because of this considerable hiatus in time plus the fact that no precipitation had ever been collected within RUM itself that it was considered necessary to collect and analyse precipitation independently for this study.
This study is intended to examine the chemistry of current bulk precipitation at RUM to assess the type of chemical components being delivered to the stockpile system via the atmosphere. It will allow comparisons to be made between past and present precipitation chemistry within the local region and between the chemistry of precipitation collected from within the mine itself as well as collections from outside the mine's direct influence. The study will also re-examine the issue of sources for the chemical components within the rain of the region that incorporates RUM, with new evidence from recent and significant atmospheric and climatic research relevant to the region (Kondo et al. 2003, Tapper, 2002, and Lobert et al. 1999).

This study is not only a simple understanding of the type of chemical components being applied to the RUM waste and LGO stockpiles by precipitation, but also an understanding of where these chemical components are ultimately derived, an inextricable link between the stockpiles and the environment within which they lay.

5.2 METHODS

A total of 11 bulk precipitation samples have been included in this study, collected from sites on the NCWP, the SCWP, the SWP and Corridor Creek (CC), a site east of the SWP, as well as a site remote from Ranger along the access road to the Jabiluka Mine. The purpose of the latter collection site was to obtain a current non-mine reference sample. Precise locations are given on the map in Figure 2.6 in Chapter 2. Due to a lack of sample volume only trace element analysis was performed on the Corridor Creek sample RW109. The 11 samples included in this study were collected during April 2000, the end of the 1999/2000 wet season, and November 2000, the start of the proceeding 2000/2001 wet season.

All other details regarding methodology for this study can be found in the methods chapter, Chapter 2. It includes details on collection, analysis, statistical techniques, and data validation techniques.

It is however important to explain here that bulk precipitation is a term used to describe a method of collecting rainfall whereby the collection vessel is continuously open throughout a given period so that both dry atmospheric fallout (sedimentation of
heavy aerosols, including dust and dry impaction of gases and light aerosols), and rainfall is collected. Thus bulk precipitation samples are representative of total atmospheric input during the time of sample collection. It is the method used in the previous studies of rainfall in the region, as mentioned above, and so for comparison purposes it has also been used in this study. That being said, it is considered here that the maximum amount of time that each sample was left in the field during this study has not resulted in any considerable dry deposition influence. See Chapter 2 for further details.

5.3 RESULTS

5.3.1 Raw Data

The analytical results of major element analysis of all rainwater samples collected are presented in Table 5.1 in micro-equivalents per litre (μeq/L) along with the respective calculations for HCO$_3^-$, the sum of the major cations H$^+$, Na$^+$, Ca$^{2+}$, Mg$^{2+}$ and K$^+$, the sum of the major anions NO$_3^-$, SO$_4^{2-}$, Cl$^-$ and HCO$_3^-$, and a difference function (DF) based on the cation-anion balance calculation and an associated calculation termed here as the relative ion deficit (RID).

The difference function is the same as that used by Noller et al. (1990) and is simply the numerical difference between the sum of cations and the sum of anions. The RID, which has been formulated for this study, is the difference between the sum of cations and the sum of anions as a percentage of the highest of these summations, either cations or anions. It therefore always assumes, and thus represents, a percentage of ion deficit, not excess. In other words it assumes that major differences between total cation and total anions are caused by not analysing all of those present, as has been the case in most rainfall studies in the Northern Territory (Likens et al. 1987, Noller et al. 1990, Gillett, et al. 1990, Ayers et al. 1993).
Table of Major cations and Anions, pH and Associated Functions of Bulk Precipitation Samples Collected from within the Ranger Uranium Mine Waste and Low Grade Ore Stockpiles and the Jabiluka Access Route

<table>
<thead>
<tr>
<th>Field No.</th>
<th>Site Code</th>
<th>Collection date</th>
<th>Nights</th>
<th>mm</th>
<th>pH</th>
<th>H⁺</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
<th>NO₃⁻</th>
<th>HCO₃⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>RW103 NCWP</td>
<td>14/04/2000</td>
<td>1</td>
<td>24.49</td>
<td>5.68</td>
<td>2.09</td>
<td>5.36</td>
<td>3.16</td>
<td>1.25</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>RW104 SCWP</td>
<td>14/04/2000</td>
<td>1</td>
<td>24.98</td>
<td>5.91</td>
<td>1.23</td>
<td>4.23</td>
<td>2.32</td>
<td>1.04</td>
<td>4.07</td>
<td></td>
</tr>
<tr>
<td>RW106 NCWP</td>
<td>21/04/2000</td>
<td>7</td>
<td>38.8</td>
<td>NA</td>
<td>NA</td>
<td>4.8</td>
<td>4.42</td>
<td>0.83</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>RW107 SCWP</td>
<td>21/04/2000</td>
<td>7</td>
<td>39.97</td>
<td>6.41</td>
<td>0.39</td>
<td>7.62</td>
<td>4.42</td>
<td>0</td>
<td>12.88</td>
<td></td>
</tr>
<tr>
<td>RW301 Jab</td>
<td>21/11/2000</td>
<td>6</td>
<td>34.14</td>
<td>4.12</td>
<td>75.86</td>
<td>9.87</td>
<td>7.8</td>
<td>12.96</td>
<td>0.066</td>
<td></td>
</tr>
<tr>
<td>RW304 NCWP</td>
<td>21/11/2000</td>
<td>6</td>
<td>41.85</td>
<td>4.2</td>
<td>63.1</td>
<td>32.44</td>
<td>11.38</td>
<td>15.19</td>
<td>0.079</td>
<td></td>
</tr>
<tr>
<td>RW307 SWP</td>
<td>21/11/2000</td>
<td>6</td>
<td>21.48</td>
<td>3.8</td>
<td>158.49</td>
<td>47.39</td>
<td>16.64</td>
<td>19.82</td>
<td>0.032</td>
<td></td>
</tr>
<tr>
<td>RW317 Jab</td>
<td>27/11/2000</td>
<td>6</td>
<td>40.2</td>
<td>3.63</td>
<td>234.42</td>
<td>20.59</td>
<td>8.64</td>
<td>25</td>
<td>0.021</td>
<td></td>
</tr>
<tr>
<td>RW321 NCWP</td>
<td>27/11/2000</td>
<td>6</td>
<td>163.56</td>
<td>3.97</td>
<td>107.15</td>
<td>8.74</td>
<td>7.58</td>
<td>13.98</td>
<td>0.047</td>
<td></td>
</tr>
<tr>
<td>RW322 SWP</td>
<td>27/11/2000</td>
<td>6</td>
<td>148.42</td>
<td>4.03</td>
<td>93.33</td>
<td>6.49</td>
<td>7.37</td>
<td>16</td>
<td>0.054</td>
<td></td>
</tr>
</tbody>
</table>

Non-chemical information in the Table includes the sample identifier number, the date of collection for each sample, the number of nights each sample was left in the field before collection, a field site location abbreviation (see text accompanying Table 5.1) and the amount of rain collected for each sample in millimetres (mm), converted from volume collected.

Table 5.1: Major cations and anions and pH of bulk precipitation collected within the area of the RUM waste and LGO stockpiles and along the Jabiluka access route. All concentrations are in μeq/L, DF = Difference factor, RID = Relative Ion Difference, (- or +) whether the RID is a deficit of anions (-) or cations (+), see text for explanations of functions. Nights = the number of nights left in the field, site code: NCWP = North Central Waste rock Pile, SCWP = South Central Waste rock Pile, SWP = Southern Waste rock Pile, Jab = Jabiluka access route site. The field numbers have been colour coded to highlight the difference between start of wet season (SOWS – red) and end of wet season (EOWS – blue) rains.
To highlight seasonal variance, the rainfall sample numbers have been colour coded according to whether they are from start of wet season collections (blue) or end of wet season collections (black), from here on in referred to as SOWS collections and EOWS collections respectively.

### Concentrations of Trace Elements Found in Bulk Precipitation Samples Collected from within the Ranger Uranium Mine and the Jabiluka Access Route

<table>
<thead>
<tr>
<th>Field No.</th>
<th>Site Code</th>
<th>Collection Date</th>
<th>Nights</th>
<th>mm</th>
<th>H⁺</th>
<th>Mn²⁺</th>
<th>Fe²⁺/³⁺</th>
<th>Cu²⁺</th>
<th>Zn²⁺</th>
<th>Ba²⁺</th>
<th>Pb²⁺</th>
<th>U⁶⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>RW103</td>
<td>NCWP</td>
<td>04/14/2000</td>
<td>1</td>
<td>24.49</td>
<td>2.1</td>
<td>0.7</td>
<td>14.5</td>
<td>1.9</td>
<td>30</td>
<td>2.7</td>
<td>0.1</td>
<td>0.6</td>
</tr>
<tr>
<td>RW104</td>
<td>SCWP</td>
<td>04/14/2000</td>
<td>1</td>
<td>24.98</td>
<td>1.2</td>
<td>1.5</td>
<td>10.6</td>
<td>0.9</td>
<td>25</td>
<td>1.8</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>RW106</td>
<td>NCWP</td>
<td>04/21/2000</td>
<td>7</td>
<td>33.8</td>
<td>NA</td>
<td>1.6</td>
<td>5.8</td>
<td>0.6</td>
<td>47.7</td>
<td>1.5</td>
<td>0.1</td>
<td>1.6</td>
</tr>
<tr>
<td>RW107</td>
<td>SCWP</td>
<td>04/21/2000</td>
<td>7</td>
<td>39.97</td>
<td>0.4</td>
<td>10.3</td>
<td>5.6</td>
<td>0.6</td>
<td>33.5</td>
<td>0.9</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>RW109</td>
<td>CC</td>
<td>04/21/2000</td>
<td>4</td>
<td>3.43</td>
<td>NA</td>
<td>5.6</td>
<td>19.9</td>
<td>2.5</td>
<td>279</td>
<td>3.2</td>
<td>0.6</td>
<td>1.0</td>
</tr>
<tr>
<td>RW301</td>
<td>Jab</td>
<td>11/21/2000</td>
<td>6</td>
<td>34.14</td>
<td>76.5</td>
<td>2.0</td>
<td>32.7</td>
<td>0.8</td>
<td>68</td>
<td>1.2</td>
<td>0.2</td>
<td>0.0</td>
</tr>
<tr>
<td>RW304</td>
<td>NCWP</td>
<td>11/21/2000</td>
<td>6</td>
<td>41.85</td>
<td>63.6</td>
<td>7.7</td>
<td>39.2</td>
<td>0.2</td>
<td>315.3</td>
<td>2.7</td>
<td>0.2</td>
<td>4.3</td>
</tr>
<tr>
<td>RW307</td>
<td>SWP</td>
<td>11/21/2000</td>
<td>6</td>
<td>21.48</td>
<td>159.7</td>
<td>16.8</td>
<td>28.8</td>
<td>0.5</td>
<td>517.6</td>
<td>2.2</td>
<td>0.4</td>
<td>0.8</td>
</tr>
<tr>
<td>RW317</td>
<td>Jab</td>
<td>11/27/2000</td>
<td>6</td>
<td>40.2</td>
<td>236.3</td>
<td>3.9</td>
<td>63.2</td>
<td>6.8</td>
<td>220.6</td>
<td>3.1</td>
<td>1.2</td>
<td>0.0</td>
</tr>
<tr>
<td>RW321</td>
<td>NCWP</td>
<td>11/27/2000</td>
<td>6</td>
<td>163.56</td>
<td>108.0</td>
<td>6.2</td>
<td>41.5</td>
<td>0.3</td>
<td>48.6</td>
<td>1.1</td>
<td>0.3</td>
<td>12.1</td>
</tr>
<tr>
<td>RW322</td>
<td>SWP</td>
<td>11/27/2000</td>
<td>6</td>
<td>148.42</td>
<td>94.1</td>
<td>4.5</td>
<td>18.2</td>
<td>0.0</td>
<td>0</td>
<td>0.9</td>
<td>0.3</td>
<td>7.3</td>
</tr>
</tbody>
</table>

**Table 5.2:** Trace element concentrations in bulk precipitation collected within the area of the RUM waste and LGO stockpiles, Corridor Creek (CC) which is still within the mine, and a site along the Jabiluka access route. All concentrations are in µg/L. See text and Table 5.1 for further details.

Table 5.2 displays the results of trace element analysis for those elements found to exist in the samples, in µg/L. Trace metals are usually measured in picograms per litre (pg/L) in rainfall due to their extremely low abundance, and therefore are usually analysed only after samples have been carefully pre-concentrated. This was not achieved in the RUM rainfall analyses and thus only a few trace elements were found above the ICPMS detection limits (see Table 3.2), and for some of these, particularly Cu⁺², Pb⁺² and U⁶⁺ their concentrations were often just on detection limits. Although lower concentrations are displayed in Table 5.2, it is considered here that anything below 0.5µg/L is well within the range of background interference and so should be treated with caution.
It should be noted that any corrections for contamination have been made in Tables 5.1 and 5.2 in accordance to the criteria set out by the section regarding contamination issues in the methods chapter.

5.3.2 Data Accuracy Test - The Cation/Anion Balance

The net difference between total cations and total anions in eq/L, and how far this varies from a zero difference or perfect balance, is often used to assess the validity of the results of a chemical analysis of a water or rainwater sample (Hem, 1985, Sequeira and Lung, 1995). The principle of this technique is that the chemistry of a water sample must obey the rule of electrical neutrality, thus the variation of the net cation-anion balance from zero and hence from electrical neutrality, is a measure of how inaccurate the analysis may be. The cation-anion balance is generally stated in the terms of a percentage of the sum of anions and cations in solution (eq/L) and is calculated as follows:

\[
B_i(\%) = \left( \sum_- - \sum_+ \right) / \left( \sum_- + \sum_+ \right) \times 100 \tag{5.1}
\]

where \( \sum_- \) is the sum of the anions and \( \sum_+ \) is the sum of the anions.

However, the technique assumes that all electrically charged species of significant concentration are analysed and accounted for. This is not the case in the samples presented here and not the case for many rainwater analyses (see for example the NADP rainfall concentration data of the USA). It is for this reason that the RID has been formulated for this study, as it is a measure of potential magnitude of the concentration of the missing ion. The usual measure, which compares the magnitude of the imbalance to the sum of both the cations and anions, hence as a percentage of the total conjugate ion concentration (for example Sequeira and Lung, 1995), assumes an analytical error and is measuring that error against the total analysis.

Table 5.1 shows that the RUM rainfall analyses are significantly unbalanced, with all except two samples, R104 and R107, having a deficit of anions as large as 79% (refer to RID values). Figure 5.1 also shows that the magnitude of this positive skewness in the cation/anion balance is highly correlated to the calculated H\(^+\) ion concentration,
particularly in the SOWS rains. This is strong evidence that the anion deficit is due to the existence of a conjugate base that has not been analysed. As will be explained later, the major control on the dramatic increases in $H^+$ concentrations, for the start of wet season rainfall at RUM, Jabiru and other parts of the Northern Territory is the presence of organic acids (Likens et al. 1987, Gillett and Ayers, 1988, Gillet et al. 1990, 1994, Noller et al. 1990, Ayers et al. 1993). Organic acids were not analysed in the RUM samples and are the likely source of the discrepancy in the cation/anion balance.

Noller et al. (1990) also concluded that significant anion deficiencies in cation/anion balances for rainfall data at Jabiru and surrounding regions was due to formate and other weak organic acids that were not analysed in their own samples. Keywood (1995) also came to the same conclusion for large ion imbalances found in rainwater samples at an array of sample sites stretching from the coast of the Northern Territory to the coast of South Australia. Interestingly, this seemed not as prevalent at a coast to inland array of sample sites in Western Australia (Keywood, 1995).

![Figure 5.1: Chart showing the linear relationship between the difference function (DF)-the difference between the total amount of cations to anions - and $H^+$ concentration. Note that the EOWS rains follow a different trend slope than the SOWS rains, when treated separately.](image)

$$\begin{align*}
y &= 8.1167 + 1.1185x \\
R &= 0.99271 \\
R^2 &= 0.98608
\end{align*}$$
The cation deficiency in samples R104 and R107 is more difficult to explain, although in such dilute samples the total amount of trace elements can explain some of this deficit, in fact including the total μeq/L of trace elements would change the RID of sample R104 from a 8.3% cation deficit to a 4.2% anion deficit, well within a more acceptable 5% error range. However, this still leaves sample R107 with a cation deficit of some 55.5%. Some of this can be attributed to the absence of the NH$_4^+$ ion in these analyses. For example, in the Noller et al. (1990) study for Jabiru East, only 3.1 kilometres from the RUM stockpiles, NH$_4^+$ represents approximately 8.6% of the total cations analysed using volume weighted mean (VWM) values.

NH$_4^+$ is an important component of the continental tropospheric aerosol being derived from ammonia (NH$_3$), the primary basic gas in the atmosphere that is readily absorbed by surfaces such as water and soil (Seinfeld and Pandis, 1998). Whilst emissions from animal waste, losses of NH$_3$ based fertilisers from soils, the ammonification of humus and subsequent emissions from soils, vegetation, and industrial wastes are all contributors to atmospheric NH$_4^+$ (Dentener and Crutzen, 1994, Seinfeld and Pandis, 1998), in tropical regions savannah fires are also known to be significant (Lobert et al. 1990; Delmas et al. 1995). There should be no doubt then, that NH$_4^+$ will be an important cation in the rainfall of the RUM area, however it is considered unlikely that it will account for the large deficit in cations of sample R107. The deficit in sample R107 therefore remains unexplained.

5.3.3 Dominant Chemistry

The results in Table 5.2 show that all of the rains are basically NaCl solutions, although the SOWS rains are distinctively enriched in NO$_3^-$ and H$^+$, so much so that H$^+$ is the dominant ion in solution for the SOWS samples. This would also indicate that within the SOWS rains subjugate bases that have not been analysed may also be important ions.
HCO$_3^-$ is a significant ion in EOWS rains and is a dominant ion in samples R104 and R107. This is not unusual in some rainfall, where HCO$_3^-$ has been measured, for example in Californian rainfall chemistry data from Hem (1985), HCO$_3^-$ is definitively one of the most dominant ions in solution. There does not seem to be a distinct pattern in the ordering of the other major components in the RUM rainfall although by weight (μg/L) SO$_4^{2-}$ is also a significant ion.

5.3.4 Major Distinguishing Features of RUM Rainfall

Figures 5.2(a) and 5.2(b) summarise the major distinguishing features of the bulk precipitation chemistry data of Table 5.1. To reveal these relationships two charts have been used that have not been previously published. They have been developed specifically by the author for this research and all detail into how they are constructed is found in methods, Chapter 2.

The TICC bar shows that the most obvious distinguishing feature of the RUM rainfall data is the large increase in ions present at the start of the wet season as opposed to the end of the wet season. This is most likely a ‘wash out’ effect, whereby a build up of chemical components in the atmosphere before the start of the wet season are ‘washed out’ as the rainfall season progresses (see later). However, other factors are involved in this, both physical and meteorological, and these are discussed in more detail later.

It should be noted that not all species are significantly more concentrated in all of the SOWS precipitation samples. Table 5.1 shows that K$^+$ is not significantly enriched in any of the SOWS rains compared to the EOWS rains and Ca$^{2+}$ and Mg$^{2+}$ are not significantly enriched in samples RW301, RW321 and RW322.
Figure 5.2(a): Diamond Compass Charts (ug/L relative) for April 2000 bulk precipitation samples (EOWS rains) and Total Ion Concentration Comparison (TICC) bar chart comparing the EOWS rains with the SOWS rains (see figure 3.5[b]). See text for detailed explanation of both types of charts. Note that the key for the Diamond Compass charts here is also applicable for figure 5.2(b) following.

### TICC Bar

**EOWS Rains**

**SOWS Rains**

### Key

<table>
<thead>
<tr>
<th><strong>Ca/Na Ratio</strong></th>
<th><strong>Wind Speed (km/h)</strong></th>
<th><strong>Wind - time of measurement - Colour Code</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sea water</td>
<td>0</td>
<td>3pm</td>
</tr>
<tr>
<td>Sample</td>
<td>1-9</td>
<td>6pm</td>
</tr>
<tr>
<td>Sample</td>
<td>10-19</td>
<td>9pm</td>
</tr>
<tr>
<td>Sample</td>
<td>10-19</td>
<td>Midnight</td>
</tr>
</tbody>
</table>

### pH Scale

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>10</td>
</tr>
<tr>
<td>9</td>
</tr>
<tr>
<td>8</td>
</tr>
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<td>7</td>
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<tr>
<td>2</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>0</td>
</tr>
</tbody>
</table>
Figure 5.2(b): Diamond Compass Charts
(ug/L) relative for November 2000 bulk precipitation samples (SOWS rains)

NCWP RW304 (41.85mm)
RW307 (21.48mm)
Jab RW301 (34.14mm)
Jab RW317 (40.2mm)
NCWP RW321 (163.56mm)
SWP RW322 (148.42mm)

---

201
The Diamond Compass charts show the relative concentrations (µg/L) of the major cations Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\) and K\(^+\), as well as the pH of each bulk precipitation sample. Combined with these chemical parameters, the Diamond Compass charts also show the direction and speed of winds measured during the days responsible for the rainfall collected in each sample. Note that average seawater composition rectangles (using data from Wilson, 1975 and Brewer, 1975) have been added to the Diamond Compasses of Figures 5.2(a) and (b) for comparison purposes, the theory being that the closer the resemblance in position and shape of the RUM rainfall rectangles to those of average seawater the more dominant the ocean is as a source. The centres of each rectangle have been highlighted for easier comparison.

The Ca/Na ratio has been highlighted in the Diamond Compasses of Figures 5.2(a) and (b) because it is often used as a simple indicator of the magnitude of terrestrial influence on rainfall chemistry (see Berner and Berner, 1996), Ca\(^{2+}\) being associated with a predominantly terrestrial source and Na\(^+\) being associated with a predominantly oceanic source.

Any combination of chemical components could have been chosen for the Diamond Compass charts used in this study, however the major cations chosen were considered most appropriate due to their ability to delineate the major differences within the rainfall and because they can be used as a direct comparison to ternary diagrams used by Noller et al. (1990), the reason for this revealed in the following.

The RUM bulk precipitation Diamond Compasses further develop the main distinguishing features of the RUM rainfall. The EOWS rains of April 2000 are relatively similar to each other, the major cation rectangles all being of similar shape and the Ca/Na ratio markers being in relatively similar positions. This is a distinguishing feature of the EOWS rains, the relative cation composition being intermediate between the two distinct compositions of the November 2000 SOWS rains, one close to that of seawater and one far from that of seawater. Apart from that already revealed by the TICC bar, the major distinguishing feature of the EOWS rains is the markedly higher pH and thus orders of magnitude lower concentrations of free
H⁺, compared to that of the SOWS rains. Although not included in the Diamond Compass charts, NO₃⁻ concentrations are partly responsible for this, since it is a subjugate base and becomes a dominant ion in the SOWS rains (see Table 5.1). The Diamond Compasses show that meteorology may be influencing the divide between the SOWS and EOWS rains, since general wind direction switches from easterly and northerly winds just before and during the EOWS rains to a much stronger northerly influence and the addition of a significant westerly direction in the SOWS rains.

The second major differentiation to be made is within the SOWS rains themselves. As has already been mentioned, two distinct compositions are evident, a group containing samples RW301, RW321 and RW322, which is relatively close to a seawater composition and a group containing RW304, RW307 and RW317, which is far from a seawater composition. The rectangles and Ca/Na ratio markers in the latter group show that the major difference between the two groups is a relative increase in Ca²⁺ at the expense of Na⁺. Importantly, RW317 represents a different set of rainfall events than the two samples of similar composition and it is also a Jabiluka sample, far from the mine location of the other two samples. RW301, the other Jabiluka sample, has a similar relationship with the two samples that are of similar composition to it. This means that the differentiating factor separating the SOWS rains into the two groups, that is, the relative concentration of Ca and Na, is largely independent of both location and time of collection. However, meteorological effects cannot be ruled out, since the wind directions have been taken from ABM measurements at Jabiru East, a location much closer and thus more relevant to RUM than the Jabiluka access road.
Figure 5.3: Results of cluster analysis of major cations and anions in the RUM rainfall data

To test the relationships shown in the Diamond Compasses cluster analysis was undertaken on the major cations and anions (disregarding H$^+$) in the RUM rainfall data. The results, shown in Figure 5.3, confirm the Diamond Compass conclusions, the cluster analysis separating the data into the same three groups, the EOWS rains and the two sets of SOWS rains. However, the cluster analysis actually categorises the seawater like SOWS groups as being more similar to the EOWS compositions. This should not be surprising considering the relative rectangle shapes of both these groups in the Diamond Compasses.

### 5.3.5 Trace Elements

$\text{Zn}^{2+}$ is by far the most dominant trace element found in solution, followed by $\text{Fe}^{2+/3+}$. Proportions of other elements vary, those found to exist were $\text{Mn}^{2+}$, $\text{Cu}^{2+}$, $\text{Ba}^{2+}$, and on a limited number of occasions, $\text{Pb}^{2+}$ and $\text{U}^{6+}$. In general, trace element concentrations show a more erratic behaviour than the major ions, a possible indication that trace element concentrations may be related to more erratic sources such as local aerosol.
When present, U\(^{6+}\) and Fe\(^{2+/3+}\) are consistently higher in the SOWS rains than in the EOWS rains. Zn\(^{2+}\) follows a similar trend to that of the major ions Cl\(^-\) and Ca\(^{2+}\), being significantly more concentrated in samples RW304, RW307, and RW317, one of the SOWS groups identified above. Anomalous high concentrations of all trace elements found in sample RW109 are probably due to a concentration effect, discussed in more detail below, due to the extraordinarily low volume of rainfall collected, only 3.43ml.

### 5.3.6 Chemical Correlations

Multivariate scatterplot matrices were used to examine correlations between chemical species within the whole data set as well as within the SOWS and EOWS sub-sets. Correlation coefficients were only used as a method of cross-referencing the graphical findings.

As expected, the three most abundant species of rainfall, SO\(_4^{2-}\), Cl\(^-\) and Na\(^+\) (see Drever, 1997), are all correlated to each other (Figure 5.4a-c). A strong correlation also exists between H\(^+\) and NO\(_3^-\) (see Figure 5.4d), again not surprising since NO\(_3^-\) is not an uncommon acidic anion in rainfall (Seinfeld and Pandis, 1998). Figures 5.4(e) and 5.4(f) show that the other common acidic anions, Cl\(^-\) and SO\(_4^{2-}\), are not so well correlated with H\(^+\). This suggests that HNO\(_3\) is an important contributor to the free acidity of rainwater at RUM and that H\(_2\)SO\(_4\) and HCl are not necessarily important contributors to acidity.

Although not presented here, there is also some evidence in the data correlation may exist between SO\(_4^{2-}\) and the major cations Mg\(^{2+}\) and Ca\(^{2+}\), although the relationships are not simple. If the SOWS and EOWS rains are considered separately, then both Mg\(^{2+}\) and Ca\(^{2+}\) are correlated to SO\(_4^{2-}\) in the SOWS rains, with the exception of sample RW307 that acts as an outlier towards an excess of SO\(_4^{2-}\) against Mg\(^{2+}\). However only Mg\(^{2+}\) seems to be correlated to SO\(_4^{2-}\) in the EOWS rains. If all samples are treated as a single dataset, then the outliers become sample RW304 with an excess of Mg\(^{2+}\) to SO\(_4^{2-}\), and samples RW301, 321 and 322, all with an excess of SO\(_4^{2-}\) to Ca\(^{2+}\).
The relationship is interpreted as being one governed by the amount of terrestrial influence in individual and groups of samples. The Diamond Compass charts of Figures 5.2(a) and 5.2(b) have already separated the RUM rainfall data into 3 groups, one group with a composition closer to seawater than all of the others (samples RW301, RW321 and RW322), one group with a composition most unlike that of seawater than the others (samples RW304, RW307 and RW317) and one group with a composition somewhat in between these two extremes (all of the EOWS rains). Thus, any bivariate plot that includes a mostly terrestrial derived component, as is Ca$^{2+}$, against an important component of sea salt aerosol, such as SO$_4^{2-}$, has the potential to separate the RUM rainfall into these three categories. This is what has been done in Figure 5.5(a). The strong positive correlation is present within the SOWS rains because SO$_4^{2-}$ can also be sourced terrestrially. In fact it is well known that as terrestrial sources become dominant rain tends to become predominantly a CaSO$_4$ solution (Berner and Berner, 1996).

The Mg$^{2+}$ and SO$_4^{2-}$ bivariate plot in Figure 5.5(b) has also separated the SOWS and EOWS rains, with correlation seeming to exist in both groups except for the potential outliers outlined above, RW304 and/or RW307. The correlation is not surprising because not only is Mg$^{2+}$ also associated with seawater (Berner and Berner, 1996) but it is a potential local aerosol component since epsomite (MgSO$_4$.7H$_2$O) and hexahydrite (MgSO$_4$.6H$_2$O) are frequently observed around the waste and VLG stockpiles of RUM, and Chlorite ((Mg,Fe$^{2+}$,Fe$^{3+}$,Mn,Al)$_{12}$[(Si,Al)$_2$O$_{20}$](OH)$_{16}$) is a ubiquitous mineral in the rocks of the stockpiles. The two potential outliers can be explained by a simple flux of Mg$^{2+}$ for RW304 and a flux of SO$_4^{2-}$, in this case CaSO$_4$ (see Figure 5.5a), for RW307.

Other general correlations existing in the data are between Mg$^{2+}$ and Cl', Mg$^{2+}$ and Na$^+$ and Ca$^{2+}$ and K'. Mg$^{2+}$, Cl' and Na$^+$ are often used as seawater reference elements in rainfall studies (Berner and Berner, 1996) so relationships between these should be expected. Once again however samples RW304 and RW307 are outliers. In the Ca$^{2+}$ and K' relationship sample RW317, the other least seawater like sample (see Figure 5.2b), is also an outlier. There is also some correlation between HCO$_3^-$ and Ca$^{2+}$ and to a lesser extent HCO$_3^-$ and Mg$^{2+}$, although only in the SOWS rains. These relationships could be related to carbonate aerosol.
Figure 5.4(a-f): Scatterplot matrices showing the correlation of major rainfall ions, sodium, chloride and sulphate (a-c) in RUM rainfall chemistry as well as the correlation between free hydrogen ions and the analysed acidic anions, nitrate, sulphate and chloride (d-f). See text for explanations.
Figure 5.5 (a-b): Scatterplot matrices showing the correlation between sulphate and the major cations calcium and magnesium. See text for explanation.

Key
(For both figure 5.5 and figure 5.6)
•  Start of wet season (SOWS) samples
•  End of wet season (EOWS) samples

Figure 5.6 (a-c): Scatterplot matrices showing the correlation between Zinc and the major ions Chloride, Sulphate and Sodium. See text for explanation.
There are no significant correlations between the trace elements. Some correlation may exist between Fe^{2+}/Fe^{3+} and Cu^{2+} and Fe^{2+}/Fe^{3+} and Ba^{2+} in the EOWS rains alone, however, there are simply too few samples to make any definite conclusion.

Some better correlations exist between the trace elements and the major ions, particularly if the SOWS rains are considered separately and especially with Zn^{2+}. These include Zn^{2+} and Cl^-, Zn^{2+} and SO_4^{2-}, Zn^{2+} and Na^+ (see Figures 5.6a-c) and a very loose correlation between Ba^{2+} and K^+. Also Pb^{2+} seems to be correlated to H^+ in the SOWS precipitation samples, although this cannot be regarded as valid due to the sub-detection limit concentrations of Pb^{2+}. Since Cl^-, SO_4^{2-} and Na^+ are major constituents of seawater, their relationship with Zn^{2+} implies that Zn^{2+} may also be sourced from sea salt aerosol.

5.3.7 Relationship between Location and Chemistry

Although not convincing, there is some evidence to suggest that a location effect may be operating within the mine due to the composition of dust influx within the direct vicinity of collectors. The SOWS Diamond Compasses in Figures 5.2(a) and 5.2(b) show increased relative concentrations of Ca^{2+} at the SWP for each collection day and increases in the relative concentrations of Mg^{2+} and K^+ at the NCWP for each collection day. Due to a concentration of carbonate rocks on the SWP (see Chapter 4) it is possible that local dust particles in that area may have high concentrations of Ca^{2+}.

Whilst the trend in Mg^{2+} is not repeated in the EOWS rains the trend in K^+ is. It is important to note here that the trace elements U^{6+}, Ba^{2+} and Fe^{2+/3+} are also enriched for each collection day for both the EOWS and the SOWS rains (see Table 5.2). A possible explanation for this enrichment is that the NCWP was the closest site to current mining operations and so would be more likely to be affected by any increased rock/soil derived aerosol that may or may not result from such activity despite dust suppression procedures (see Chapter 6).
Since no Jabiluka samples were collected during the April 2000 EOWS expedition no conclusions can be made regarding the difference between the Jabiluka and RUM samples for the entire dataset. Considering the SOWS rain samples alone, there does not seem to be any significant difference between the concentrations of major ions between the two locations. There is some evidence however, although once again not convincing, that Mn$^{2+}$ and U$^{6+}$ are depleted in the Jabiluka SOWS samples and that Cu$^{2+}$ is enriched. However the differences in Mn$^{2+}$ are minimal, the Cu$^{2+}$ values are bordering on the detection limits of the ICPMS and the Jabiluka sample RW317 was the sample affected by U$^{6+}$ contamination (see Chapter 2). That being said Mn$^{2+}$ and obviously U$^{6+}$ are enriched in the rocks of Ranger (see Chapter 5).

5.3.8 Dilution / Concentration Effect

Likens et al. (1987) concluded that dilution may be an important factor controlling the ionic strength of precipitation at Katherine, at least on an annual basis. This was a similar conclusion to the Likens et al. (1984 in Likens et al. 1987) study of rainfall at Hubbard Brook, New Hampshire, in the United Kingdom. In a study of convective rainfall over an equatorial forest in Africa, Cautenet and Lefevre (1994) found a reduction of aerosol scavenging with increasing rainfall intensity. This decrease in scavenging efficiency, which equated to a dilution effect, seemed to be more important for elements derived from aerosols than those from gases. One aspect of a model developed by Xing and Chameides (1990) shows that over extended periods of rainfall, the rate of wet removal of atmospheric components ceases to be controlled by the microphysical parameters of the rain itself and instead is limited by the rate at which atmospheric components can be re-supplied to the area in which the rainfall is occurring, the rainfall column.

Theses studies imply that there should be some type of negative relationship between the amount of rain collected and the concentration of species in the rain samples, at least at the extremities of volumes collected, that is, in samples of extremely low volume and in samples of extremely high volume. If this is the case then it will be important to take such an effect into account when calculating annual total input loads to the RUM waste and VLG stockpiles (see Chapter 6).
In bulk precipitation collection, like the RUM samples, extremely low volumes have the added possibility of being affected by direct aerosol influx. In fact extremely low volume rainfall samples (around 2mm and below) are sometimes completely discarded in rainfall studies due to the possibility of enhanced contamination returning spurious results (Ayres et al. 1993).

There is no definitive negative correlation between the amount of rain collected and the total concentration of ions in the RUM rainfall chemical data, however the data is suggestive of a negative correlation occurring in the EOWS samples alone for a limited number of trace elements, a concentration effect occurring in sample RW109 for some trace elements, and a dilution effect occurring in the two samples of extraordinary large volume (samples RW321 and RW322).

Figure 5.7(a) shows the relationship between volume and the total amount of major cations and anions analysed disregarding free H⁺, HNO₃⁻ and NO₃⁻, since these are the ions that effectively separate the EOWS rains from the SOWS rains. This relationship is similar to that of most of the ions when plotted against volume individually. The potential dilution effect on samples RW321 and RW322 can be clearly seen however when considered against the EOWS rains it seems that no dilution has occurred at all. In fact even considering the SOWS rains alone it seems that the relationship is merely that already highlighted by the Diamond Compass charts of Figure 5.2(b) whereby samples RW301, RW321 and RW322 are compositionally different from the others.

The only major cation that shows any relationship capable of being interpreted as being a potential negative correlation is that of Na⁺ (Figure 5.7(b), but this would only be for the two large volume samples RW321 and RW322. This equates to an approximate 37-38% decrease in sodium with a 307% (nearest %) increase in volume. The problem with taking this into account in any input calculations is two-fold. Firstly, if there is a relationship it may not be linear and thus difficult to calculate without further data points. Secondly, the effect may only operate at certain volumes and above whereby the rain column supply is totally exhausted, without further data there is no way of knowing at which volume this is. Whatever the case, the fact that the relationship only occurs for Na⁺ may suggest that it is a statistical artefact, not a real effect, and even if real, events of such magnitude are rare.
Sample RW109 does contain relatively high amounts of trace elements compared to other EOWS samples however only for Pb\(^{2+}\) and Zn\(^{2+}\) can they be considered to be anomalous (see Table 5.2). This has already been outlined in the methods Chapter (Chapter 2) and thus concentrations in RW109 should be treated accordingly.

![Diagram](image)

**Figure 5.7(a-b):** Relationship between the total amount of rain collected in each sample and the total major ion concentrations disregarding free H\(^+\), HNO\(_3\)\(^-\) and NO\(_3\)\(^-\) (a) and the total amount of rain collected and Na\(^+\) (b).

A negative relationship can be found in the EOWS rains for the trace elements Ba\(^{2+}\), Cu\(^{2+}\) and Fe\(^{2+/3+}\) however it is considered here that there are simply too few data points to know if this relationship is real. In the case of this study anyway, the concentrations of most trace elements, except that of Zn\(^{2+}\), are probably far too low to make any significant contribution to the stockpile of RUM.

In summary, the RUM rainfall data set does not reveal any consistent trend by which a dilution or concentration effect factor can be measured. Thus no corrections have been made for samples RW321 and RW322.
5.4 DISCUSSION

5.4.1 Comparison with other Studies in the Region

Table 5.3 compares concentration ranges for major ions found in the limited number of bulk precipitation samples analysed in this study with arithmetic means and their related standard deviations from Noller et al. (1985), a study that has been identified as a possible data source for rainfall input calculations to the RUM waste rock stockpiles in this research. The Noller et al. (1985) concentration averages in Table 5.3 are for each month of the 1982-83 wet season that is relevant to this study. Noller et al. (1985) do not give a standard deviation for their November data and so December data is used here instead, the RUM November data in this study represents a relatively late period of the month anyway, and so comparisons can still be made. The April data from Noller et al. (1985) has been combined with their May data because this is also how it was presented in the 1985 publication. The latter should make little difference for comparison purposes since it encompasses only until May 4th. It should be noted that the Noller et al. (1985) rainfall samples were also weekly bulk precipitation rainfall collections as are the majority of those collected for this study.

<table>
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<tr>
<th>Data Source</th>
<th>Rainfall Period/Type</th>
<th>pH</th>
<th>Cl-</th>
<th>SO42-</th>
<th>NO3-</th>
<th>Ca2+</th>
<th>Mg2+</th>
<th>Na+</th>
<th>K+</th>
</tr>
</thead>
<tbody>
<tr>
<td>RUM (this study)</td>
<td>November</td>
<td>3.63-4.2</td>
<td>6.49-47.39</td>
<td>7.37-16.64</td>
<td>12.96-25</td>
<td>1.6-21.46</td>
<td>1.42-16.05</td>
<td>6.06-12.85</td>
<td>1.6-3.4</td>
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<td></td>
<td>April</td>
<td>5.68-6.41</td>
<td>4.23-7.62</td>
<td>2.32-4.42</td>
<td>0-1.25</td>
<td>2.26-4.51</td>
<td>0.89-2.56</td>
<td>3.62-4.92</td>
<td>1.01-3.37</td>
</tr>
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<td>Noller et al. (1985)</td>
<td>December</td>
<td>29 (2)</td>
<td>16 (8)</td>
<td>12 (6)</td>
<td>4.5 (4.4)</td>
<td>5.5 (5.3)</td>
<td>16 (10)</td>
<td>4.6 (2.6)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>April/May</td>
<td>12 (19)</td>
<td>2.1 (0)</td>
<td>2.4 (1.4)</td>
<td>1 (1)</td>
<td>1.7 (0.8)</td>
<td>5.5 (1.8)</td>
<td>2.2 (1.2)</td>
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</tr>
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<td>Berner and Berner (1996)</td>
<td>Continental</td>
<td>4.0-6.0</td>
<td>5.6-56.4</td>
<td>20.8-218.7</td>
<td>6.5-21</td>
<td>5-149.7</td>
<td>4.1-41.1</td>
<td>8.7-43.5</td>
<td>2.6-7.7</td>
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<td>1-10</td>
<td>1-10</td>
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<td>1-10</td>
<td>1-10</td>
<td>1-10</td>
</tr>
<tr>
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<td>Marine</td>
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<td>28.2-282.1</td>
<td>20.8-62.5</td>
<td>1.6-8.1</td>
<td>10-74.9</td>
<td>32.9-123.43</td>
<td>43.5-217.5</td>
<td>5.1-15.3</td>
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</table>

Table 5.3: Comparison of RUM rainfall chemistry with rainfall chemistry for Jabiru East from Noller et al. (1985) and with the results of a compilation of rainfall chemistry data from around the world by Berner and Berner (1996). All values are in μeq/L to which the Berner and Berner (1996) data has been converted to. Noller et al. (1996) data are arithmetic means followed by standard deviations in brackets.
From Table 5.3 it is evident that there is no significant difference in rainfall chemistry between the SOWS rains of 1982/83 and 2000/2001 or between the EOWS rains of 1982/83 and 1999/2000 when taking into consideration the standard deviations of the Noller et al. (1985) data. Some minor differences occur:

- NO$_3^-$ is a little higher in November and slightly lower in April in the RUM data, however the Noller et al. (1985) data does overlap with the RUM concentration ranges when standard deviations are included;
- Na$^+$ is higher in the Noller et al. (1985) data however the December values overlap with the RUM data;
- Although both data sets show significant overlap in Cl$^-$ values there is much greater variance in SOWS rains at RUM and less variance in EOWS rains at RUM;
- Ca$^{2+}$ concentrations are higher in the EOWS rains of RUM with no overlap occurring with the Noller et al. (1985) data, however both ranges are small and the gap between them is less than 1μeq/L suggesting that concentrations outside the standard deviation in the Noller et al. (1985) data probably overlaps with RUM values.

These differences may be related to variables such as the position of the wet season during sampling (that is, the number of rainfall events that had already taken place for the SOWS rain collections) and a related ‘washout effect’ (see above), rainfall volume, number of rainfall events during analysis, location within the mine or simply the small number of samples represented in the RUM data. The important point is that these differences are not significant enough to conclude that the rainfall chemistry for November/December and April/May within the wet season at Jabiru/RUM has changed to a degree that the 1982/83 Noller et al. (1985) chemical data could be considered redundant. It can thus be assumed that the chemistry of rainfall incident to the RUM waste and LGO stockpiles in 1999-2000 is not significantly different from the rainfall chemistry at Jabiru during the 1982/83 wet season, at least in terms of major ion concentrations, and hence rainfall chemistry in the area has not changed in the past two decades. Therefore, the Noller et al. (1985) dataset, one that encompasses
the duration of an entire wet season, can be used for calculating the chemical input from precipitation to the RUM stockpiles in this study.

It is also important to note that 1982 and 1983 have been classified as years of a strong El Niño-Southern Oscillation (ENSO) event (Tapper, 2002) where as 1999 and 2000 were not (ABM data). ENSO events cause a breakdown of the Normal Walker Circulation over the maritime continent region of SE Asia and Northern Australia. They are characterised by strong differences in air pressure between Tahiti and Darwin (the Southern Oscillation Index [SOI]), where Darwin air pressure becomes higher than that of Tahiti as the major tropical convective zone moves east into the Pacific Ocean. The major effect of this has been identified as a late start and early finish of the wet season over the Indonesian Archipelago with greatest effect also on the start and finish of the wet season over northern Australia (Tapper, 2002). Thus Table 5.3 indicates that the ENSO event of 1982/83 has not translated into any significant effect on the rainfall chemistry at the start and end of the wet season at the Jabiru/RUM location in the Northern Territory of Australia, at least according to the chemistry of the corresponding periods in the year 2000.

Noller et al. (1985) compared their own results with those of Galloway et al. (1982), who analysed rainfall from the 1980/81 wet season at Katherine, and also concluded from the comparison that the late arrival of the monsoon in 1982/83 (a late February arrival) did not affect precipitation chemistry. The direct comparison is somewhat dubious however, considering Katherine is much further inland than Jabiru and the 1980/81 wet season was a period of negative SOI values anyway, although not significant enough in duration to be classified as an ENSO event. It is important to point out that despite the late arrival of the monsoon, the total amount of rain for the wet season in the Jabiru area was close to average.

Taking into consideration that the rainfall samples collected by Gillett et al. (1994) at Jabiru during the 1984/85 wet season began much later (late December) than the SOWS rains of this study, that they extended into the monsoon period, and that they were storm event wet-only precipitation samples, the RUM data also compares reasonably well with the concentration ranges of major ions in the Gillett et al. (1994) study.
Comparison of the RUM data with other data from the Northern Territory tends to show differences that are related to each site's distance from the coast or the amount of time bulk samplers were left in the field. The extensive study presented by Likens et al. (1987) at Katherine over the period 1980-1984 shows that Katherine rainfall seems to have greater amounts of $\text{SO}_4^{2-}$, $\text{Cl}^-$, $\text{Ca}^{2+}$ and $\text{K}^+$ than RUM, all those components shown to have significant continental sources (Berner and Berner, 1996). This should be expected since Katherine is located some 170 kilometres further inland than RUM from the northern coastline (approximately three times the distance from the coast than RUM).

The corresponding periods in the Ayers et al. (1993) data show that Darwin rainfall is consistently higher in $\text{SO}_4^{2-}$, $\text{Na}^+$ and $\text{Cl}^-$ than RUM, consistent with what would be expected considering Darwin’s coastal location and a corresponding greater influence of sea salt aerosol. Comparison of RUM data with the Keywood (1995) study suggested that Kapalga experiences higher concentrations of $\text{SO}_4^{2-}$, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$ and $\text{K}^+$ in its rainfall, a consequence of the fact the bulk samplers for that study were left in the field for a period of three months and thus collected far greater dry deposition volumes of terrestrial derived aerosol.

Although some interpretations may be different in this study, the RUM rainfall data reveals the same major trends identified in all similar rainfall studies of the region, including the significantly higher concentrations of all major ions, particularly that of $\text{H}^+$, at the start of the wet season compared to the rest of the wet season, the excess of cations in the ionic balance which studies have identified as the failure to analyse for organic acid anions and the large proportion of ‘excess’ or NSS-$\text{SO}_4^{2-}$ throughout all of the wet season rains (Keywood, 1995, Likens et al. 1987, Galloway et al. 1982, Nollet et al. 1985, 1990, Gillett et al. 1990, 1994, Ayers et al. 1993, Wetselaar and Hutton, 1962, Ayers and Gillett, 1988).
5.4.2 Comparison with International Rainfall Chemistry Datasets

Table 5.3 also contains concentration ranges for various ions that are characteristic of different rainfall environment locations around the world, according to the database presented by Berner and Berner (1996). Comparing the data compiled by Berner and Berner (1996) with the RUM data shows that RUM rainfall chemistry is similar to the chemistry of remote continental rainfall around the world. Once again, as has already been done in the Diamond Compasses of Figures 5.2(a) and (b), samples RW304, RW307 and RW317 are different from the other samples in that they have chemical characteristics more like that of normal continental rainfall, specifically in regards to the ions Mg$^{2+}$, Ca$^{2+}$ and Cl$. Noller et al. (1990) also classified rainfall at Jabiru as that of remote continental rainfall, with a relative dominance of known continental derived ions over marine components but with a definitive lack of total ionic abundance compared to most other continental rainfall locations around the world.

5.4.3 Meteorological Relationship

Noller et al. (1990) and Gillett et al. (1990) separate their Jabiru rainfall datasets into monsoon and non-monsoon rainfall. The non-monsoonal rains in both these studies are referred to as transitional, the name given to the period when the Intertropical Convergence Zone (ITCZ) moves north and south across the maritime continent region (normally March-April and October-November), taking with it the monsoon. Both Noller et al. (1990) and Gillett et al. (1990) argue that the transition rains are characterised by higher ionic concentrations and lower pH, although acknowledge that it is the transition period at the start of the Northern Territory wet season, when this is most prominent. They also both refer to the major meteorological difference between the monsoon and the transition as a change in near surface wind direction from the predominance of easterly trades in the transition periods to a NW source in the monsoon. Noller et al. (1990) specifically identify the easterly trades to be associated with isolated convective storm events and higher concentrations of terrestrial derived components in the rainfall compared to the monsoon, which has a chemical signature closer to that of seawater.
However, the Diamond Compass charts presented here in Figures 5.2(a) and (b) suggest that the characterisation of the wet season rainfall may not be that simple. The RUM SOWS rain in Figure 5.2(b) is accompanied by a dominance of northerly winds, although easterly and westerly directions are also prominent, but weaker in strength. Importantly, it does not seem that the RUM SOWS rain is being influenced by consistent easterly trade winds as the EOWS samples of R103 and R104 are in Figure 5.2(a). Yet, the RUM SOWS rain shows two distinctly different cation compositions, one similar to that of seawater and one far from it. If wind direction alone were to identify transition meteorology, then the RUM SOWS rain would have to be categorised closer to monsoon events, but if this were so, then the large deviation from the seawater composition should not exist. If however, the RUM SOWS rain were to be described as transition rains because of its very early position within the wet season, long before the monsoon actually arrives, then the proximal seawater cation compositions should not exist. This paradox may not exist, if the Noller et al. (1990) characterisation is not entirely correct.

To illustrate their conclusions, Noller et al. (1990) use ternary diagrams of the major cations $\text{Ca}^{2+}$, $\text{Mg}^{2+}$ and $\text{Na}^{+} + \text{K}^{+}$ for each month during the 1982/83 wet season at Jabiru, the same cations used in the Diamond Compasses. However, upon closer examination of these diagrams (Figure 5.8) it is difficult to understand how they support the conclusion that monsoon rains are necessarily more oceanic than transition rains.

Referring to Figure 5.8, a small group of monsoon related samples are definitely closer to the seawater reference point in January and April/May of 1983 than are the other samples in those particular months. However, another group of monsoon samples in the April/May diagram are definitively more related to the non-monsoon samples and in the February diagram there is no distinct difference in proximity to the seawater reference point between monsoon and non-monsoon samples. It seems then, that the Noller et al. (1990) data does not show any clear distinction between the monsoon related rainfall and non-monsoon or transitional related rainfall in regards to proximity to seawater composition, a result consistent with the results of this study. It is a result also consistent with conclusions by Likens et al. (1987) for a study of air mass back trajectories for rainfall at Katherine over the period 1980-1984. Likens et
Figure 5.8: The Noller et al (1990) ternary diagrams showing the relative concentrations of the major cations of rainfall from all the Noller et al (1990) collection sites compared to the relative composition of average seawater. The rainfall was collected during December 1982 and January, February, March and April of 1983. The outlines show sets of samples grouped according to Noller et al (1990) classification, M indicates the presence of the monsoon trough. See text for details. All diagrams were taken from Noller et al (1990) without alteration.
al. (1987) found that no trajectory direction, including the NW direction proposed by Noller et al. (1990) to be associated with the monsoon, contained increased concentrations of sea salt components in the related rainfall.

All this being said, one clear distinction can be made in the Noller et al. (1990) ternary diagrams of Figure 5.8 that is consistent with the Diamond Compasses of this study and with conclusions by Likens et al. (1987). The distinction is that the SOWS rain, the rain characterised by its position at the very start of the wet season before the monsoon arrives, can be differentiated by its extreme variation in cation chemistry, from seawater like to non-sea water like, particularly in regards to variations in Ca\(^{2+}\) concentrations.

The distinction outlined above is in addition to those already revealed by the results of the RUM rainfall study, as well as by Noller et al. (1990) and Likens et al. (1987). The SOWS rain also has much higher concentrations of H\(^{+}\), NO\(_3\)\(^{-}\), SO\(_4\)\(^{2-}\) and Na\(^{+}\). It is argued here that all of the distinctive chemical characteristics of the SOWS rain, and the fact that the monsoon rains can also have terrestrial influence, can be explained by the following:

- that the early transition period in which the SOWS rain falls is not characterised by a dominance of easterly trade winds, rather it corresponds to a period of highly variable surface and near surface winds of relatively little strength, where the easterly trades have already broken down;
- winds from the ocean, allegedly those from the NW, may be of low enough strength at times to reduce the distance that large amounts of sea salt can be transported inland;
- low winds on the ocean may reduce the amount of sea salt that is transferred to the atmosphere to begin with, at least enough so that it is easily swamped by any terrestrial influences;
- persistent continental low pressure over the northern Australian region during the monsoon allows a large amount of re-circulation to occur (Sturman and Tapper, 1996), hence even monsoon winds have the potential to have significant local influence; and
as the wet season begins ‘washout’ quickly reduces the amount of components that have been allowed to build up in the local atmosphere because of the above meteorological conditions. The resulting reduction in supply of components to the rain column and cloud formation regions reduces the concentrations of many ions in rainfall as the wet season continues.

The above meteorological conditions are brought about because the “top end” of the Northern Territory of Australia is located within the maritime continent climate region, one of three locations around the world that experiences enhanced tropical convective activity, along with the Amazon Basin and central Africa. It is also the region of greatest movement, north and south, of the ITCZ (Figure 5.9a-c), the zone where tropical easterly airflow from each hemisphere converges near to the equator and ascends. The increased movement of the ITCZ over the maritime continent is related to the large differential heating that occurs between the Asian and Australian continents during summer/winter, as the ITCZ tends to follow those areas of highest solar radiation, although many other factors are involved that sometimes show variation in this behaviour (Tapper, 2002, Xie, 1998).

As northern Australia is tilted towards the sun on the approach to summer, and so becomes heated, the ITCZ is drawn south reaching as far as Jabiru and RUM around January (refer to Figure 5.9a). As can be seen by the near surface stream lines related to the ITCZ (Figure 5.9a), this movement brings with it a reversal of low-level wind direction over the Indonesia-Australian region, from dry easterly trade winds from the Australian continent, to warm moist west to NW winds from SE Asia, the winds of the monsoon. During the period where the ITCZ is moving south across the Maritime Continent region, the October-November transition period, lateral wind movement over the Jabiru area slows almost to a complete halt as local convective cells begin to form over the “top end” (refer to Figure 5.9b). As Figure 5.9(b) and (c) show, at this time RUM experiences very little wind at 500 metres elevation and from no particular direction. By January this cell had moved to the east slightly and the NW monsoon
flow should begin to appear (refer to Figure 5.9c). By April, the easterly trade winds have been re-established and more consistent stronger winds begin to dominate.

Figure 5.10 confirms this model for RUM, whereby 3 hourly surface wind directions from 12 noon to 12 midnight at Jabiru east have been plotted for each month of the 1999/2000 wet season. The 3pm and 6pm data points have been highlighted due to the reasons explained earlier (section 5.2). November 2000, the month of the collections for this study has been included in the display. The pattern is clear; the easterly trades have broken down by the end of October, when a short period of highly variable wind directions occurs through November. Northerly to westerly winds begin to dominate as the monsoon arrives in December until the easterly trades begin to be re-established in April.
Figure 5.9(a): Mean position of the ITCZ during January and July and streamlines of near-surface windflow in the tropics. Note the direction of the near surface windflow in January, generally a monsoon month. See text for further details. (from Sturman and Tapper, 1996 in Tapper, 2002)

Figure 5.9(b): Regional scale wind speed at 500 metres in January, April, July and October. Isotachs are at 2 m/s intervals and winds > 2 m/s are shaded. Note the lack of wind speed over RUM during October, the lead up month to the start of the wet season. See text for further details (from McBride, 1992 in Tapper, 2002)

Figure 5.9(c): Regional scale low-level winds in January, April, July and October, showing the seasonal reversal of the monsoon flows. Wind strength is indicated by the length of the arrow. Note the lack of direction and strength over RUM during October, the lead up month to the start of the wet season. See text for further details. (from McBride, 1992 in Tapper, 2002)
Figure 5.10: Daily 12noon, 3pm, 6pm, 9pm and 12 midnight wind direction records for each month of the 1999/2000 wet season at the Jabiru East airport. Note that the 3pm and 6pm wind directions have been highlighted because these are the directions most commonly associated with the prevailing surface wind before and during the rainfall event (as observed). The 3pm and 6pm winds were also characterised as those of the greatest wind speed. Data is from Australian Bureau of Meteorology database. See text for further details.
5.5 IDENTIFYING THE SOURCES OF INDIVIDUAL CHEMICAL COMPONENTS IN RAINFALL AT RUM

5.5.1 Non-Sea Salt Calculations and General Classification

The excess, or non-sea salt (NSS) ratio, is used to determine the amount of a particular component that is in excess to that derived from sea salt and hence, how much of the component is not derived from the ocean. It is a general parameter based on the premise that despite the complexity in the types and amounts of chemical reactions that have been found to be occurring within all levels of the atmosphere the sources of the chemical components measured in rainfall are either oceanic or terrestrial in origin, the latter including anthropogenic pollutants. It is thus an initial basic tool for rainfall chemistry source studies and is used here for this purpose.

NSS calculations are usually based on Na\(^+\), Cl\(^-\) and Mg\(^{2+}\) as the sea salt reference ion because these elements show the least variation in relative concentration from seawater in rainfall over the ocean (Berner and Berner 1996, Wadleigh et al. 1994, 1996 and de Caritat et al. 1997). Mg\(^{2+}\) cannot be used as a sea salt reference at RUM because it has a potential local source; it is one of the most abundant elements within the rocks of RUM and a dominant metal in sulphates found to be prevalent on the surfaces of the waste and LGO stockpile (see Chapter 4).

Choosing between Cl\(^-\) and Na\(^+\) can be difficult. For marine rain Na\(^+\) is usually preferred over Cl\(^-\) because Cl\(^-\) can be gained from pollution sources as well as HCl loss from acidified marine sea salt aerosols, but over continents Na\(^+\) can be introduced by mineral aerosol (Berner and Berner, 1996, Keene et al. 1990). Figure 5.11 is a bivariate scatterplot of Cl\(^-\) and Na\(^+\) in the RUM rainfall. The slope of the line applied to the scatterplot represents the Cl\(^-\)/Na\(^+\) ratio of average seawater composition. If it is assumed that the only changes in the relative proportions of Na\(^+\) and Cl\(^-\) can be by addition of either cation, and hence there is no preferential fallout of one cation over the other during transport over the continent (disregarding isotopic differentiation) then Figure 5.10 implies that Cl\(^-\) has been enriched relative to sea salt in the RUM rainfall for three samples, those already identified as having dominant terrestrial signatures in relative cation chemistry (see Figures 5.2a and b). For this reason Cl\(^-\) cannot be used as a sea salt reference element in this study. Keywood et al. (1997)
found that Cl\textsuperscript{−} decreased relative to Na\textsuperscript{+} over inland Western Australia due to the preferential loss of Cl\textsuperscript{−} from the sea salt aerosol to HCl gas by incorporation of H\textsubscript{2}SO\textsubscript{4} and NO\textsubscript{3}\textsuperscript{−}. Although this does equate to preferential fallout, Cl\textsuperscript{−} was still the variant and not Na\textsuperscript{+}.

**Figure 5.11**: Discriminating between Na\textsuperscript{+} and Cl\textsuperscript{−} for use as the seawater reference element in NSS-calculation for RUM rainfall chemistry source studies. To do this a comparison has been made between the RUM rainfall Cl\textsuperscript{−} and Na\textsuperscript{+} relationship to that of the Cl/Na\textsuperscript{+} ratio in average seawater. Average seawater concentrations have been taken from Wilson (1975) at 35% o salinity. See text for further details.

NSS calculations for the RUM data are presented in Figure 5.12 expressed as percentages. The derivation is as follows;

\[
\text{NSS-(component)}\% = 100 - ((\text{mg/L of component/mg/L of Na}\textsuperscript{+} \text{ in sea salt}) / (\text{mg/L of component/mg/L of Na}\textsuperscript{+} \text{ in rain}) \times 100)
\]

Figure 5.12 clearly suggests that the major chemical components of the RUM rainfall can be separated into two groups; one derived almost entirely from continental sources, consisting of Ca\textsuperscript{2+}, SO\textsubscript{4}\textsuperscript{2−} and K\textsuperscript{+}; and one that has a significant sea salt source
but with possible terrestrial fluxes and highly variable source strengths, consisting of Mg$^{2+}$ and Cl$^-$. Figure 5.12 also suggests that according to NSS values there is no significant difference in terrestrial source strength for the terrestrially sourced group, Ca$^{2+}$, SO$_4^{2-}$ and K$^+$, throughout the entire dataset. That being said lower NSS values occur for SO$_4^{2-}$ with samples R103 and R104 and the Ca$^{2+}$ enrichment outlined above in samples RW304, RW307 and RW317 is also evident in the NSS calculations. Both R103 and R104 were only left in the field overnight, and it has already been explained that SO$_4^{2-}$ was the only ion possibly affected by the different field collection times used in this study (see Chapter 2). Thus NSS-SO$_4^{2-}$ has been affected accordingly.

![Non Sea Salt (nss) Calculations for RUM Rainfall Chemistry](image)

**Figure 5.12:** Non sea salt (NSS) calculations for Cl$^-$, SO$_4^{2-}$, Ca$^{2+}$, K$^+$ and Mg$^{2+}$ in the RUM rainfall samples. Na$^+$ has been the used as the seawater reference element and the average concentrations of seawater have been taken from Wilson (1975) at a 35% salinity. See text for further details.
It is important to understand that NSS calculations are not a measure of how much of a particular component of a rain sample has or has not been supplied by an air mass originating from the ocean, although this is how they are popularly used. They are instead only precise calculations of how much a certain proportion of a chemical component varies from the proportion in which it is found in “average seawater or sea salt”. This leads to three main problems that one needs to be aware of when dealing with NSS calculations.

Firstly, sea salt is not the only source of aerosol over the ocean, marine aerosol composition can be effected by large terrestrial sources such as deserts and volcanoes if it is within the associated transport pathways (Chester, 1990). Thus it is possible that a rain-producing air mass containing marine aerosol may already have terrestrial chemical signatures before it reaches a land mass.

Secondly, sea salt aerosol is not the only contribution the ocean makes to rainfall chemistry, particularly in regards to $\text{SO}_4^{2-}$; estimates suggest that almost 28% of all the sulfur released to the marine atmosphere by the ocean may be derived from biogenic reduced sulfur species (using data from Bates et al. 1992 and Ericksson, 1960, sourced from Berner and Berner, 1996) such as dimethyl sulfide ($\text{[CH}_3\text{]_2\text{S}$).

Finally, it is not the bulk seawater that produces the sea salt aerosol, rather the thin layer of water at the air-sea interface (estimates of thickness range from a monomolecular layer to several hundred micrometres), commonly known as the sea surface micro-layer (Blanchard, 1963 in Horne, 1969, Horne, 1969, Liss, 1975 and Chester, 1990). This is because the transfer process from the sea to the atmosphere involves the production of fine sea spray at the sea surface, either by the bursting of bubbles, wind collection of spume from waves, wind induced ocean chop, direct splash from waves and even rain droplets (Monahan, 1985 and Horne, 1969). It has been proposed that the sea surface micro-layer is a loose hydrated gel film of inter-tangled macromolecules (free and condensed), colonised by bacteria and that it has a chemical signature markedly different from that of the underlying seawater (Seiburth, 1983 in Chester, 1990, Chester, 1990 and Liss, 1975).
Whilst the proportions of most major elements may not be significantly different in the micro-layer compared to the average sea salt composition, many trace elements can be enriched in this layer by as much as $10^3$ to $10^7$ times (Chester, 1990). Added to this, and clouding any attempt to measure the amount of fractionation, is the fact that the sea surface micro-layer is itself the site of atmospheric deposition of elements on the ocean and thus it is a place where aerosols are, in effect, recycled. It is possible therefore that some trace elements in the sea salt aerosol may have actually originated from terrestrial sources despite being directly sourced from the sea surface.

5.5.2 Sodium

It is assumed that $\text{Na}^+$ is sourced completely from oceanic sea salt aerosol for the NSS calculations. Figure 5.11 shows that whilst the presence of $\text{Na}^+$ salts in mineral aerosol cannot be ruled out $\text{Na}^+$ can be considered here to be the least likely major element analysed in this study to be sourced to any significant degree from mineral aerosol.

It is possible that the burning of vegetation could introduce $\text{Na}^+$ into rainfall since biomass burning is a potential source of $\text{Na}^+$ (Berner and Berner, 1996) and supervised prescribed burning certainly occurs in the region incorporating RUM. Also, recent analysis of vegetation proximal to RUM does reveal the presence of proportionally significant $\text{Na}^+$ concentrations in some of the samples (Kilby, unpublished, 2001).

Burning of the tropical savannah in the Northern Territory and the rest of Australia’s northern tropics, mostly through fire management practices, but also as the result of lightning strikes and arson, begins as soon as the wet season rains cease around March or April and does not end until the wet season begins in November and even December (personal communication Russel-Smith, 2003). Figure 5.13 is a map of the entire northern tropics region in Australia showing the areas affected by fire in the year 2000, the year the rainfall in this study was collected. The predominance of late dry season to early wet season burning is clearly evident. These late dry season burns have the potential to influence rainfall chemistry at the start of the wet season and it has been suggested as a potential source for various chemical components in SOWS
rains in the Jabiru area (Noller et al. 1990). This may be the reason behind a relatively small increase in Na$^+$ concentration in the SOWS rain of this study.

![Map of Fire Affected Areas in Australia's Tropical Savannas for the Year 2000](image)

**Figure 5.13:** A map of the fire affected areas of the northern tropical savannah region of Australia and the location of the area incorporating Ranger Uranium Mine and Jabiru. The map has been taken from the Tropical Savannahs CRC web site: [http://savannah.ntu.edu.au/research/projects/fire_maps_tropical_savannahs.html](http://savannah.ntu.edu.au/research/projects/fire_maps_tropical_savannahs.html). The map was produced from NOAA-AVHRR satellite images by the W.A. Department of Land Administration (DOLA).

### 5.5.3 Calcium

Ca$^{2+}$ is primarily of continental origin (Berner and Berner, 1996). NSS-Ca$^{2+}$ values for RUM rainfall samples suggest that 83% to a little over 97% of the Ca$^{2+}$ originates from sources, other than sea salt. The primary source of Ca$^{2+}$ in continental rains is CaCO$_3$ in aerosol derived from soil, gypsum (CaSO$_4$) being a common contributor, and in some places even CaCl$_2$ can contribute to the Ca$^{2+}$ content of rainfall (Berner and Berner, 1996). Such salts are normally the first to precipitate out of soils (Simpson and Herczeg, 1994) and are thus readily available at the surface. Simpson and Herczeg (1994) use Ca/Na ratios above 1.0 to identify significant regional dust input to rainfall in South Eastern Australia. The Diamond Compass charts of Figure 5.2(b) show that Ca/Na ratios climb above 1.0 for the 3 SOWS samples RW304, 307
and 317, confirming the terrestrial influx proposed for these samples. Whilst Na does increase in these three SOWS rains, Ca is as much as 13 times more concentrated than in the other SOWS rain.

Except for the three samples mentioned, Ca concentrations in the rainfall collected fall well within those stated by Berner and Berner (1996) for remote unpolluted continental rain (0.02-0.2mg/L), hence there is no reason to suspect that Ca is from anything other than natural continental sources. Major pollution sources for Ca, such as cement manufacturing and major coal burning facilities, do not exist in the vicinity of RUM.

A contribution from plant particle aerosol, particularly those produced by biomass burning, cannot be ruled out. Biomass burning is a potential source of Ca (Berner and Berner, 1996, Yamasoe et al. (2000) and data from Kilby (2001) shows that Ca is present in considerable proportions, relative to other cations, in vegetation around the Magela Creek and Ranger area.

5.5.4 Potassium

NSS-K suggests that in all samples over 87% of K is from a non-sea salt origin. As has already been pointed out, disregarding the three samples RW304, RW307 and RW317, K correlates (non-linear) with Ca in the RUM rainfall. This is consistent with a situation where K is derived from a mineral aerosol base, as is Ca, but from a less soluble mineral compared to that responsible for most of the Ca. If the time of contact between the rainwater and the mineral aerosol is short, then fractionation will occur towards mineral salt components due to their high solubilities compared with the K-bearing soil dust minerals such as illite, feldspars and micas. Thus fluxes of mineral aerosol to the rain column before a rain event may result in only the Ca being enriched in the filtered solution collected. This is similar reasoning to that used to explain the lack of SiO in rainfall despite the presence of elements such as K that are derived predominantly from silicate minerals, that is, SiO is more secure in silicate structures than is K, and thus K is preferentially taken into solution in earlier stages of mineral-water reaction (Berner and Berner, 1996).
Biogenic aerosol created by the release of plant exudates to the atmosphere has been used to explain the presence of K\(^+\) in rains of the Amazon basin where dust is minimal (Lawson and Winchester, 1979) and it is thought that such processes are favoured in regions of high heat and humidity. However, unless Ca\(^{2+}\) is also introduced by biogenic aerosol, the reasonably strong relationship K\(^+\) has with Ca\(^{2+}\) suggests a similar source. A total lack of correlation with SO\(_4^{2-}\), the probable anion of the plant exudate salt, also suggests a minimum, if any, contribution by biogenic exudates, although much higher SO\(_4^{2-}\) concentrations from another source would probably mask such a relationship anyway.

Although biomass burning is a potential contributor to K\(^+\) in rainfall (see Berner and Berner, 1996, Yamasoe et al. 2000), there is no significant difference in K\(^+\) concentrations between the SOWS and EOWS rain that would suggest that late dry season and early wet season burning in the Northern Territory is an important K\(^+\) source. Vegetation analysis by Kilby (2001) shows that plant matter in the vicinity of RUM may not be a reliable source of K\(^+\) anyway.

### 5.5.5 Sulphate

As in many parts of the world SO\(_4^{2-}\) source studies have received particular attention in the Northern Territory due to the presence of large proportions of excess SO\(_4^{2-}\), a phenomenon generally equated to pollution and 'acid rain' (Seinfeld and Pandis, 1998). Pollution derived SO\(_2\) species form SO\(_4^{2-}\) through two main processes. Firstly SO\(_2\) gas reacts with OH\(^-\) molecules to form the strong acid, H\(_2\)SO\(_4\), which then quickly dissociates to release free H\(^+\) ions and the subjugate base, SO\(_4^{2-}\). Secondly, SO\(_2\) is dissolved into liquid aerosol particles or cloud droplets, where it reacts with H\(_2\)O\(_2\) or O\(_3\) (in cloud droplets) to form H\(_2\)SO\(_4\), and subsequently SO\(_4^{2-}\) upon disassociation.

Some 86% of total SO\(_4^{2-}\) in weekly rainfall collections by Noller et al. (1990) at Jabiru East was excess (VWM, all samples). RUM samples are similar with NSS-SO\(_4^{2-}\) ranging between 77.5% and 90.6% of total SO\(_4^{2-}\). Noller et al. (1990) calculated the likely contribution of local anthropogenic sources of SO\(_2\) to both dry and wet deposition in the Jabiru area; these included an oil-fired electricity generation station, a calciner plant and a plant producing H\(_2\)SO\(_4\) from elemental sulphur via the contact
process at RUM as well as an oil fired electricity station, a calciner and open vats of H$_2$SO$_4$ at Nabarlek, some 43 kilometres north east of Jabiru. They concluded that local anthropogenic sources were insignificant. During the 1999/2000 environmental monitoring period at RUM, some 148.379 tonnes of SO$_2$ was estimated to have been emitted from RUM (ERA, 2000).

However, estimates of total S emissions into the atmosphere of the entire northern Australian tropics by Ayres and Gillett (1988) suggested that some 80% were believed to be from anthropogenic sources, and some 87.5% of this, originated from the Mount Isa smelters alone (Pb, Zn, Ag Mine in Queensland, Australia). The Mount Isa smelters are approximately 1280 kilometres south east of Jabiru and so it is difficult to predict exactly how much they contribute to NSS-SO$_4^{2-}$ at RUM. Likens et al. (1987) also sighted the Mount Isa smelters as a potential source of S to rainfall at Katherine.

Concerning rains from Katherine and Jabiru, both Likens et al. (1987) and Noller et al. (1990) respectively, acknowledge the fact that despite the large excess SO$_4^{2-}$, the total concentrations of SO$_4^{2-}$ are very low relative to other remote locations around the world. Similar results are seen in this study, in fact even the highest concentrations in the RUM data fall well short of the range set by Burner and Burner (1996) for remote, unpolluted continental rainfall. This is an important observation, since it means there is no need to invoke a strong pollution source if total concentrations are already very low; natural sources may be sufficient providers of S species to the atmosphere. Contrarily, a strong pollution source may not necessarily need to be proximate to the sample site to influence the rainfall chemistry.

Potential natural sources of SO$_4^{2-}$ include mineral aerosol, reduced S species from vegetation emissions, soil desorption from soil surfaces, in particular in tropical coastal areas with large tides, volcanic emissions and biomass burning (Berner and Berner, 1996). All these sources, except volcanic emissions, are present in the RUM region. Calculations made by Ayers and Gillett (1988) set bushfires and soil emissions as the prime sources of natural S to the atmosphere in tropical Australia. As has been already stated above, biomass burning of predominantly anthropogenic origin occurs throughout the dry season and well into the start of the wet season in the
tropical Northern Territory. S-products in the atmosphere from this source in November and early December may explain why SO$_4^{2-}$ is distinctly more concentrated in the SOWS rains compared to the EOWS rains at RUM. It has been found that biomass burning is also an important S source in remote continental areas such as the Amazon Basin and West Africa (Yamasoe et al. 2000, Berner and Berner, 1996).

It should be noted that biomass burning is also a significant source of CO and CH$_4$, the primary regulators of OH$^-$ radical abundance in the atmosphere (Hurst and Griffith, 1994). Thus, biomass burning in the Northern Territory may result in lengthened lifetimes and subsequently greater transport distances for trace gases such as SO$_2$, possibly resulting in a more ubiquitous dispersion of SO$_2$ throughout the entire territory region.

However, an important observation is that NSS-SO$_4^{2-}$ calculations for the RUM samples (refer to Figure 5.12) suggest that whilst concentrations of SO$_4^{2-}$ may have increased significantly, they have not done so relative to Na$^+$. This suggests that whilst terrestrial source strength has increased, so too has that of the ocean, or that Na$^+$ is also sourced from the same terrestrial source as that of SO$_4^{2-}$. This would also explain why throughout the RUM samples, SO$_4^{2-}$ seems to be correlating with Na$^+$ (Figure 5.4b), Cl$^-$ (Figure 5.4c) and to a much lesser extent, Mg$^{2+}$ (Figure 5.5b), all species associated more commonly with an oceanic source. However, this can also be explained if the air masses responsible for the rain at RUM already contained excess sulphate before they reached the Australian continent. Then, any increase in the contribution of oceanic derived air to the chemistry of the rain, despite influxes of continental materials, would see some correlation of SO$_4^{2-}$ with the oceanic species. This is a very possible proposition, since SO$_4^{2-}$/Na$^+$ ratios in marine rainfall and marine aerosol are almost always greater than those of seawater. The reason for this has been long debated, some researchers have suggested various processes of enrichment at the sea-surface micro-layer (Komabayasi, 1962, Martin and Lubke, 1964, Bloch et al. 1966 in Horne, 1969), others have suggested fractionation during the formation of sea salt from seawater (Garland, 1981), however more recent studies suggest that SO$_4^{2-}$ may simply be enriched over the ocean via long distance transport from continents and pollution sources (Andrae et al. 1986, Savoie et al. 1989, Chester,
1990). However, enrichment can also be explained by the production of (CH$_3$)$_2$S, dimethyl sulfide (DMS), in the ocean, particularly in biologically productive parts of the ocean surface, and the subsequent reaction path in the atmosphere to SO$_4^{2-}$ (Berner and Berner, 1996, Yang et al. 1998). It has been estimated that DMS may represent half of the entire global flux of biogenic S to the atmosphere (Andreae, 1990).

These conclusions are important to rainfall at RUM because the Indonesian archipelago and Papua New Guinea (PNG) have numerous active volcanoes and frequent large forest fires (mostly anthropogenic) and the relatively warm shallow waters of the continental shelf that extends almost to Timor and PNG from tropical Australia, has relatively higher biological activity compared to the deep ocean (Considine, 1984 in Noller et al. 1990). Thus, relatively large proportions of excess SO$_4^{2-}$ may already be a characteristic of the air mass responsible for rainfall in the RUM region, before it interacts with more regional continental sources.

It has already been explained that the relationship between SO$_4^{2-}$ and Ca$^{2+}$ in RUM rainfall (refer to Figure 5.5a) seems to suggest that SO$_4^{2-}$ has an additional or different source to Ca$^{2+}$. The chemistry of local atmospheric aerosol collections over Jabiru in 1984 and 1985 revealed that some 67% of S existed in the gas phase as SO$_2$ while the remaining 33% existed in the SO$_4^{2-}$ particle phase (Gillett et al. 1994). It is difficult to make any precise conclusion from this result, however it is evidence to suggest that most SO$_4^{2-}$ is derived from SO$_2$ rather than direct mineral aerosol.

It is important to point out here that when Wetselaar and Hutton (1962) examined filter papers from the filtering of wet-only rainfall samples collected at Katherine during the 1958/1959 wet season, they found that those that corresponded to SOWS rain was dominated by plant particles, where as the others were dominated by soil particles. It can be postulated that SO$_4^{2-}$ is derived predominantly from a background marine aerosol, which has significant terrestrial influence, accompanied by a SO$_2$ source from bushfires in the SOWS rain, where as Ca$^{2+}$ is in the same background marine aerosol but influenced by fluxes of local mineral aerosol in the SOWS rains.
5.5.6 Magnesium

Mg$^{2+}$ is normally of sea salt origin in coastal areas and continental origin in inland areas (Berner and Berner, 1996). Figure 5.12 shows that both of these sources may fluctuate in strength at RUM, although the NSS-Mg$^{2+}$ values clearly separate Mg$^{2+}$ from other components (except Cl$^-$) as having a greater oceanic influence. Some of the RUM rains seem to have no continental contribution of Mg$^{2+}$ at all. General positive correlation of Mg$^{2+}$ with Na$^+$ and Cl$^-$ is further evidence that Mg$^{2+}$ is heavily influenced by an oceanic source.

Mg$^{2+}$ is a prominent cation in vegetation in the RUM area (using data from Kilby, 2001) so biomass burning is a potential source, and Mg$^{2+}$ is a common component of soils (Berner and Berner, 1996). At Ranger, Mg$^{2+}$ is enriched in stockpile surface soils as well as the waste rock (see Chapter 4). This enrichment may have provided a local source for the extraordinarily high concentration of Mg$^{2+}$ in sample RW304, a sample from location site NCWP which is situated closest to the active mine pit and hauling traffic. The fact that NSS-Mg$^{2+}$ calculations are highly variable may also be evidence that Mg$^{2+}$ is sporadically sourced from soil/dust aerosol influx to the rain column or directly to the collection vessel.

5.5.7 Chloride

The major source of Cl$^-$ in the atmosphere and rainwater are the world’s oceans (Hem, 1985, Berner and Berner, 1996, Chester, 1990, Langmuir, 1997, Keene et al. 1999). Most of the earth’s Cl$^-$ exists in the oceans, and sea salt aerosol from the oceans surface is estimated to contribute some 89% of the total reactive inorganic Cl$^-$ released to the global atmosphere per year (using global budget estimates from Keene et al. 1999). However, although some of this aerosol is converted to volatile compounds that remain in the atmosphere, most is deposited back to the ocean with the super-micron sea salt aerosol within an average of approximately 1.5 days (Keene et al. 1999). Thus, Cl$^-$, like any other sea salt derived component, dramatically decreases over the continent with distance from the coast as has been documented in Australia (see Keywood, 1995, 1997). Thus it is possible that other sources of Cl$^-$ may be important at localised, continental sites.
The major continental contributors of Cl\textsuperscript{−} are considered to be volcanoes, biomass burning, denuded soil surfaces (producing dust), the burning of fossil fuels (mainly automobiles and coal combustion) and waste incinerators (via the burning of polyvinyl chloride [PVC]) (Keene et al. 1999 and Berner and Berner, 1996, Yamasoe et al. 2000).

At RUM, only four rainwater samples have NSS-Cl\textsuperscript{−} values over 17%, none of these reach greater than a 69% NSS contribution. Like Mg\textsuperscript{2+}, this clearly separates Cl\textsuperscript{−} from other ions in terms of having a more dominant oceanic source. However in three samples, the SOWS samples RW304, RW307 and RW317, Cl\textsuperscript{−} increases by as much as 7 times that of other SOWS samples, outstripping corresponding increases in Na\textsuperscript{+} to mount NSS-Cl\textsuperscript{−} values greater than 50% of total Cl\textsuperscript{−}. One sample from the EOWS rain, sample R107, also has a NSS-Cl\textsuperscript{−} value close to 50%, however the Cl\textsuperscript{−} concentration in this sample has only increased by approximately 60%. Still, it does suggest that Cl\textsuperscript{−} may have an alternative source to sea salt, albeit an inconsistent one, and in some cases it may be a significant contributor to total Cl\textsuperscript{−}.

Although no published studies in the area have given Cl\textsuperscript{−} derivation any particular attention, an examination of the data from these studies reveals that excess Cl\textsuperscript{−} is not uncommon (using data from Noller et al. 1990, Gillett et al. 1990, Likens et al. 1987, Ayers et al. 1993 and Gillett et al. 1994) for rainfall at Jabiru East Airport, Jabiru, Katherine and Darwin. The only study to actually acknowledge the presence of significant excess Cl\textsuperscript{−} is that of Gillett et al. (1994), in which case it is used as evidence to suggest that HCl may contribute to acid deposition at Jabiru.

Ca\textsuperscript{2+}, SO\textsubscript{4}\textsuperscript{2−}, Na\textsuperscript{+} and Mg\textsuperscript{2+} all correlate to some degree, with Cl\textsuperscript{−} in the RUM rainfall, but only Ca\textsuperscript{2+} shows similar extraordinary increases in concentration for the three SOWS samples mentioned above as well as corresponding increases in NSS-Ca\textsuperscript{2+}. This suggests that in these three samples alone, additional Cl\textsuperscript{−} may have the same source as that of excess Ca\textsuperscript{2+}, which is suggested here to be either a soil dust signature, possibly even CaCl\textsubscript{2} itself, as has already been noted as a potential soil/dust component of rainfall (Berner and Berner, 1996), or biomass burning.
According to estimates by Graedel and Keene (1996) and comparing these with data from Keene et al. (1999), mineral dust aerosol from areas of deflation is the largest continental source of Cl in the atmosphere (15Tg per yr-1). Another significant continental source of Cl is biomass burning. Cl concentrations correlate strongly with SO$_4^{2-}$ in the RUM data and Cl/Na weight ratios in some of the vegetation near RUM (using data from Kilby, unpublished, 2001) are similar to those in the three SOWS samples with excess Cl. In fact it has been found that savannah grasses contain much higher amounts of chlorine than wood or forest fuels (Lobert et al. 1999). Recent atmospheric global Cl flux models identify biomass burning in northern tropical Australia as an area of significant Cl supply to the atmosphere (Lobert et al. 1999).

Considering automobile emissions have been previously disregarded as pollution sources of any significance in the Northern Territory (Noller et al. 1990) and no other major fossil fuel burning facilities or concentration of incinerator plants are present in the vicinity of RUM, the evidence supports a notion of Cl originating primarily from sea salt and biomass burning with influxes of mineral aerosol contributions.

5.5.8 Nitrate

Most NO$_3^-$ in rain is derived from reactive nitrogen oxide gas species (Nox), either directly from nitrogen oxide (NO$_2$) or indirectly from nitric oxide (NO) (Berner and Berner, 1996, Seinfeld and Pandis, 1998 and Tie et al. 2002,). In the atmosphere NO$_2^-$ is converted to HNO$_3$ by catalytic reaction with OH molecules, which in turn completely dissociate to form NO$_3^-$ and H$^+$ ions. NO is converted to NO$_2^-$ in the atmosphere by reaction with ozone (O$_3$), hydrogen peroxides (HO$_2$) or various organic peroxides (Atkinson 2000, Berner and Berner 1996, Seinfeld and Pandis 1998).

Important processes that can contribute to the amount of NOx (NO + NO$_2$) in the atmosphere are the photochemical oxidation of N$_2$O in the stratosphere, the chemical oxidation of NH$_3$ in the atmosphere, biologically induced nitrogen fixation processes in soils (which eventually result in the release of gases such as N$_2$, NH$_3$, NO and N$_2$O to the atmosphere) and one of the most important to the amount of NO$_3^-$ in rainfall, nitrogen fixation with oxygen (to form NO) by high temperature combustion (Berner and Berner, 1996). The most common combustion processes relative to the production
of NO$_3^-$ precursors are the burning of fossils fuels, biomass burning and lightning (Berner and Berner, 1996, Seinfeld and Pandis, 1998 and Tie et al. 2002.).

Ayers and Gillett (1988) estimated that, at the time of publication, bushfires accounted for some 83% of total nitrogen input to the tropical Australian atmosphere, with soils, lightning, power stations (coal and oil fired) and negligible emissions from automobiles making up the difference. It is assumed that little change in the relative proportions of different components would have occurred (if correct), except in the obvious case of an increase in that derived by the burning of fossil fuels with increased populations. According to ERA calculations (2000) the Ranger Mine operations emitted approximately 362.319 tonnes of NOx to the air over the Ranger environmental monitoring period of September 1999 to August 2000, insignificant compared to estimates by Ayers and Gillett (1988).

The Ayers and Gillett (1988) calculations imply maximum concentrations of NO$_3^-$ in rainfall contributed by lightning to be 0.85μM/L, by bushfires to be 14μM/L, and by soils to be 1.2μM/L. In the RUM data NO$_3^-$ concentrations are an order of magnitude higher during the SOWS rain compared to the EOWS rain (refer to Table 5.1). If it is assumed that the effect of bushfires is limited to the first rains of the wet season, because of the effect of washout and the absence of bushfires during the monsoon season, and that it is possible that soil emissions are significantly lower in vegetated tropical forests compared to freshly burnt areas as is suggested by Levine et al. (1988), and Hänsler (Max Plank Institute Press Release, 2002), and hence lower at the end of the wet than at the start of the wet, then the Ayers and Gillett (1998) concentration estimations for NO$_3^-$ in rainfall fit extraordinarily well with the NO$_3^-$ concentrations in the RUM rainfall data (see Figure 5.14).
Figure 5.14: Ayers and Gillett (1988) calculations regarding the μeq/L contributions of lightning, soils and biomass burning to NO₃⁻ in rainfall at Jabiru are compared to the RUM rainfall NO₃⁻ concentrations. It has been assumed that biomass burning and soil contributions are limited after the start of the wet season due to a reduction in fires and the reduction in soils exposed to the atmosphere as the wetlands fill with water. It is shown that if this assumption is made then the Ayers and Gillett et al. (1988) calculations fit with the RUM rainfall NO₃⁻ concentrations.

A number of discrepancies may be present in the estimations above due to the uncertainty in many of the physical parameters of the processes involved. For instance Tie et al. (2002), points out that estimates of NOx production rates by individual lightning flashes range from 0.23 X 10²⁶ to 21 X 10²⁶ NO molecules for each cloud-to-ground flash. Also fire frequencies, fuel loads and burning efficiencies of different savannah regions are poorly known (Hurst et al. 1994), hence making uncertain calculations regarding exact emissions from biomass burning.

That being said, recent studies of concentrations of reactive nitrogen (NOy = NOx + all compounds that are products of NOx oxidation, eg HNO₃, NO₃⁻, HONO etc. HNO₃ being the major one in the atmosphere [Seinfeld and Pandis, 1998]) over Australia and the western Pacific, which includes much of Indonesia, in August to October of 1998 and 1999 (the lead up to the first sampling season in this study) found plumes from biomass burning were causing high concentrations of NOy and CO in the
boundary layer (approximately the bottom three kilometres of the atmosphere) directly over northern Australia (Kondo et al. 2003). These plumes had been trapped in the boundary layer by descending air in the free troposphere (above the boundary layer) caused by nearby high pressure systems in the north west. They also observed a tight correlation of CO and NOy, again above five kilometres, and concluded that this was consistent with the biomass burning source in the boundary layer. Figure 5.15 shows concentration contours for NOy and CO within cross-section slices of the atmosphere through the tropics above northern Australia and the maritime continent region developed from the Kondo et al. (2003) study. The approximate position of RUM has been included in the cross-sections of Figure 5.15 to show that RUM is located well within the boundary layer store of the biomass burning products. The correlation between NOy and CO can also be clearly seen in the atmospheric cross-sections.

Kondo et al. (2003) also acknowledged that during upward transport by active convection, lightning can add a significant amount of NO to the biomass burning plumes already rich in NOy and CO. However, in such circumstances where both processes were operating adjacently, they found it very difficult to separate and quantify the exact contributions made to NOy concentrations by each process. In both years, 1998 and 1999, upper tropospheric air over northern Australia was dominated by air from Indonesia (using 14-day back trajectories) where it was concluded that lightning was the major source of NOy (Kondo et al. 2003). However, it should be noted that earlier work by Wetselaar and Hutton (1962) at Katherine found no correlation between NO$_3^-$ and observed lightning activity for storm event rainfall.

Therefore, it seems that NO$_3^-$ in the RUM rainfall is primarily sourced from both biomass burning and lightning. It is difficult to quantify the exact contributions made by each of these potential sources, however previous estimations by Ayers and Gillett (1988), the atmospheric concentration cross-section diagrams assembled from more recent research (Kondo et al. 2003) and the earlier observations and analysis of Katherine rainfall by Wetselaar and Hutton (1962) suggests that biomass burning is the major factor in supplying the order of magnitude higher NO$_3^-$ concentrations of the SOWS rains. As has already been noted, biomass burning in Northern Australia extends well into the period where SOWS rain has already begun to fall.
Despite the known relationship between lightning and NO production in the atmosphere, observations are yet to be made in the tropical savannah region of the Northern Territory that directly link the amount of electrical activity in a storm event with the amount of NO$_3^-$ in the rain produced by that particular storm.

### 5.5.9 Free Hydrogen Ions (pH)

The SOWS rain at RUM has free H$^+$ ion concentrations two orders of magnitude greater than the EOWS rains. As previously mentioned, the strong correlation between the cation/anion difference and H$^+$ concentrations in the RUM rainfall suggests that the subjugate base or bases responsible for the H$^+$ have not been analysed. Similar conclusions were made by Galloway et al. (1982) and Noller et al. (1990) for rainfall chemistry at Katherine and Jabiru respectively.

Studies by Gillett and Ayers (1985), Likens et al. (1987), Gillett et al. (1990 and 1994) and Ayers et al. (1993) have identified the missing acidic anions belonging to organic acids, particularly formic (HCOOH) and acetic (CH$_3$COOH) but also small proportions of other organic acids. Further, these studies have all concluded that organic acids are the main contributors to acidity in rainfall at Jabiru, Katherine and Darwin. Calculations by Gillett et al. (1990 and 1994) showed that organic acids contributed as much as 41-55% of the H$^+$ ions at Jabiru in the wet seasons between 1982/83-84/85, and calculations by Likens et al. (1987) showed that they contributed a maximum of 57-74% at Katherine (as high as 94% for one sample) over the 1980/81-83/84 wet seasons.

Gillett et al. (1994) showed that by using the general hypothesis that free acidity in rainwater results from the balance between acid anions and the neutralising capacity of atmospheric NH$_4^+$ and Ca$^{2+}$ (representing soil dust carbonates) on the other, predictions of H$^+$ concentrations could be made that correlated closely (a single outlier existed in 10 samples) with actual H$^+$ ion measurements. Importantly they found that this occurred when using additions of formate (HCOO$^-$), acetate (CH$_3$OO$^-$), NSS-SO$_4^{2-}$, NSS-Cl$^-$ (based on Na$^+$ as the conservative sea salt species) and NO$_3^-$ concentrations for the acidic anions and Ca$^{2+}$ and NH$_4^+$ concentrations for the neutralising species; hence these species were the major species responsible for free...
H⁺ concentrations. On the basis of this, the major species contributing to the free acidity in rainfall at Jabiru in the 1984/85 wet season were apportioned by Gillett et al. (1994) in the following way: HCOO⁻ (32.9%); SO₄²⁻ (25.9%); Cl⁻ (20.4%); NO₃⁻ (12.2%) and CH₃COO⁻ (8.5%).

Based on this finding by Gillett et al. (1994) the same calculations have been made for the RUM data for the low pH rain fall in the SOWS rains and are presented in Table 5.4. However, since both of the organic acid anions, HCOO⁻ and CH₃COO⁻, and NH₄⁺ were not analysed for in the RUM rainfall, the equation used by Gillett et al. (1994) has been re-arranged into the following;

\[(y - x) = [\text{NO}_3^-] + [\text{NSS-SO}_4^{2-}] + [\text{NSS-CI}^-] - [\text{Ca}^+] - [\text{H}^+] \quad (1)\]

where 'y' represents the concentration of the missing NH₄⁺ and 'x' is the combined concentrations of the missing HCOO⁻ and CH₃COO⁻. Thus, the function '(y-x)' in the equation above represents the H⁺ ions unaccounted for in the RUM rainfall by the acid anions analysed, if Gillett et al. (1994) correctly identified all of the major contributing species to rainwater acidification in the area. Hence the value in Table 5.4 labelled 'unaccounted' represents the percentage of the concentration of H⁺ that can be attributed to the function '(y-x)'. Although a significant proportion of the total concentration of cations analysed may be NH₄⁺, as much as 8.6% according to data from Noller et al. (1990), it can be safely assumed that most of the '% unaccounted' in Table 5.4 is made up of the missing organic anions.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>% Unaccounted</th>
<th>%NO₃⁻</th>
<th>%Cl⁻</th>
<th>%SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>RW301</td>
<td>74.2</td>
<td>17.1</td>
<td>0.0</td>
<td>8.7</td>
</tr>
<tr>
<td>RW304</td>
<td>29.8</td>
<td>24.1</td>
<td>30.5</td>
<td>15.7</td>
</tr>
<tr>
<td>RW307</td>
<td>57.6</td>
<td>12.5</td>
<td>20.5</td>
<td>9.4</td>
</tr>
<tr>
<td>RW317</td>
<td>81.6</td>
<td>10.7</td>
<td>4.5</td>
<td>3.2</td>
</tr>
<tr>
<td>RW321</td>
<td>79.3</td>
<td>13.0</td>
<td>1.4</td>
<td>6.3</td>
</tr>
<tr>
<td>RW322</td>
<td>75.8</td>
<td>17.1</td>
<td>0.0</td>
<td>7.0</td>
</tr>
</tbody>
</table>

Table 5.4: Calculations for the contribution to free hydrogen ions of HNO₃, HCl and H₂SO₄. These acids have been displayed in the Table under the headings of their appropriate acid anions, those analysed in the RUM rainfall. Calculations are based on findings by Gillett et al. (1994) for rainfall at Jabiru. Note that % unaccounted represents the function '(y-x)' in equation (1), see text for details.
That being said the calculations show that in the RUM SOWS rain out of the three inorganic acidic anions analysed, NO$_3^-$ contributes most to the free acidity followed by SO$_4^{2-}$, with Cl$^-$ hardly contributing at all except in the three samples RW304, RW307 and RW317. A relatively strong correlation between H$^+$ and NO$_3^-$ (Figure 5.4d), a very weak correlation between H$^+$ and SO$_4^{2-}$ (Figure 5.4e) and almost no correlation between H$^+$ and Cl$^-$ (Figure 5.4f) in the RUM data is evidence to support the trend in these calculations. Most important however, is the fact that these calculations suggest that anywhere from 30-82% of the free H$^+$ ions in the SOWS rains remain unaccounted for by the three acid anions analysed, and thus, according to the studies mentioned above, are probably sourced from the organic acid anions HCOO$^-$ and CH$_3$COO$^-$ amongst others. Considering organic acids are weak acids, and thus do not disassociate completely, a substantial concentration of them must exist in the RUM rainfall.


Gillett et al. (1990) found that HCOO$^-$ and NO$_3^-$ showed significant positive correlation in the wet season of 1983/84 at Jabiru, which they interpreted as being an indication that both anions were from the same source. They argued that since NO$_3^-$ is probably sourced predominantly from bushfires, then formic acid or its precursors are also sourced from biomass burning.
Gillett et al. (1990) also suggested that a photochemical source for HCOO' was possible through OH' oxidation of VOCs such as Isoprene (CH2:C(CH3)CH:CH2). Radiocarbon isotopic analysis of formic and acetic acids in Europe shows that even in semi-urban and urban air, significant proportions of these acids are derived from VOCs of biogenic continental origins rather than from fossil fuel burning (Glasius et al. 2001). Souza et al. (1999) also suggests that this is the case for the winter months in Sao Paulo, Brazil. Recent reports from ongoing research in the Amazon region of Brazil by the Max Planck Institute for Chemistry, reveal that two of the rainforest trees tested released isoprene through their leaves in a much greater abundance in the dry season than in the wet, leading to a far greater concentration of the gas in the atmosphere, enough to influence the global carbon cycle if considered as a worldwide phenomena (Hänsler, Max Planck Institute Press Release, 2002).

This does not correspond well with measurements of isoprene at Jabiru, where it was found to be in significantly less concentration in a dry season month compared to the wet season (Alligators Rivers Research Institute, 1987 in Gillett et al. 1990). This may have something to do with the fact that there is less vegetation available to produce it, since much of the vegetation around Jabiru would have been consumed in dry season fire control practices. If isoprene and other alkenes are contributors to organic acids, it would thus seem that they are more important during the wet, when vegetation is once again at maximum volume and mass.

Kesselmeier ( in Hänsler, Max Planck Institute Press Release, 2002) also reveals from the ongoing research in Brazil by the Max Planck Institute for Chemistry, that formic and acetic acid levels, among others, rose three to four times that of the wet season measurements in the dry season, due to state controlled clearance of the forest by fire. If biomass burning produces similar trends in organic acid concentrations in the atmosphere above Jabiru as it does in the Amazon of Brazil, and there seems to be no reason why this would not be the case considering the fire management practices in the Northern Territory (already explained above– see Figure 5.12), and this is a season where isoprene levels are low above Jabiru (Gillett et al. 1990), then isoprene may not the prime producer of high organic acid concentrations at Jabiru and RUM. Instead, it may simply be a matter of emissions from biomass burning that has
extended into the period that coincides with the first infrequent rains of the wet season.

Analysis of formic and acetic acids in gases and aerosols during the wet season of 1984/85 by Gillett et al. (1994) showed that, at least during that season, there was significantly more formate in the gas phase in December/January than the rest of the season. Acetate did not seem to behave the same as formate, unlike other studies from around the world (Gillett et al. 1994). Ayers et al. (1993) have explained a similar lack of correlation between the two gases at Darwin by the fact that the ionisation of acetic acid increases dramatically between pH 4.5 and pH 5.5, therefore acetate concentrations may not necessarily decrease as the wet season progresses because the associated increase in pH tends to cross this ionisation boundary. The marked decrease in concentration of formate that occurred nearing the end of January in 1985 directly coincided with an increase in the incidence of rain that marked the beginning of the more consistent rains of the monsoon.

It is known that almost all of the organic acids in the atmosphere at Jabiru are in the gas phase (Gillett et al. 1994), and the gas-phase oxidation of these acids is slow, in fact a life time of greater than 10 days when considering reaction with the OH radical (Sanhueza at al, 1996). Lifetimes of this magnitude mean that organic acids can be transported over long distances and that removal of these acids from the atmosphere is normally only by wet or dry deposition and not reaction (Sanhueza at al, 1996). Hence if rainfall is infrequent and of small volume, then organic acids have the potential to build up in the atmosphere via local production and transport processes, particularly by production processes that are relatively constant. VOCs such as isoprene have very short atmospheric lifetimes (for example Isoprene has a 1.7 hour lifetime with the OH radical [Seinfeld and Pandis, 1998]) and their removal is dominated by reaction pathways. This large difference in atmospheric lifetimes between organic acids and their precursor VOCs means that the constant daily production of VOCs such as isoprene by plants, is a potentially efficient mechanism of organic acid addition in the atmosphere during infrequent rainfall periods. Hence plant emission of precursor gases are still probably important contributors to organic acids in rainfall in SOWS rain in the Northern Territory and may become significant in later parts of the wet
season that also experience low and infrequent rainfall but where burning has all but ceased.

That being said, considering the definitive effect biomass burning seems to have on NO$_3^-$ and CO concentrations in the boundary layer above northern Australia and the extent of late dry season fire effected areas across this entire region, it seems difficult to see how this is not the major contributor to the higher concentrations of organic acids in the SOWS rains.

Whatever the case, what is clear is that the high concentrations of free H$^+$ ions at the start of the wet season at RUM are mostly derived from weak organic acids, particularly formic and acetic. In the RUM rainfall, HNO$_3$, H$_2$SO$_4$ and to a lesser extent HCl also contribute to free H$^+$ but to a much smaller degree.

5.5.10 Trace Elements

Using the average crustal concentration of Al, Rahn et al. (1979) tabulated crustal enrichment factors ($EF_{crust} = \frac{\text{Element / Al}_{\text{air}}}{\text{Element / Al}_{\text{crust}}}$) for some 70 elements in over 100 samples from the world aerosol. The geometric means of all results for each element showed that U, Fe, Mn and to a lesser extent Ba (considering only those elements found in this study presented in Table 5.2) can all be classified as non enriched elements (NEEs) within an order of magnitude, compared to the average crustal composition, in the world aerosol. In other words, these elements have predominantly crustal sources. However, the other elements found in the RUM rainfall showed average enrichment in the Rahn et al. (1979) data of approximately 100 times for Cu, 200-300 times for Zn and over 1000 times for Pb, suggesting that in the world aerosol these elements do not have a strong crustal source. They were part of a group of some 30 elements that were classified as anomalously enriched elements (AEEs).

Atmospheric Interference Factors (AIF = [total anthropogenic emissions / total natural emissions] x 100) developed by Lantzy and Mackenzie (1979) and presented in Chester (1990) suggest that on a global scale, Zn, Cu and Pb in the atmosphere are predominantly sourced from anthropogenic emissions, that is, industrial particulate and fossil fuel, where as Fe and Mn are sourced from predominantly natural crustal
emissions, that is, continental dust and volcanic dust and gas. U and Ba were not considered in this study, neither was biomass burning or the ocean considered as potential sources. Chester (1990) also suggested that earlier research (Robinson and Robbins, 1971) had suggested that only 10% of the total influx of anthropogenic components was sourced from the southern hemisphere. Thus, it is conceivable that for remote southern hemisphere sites, such as RUM, anthropogenic sources may not be as important as Lantzy and Mackenzie’s (1979) study suggests.

RUM is required to estimate the total emissions to the air produced by the entire mine operations each monitoring year. Table 5.5 presents these estimations, for those elements of interest here, for the environmental monitoring period of September 1999 to August 2000. The figure for U represents that from both the Calciner Stack and Product Stack, the two U sources, combined.

<table>
<thead>
<tr>
<th>Element Emitted</th>
<th>Amount Emitted (kg)</th>
</tr>
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<tbody>
<tr>
<td>Mn and compounds</td>
<td>354</td>
</tr>
<tr>
<td>Pb and compounds</td>
<td>100</td>
</tr>
<tr>
<td>Cu and compounds</td>
<td>97</td>
</tr>
<tr>
<td>Ni and compounds</td>
<td>71</td>
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<tr>
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<td>68.2</td>
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<td>Zn and compounds</td>
<td>12</td>
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</tbody>
</table>

Table 5.5: Estimated emissions to the air from the RUM site of selected trace elements. Data taken from ERA (2000).

The data in Table 5.5 suggests that it is possible that some of the trace elements may be sourced from the RUM operations, particularly for those elements found in small proportions within the rain, such as Mn, Pb, U and Cu. However, the highest Cu value was found in a non-mine bulk precipitation sample, sample RW317. The same sample also contained the highest amount of Pb and Fe as well as significant proportions of Ba and Zn. If concentrations of anthropogenically derived components in rainfall are higher closer to their point source, then this result is contrary to expectations. Also contrary to the suggestion that trace elements are sourced from
RUM emissions is the fact that very little Zn, one of those elements thought to be predominantly sourced from anthropogenic emissions, is emitted into the air from RUM compared to other trace elements, yet it is by far the most abundant trace element in the RUM rainfall samples. Also, Ni was not found in the RUM rainfall yet it is one of the most prominent of the trace elements emitted by RUM.

Whilst the analytical data does not seem to support the possibility that trace element concentrations in the RUM rainfall are dependant on emissions from RUM, it does not necessarily rule out the possibility that emissions from RUM at least contribute, even if in small and inconsistent amounts, to the presence of certain trace elements in RUM rainfall.

It has already been stated that one of the major problems with determining the strength of oceanic sources using enrichment factors relative to sea water concentrations (for example EF_{sea} and NSS-values) is that it is the sea surface micro-layer that supplies the aerosol to the atmosphere, which is highly enriched in many trace elements relative to the bulk sea water composition. Using analyses of samples collected by the Bubble Interfacial Micro-layer Sampler (BIMS), Weisel et al. (1984) calculated relative oceanic enrichment factors (REF_{sea} = EF_{sea} / BIMS EF_{sea}) for 7 elements in the marine aerosol of the North Atlantic Ocean and two locations in the North Pacific Ocean. The results suggested that the sea surface is a trivial source for Mn and Pb in the marine aerosol, even at remote oceanic locations, however it can become a non-trivial source for Zn and Cu in such regions.

From this evidence alone, it would seem plausible to conclude that, assuming no significant anthropogenic source, Mn^{2+}, Fe^{2+/3+}, U^{6+} and Ba^{2+} in RUM rainfall are mineral aerosol derived components, where as Zn^{2+} and Cu^{2+}, although probably mostly of terrestrial origin, may be sourced in part at least, from the ocean. It should also be noted that all of these elements, except Zn^{2+}, are found in concentrations in rocks at Ranger that make it possible for dust from these rocks to be a direct local source of mineral aerosol. However, Zn^{2+} does not seem to be in any abundance in any rock type at Ranger that could explain its relatively high concentrations in the rainfall.
It is obvious from the studies mentioned above that NSS trace element calculations cannot be used to examine the marine/terrestrial source strengths for the trace elements in RUM rainfall; extreme enrichment of trace elements already exists in the marine aerosol. Even the BIMS enrichment factors for these elements are at least an order of magnitude less than those found in the remote marine aerosol at Enewetak in the North Pacific by Weisel et al. (1984). Whether a background global aerosol signature is present or trace elements are significantly partitioned in the creation of aerosol from the sea surface micro-layer or simply that the BIMS incorporates too much of the water beneath the micro-layer is irrelevant. It is considered here that the marine aerosol itself is the best representation of a marine source for trace elements in rainfall and it has thus been used to formulate a non-marine aerosol (NMA) value for trace elements at RUM, which are presented in Table 5.5.

The NMA calculation is exactly the same as the NSS calculation used above except that the bulk seawater concentrations have been multiplied by the EF_{sea} values for each element calculated by Weisel et al. (1984) for aerosol at Enewetak. The Enewetak values have been chosen due to the lack of aerosol trace element data available for marine locations closer to RUM and because it is considered the most pristine marine location in the Weisel et al. (1984) data.

According to the NMA trace element calculations all elements in the RUM rainfall are derived mostly from terrestrial sources with only Zn^{2+} showing a marine source of greater than 10%. Only on limited occasions do elements other than Zn^{2+} have NMA values less than 95%. Fe^{2+/3+}, Zn^{2+} and to a lesser extent Mn^{2+} seem to have a stronger marine aerosol source in the EOWS rains compared to the SOWS rains. Cu^{2+} on the other hand seems to have a stronger marine aerosol source in the SOWS rains, however because most of the NMA-Cu^{2+} values are based on Cu^{2+} concentrations that are on the limits of detection for the ICPMS used in this study, the NMA-Cu^{2+} values are questionable. For those Cu^{2+} concentrations that are above the detection limits of analysis, NMA values are above 99%.
RUM Rainfall Trace Element Non Marine Aerosol (NMA) calculations

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>NMA-Zn</th>
<th>NMA-Pb</th>
<th>NMA-Mn</th>
<th>NMA-Fe</th>
<th>NMA-Cu</th>
</tr>
</thead>
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<tr>
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<td>94.0</td>
<td>95.7</td>
<td>99.2</td>
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<td>97.6</td>
<td>94.9</td>
<td>98.4</td>
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<td>NA</td>
<td>98.0</td>
<td>91.7</td>
<td>98.1</td>
</tr>
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<td>NA</td>
<td>99.7</td>
<td>91.7</td>
<td>97.9</td>
</tr>
<tr>
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<td>NA</td>
<td>96.0</td>
<td>96.4</td>
<td>96.3</td>
</tr>
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<td>96.3</td>
<td>NA</td>
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<td>99.4</td>
<td>94.3</td>
<td>91.8</td>
</tr>
<tr>
<td>RW317</td>
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<td>98.6</td>
<td>98.1</td>
<td>98.3</td>
<td>99.6</td>
</tr>
<tr>
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<td>98.1</td>
<td>NA</td>
</tr>
<tr>
<td>RW322</td>
<td>197.5</td>
<td>NA</td>
<td>98.9</td>
<td>95.7</td>
<td>NA</td>
</tr>
</tbody>
</table>

Table 5.6: NMA-calculations for RUM rainfall trace element data. Note that all concentrations under the 0.5μg/L have not been included in the calculations due to the arbitrary cut off explained previously. See text for details and explanation of results.

It is concluded then that all of the trace elements found in RUM rainfall have a strong terrestrial source, probably of mineral aerosol derivation. Since concentrations are generally higher in the SOWS rains, and biomass burning has been identified as a probable significant source of some major ions during this period, biomass burning is also a potential source for trace elements. In fact Yamasoe et al. (2000) believe that savannah and tropical forest biomass burning could be responsible for 2 and 3% of the global budget of Cu$^{2+}$ and Zn$^{2+}$ respectively. It has also been found that the marine aerosol may be a non-trivial source for Zn$^{2+}$ in rainfall in the Ranger area. Although it is impossible to rule out the possibility that some Zn$^{2+}$ is sourced from the burning of fossil fuels, in particular direct emission from diesel powered haulage and water tanker vehicles operating at RUM, it is considered here to be of negligible contribution, if any at all.

It cannot be known just how much of the concentration of different trace elements in the RUM rainfall is the result of a background aerosol component much greater than the Enewetak aerosol EF$_{sea}$ values used in the NMA-calculations here. Weisel et al. (1984) EF$_{sea}$ values for aerosol at Hawaii are at least an order of magnitude greater.
than those of Enewetak, and so if the marine aerosol reaching RUM is not as pristine as the Enewetak values then a much greater proportion of the trace elements found in the rainfall at RUM would be from the marine aerosol or at least an external background source.

The external or foreign aerosol entering the ‘top end’ region of the Northern Territory at the start of and during the wet season may have come from a number of different regions, one of which includes Indonesia. Biomass burning and fossil fuel combustion in Indonesia are thus potential sources of such elements as Zn$^{2+}$. The Mount Isa smelter facility in NW Queensland may also be a contributor of Zn$^{2+}$ to the atmosphere above RUM, although the easterly trade winds seem to have broken down by the time the wet season starts. What is an obvious result of the trace element study of RUM rainfall is that further research is needed into trace elements in rainfall in northern Australia, particularly the isotopic composition of Pb and S, to ascertain external region or point source influences.

It seems that even at some of the remotest marine rainfall sites, like that of Paradise in Fiordland, in New Zealand’s south island, sea salt contribution calculations infer minimal sea salt origin for trace elements (<5% for any trace element at Paradise) and distant pollution sources may still be of influence (Halstead et al. 2000). Until more is known about the global distribution of trace elements in the actual sea-surface micro-layer and the exchange processes between this layer and the atmosphere in regards to trace elements, it is believed here that the remote marine aerosol itself is a better representation of a marine source, hence the introduction of the NMA calculation. By using a remote marine aerosol reference instead of a sea salt aerosol, the potential strong terrestrial background signature in the remote marine atmosphere is discarded from the equation.

All the trace element concentrations in this study are far greater than those of remote marine rainfall sites (see Halstead et al. 2000), probably a reflection of the terrestrial characteristics of rainfall in this area (Noller et al. 1990).
5.6 A Model for the Rainfall Chemistry at RUM

Based on the evidence produced here, it is possible to conceptualise the general chemical pattern of bulk precipitation incident to RUM over the wet season.

A consistent and relatively strong (in comparison to the wet season) easterly trade wind flow brings dry air over RUM during the dry season. As the early transition begins in accordance with the southern movement of the ITCZ, the easterly trades break down and near surface and surface winds at RUM slow and turn towards the north, although with high variability, bringing with them moist air. This is due to a cell of regional convection occurring over RUM and its surrounds. At this time the boundary layer over RUM has become a relatively stagnant air mass acting as an atmospheric late dry season store.

Unique to the atmosphere in this period is the presence of relatively large amounts of organic material and gases, NOy and sulfur products (mainly SO2) from the extensive regional late dry season burning of vegetation. Burning is observed to occur well into the transition period, some from lightning strikes, but most from human activity, particularly in Arnhem Land, to the NE of Jabiru (personal communication Russel-Smith, 2003 and own observations). The resulting chemistry of the rain produced by the local convective thunderstorms occurring at this time are thus enriched in and dominated by SO4^{2-}, NO3^- and organic acid anions, particularly formate and acetate. A high incidence of lightning over the region during this period may increase NO production and thus NO3^- concentrations even further. The end result is that the pH of early transition rainfall is acidic, sometimes as low as 3.6-3.7. In dilute remote tropical rainfall, such low pH equates to free H^+ being the most abundant chemical component.

The local nature of the rainfall in the early transition combined with continued burning in some locations and possible influxes of local dust sources to the rain column, may be responsible for significant terrestrial influxes, particularly towards Ca^{2+} and Cl^- enrichment, in bulk precipitation samples in this period.
As the wet season progresses and rain becomes more frequent, as do large volume events, the washout effect quickly depletes the boundary layer store and non-monsoon and monsoon rainfall events become less concentrated with the related chemical components. This is probably also related to a decrease in potential local aerosol sources due to such processes as increases in regional soil moisture, inundation of seasonally dry lowlands, creeks and rivers, the revegetation of the extensive areas effected by burning and the dramatic decrease in the amount of burning occurring. The low velocities of the general surface wind flow also work to ensure local aerosol sources may not be as relevant after the initial period of rainfall.

The relatively short period of monsoon dominance is associated with a consistent NW surface wind direction as the region of local convection moves to the east and the monsoon system moves in. More consistent rainfall chemistry is experienced at this time, but this does not necessarily translate into a chemistry that is distinguishable from individual non-monsoon rain events.

As the ITCZ moves north in the late transition, the easterly trades are re-established. A combination of lower rainfall frequency, easterly terrestrial sources and early dry season burning practices from the mine may be responsible for slightly increased concentrations of chemical components in these last rains that have been observed by others (Ayers et al. 1993).

5.7 CONCLUSIONS

There is no significant difference between the weekly bulk precipitation chemistry of this study at RUM and the relative periods in the weekly bulk precipitation study by Noller et al. (1985) for the 1982/83 wet season. The patterns and characteristics in the chemistry of the rainfall collected in this study also match those observed throughout the region in previous studies. Thus no significant change in rainfall chemistry has occurred in the RUM area for almost two decades. Hence the concentrations and input calculations by Noller et al. (1985) can be utilised as a more statistically viable database for bulk precipitation input calculations to the waste rock stockpiles of RUM in this project.
There is no evidence in the data presented here to conclude that there is any significant difference in major ion chemistry between bulk precipitation within the mine and that at the Jabiluka Lease site, suggesting that the mine does not have a significant localised effect on bulk precipitation chemistry for major ions. This conclusion is made despite the suggestion found in the dilution/concentration effect analysis that some ions may be depleted slightly at the Jabiluka site. In other words, the dilution effect that has occurred in samples RW321 and RW322 may be “overprinting” the location effect. There is some evidence to suggest that the trace elements Mn$^{2+}$ and possibly U$^{6+}$ are enriched in the bulk precipitation within the mine whilst Cu$^{2+}$ is enriched at the Jabiluka site. More sampling is needed to know if this is actually occurring but it may be evidence that some trace element recycling is occurring within the mine.

There is some evidence to suggest that enrichment of Mg$^{2+}$, K$^+$, Ba$^{2+}$, Fe$^{2+}$ and U$^{6+}$ occurred at the NWP site compared to other sites in the mine. More evidence would be needed to prove this beyond doubt, however it would not be surprising considering this site was closest to and down wind of, the currently operating pit, hence closest to blasting operations, as well as haulage traffic to and from the waste rock stockpiles.

RUM experiences rainfall of significantly different chemical composition at the start of the wet season, the early transition, compared to that of all other rainfall throughout the wet season, the latter being relatively consistent and similar in composition. The early transition rains (SOWS rain) are characterised by high concentrations of H$^+$, NO$_3^-$, SO$_4^{2-}$, and to a lesser extent Na$^+$ and Cl$^-$. Significant but erratic fluxes in Ca$^{2+}$ and Cl$^-$, and possibly Zn$^{2+}$ concentrations are also a distinguishing feature of the early transition rains as is the fact that they fluctuate from a cation composition similar to that of seawater to far from it.

The relative abundance of the cations Ca$^{2+}$, K$^+$, Mg$^{2+}$ and Na$^+$ cannot be used to distinguish between monsoon rain and non-monsoon rain, nor even early transition and all other rain, because non-monsoon rain can have a similar relative abundance of these elements to that of monsoon rain as can some individual early transition (SOWS) rains. This is contrary to the separation of monsoon and non-monsoon
rainfall at Jabiru made by Noller et al. (1990, 1985) despite the fact their own data proves otherwise.

In the light of more recent atmospheric research over the ‘top end’, it is considered here that there can be little doubt that orders of magnitude enrichment of organic acid anions and NO$_3^-$ found in the SOWS rain of this study and other studies throughout the north of the Northern Territory region in the past, is the direct result of late dry season burning practices and natural fires pumping organic material, NO and NO products into the atmosphere. Biomass burning is the only consistent widespread source that could supply large quantities of these components to every individual convective storm event. Whilst some NO$_3^-$ may be supplied by high temperature combustion from lightning, NO$_3^-$ is not the major contributor to free H$^+$ ions in the RUM rainfall, rather organic acids are. This is consistent with conclusions by Noller et al. (1990) and Gillett et al. (1990, 1994) for rainfall at Jabiru in 1982/83, 1983/84 and 1984/85 respectively. Thus lightning is not the cause of natural acid rain in the Northern Territory although it may contribute to a small degree.

A marine aerosol that probably already has a significant terrestrial signature may be a significant source of Na$^+$, Cl$^-$, SO$_4^{2-}$, Mg$^{2+}$, Ca$^{2+}$ and K$^+$ throughout the wet season. A more regional terrestrial aerosol is also probably an important contributor of some of these ions through the wet season but becomes a little more important at the end of the wet season when the easterly trade winds are re-established. At the start of the wet season, late dry season and early wet season biomass burning is responsible for NO$_3^-$ and large increases in SO$_4^{2-}$ and to a lesser extent Na$^+$ and Cl$^-$ across the entire region. At the same time localised mineral aerosol fluxes, or perhaps even localised enrichment of aerosol from biomass burning, are responsible for sporadic increases in Ca$^{2+}$, Cl$^-$ and Mg$^{2+}$. K$^+$ may not show the same fluxes due to differences in mineralogy and the associated solubilities.

All trace elements found in the RUM rainfall are derived from non-marine aerosol sources, all except Zn$^{2+}$ can be potentially sourced from the rocks of Ranger and Cu$^{2+}$ and Zn have been found elsewhere to be associated with biomass burning in savannah and tropical forests. Zn$^{2+}$ has a potentially higher proportion related to a marine aerosol source.
It is suggested here that there is a potential for the marine aerosol arriving in the Northern Territory to already have a significant terrestrial signature and that this may be the reason why large NSS-values are seen throughout the RUM rainfall for $K^+$, $SO_4^{2-}$, $Ca^{2+}$ and trace elements. This would also explain the large amount of ‘excess’ sulphate found throughout the region in other studies, which has not been adequately explained.

It is concluded that the most dominant meteorological effects on rainfall chemistry in the region is the development of an area of low wind strength and variable northerly direction in the early transition, a situation that brings with it locally derived convective storms. This is enhanced by an atmospheric inversion above the boundary layer over RUM. Possibly even more important than this is the washout effect, in other words how much rain falls, and how often.
CHAPTER 6

THE CHEMISTRY OF DUST SUPPRESSION WATER AND ITS CONTRIBUTION TO TOTAL CHEMICAL INPUT TO THE STOCKPILE SYSTEM COMPARED TO RAINFALL

6.1 INTRODUCTION

Rainfall is an obvious external source of chemical components into the stockpile hydro-geochemical system at RUM. However, another potential contributor of chemical components, and one that has never been included in any previous thinking on the hydro-geochemistry of the RUM stockpiles, is dust suppression water. Dust suppression water is the term used here to refer to the water applied to the haulage roads at RUM by mobile sprinkler systems, mounted to water carts (water tanker trucks) in order to minimise the formation and transport of dust into both the working environment of the mine and the environment of the area surrounding the mine.

To date, dust suppression water has not been ‘on the radar’ in the environmental management of RUM. This is not surprising, since unless dust suppression water has been enhanced by the addition of chemical based dust suppressants such as calcium chloride, magnesium chloride, hydrated lime or sodium silicates (Organiscak et al. 2003), mines tend not to seek the identity or quantity of chemical components being applied with it.

The chemistry of dust suppression water at RUM is complex, it is derived from RP2, the mine’s central retention pond, which itself has a complex set of influences on its chemistry and one that changes seasonally and through time. So to understand the chemistry of dust suppression water and the types and concentrations of chemical components it may be adding to the stockpile system, one must understand the chemistry of RP2.
It is the hypotheses of this study, that despite the obvious orders of magnitude greater volumes of solution that is supplied to the stockpiles by rainfall, the orders of magnitude greater concentration of ions that will be in RP2 will make dust suppression a measurable contributor to chemical input to the stockpile system, at least where dust suppression water is applied.

This study will first examine the water chemistry of RP2, and in doing so the chemistry of dust suppression water, and then calculate and compare the total input of ions it supplies to the stockpiles with that of rainfall. The period of focus for the comparative calculations will be for the 1999/2000 wet season through to the 2000/2001 wet season, since most of the water samples for this research span the year 2000, encompassing the end of the 1999/2000 wet season and the start of the 2000/2001 wet season.

6.2 METHODS

Dust suppression water is sourced from RP2. This water body was sampled four times, once at the end of the wet season in April 2000 (sample R110), twice in the dry season in August 2000 (samples RW207 and RW217) and once at the start of the following wet season in November 2000 (sample RW312). The double sampling of the pond in August was accomplished due to the fact that during the dry season excess water from the operating pit, Pit 3 (P3) is redistributed into RP2. Thus RP2 was sampled before (RW207) and after (RW217) a major period of water redistribution from P3 to compare differences in pond chemistry.

A sample of dust suppression water was also collected directly from the sprinkler of a water cart in May 2002 (sample RW404) for an actual dust suppression water representation and to compare chemistry with previous RP2 samples (see Chapter 2).

Electrical Conductivity (EC), Dissolved Oxygen (DO), eh, pH and temperature were all measured in the field with the appropriate calibrated probes. Total alkalinity, assumed here to be predominantly HCO₃⁻ due to pH and temperature (see methods chapter) was calculated from alkalinity titrations (using methyl orange as the indicator) performed in the field, no more than 3 hours after collection. Major anions

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were analysed by IC, major cations were analysed by ICPAES and trace elements were analysed by ICPMS. All samples were filtered with a 0.45micron cellular nitrate filter in the field directly upon collection. Only brief methodology has been given here, if further detail is required refer to Chapter 2.

Historical chemical data was retrieved from the RUM Environmental Department’s database to examine long-term changes in chemistry though time.

### 6.3 THE CHEMISTRY OF DUST SUPPRESSION WATER

#### 6.3.1 Results of Chemical Analysis

Table 6.1 displays the concentrations in millimoles per litre (mM/L) of the major cations and anions analysed in the four RP2 water samples and the single dust suppression water sample along with their respective in-field parameters pH, EC, DO, alkalinity (HCO₃⁻) and temperature. The equivalent sum of the cations and anions are also given as is the ion balance and relative ion difference (RID).

The ion balance is the usual method of testing the validity of a chemical analysis of a water sample (Hem, 1985 and see Sequeira and Lung, 1995) and is simply the net difference between the sum of the major cations and the sum of the major anions in eq/L as a percentage of the total sum of all major ions. In principle the further this percentage varies from zero, a perfect ion balance, the more inaccurate the analysis may be, assuming all major components have been analysed. Although NH₄⁺ and P⁵⁺ species (anions) have not been analysed in this study, the balances of all of the RP2 waters are under 10% and thus the analyses can all be considered valid (see Chapter 6 for a more detailed explanation of this).

The RID has been explained previously (see 5.3.1) but basically it differs from the ion balance in that it is the net cation/anion difference as a percentage of the highest of the two ion summations. Thus the RID is a measure of an ion deficit and assumes that this deficit is caused by a missing ion in the analysis. It so happens that most of the RIDs show the possibility of a missing cation, potentially the NH₄⁺ ion, already mentioned previously.
Table of Major cations and Anions (mM/L), In-field Parameters and Associated Functions of dust suppression water and its source water (RP2) at Ranger Uranium Mine

<table>
<thead>
<tr>
<th>Field No.</th>
<th>Origin Code</th>
<th>Sample Date</th>
<th>pH</th>
<th>Eh (mV)</th>
<th>EC (µS/cm³)</th>
<th>Temp. (°C)</th>
<th>DO</th>
<th>Alk. (HCO₃⁻) (mM/L)</th>
<th>F⁻</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
<th>NO₃⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>R110</td>
<td>RP2</td>
<td>17/04/2000</td>
<td>6.54</td>
<td>189.4</td>
<td>893</td>
<td>30.8</td>
<td>0.47</td>
<td>0.005</td>
<td>0.05</td>
<td>4.93</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>RW207</td>
<td>RP2</td>
<td>5/08/2000</td>
<td>7.62</td>
<td>151.3</td>
<td>957</td>
<td>8.17</td>
<td>31</td>
<td>0.8</td>
<td>0.11</td>
<td>1.10</td>
<td>5.14</td>
<td>0.05</td>
</tr>
<tr>
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<td>RP2</td>
<td>13/08/2000</td>
<td>7.54</td>
<td>147.4</td>
<td>905</td>
<td>6.98</td>
<td>31.3</td>
<td>1.12</td>
<td>0.016</td>
<td>0.08</td>
<td>4.72</td>
<td>0.05</td>
</tr>
<tr>
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<td>RP2</td>
<td>25/11/2000</td>
<td>8.38</td>
<td>178.4</td>
<td>1005</td>
<td>9</td>
<td>33</td>
<td>0.95</td>
<td>0.014</td>
<td>0.15</td>
<td>5.25</td>
<td>0.05</td>
</tr>
<tr>
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<td>7.11</td>
<td>77.3</td>
<td>1282</td>
<td>9.2</td>
<td>NA</td>
<td>0.51</td>
<td>0.013</td>
<td>0.11</td>
<td>7.15</td>
<td>0.04</td>
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</table>

<table>
<thead>
<tr>
<th>Field No.</th>
<th>Origin Code</th>
<th>Sample Date</th>
<th>H⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Si</th>
<th>Cat. Sum (-Si) (meq/L)</th>
<th>Anion Sum (meq/L)</th>
<th>Balance %</th>
<th>RID %</th>
</tr>
</thead>
<tbody>
<tr>
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<td>RP2</td>
<td>17/04/2000</td>
<td>0.00029</td>
<td>0.33</td>
<td>4.48</td>
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<td>0.06</td>
<td>0.15</td>
<td>9.98</td>
<td>10.43</td>
<td>-2.22</td>
<td>4.34 (-)</td>
</tr>
<tr>
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<td>0.36</td>
<td>4.73</td>
<td>0.39</td>
<td>0.06</td>
<td>0.20</td>
<td>10.64</td>
<td>11.24</td>
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<td>5.37 (-)</td>
</tr>
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<td>0.35</td>
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<td>0.30</td>
<td>0.06</td>
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<td>9.95</td>
<td>10.70</td>
<td>-3.63</td>
<td>7.01 (-)</td>
</tr>
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<td>RP2</td>
<td>25/11/2000</td>
<td>0.00000</td>
<td>0.41</td>
<td>5.41</td>
<td>0.35</td>
<td>0.08</td>
<td>0.21</td>
<td>12.08</td>
<td>11.66</td>
<td>1.77</td>
<td>3.59 (+)</td>
</tr>
<tr>
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<td>5/05/2002</td>
<td>0.00008</td>
<td>0.64</td>
<td>8.04</td>
<td>0.48</td>
<td>0.08</td>
<td>0.20</td>
<td>17.92</td>
<td>14.97</td>
<td>8.97</td>
<td>16.46 (+)</td>
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</table>

Table 6.1: Major cations and anions in mM/L, in-field parameters and associated functions of dust suppression water and its source water, Retention Pond 2 (RP2), at RUM. RID = Relative Ion Difference with (-) if a deficit of anions and (+) if a deficit of cations, see text for explanation of functions. Note that major species are displayed in their most common oxidation state for that found in natural waters (from Hem, 1985).

Trace element analysis results for the samples are displayed in Table 6.2, concentrations are given in micrograms per litre (µg/L). Only those elements found to exist within the water samples are displayed.
Table of Trace Elements (µg/L) of dust suppression water and its source water (RP2) at Ranger Uranium Mine

<table>
<thead>
<tr>
<th>Field No.</th>
<th>Origin Code</th>
<th>Sample Date</th>
<th>Al</th>
<th>P</th>
<th>Sc</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Ga</th>
</tr>
</thead>
<tbody>
<tr>
<td>R110</td>
<td>RP2</td>
<td>17/04/2000</td>
<td>39</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>1114</td>
<td>69</td>
<td>6</td>
<td>8</td>
<td>5</td>
<td>23</td>
<td>1</td>
</tr>
<tr>
<td>RW207</td>
<td>RP2</td>
<td>5/08/2000</td>
<td>22</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1263</td>
<td>125</td>
<td>0</td>
<td>1</td>
<td>4</td>
<td>21</td>
<td>0</td>
</tr>
<tr>
<td>RW217</td>
<td>RP2</td>
<td>13/08/2000</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>940</td>
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<td>10</td>
<td>64</td>
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<tr>
<td>RW312</td>
<td>RP2</td>
<td>25/11/2000</td>
<td>149</td>
<td>3</td>
<td>5</td>
<td>2</td>
<td>3</td>
<td>518</td>
<td>147</td>
<td>2</td>
<td>6</td>
<td>7</td>
<td>11</td>
<td>3</td>
</tr>
<tr>
<td>RW404</td>
<td>dust sup.</td>
<td>5/05/2002</td>
<td>NA</td>
<td>0</td>
<td>11</td>
<td>0</td>
<td>0</td>
<td>700</td>
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<td>11</td>
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<td>0</td>
<td>99</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Field No.</th>
<th>Origin Code</th>
<th>Sample Date</th>
<th>As</th>
<th>Se</th>
<th>Rb</th>
<th>Sr</th>
<th>Y</th>
<th>Mo</th>
<th>Cd</th>
<th>Ba</th>
<th>Pb</th>
<th>Th</th>
<th>U</th>
</tr>
</thead>
<tbody>
<tr>
<td>R110</td>
<td>RP2</td>
<td>17/04/2000</td>
<td>0</td>
<td>6</td>
<td>6</td>
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<td>0</td>
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<td>0</td>
<td>0</td>
<td>2398</td>
</tr>
<tr>
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<td>RP2</td>
<td>5/08/2000</td>
<td>0</td>
<td>4</td>
<td>6</td>
<td>55</td>
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<td>33</td>
<td>0</td>
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<td>0</td>
<td>0</td>
<td>3434</td>
</tr>
<tr>
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<td>RP2</td>
<td>13/08/2000</td>
<td>0</td>
<td>1</td>
<td>4</td>
<td>49</td>
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<td>5831</td>
</tr>
<tr>
<td>RW312</td>
<td>RP2</td>
<td>25/11/2000</td>
<td>1</td>
<td>5</td>
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<td>132</td>
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<td>98</td>
<td>1</td>
<td>48</td>
<td>1</td>
<td>3</td>
<td>6647</td>
</tr>
<tr>
<td>RW404</td>
<td>dust sup.</td>
<td>5/05/2002</td>
<td>1</td>
<td>6</td>
<td>5</td>
<td>80</td>
<td>0</td>
<td>17</td>
<td>0</td>
<td>23</td>
<td>0</td>
<td>0</td>
<td>2787</td>
</tr>
</tbody>
</table>

Table 6.2: Trace elements in µg/L for dust suppression water and its source waters, Retention Pond 2 (RP2), at RUM.

6.3.2 General Chemistry

It is clear from Table 6.1 that both the dust suppression water and the RP2 samples are dominated by Mg$^{2+}$ and SO$_4^{2-}$, so much so that they can be described as MgSO$_4$ waters. HCO$_3^-$, Ca$^{2+}$ and Na$^+$ are in much less but still significant concentrations. Table 6.2 shows that U$^{6+}$ and Mn$^{2+}$ are by far the most significant trace elements in solution, and in fact by weight per unit of volume U$^{6+}$ is equal to or greater in concentration than the major ions, F, Cl, NO$_3^-$, K$^+$ and Si. Other trace elements of significance include Fe, Al, Zn, Sr, Mo, and Ba. Co, Ni, Cu, Se and Rb are also consistently present although generally in concentrations less than 10µg/L.
It can be assumed that the SO$_4^{2-}$ ion will be very important in the major chemistry of the dust suppression related waters. Ca$^{2+}$ may be associated with SO$_4^{2-}$ in “ion pairs” as will some of the Mg$^{2+}$, although SO$_4^{2-}$ generally needs to be above 1000mg/L (10.4mM/L) for such pairing to be accounting for large proportions of both these cations (Hem, 1985). Total dissolved solids (TDS) may also not be great enough in these waters for any significant complexing to have occurred with the monovalent cations of Na$^+$ and K$^+$, that is except for the single dust suppression water sample, which has a TDS of approximately 940mg/L (based only on the analyses in Tables 6.1 and 6.2). In this sample, at least some of the Na$^+$ will probably form “ion pairs” with the HCO$_3^-$ and SO$_4^{2-}$ ions.

HCO$_3^-$ concentrations in the dust suppression water and source water are too low to contribute to any significant complexes of Mn$^{2+}$ but the MnSO$_4$(aq) ion pair is probably important in these waters, once again given their relatively high concentrations of SO$_4^{2-}$. In oxidised conditions, the hexavalent U$^{6+}$ ion is the most stable in solution and it is usually present in natural waters as the relatively mobile uranyl ion (UO$_2^{2+}$) (Hem, 1985). The uranyl ion has a strong affinity for forming relatively strong carbonate complexes in natural waters (Garrels and Christ, 1965, Hem, 1985, Langmuir, 1997). According to general eh-pH diagrams constructed for the U-O$_2$-H$_2$O-CO$_2$ system (see for example Langmuir, 1997, Brookins, 1988 and Garrels and Christ, 1965), the eh and pH conditions measured for the dust suppression water and RP2 samples and their respective HCO$_3^-$ concentrations would favour the U-carbonate complexes UO$_2$(CO$_3$)$_2^{2-}$ and UO$_2$(CO$_3$)$_3^{4-}$, the latter at the higher end of the pH range. However the uranyl ion is also known to be associated with SO$_4^{2-}$ (Hem, 1985) and given the dominance of SO$_4^{2-}$ in the dust suppression water related samples, this association is most likely the most dominant (see Chapter 7).

6.3.3 Changes in Chemistry

Table 6.1 shows pH is near neutral for all samples except that of the start of wet season (SOWS) RP2 sample which deviates significantly from neutral to a pH of 8.38. Eh, on the other hand, ranges within a consistent band of between 147.4mV to 189.4mV for all samples except that of the dust suppression water sample, which has a relatively reduced propensity to oxidise with an Eh measurement of 77.3mV. The
Eh of the dust suppression water sample is consistent with its environment, having been sourced from an enclosed tank with no direct contact with the atmosphere until sampling.

DO values also fall into a consistent range except for one sample, the end of wet season (EOWS) RP2 sample R110, for which a much lower value was recorded. The range of between 6.92mg/L to 9.2mg/L of DO found in these samples is well within a respectable range for waters in equilibrium with the atmosphere of 7.05 to 8.32 mg/L for 35°C and 25°C respectively (Manahan, 2005). This is similar to temperatures of the RP2 and dust suppression water samples. The limited variations in these samples can easily be explained by slight variations in measuring technique and environmental conditions, such as wind velocity, during measurement. However the 3.34mg/L of DO recorded for sample R110 is too low for such an explanation, and no notable physical or chemical difference that is consistent with this low value is present in this sample either. As has already been explained in the relevant section in the Methods Chapter of this thesis, the cause of this low value is likely a partially blocked membrane on the DO probe, which has subsequently reduced the rate of diffusion through it and thus lowered the recorded amount of DO. A more detailed discussion of this is found in Chapter 2.

Figure 6.1 is a bar chart showing the relative proportions of the major to minor ions analysed in each sample in terms of mM/L. F⁻ has not been included due to the potential analytical problems associated with this ion during the analysis of the earlier expedition samples (see explanation of this in Methods chapter) Due to the ‘swamping’ effect that Mg²⁺ and SO₄²⁻ proportions would have on these diagrams, Mg²⁺/SO₄²⁻ ratios (in mM/L) have been used instead to demonstrate their relative proportions in each sample.
Figure 6.1: Relative Concentration of Major Ions with $\text{Mg}^{2+}$ and $\text{SO}_4^{2-}$ separated due to their extremely large concentrations 'swamping' the other ion proportions. $\text{F}^-$ has not been included due to the problems associated with $\text{F}^-$ analysis on the IC for the April 2000 expedition samples (i.e. R101) – see Methods Chapter for further details. $\text{Mg}^{2+}$ and $\text{SO}_4^{2-}$ have been included as a separate ratio ($\text{Mg}^{2+}/\text{SO}_4^{2-}$). See text for further details.

Figure 6.1 shows that some variation occurs in relative chemistry between the RP2 samples and the dust suppression water sample. $\text{Mg}^{2+}/\text{SO}_4^{2-}$ ratios progressively increase from the end of wet season (EOWS) RP2 sample of April 2000 to the EOWS dust suppression water sample of May 2002. Table 6.1 shows that this has been caused by a progressive increase in $\text{Mg}^{2+}$ concentrations relative to $\text{SO}_4^{2-}$. Relative
HCO$_3^-$ concentrations seem to decrease at the end of the wet season at the expense of Ca$^{2+}$, although Table 6.1 reveals that this is a consequence of absolute decreases in HCO$_3^-$ in both end of wet season samples. There is a significant spike in relative HCO$_3^-$ concentrations in the second dry season RP2 sample, probably a result of a P3 water chemical influence, since the difference in RP2 water level between the two dry season RP2 samples was significant as a result of pumping P3 water into RP2.

Cl$^-$ concentrations are greater in the start of wet season (SOWS) November 2000 RP2 sample relative to other samples, where as Mn$^{2+}$ concentrations are less in this sample. The dust suppression water sample has a relatively larger proportion of Ca$^{2+}$ but less Mn$^{2+}$ and U$^{6+}$. The first dry season RP2 sample of August 2000 has relatively more Na$^{2+}$ whilst the second dry season sample, sampled after a significant amount of water from P3 had been introduced into it, shows an increase in Si compared to all other samples. Along with the SOWS RP2 sample of November 2000, the second dry season RP2 sample shows a significant increase in U$^{6+}$.

Figure 6.2 displays absolute concentrations of major and minor ions in the RP2 and dust suppression water samples. It shows that the dust suppression water sample is significantly enriched in Mg$^{2+}$, SO$_4^{2-}$, Ca$^{2+}$ and to a lesser extent Na$^+$, compared to the rest of the samples and the SOWS sample, RW312, is enriched in Mg$^{2+}$, Ca$^{2+}$, Na$^+$, K$^+$, Cl- and to a lesser extent U$^{6+}$ and SO$_4^{2-}$, compared to the other RP2 samples. It also shows that both the end of wet season samples, R110 and RW404 have as much as half the amount of HCO$_3^-$ as the other samples.
Figure 6.2: Examination of major ion concentrations in RP2 and dust suppression water samples. (A) Major ion concentrations including \( \text{Mg}^{2+} \) and \( \text{SO}_4^{2-} \) and (B) major ion concentrations excluding \( \text{Mg}^{2+} \) and \( \text{SO}_4^{2-} \) to avoid 'swamping effect'.
Table 6.2 suggests that the SOWS period is not only a period of increased concentrations of some of the major elements but also a period of increased trace element concentrations. RW312, the SOWS 2000 sample, has significantly higher concentrations of Al, Sr, and Mo and to a lesser extent Rb, Fe, and Ba compared to all of the other samples analysed. The trace elements Y, V, Cd, Th and Cr were also found in small proportions in sample RW312 and not found at all, except for 1μg/L of Cr in sample R110, in any other samples. Co and Zn were the only trace elements that the dust suppression water sample, RW404, had in greater amounts than the other samples. Other differences between the samples include the fact that the dry season samples seem to be depleted in Co, Ni, and Sc compared to the rest of the samples where as the dust suppression water sample seems to be depleted in Fe, Ni, and Cu.

It can be concluded then, from the analyses presented in Tables 6.1 and 6.2, that there is a significant difference in the chemistry of RP2 between the November 2000 SOWS samples and all other samples for that year, but only in terms of absolute concentrations of ions and pH. Not unlike that of the SOWS rainfall, the SOWS RP2 chemistry is marked by a significant increase in the concentration of many major and trace ions. It can also be concluded from the analyses in Tables 6.1 and 6.2 that the dust suppression water sample of the EOWS period of 2002 is also significantly different from all of the RP2 samples, in that it has a lower Eh and much higher concentrations of some of the major ions.

Table 6.3 compares concentrations for some of the ions in the dust suppression water sample from this research with those from an analysis of an RP2 water sample collected by the ERA Environmental Department at a similar time. Comparing the ERA RP2 data with like components of the dust suppression water sample suggests that the dust suppression water has not undergone any significant change, as far as total concentrations are concerned, during its transfer from the retention pond to the tanker from which it was sampled. Although Mg$^{2+}$ is still higher in the dust suppression water sample compared to the ERA RP2 data, the difference is much reduced compared to the difference observed with the data from this study. Thus, the difference between the dust suppression water sample and the RP2 samples of this study cannot be attributed to the different environments of the retention pond and the
water cart; rather it is a change in the concentrations of ions in RP2 at the time the sample was taken. The fact that all ERA samples show little variation to the corresponding sample from this research is evidence that the similarity between the dust suppression water sample and its corresponding ERA sample is not a chance occurrence and thus, that the conclusion made is valid.

### Comparison between Dust Suppression Water Sample and ERA RP2 Sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Date of Collection</th>
<th>pH</th>
<th>EC</th>
<th>Mg^{2+}</th>
<th>SO_{4}^{2-}</th>
<th>Mn^{2+}</th>
<th>Fe^{6+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>RW404</td>
<td>5/05/2002</td>
<td>7.11</td>
<td>1282</td>
<td>8.04</td>
<td>7.15</td>
<td>700</td>
<td>2787</td>
</tr>
<tr>
<td>ERA sample</td>
<td>8/05/2002</td>
<td>7.4</td>
<td>1310</td>
<td>7.08</td>
<td>7.28</td>
<td>808</td>
<td>3196</td>
</tr>
</tbody>
</table>

**Table 6.3:** Examination of difference in chemistry between dust suppression water sample from this study and an RP2 sample collected by ERA at a similar time, only three days apart. Only four ions, pH and EC were analysed by ERA for monitoring purposes on that particular date and thus not other ions can be compared.

Thus, not only has the chemistry of RP2, and hence dust suppression water, changed significantly in the SOWS period of 2000 compared to the rest of the year, but it has also changed significantly from the EOWS period of 2000 to the same period in 2002. In other words, not only does the data from Tables 6.1 and 6.2 prove that dust suppression water chemistry is changing within the year, it also proves that there are long term changes in chemistry occurring as well. These changes need to be addressed in order to understand the chemistry of dust suppression water.

### 6.3.4 Understanding Changes in Dust Suppression Water Chemistry in a Long-term Context

It is important to understand the changes in RP2, and hence dust suppression water, chemistry revealed above in a long-term context. After all, it is only in a long-term context that the dust suppression water input considerations for the year 2000 that follow later, can be understood in terms of reproducibility and applicability.

The only way to do this is to examine the existing database of RP2 water chemistry held by the ERA Environmental Department. Compared to the chemistry presented in Tables 6.1 and 6.2 the ERA database for RP2 is limited in that not as many chemical
components have been measured. Also, in many circumstances, for those ions that have been measured, the consistency of measurement varies. That being said for pH, conductivity and concentrations of $\text{Mg}^{2+}$, $\text{SO}_4^{2-}$, $\text{U}^{6+}$ and $\text{Mn}^{2+}$ the consistency of measurement is relatively good and long term trends can be identified.

Figure 6.3 is a time series plot of pH, Conductivity and concentrations of $\text{Mg}^{2+}$, $\text{SO}_4^{2-}$, $\text{U}^{6+}$ and $\text{Mn}^{2+}$ from 1994 until the end of April 2002 using the ERA database of RP2 water chemistry. This time period basically corresponds to the mining of orebody No.3 (see Chapter1). Five major trends can be identified in Figure 6.4.

1. A significant and consistent peak in all parameters occurring around October to December every year. In some instances, for example the first peak in Conductivity, this peak is skewed, so that a prominent lead is present, but a sharp drop off provides little to no tail. The consistency of this peak suggests it is part of a cycle.

2. A secondary and less consistent peak occurring around May to July.

3. An even less consistent tertiary peak occurring in some years around March.

4. A trend of increasing conductivity and concentrations of $\text{Mg}^{2+}$ and $\text{SO}_4^{2-}$ that began in 1999 but is more prominent from 2001 onwards.

5. A significant trend of increasing concentrations of $\text{U}^{6+}$ that began in 1999.

It should be clear then that the higher concentrations of some chemical components in the SOWS RP2 sample, RW312, compared to the other RP2 samples of 2000, corresponds with the timing of the most prominent and consistent cycle outlined above, one of increased concentrations around the SOWS period. The precise location of sample RW312 in reference to this cycle is shown in the time series plot of Figure 6.3. As can be seen its timing coincides with the lead to the peak in conductivity, $\text{Mg}^{2+}$, $\text{SO}_4^{2-}$ and $\text{U}^{6+}$ that reaches its maximum at the beginning of January 2001.
Figure 6.3: Time series data for the chemistry of Retention Pond 2 (RP2) at Ranger Uranium Mine from 1994 to 2002. The parameters of pH and Conductivity as well as the concentrations of Magnesium, Sulphate, Uranium and Manganese are shown. Data is sourced from ERA Environmental Department. The red rectangle represents the area shown in the close-up below, used to highlight the period covered by the water sampling during this research. The location in time of the samples analysed for this study are shown in the close-up chart so that concentrations can be compared to those in Table 6.1. The latest ERA sample of December for each year has been highlighted to show seasonal relevance of trends and cycles. See text for further details.

<table>
<thead>
<tr>
<th>Date</th>
<th>Cond (µS/cm)</th>
<th>SO₄ (mg/L)</th>
<th>Mg (mg/L)</th>
<th>U (µg/L)</th>
<th>Mn (µg/L)</th>
</tr>
</thead>
<tbody>
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<td>27/12/2001</td>
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<td>800</td>
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</tr>
</tbody>
</table>

RP2 Chemistry from 1994 - 2002

The latest ERA sample of December for each year has been highlighted to show seasonal relevance of trends and cycles.
The decrease in Mn$^{2+}$ in sample RW312 compared to the rest of the RP2 samples analysed in this study is explained by an extraordinary period of elevated Mn$^{2+}$ concentrations that began in the SOWS period of 1999 and extended through most of the 2000 dry season (refer to Figure 6.3). Figure 6.3 shows that the concentration of Mn$^{2+}$ in this period was higher than the following cyclical SOWS peak, therefore whilst sample RW312 still represents part of the SOWS peak cycle, it has less Mn$^{2+}$ than the other RP samples in this study.

Figure 6.3 also shows that the increased concentrations in RP2 water (from ERA data) and the dust suppression water sample (RW404 in this study) of the 2002 EOWS period corresponds to the tertiary peak observed in Figure 6.3 (number 3 above). It should also be clear why the EOWS 2002 RP2 water should have significantly higher concentrations of major elements than it did for the same period in the year 2000. Not only does the EOWS 2000 peak seem to be less prominent than the 2002 peak (see the 2000 sample period of this study marked on the time series chart, Figure 6.3), but the trend of increasing concentrations in the major elements that has occurred since 2001 has ensured that the 2002 EOWS peak in concentration is greater than its 2000 predecessor.

6.3.5 The Causes of the Major Cycles and Trends in Dust Suppression Water Reservoir Chemistry

RP2 captures run-off from the waste and LGO stockpile area, the ore stockpile area and the mine/mill area (ERA, 2000)(refer to map of Figure 2.1). However there are other inputs into RP2 and these are shown in Figure 6.4. Figure 6.4 is a record of the RP2 water input balance for the 1999/2000 environmental monitoring period for the mine. As is shown RP2 is also used as a dump for water that has accumulated in P3 during the wet season from the wet season rains and from overflow from RP2 itself (see also ERA, 2000). Water is also pumped into RP2 from SUMP98 (a sump that collects water from the WWP – see Figure 2.1), and from the LGO sump (a sump collecting water from the CWP) during the dry season. A more continuous supply of water to RP2 is derived from the mill, water that originates from RP2 in the first place with a recycling return factor of approximately 60% (ERA, 2000). However, the RP2
water that goes to the mill is used for cooling in the power station only and so the returned water has no known chemical inputs.

**Figure 6.4:** Total volume of water entering RP2 from each source every month and the corresponding total volume of water in RP2. Note that wet season runoff and dry season input from P3 are the main influences on the amount of water in RP2 as far as inputs are concerned. P3 = Pit No. 3., the current working open cut pit. LGO sump = low grade ore sump collecting water from Central Waste-rock Pile. Recycle = RP2 water returned from its use in the mill. Sump98 = sump collecting water from the Western Waste-rock Piles. Runoff = calculated from catchment that includes mill area, ore stockpiles and waste and LGO stockpiles. See text for further details. All data sourced from ERA (2000).

The result is a dust suppression water supply with numerous inputs at various times throughout the year, and hence the potential for dust suppression water chemistry to be affected and change accordingly. If any of these inputs are responsible for changes in the chemistry of the dust suppression water reservoir, then it is also possible that any changes in the long-term supply of those particular inputs may cause long-term changes in chemistry.
An investigation was undertaken to examine the relationship between RP2 chemistry and its inputs. This investigation was carried out using the 1999/2000 water balance for RP2, the major and minor ion concentrations for 2000 from this study (Table 6.1) and monthly averaged ERA time series data for those months corresponding with the 1999/2000 RP2 water balance.

The investigation revealed that a number of factors were controlling different ions at various times throughout the 1999/2000 period, and most of the time it was an interplay between many. However, in general, most changes in chemical concentrations in RP2 in the 1999/2000 period can be related to the amount of inputs that were carrying chemical components as well as the total volume of water in RP2 at any one point in time. Some ions showed clearer associations than others and these are presented in Figure 6.5. Mg$^{2+}$ seems to have relatively good positive association with the total volume of water in RP2 and the external inputs from the LGO sump (CWP sump), P3 and sump98 (see Figure 6.5a). U$^{6+}$ seems to have some association with all of the inputs and the total volume of water in RP2 but also shows reasonable correlation to run-off and RP2 water volume as well as sump98 water alone (see Figure 6.5b, c, d and e). SO$_4^{2-}$ on the other hand seems to be dominated simply by the concentration/dilution effects of the amount of water in RP2 at any one point in time (see Figure 6.5f).

Mn$^{2+}$ concentrations are a little more difficult to explain in terms of the RP2 water balance. There is some hint of association between Mn$^{2+}$ and P3 input, but only during the months of smallest input volume, from September 1999 through to January 2000. There also seems to be some negative association between Mn$^{2+}$ and the amount of run-off received by RP2, but only for the period of November through to March. The most prominent relationship seems to be a negative relationship with pH as is shown in Figure 6.6 suggesting that a pH control may be overprinting any other relationship.
Figure 6.5: The relationships between the major ions, magnesium, sulphate and the minor ion, uranium and various input components of the RP2 1999/2000 water balance. Outliers have been highlighted in colour and labeled according to the water balance month. Note that Balance = the total volume of water measured (not calculated) in the RP2 reservoir at the end of that month. See text for further details. Data is sourced from ERA (2000) and ERA data (2002).
Although the relationship between the RP2 water balance and RP2 chemistry is complex, a separation of RP2 chemistry throughout the 1999/2000 monitoring period can be made.

1. **October to November 1999** - A period of increasing concentrations of most major and minor species. A low RP2 water volume was easily affected by the introduction of run-off from the SOWS rains. Whilst the October input of P3 water had \( U^{6+} \) concentrations as much 9-12000\( \mu \)g/L (based on 1998, 2001 and 2002 values from ERA – 2000 values were unavailable) and thus probably contributed to higher concentrations in this month, by November these dropped dramatically, yet \( U^{6+} \) concentrations in RP2 continued to rise. This can be explained by the fact that November coincided with the first reasonable rains of the wet season, the beginning of sump98 input for the year, which in November averaged 7388.584\( \mu \)g/L (ERA data) and an increase in P3 input. Also, if November coincides with overflow release from LGO, caused by increased run-off, then the LGO may also contribute significantly at this time (although it is classed as run-off according to ERA). In November 2000,
a sample and duplicate from the LGO, taken for this research, revealed over 48mg/L U$^{6+}$ (see Chapter 7).

2. December 1999 – A slight decrease in the SOWS rains run-off accompanied by a 20% increase in RP2 volume led to a decrease in concentrations, particularly for U$^{6+}$. However this period marked the beginning of a significant increase for Mn$^{2+}$, suggesting oxidation/reduction environments in run-off catchments may have been of some influence. Only slight decreases for Mg$^{2+}$ and SO$_4^{2-}$ during this month suggest that for the major elements, December can be included with October and November. Note that this entire period, October through to December, corresponds to the most prominent cyclical increase in ion concentrations identified above.

3. January 2000-September 2000 – A period of fluctuating but low concentrations relative to period one and two above. Different ions show slightly different behaviour during this period. SO$_4^{2-}$ tends to follow water volume in RP2 and thus from January through to May, the period of largest water storage volumes in RP2, SO$_4^{2-}$ is at its lowest. The large RP2 volumes are caused by large amounts of run-off from January to March, associated directly with the high volume monsoon rains (refer to Chapter 5). Unlike the other ions, SO$_4^{2-}$ returns to values similar to the October-December levels from June to August as water volume in RP2 halves. Mg$^{2+}$ fluctuates at low levels with small increases in February, May and August. Mn$^{2+}$ begins to drop away in January and fluctuates with small peaks in January, March, June/July. U$^{6+}$ initially increases in this period (January and February), possibly due to an almost tripling of input from Sump98 in January and February, which according to ERA data, averaged 10257.05μg/L during January resulting in by far the largest total contribution of $^{238}$U to RP2 from Sump98 for the 1999/2000 period, some 636kg (calculated using ERA data for Sump98 and ERA water balance data – Figure 6.1). In March and April U$^{6+}$ decreases, as do inputs, although total water volume in RP2 remains high. May and June see the lowest concentrations of U$^{6+}$ all year possibly due to the fact that except for that from the LGO, there is little no other input water. A return to
March/April levels is seen in July through to September, the data suggesting that this is due to a large influx of P3 water, whilst RP2 volume remains relatively low.

Thus, although the relationship between RP2 input and RP2 chemistry is relatively complex, particularly during the dry season, the major annual cycle is explained. Importantly however, the investigation above has also alluded to the causes of the longer-term trend of elevated concentrations that is now being experienced in RP2.

As has been outlined above, and can be seen in Figure 6.3, $U^{6+}$ began increasing to elevated baseline levels at the end of the 1997/1998 wet season. $Mg^{2+}$ and $SO_4^{2-}$ also began increasing at this time, although to a much lesser extent, both these ions showing greater increase from 2001. It is proposed here that there are 4 significant events or external influences that caused this.

The first of these causes was the development of the WWP and the subsequent development of the Sump98 reservoir from 1997 to 1999. Figure 6.7, a series of aerial photographs of the mine from 1997-2002, shows that prior to 1999 Sump98 did not exist. It has been shown that $U^{6+}$ concentrations in RP2 seem to have more of an association with Sump98 input than do other ions (see Figure 6.5c and d), at least for the 1999/2000 monitoring period. Thus, whilst the development of Sump98 and the subsequent transferral of this water into RP2 may have influenced the concentration of most ions in RP2 at this time, $U^{6+}$ may have been influenced more so. Whatever the case, Sump98 input represents an input of $U^{6+}$ that did not exist prior to 1998.
Figure 6.7: Aerial photographs showing the major developments of the mine since 1997 that have affected the chemistry of RP2, the central retention pond at RUM. In 1997 the NCWP was relatively stable, P3 had yet to reach significant non-oxidised mineralogy, Sump98 had not been developed yet and all stockpiles were growing slowly.

By 1999 the WVWP had begun to be developed due to large increases in total rock mined from P3. Sump 98 was developed as a collection pond for the WVWP. Freshly mined LGO weathered material is placed near the LGO sump.

In 2002 mining had reached well beyond the oxidised zone in P3. This less oxidised LGO material was placed in the WVWP, a new developing pile, the NWP, as an extension of the NCWP to the east, infilling RP4, and on top of the CWP. Not only had the amount of waste and LGO material in RP2’s catchment significantly grown, but so too had the amount of ore in the ore stockpiles.
Secondly, there has been an increase in the baseline chemical concentrations of Mg\textsuperscript{2+}, SO\textsubscript{4}\textsuperscript{2-} and U\textsuperscript{6+} in P3 water since 1999 and as has already been explained above, P3 water is a major input to RP2. This increase is shown in Figure 6.8. Three factors may explain this:

1. The development of the NWP in 2001 (refer to Figure 6.7) and the subsequent release of leachate water from this pile into P3.

2. The increasing depth of P3 as mining has progressed and the subsequent interaction of P3 water and water flowing into P3 with unoxidised fresh rock. From very basic observations made in the bottom of P3 in 1999, 2000 and 2002 made during this study, it seems that some time between 2000 and 2002 P3 has intercepted schists with notable sulfides as smears on foliation planes, pods between foliation planes and veinlets at angles to foliation (mainly Pyrite – see Chapter 4 and Figure 4.21). The oxidation of these sulfides may help to produce localised acid conditions and consequently help to release more elements into solution. The relative absence of weathering at such mining depths will also mean that mineral weathering rates will be higher in comparison to the leached upper levels of the Pit profile. It should be noted that pH has also increased in P3 water from a range of approximately pH 6 to pH 7 to a range of pH 7.5 to pH 9.5 (Figure 6.8b). This may be simply due to an increase in volume of alkalinity producing silicate reactions. U\textsuperscript{6+} solubility is highly dependant on pH and as pH increases above neutral the more U\textsuperscript{6+} can be potentially held in solution (see Figure 7.12). Figure 6.8(c) shows that, according to ERA data, whilst there is no linear relationship between U\textsuperscript{6+} and pH in P3 water, the increases in pH have certainly allowed more U\textsuperscript{6+} to be present when possible. Thus pH has also been favourable for increased concentrations of U\textsuperscript{6+} in the P3 reservoir.

3. Since other factors are also responsible for increasing concentrations in RP2, and since RP2 is often pumped back into P3 during the monsoon rainfall period of January – April, recycling of the RP2 water itself may also help to increase concentrations in P3.
Thirdly, the infilling of Retention Pond 4 (RP4) at the end of 2000 with LGO material and the subsequent extension of the NCWP to the east has substantially increased the amount of LGO material in the RP2 catchment. The NCWP was a relatively stable stockpile of waste grade material with a limited cover of vegetation in 1999 and early 2000. RP4 drains into RP2 and the results of an analysis of the remainder of RP4 sampled on 16th May 2002 for this study revealed a concentration level of 17.981 mg/L $U^{6+}$, 1211 mg/L $SO_4^{2-}$ and 356 mg/L $Mg^{2+}$. Such $U^{6+}$ concentrations were approximately 240 times those of the same period in 1999 (comparing with ERA data) and so this expansion will be a significant influence on RP2 chemistry.
Finally, accompanying these changes in external influences is the fact that the amount of material entering the waste and LGO stockpiles increased substantially as of the 1996/1997 financial year (FY). The total amount of waste and LGO entering the waste and LGO stockpiles each year has been calculated here utilising information found in the ERA Ranger Uranium Mine End of Year Reports and is presented in Figure 6.9. All waste diversion and stockpile reductions from using waste as construction material (mainly the tailings dam walls) has been taken into account with these calculations. Figure 6.9 shows the cumulative growth of the total amount of material (by weight) in the waste and LGO stockpiles, the total amount of waste and LGO entering the stockpiles each year and the breakdown of how much of this annual addition to the stockpiles was waste and how much was LGO.

Figure 6.9 shows that in the five years from 1996 to 2001 the total amount of material (by weight) in the waste and LGO stockpile system almost doubled. In fact in the 2000/2001 FY, the period where further increases in RP2 chemical concentrations occurred, over 8 million tonnes of material was distributed into the waste and LGO stockpiles, more than double the maximum in years previous to 1996. Possibly even more crucial in regards to the early increase in $\text{U}^{6+}$, Figure 6.9 shows that over the 1997/1998 FY and 1998/1999 FY LGO outstripped waste by almost three to one (2.85:1). Hence, not only did the amount of material available to potentially react with rainwater during this period significantly increase, but so did the relative proportion of leachable uranium. The aerial photographs of Figure 6.7 show visually, the growth of the stockpiles that occurred as a consequence of the increase in tonnage mined.
Figure 6.9: RUM waste and low grade ore (LGO) stockpile construction history in terms of tonnage (million tonnes) of material added. The stockpile growth is represented by the accumulated LGO and waste, the dotted line, on the right hand side y-axis. All calculations have taken into account material being taken directly from the stockpiles and diverted from the stockpiles each year during mining, for use in constructions such as the original tailings dam wall. Note that each year represents a financial year except for 2001 and 2002. In 2001 ERA Ltd. changed their reporting practices to calendar years and thus 2001 on the chart represents the rest of the 2001 year, hence only 6 months. 2002 represents a full calendar year. All data was sourced from ERA annual reports.

6.4 RAINFALL INPUT CALCULATIONS

6.4.1 Major Ions

Major ion deposition from rainfall at RUM (in kg/Ha) and the total ion input to the RUM waste and LGO stockpiles attributable to rainfall (in kg) are presented in Tables 6.4 and 6.5 respectively. It should be understood that the total input (Table 6.5) is that left on the stockpile surfaces and that which enters through the stockpile surfaces after run-off has been subtracted, whereas the deposition calculation (Table 6.4) is all that delivered by rainfall per Hectare. A set of calculations has been made for each month.
of the 1999/00 wet season, the 2000/01 wet season and the 2001/02 wet season along with the totals for each season.

Major Ion Deposition (kg/Ha) from Bulk Precipitation at RUM for the 1999/00, 2000/01 and 2001/02 wet seasons

<table>
<thead>
<tr>
<th>Year</th>
<th>Rainfall</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>K⁺</th>
<th>Na⁺</th>
<th>Total-N</th>
<th>SO₄²⁻</th>
<th>Cl⁻</th>
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</thead>
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<tr>
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<td>0.07</td>
<td>0.17</td>
<td>1.68</td>
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<td>1.54</td>
<td>1.77</td>
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<td>2.41</td>
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<tr>
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<td>0.39</td>
<td>0.18</td>
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<tr>
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<td>0.02</td>
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<td>1.18</td>
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<td><strong>0.79</strong></td>
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<td>0.19</td>
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<td>0.01</td>
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<td>0.01</td>
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<td><strong>1.67</strong></td>
<td><strong>5.06</strong></td>
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<td><strong>1.03</strong></td>
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Table 6.4: Calculations of the amount in kg/Ha of major ions delivered to RUM for each month and for the whole season of the 1999/00, 2000/01 and 2001/02 wet seasons.
### Total Major Ion Input to the RUM Waste and LGO Stockpile System (kg)

<table>
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<tr>
<th></th>
<th>Ca(^{2+})</th>
<th>Mg(^{2+})</th>
<th>K(^+)</th>
<th>Na(^+)</th>
<th>Total-N</th>
<th>SO(_4(^{2-}))</th>
<th>Cl(^-)</th>
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<tr>
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<td>6.48</td>
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<td>162.12</td>
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<td>7.42</td>
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<td>33.37</td>
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<td>169.52</td>
<td>22.60</td>
<td>18.84</td>
<td>90.28</td>
<td>99.83</td>
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<td>14.26</td>
<td>75.61</td>
<td>86.69</td>
</tr>
<tr>
<td>December</td>
<td>10.92</td>
<td>7.28</td>
<td>20.63</td>
<td>46.12</td>
<td>21.85</td>
<td>327.26</td>
<td>535.27</td>
</tr>
<tr>
<td>January</td>
<td>12.64</td>
<td>8.43</td>
<td>23.88</td>
<td>53.38</td>
<td>25.28</td>
<td>378.72</td>
<td>126.42</td>
</tr>
<tr>
<td>February</td>
<td>18.44</td>
<td>11.85</td>
<td>7.90</td>
<td>96.13</td>
<td>35.56</td>
<td>216.98</td>
<td>345.03</td>
</tr>
<tr>
<td>March</td>
<td>0.01</td>
<td>1.87</td>
<td>5.61</td>
<td>14.02</td>
<td>1.87</td>
<td>86.79</td>
<td>89.72</td>
</tr>
<tr>
<td>April/May</td>
<td>0.96</td>
<td>0.96</td>
<td>2.89</td>
<td>7.22</td>
<td>0.96</td>
<td>44.68</td>
<td>46.18</td>
</tr>
<tr>
<td>Season Total</td>
<td>52.23</td>
<td>71.36</td>
<td>238.66</td>
<td>321.77</td>
<td>118.62</td>
<td>1220.33</td>
<td>1329.13</td>
</tr>
</tbody>
</table>

**Table 6.5:** Calculated input to the Waste and LGO stockpiles of RUM for each major ion attributable to bulk precipitation and after considering that lost from direct run-off. A ROC of 0.3 has been used, see text for details.

The calculations have been made using data from Noller et al. (1985) of total monthly input (kg/Ha) from bulk precipitation at Jabiru East during the 1982/83 wet season. Jabiru East is only 3.1km from the RUM waste and LGO stockpiles and so rainfall at Jabiru East is considered representative of the rainfall incident to the RUM stockpiles. It has already been shown in Chapter 5 that there has been no significant change in the chemistry of bulk precipitation from the 1982/83 wet season to the samples collected at RUM for this research in the year 2000. The use of the Noller et al. (1985) data to calculate bulk precipitation input to the RUM waste and LGO stockpiles for this
research is therefore considered a valid approach. This approach is more accurate than using the chemistry of bulk precipitation collected during this research because of the limited number of samples collected in this study, where as the Noller et al. (1985) data represents an entire wet season of rainfall collection.

The Noller et al. (1985) total monthly input (kg/Ha) figures were converted to monthly kg/Ha/mm figures using the total rainfall (in mm) recorded for each month of the 1982/83 wet season (provided in Noller et al. 1985 and in ABM data). The monthly kg/Ha/mm figures have then been used as standard multipliers against total recorded monthly rainfall figures for the 1999/00, 2000/01 and 2001/02 wet seasons (ABM data). The result is input figures for the RUM stockpiles for each major ion for each month of the seasons in question at RUM.

Importantly however, each month of the seasons in question is multiplied by the multiplier (the kg/Ha/mm figure above) corresponding to the 1982/83 wet season month of similar chemistry and rainfall volume to that particular month. For instance, the total input calculation for November 1999 has been multiplied by the kg/Ha/mm figure derived for the month of December 1982 because both are start of wet season months (SOWS) and hence have similar chemistry (refer to Chapter 5 and directly below for explanation) and because the December 1982 rainfall volume of 148mm is considered a closer representation of the November 1999 volume of 226mm, than the 1982 November month, where only 69mm was recorded. As has already been explained in Chapter 5, the RUM bulk precipitation data suggests that if concentration and dilution effects are affecting the RUM rainfall chemistry, it is occurring at the extreme ends of the rainfall volumes collected, thus November 1999 will be more closely related to December 1982 than November 1982.

Complications derived from concentration and dilution effects are also avoided by using the total monthly input figures rather than the other measures presented in the Noller et al. (1985) publication. Such large scale effects have been shown to exist in the region by Likens et al. (1987).
It should also be clear from the above explanation that to perform the calculation the rainfall season in the Jabiru area has been split into two periods of distinctly different chemistry, the start of the wet season (often limited to only two months – see Chapter 5 and see Noller et al. 1985 data), and the rest of the wet season. Evidence from this study (see Chapter 5) and the data in Noller et al. (1985) prove that the start of the wet season rainfall, in the vicinity of RUM, has the potential to have distinctly higher concentrations of ions than the rest of the year and more importantly consistently supplies significantly larger amounts of ions to the ground than the rest of the year.

Noller et al. (1990) separates rainfall differently, preferring a monsoon and non-monsoon categorisation. However it is argued here that the data presented in the Noller et al. (1985) publication suggests that such a separation only creates one extra category when considering monthly rainfall chemistry over the entire season, a category consisting of the end of wet season rains where concentrations increase slightly after the monsoon period has departed. This was recognised by Noller et al. (1985, 1990). In any case, such a separation cannot be made here; it would require the collection of every rainfall event throughout the season along with a detailed understanding of the weather systems presiding over each event.

The run-off coefficient (ROC) used to calculate input after run-off was 0.3, taken from recent work by Puhalovich et al. (2002) on the NWP after an analysis of much of the 2001/02 wet season and considering results from Daniel et al. (1983, in Morin et al. 1991) for the Rum Jungle stockpiles, although the latter were more conservative figures, an estimated ROC range of 0.1-0.22.

6.4.2 Trace Elements

Table 6.6 displays the calculations for the total bulk precipitation trace element input (kg) to the RUM waste and LGO stockpiles, and takes into consideration that lost from run-off, for the rainfall seasons of 1999/00, 2000/01 and 2001/02.
Total Trace Element Input to the RUM Waste and LGO Stockpile System

<table>
<thead>
<tr>
<th>Year/Season</th>
<th>Mn</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>Ba</th>
<th>Pb</th>
<th>U</th>
</tr>
</thead>
<tbody>
<tr>
<td>1999/00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>October</td>
<td>1.82</td>
<td>5.01</td>
<td>0.03</td>
<td>13.76</td>
<td>0.20</td>
<td>0.04</td>
<td>1.39</td>
</tr>
<tr>
<td>November</td>
<td>2.48</td>
<td>6.84</td>
<td>0.04</td>
<td>18.80</td>
<td>0.27</td>
<td>0.06</td>
<td>1.89</td>
</tr>
<tr>
<td>December</td>
<td>0.79</td>
<td>1.57</td>
<td>0.17</td>
<td>6.51</td>
<td>0.30</td>
<td>0.03</td>
<td>0.12</td>
</tr>
<tr>
<td>January</td>
<td>1.52</td>
<td>3.05</td>
<td>0.33</td>
<td>12.64</td>
<td>0.57</td>
<td>0.05</td>
<td>0.24</td>
</tr>
<tr>
<td>February</td>
<td>1.86</td>
<td>3.72</td>
<td>0.40</td>
<td>15.42</td>
<td>0.70</td>
<td>0.07</td>
<td>0.29</td>
</tr>
<tr>
<td>March</td>
<td>1.20</td>
<td>2.40</td>
<td>0.26</td>
<td>9.94</td>
<td>0.45</td>
<td>0.04</td>
<td>0.19</td>
</tr>
<tr>
<td>April/May</td>
<td>0.88</td>
<td>1.76</td>
<td>0.19</td>
<td>7.29</td>
<td>0.33</td>
<td>0.03</td>
<td>0.14</td>
</tr>
<tr>
<td><strong>Season Total</strong></td>
<td><strong>10.55</strong></td>
<td><strong>24.34</strong></td>
<td><strong>1.41</strong></td>
<td><strong>84.37</strong></td>
<td><strong>2.83</strong></td>
<td><strong>0.33</strong></td>
<td><strong>4.26</strong></td>
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<tr>
<td>2000/01</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>October</td>
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<td>2.45</td>
<td>0.01</td>
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<td>0.10</td>
<td>0.02</td>
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<tr>
<td>November</td>
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<td>0.03</td>
<td>18.07</td>
<td>0.26</td>
<td>0.06</td>
<td>1.82</td>
</tr>
<tr>
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<td>6.56</td>
<td>0.30</td>
<td>0.03</td>
<td>0.12</td>
</tr>
<tr>
<td>January</td>
<td>2.44</td>
<td>4.89</td>
<td>0.53</td>
<td>20.27</td>
<td>0.92</td>
<td>0.09</td>
<td>0.38</td>
</tr>
<tr>
<td>February</td>
<td>2.12</td>
<td>4.25</td>
<td>0.46</td>
<td>17.62</td>
<td>0.80</td>
<td>0.08</td>
<td>0.33</td>
</tr>
<tr>
<td>March</td>
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<td>10.91</td>
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<td>0.05</td>
<td>0.21</td>
</tr>
<tr>
<td>April/May</td>
<td>0.39</td>
<td>0.78</td>
<td>0.08</td>
<td>3.23</td>
<td>0.15</td>
<td>0.01</td>
<td>0.06</td>
</tr>
<tr>
<td><strong>Season Total</strong></td>
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<td><strong>23.16</strong></td>
<td><strong>1.57</strong></td>
<td><strong>83.40</strong></td>
<td><strong>3.02</strong></td>
<td><strong>0.33</strong></td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>October</td>
<td>1.48</td>
<td>4.07</td>
<td>0.02</td>
<td>11.18</td>
<td>0.16</td>
<td>0.04</td>
<td>1.13</td>
</tr>
<tr>
<td>November</td>
<td>0.92</td>
<td>2.54</td>
<td>0.01</td>
<td>6.98</td>
<td>0.10</td>
<td>0.02</td>
<td>0.70</td>
</tr>
<tr>
<td>December</td>
<td>0.96</td>
<td>1.92</td>
<td>0.21</td>
<td>7.98</td>
<td>0.36</td>
<td>0.03</td>
<td>0.15</td>
</tr>
<tr>
<td>January</td>
<td>1.11</td>
<td>2.23</td>
<td>0.24</td>
<td>9.24</td>
<td>0.42</td>
<td>0.04</td>
<td>0.17</td>
</tr>
<tr>
<td>February</td>
<td>2.60</td>
<td>5.21</td>
<td>0.56</td>
<td>21.60</td>
<td>0.98</td>
<td>0.09</td>
<td>0.41</td>
</tr>
<tr>
<td>March</td>
<td>0.69</td>
<td>1.38</td>
<td>0.15</td>
<td>5.72</td>
<td>0.26</td>
<td>0.02</td>
<td>0.11</td>
</tr>
<tr>
<td>April/May</td>
<td>0.35</td>
<td>0.71</td>
<td>0.08</td>
<td>2.94</td>
<td>0.13</td>
<td>0.01</td>
<td>0.06</td>
</tr>
<tr>
<td><strong>Season Total</strong></td>
<td><strong>8.12</strong></td>
<td><strong>18.06</strong></td>
<td><strong>1.27</strong></td>
<td><strong>65.64</strong></td>
<td><strong>2.42</strong></td>
<td><strong>0.26</strong></td>
<td><strong>2.73</strong></td>
</tr>
</tbody>
</table>

Table 6.6: Calculated input of trace elements to the Waste and LGO stockpiles of RUM attributable to bulk precipitation and after considering that lost from direct run-off. A ROC of 0.3 has been used, see text for details.

There is no published rainfall trace element chemical data available for the region incorporating RUM, therefore the calculations of Table 6.6 rely in total on the trace element chemistry of bulk precipitation from this research, presented in Chapter 5. It should be acknowledged that the data in Table 6.4 is reliant on a limited number of samples and as such, will not be as accurate as the major ion calculations above.
A similar method of calculation has been used as that described above. Volume weighted mean (VWM) concentrations for each trace element were calculated for each collection period, the SOWS period and the EOWS period. These were then converted to a μg/L/mm measure to be used as a multiplier for each month of each wet season’s recorded rainfall. The SOWS period multiplier was used only for start of wet season rains up to and including the month of December and the EOWS multiplier was used for the rest of the wet season, starting with January. This separation is the same separation outlined above and hence made for the same reasons.

6.5 THE POTENTIAL CONTRIBUTION FROM DUST SUPPRESSION WATER

6.5.1 Factors Influencing the Significance of Dust Suppression Water

A comparison of Tables 6.1 and 6.2 of the dust suppression water source chemistry (RP2 and dust suppression water) with Tables 5.1 and 5.2 (Chapter 5) of the RUM bulk precipitation chemistry shows just how more concentrated with ions the dust suppression water is compared to the rainfall, containing orders of magnitude more major ions per unit volume. For example in November 2000 RP2 had 631 times the concentration of SO$_4^{2-}$ than did the rainfall incident to the SWP at that time. Although there seems to be significant amounts of Zn in the rainfall, it is also evident that the dust suppression water contains considerably higher concentrations of trace elements, in particular for those typically not found in rainfall to any significant degree, such as Mn and U. These differences translate into dust suppression water having up to orders of magnitude higher application rates of elements to the stockpiles on a weight per unit volume per unit area (for example mg/L/m$^2$), the differences being in accordance with the differences seen in the concentrations. However, whether these higher concentrations translate into any significant contribution to the stockpiles is another question.

In an overall stockpile assessment the dust suppression water may not be that important as there are some significant variables that work to reduce the importance of dust suppression water on the stockpiles. Firstly, rainfall has a greater coverage of the stockpiles than dust suppression water, in that it falls across the entire surface of
the stockpiles, where as dust suppression water is only applied to certain sections and only those areas accessible to the water carts. Secondly, dust suppression water is not applied evenly over all of the surfaces to which it is applied, in that more is applied to those areas where dust is more likely to be generated, for instance on working platforms where waste is being dumped. Thirdly, dust suppression water application will reduce to some extent during the wet season, due to the afternoon storm events replacing the need to for dust suppression water to suppress dust in the afternoons.

That being said there are some situations whereby dust suppression water may provide significant contributions to the stockpiles. Firstly, it is in effect the only source of external input for the environmentally important trace elements of Mn and U. Secondly, during the dry season dust suppression water is obviously the only external input to the stockpiles. Thirdly, dust suppression water may be important on a local basis due to it being concentrated in certain areas, such as working platforms, where dust generation potential was high. Finally, dust suppression water may be localised to the platform surface or just beneath, due to the fact that there is no run-off (except for small amounts on ramps) and its small relative volume does not penetrate the surface platform structure, and so this fact combined with points two and three above may result in dust suppression water deposits being significant to water – platform surface interaction during the start of wet season rains.

6.5.2 Estimating the Contribution of Ions to the Stockpile System by Dust Suppression Water

To estimate the contribution of dust suppression water to any degree of accuracy is not possible at RUM without completing a long term mine based monitoring program of water cart movement and the exact application methods. No record of water cart movement, water cart refilling or even water cart application rates have been kept at RUM, thus a an approximation of dust suppression water input to the stockpiles based on real data cannot be made. Instead, what is accomplished here, is a scenario based estimation using approximate minimum application rates for water carts and a specific surface area of application, which can be used as a basis for comparison with rainfall input.
Two surfaces were chosen for this estimation. The first was that of a small expanding stockpile surface on the western edge of the NCWP observed in the May 1999 annual aerial photograph (Figure 6.10). This area was chosen specifically because a recent dust suppression water application had been captured in the aerial photograph and thus the traverse used by the water cart for the application was known, hence its distance could be measured. Observations made in the field of water cart traverses on working stockpile platforms confirm that the traverse preserved by the wet ground in Figure 6.10 is typical of that near an expanding stockpile front. The second surface is that of the main transport road bisecting RP2 from RP4 (now the grade 3 stockpile). This section of road was chosen, not only because it was a measurable distance but also because, as the main transport route to and from the working pit, it is one of the most regularly treated areas (with dust suppression water) of the mine and thus can be used as an example of known long term regular use of the dust suppression water in the one location, unlike the other scenario. Run-off from this road will still enter the RUM retention pond system (into RP2) and thus it is also an important part of environmental management at RUM.

*Figure 6.10* Example of Dust Suppression water applied to a working platform of weathered material. Note the dark mark indicating dampness and a recent application. This area is used in calculations in the text.
dust suppression water input estimates in the two scenarios were achieved by the following simple calculation:

\[
\text{Dust Suppression Water Input} = \text{Conc.} \times N_{\text{app}} \times (D/S \times R_{\text{app}})
\]

[6.1]

where \(N_{\text{app}}\) is the number of applications, \(D\) is the distance in metres of the water cart traverse, \(S\) is the average speed in m/sec at which the water cart is travelling when applying the dust suppression water and \(R_{\text{app}}\) is the application rate in L/sec from the sprinkler system on the water cart. Note that the function in brackets calculates the amount of dust suppression water applied for each traverse of the water cart.

No information was supplied by RUM that allowed for accurate representations of \(R_{\text{app}}\). Thus \(R_{\text{app}}\) was estimated using information from Haviland (2004) of Magnum Australia. Two spray valves running at 22L/sec each (most common spray valves used on water carts in Australia – Haviland, 204) have been assumed for the RUM water carts in light of the fact that at least two were observed on the water carts when in the field.

The total length of the traverse and hence \(D\) in [6.1], is approximately 312m for that of Figure 6.10(a) and 400m for that of Figure 6.10(b). The actual speed that the RUM water carts complete such traverses is not known, and will change depending on the driver and conditions, amongst other variables. So, to remain conservative, the maximum speed limit of 30km/h (8.3m/sec) for all vehicles working within the mine area has been used here for \(S\) in [6.1].

\(N_{\text{app}}\) differs between each scenario. An arbitrary, but conservative figure of 5 traverses per day for 5 days per week (RUM operated only 5 days per week for the calculation period) has been used for both the road and the stockpile. The daily figure may be as much as double this or greater based on observations of an active part of the CWP in May of 2002. For simplicity the two scenarios here are dry season scenarios only, so that the change in dust suppression water chemistry over the wet season does not have to be taken into account, nor do adjustments need to be made due to rain. All four
completely dry months of the year 2000 dry season (June, July, August and September) are accounted for in the calculation of dust suppression water input for the road scenario due to the consistency of use of the road. The stockpile scenario includes only August of the 2000 dry season due to the fact that the area of a working stockpile platform expands with time, that there is normally more than one active stockpile platform at any one point in time, and because August can incorporate the more detailed chemical results of this study (August 2000 expedition samples of RP2).

The results of the calculations for all selected elements and ions are presented in Table 6.7. Concentrations of Mg$^{2+}$, SO$_4^{2-}$, Ca$^{2+}$, K$^+$, Na$^+$, Mn and U have been taken from monthly averaged ERA data (see above) due to the frequency of sampling and analysis by ERA for those ions (3-6 times monthly) over the four month period in question. Cl$^-$ and NO$_3^-$ concentrations have been taken from analyses from this study for August, from ERA data for June and September, and an extension of June values for July, due to the lack of analyses by ERA for these ions.

Two comparisons with bulk precipitation are made, the first for the area represented by each region in question, in the case of the stockpile scenario this is for the whole section of stockpile as outlined in Figure 4.10(a), and the second for the entire area of the RUM waste and LGO stockpiles taken from Table 6.5. Note that the rainfall comparison is for the entire 2000/2001 wet season, as it needs to be for a legitimate comparison of input.
Table showing estimates of dust suppression water input compared to Rain input for major ions

<table>
<thead>
<tr>
<th>Ions - elements</th>
<th>Dust Sup. Input</th>
<th>Rainfall Input</th>
<th>Dust Sup. contribution</th>
<th>Rainfall Input</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stockpile</td>
<td>Road Total kg - August</td>
<td>Rain stockpile (kg)</td>
<td>Rain road (kg)</td>
<td>Total Rain 2000/2001 (kg)</td>
</tr>
<tr>
<td>Mg</td>
<td>20.4</td>
<td>112.1</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>191.5</td>
<td>756.4</td>
<td>8.5</td>
<td>8.8</td>
</tr>
<tr>
<td>Ca</td>
<td>2.7</td>
<td>13.7</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>K</td>
<td>0.4</td>
<td>1.9</td>
<td>1.3</td>
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<tr>
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</tr>
<tr>
<td>Si</td>
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</tr>
<tr>
<td>Mn</td>
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<tr>
<td>U</td>
<td>0.6</td>
<td>2.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.7: Table showing estimates of dust suppression water input for major ions as well as Si, Mn and U for two scenarios on the RUM waste and LGO stockpiles. See text for details and refer to Figure 6.10 for location of scenario locations. These estimations are for illustrative purposes only, to highlight the potential input that dust suppression water may make to localised areas within the stockpiles and compared to that of the other major input of ions, rainfall. See text for further details.

6.5.3 The Significance of Dust Suppression Water – Discussion

The calculations of dust suppression water input in Table 6.7 are conservative estimations based on scenarios developed from observed frequencies of water cart movements within the mine in certain locations; they cannot be used as actual input measurements. However, considering the conservative approach taken in regards to all estimations it can still be concluded that Table 6.7 shows that dust suppression water is an extremely significant input to the RUM waste and LGO stockpile system. This is particularly the case for localised regions within the stockpiles where high levels of mining vehicle activity have occurred at times, but especially where this activity is maintained over long periods, such as main access roads to the large stockpiles. For instance in the example scenario developed above, the conservative
estimates suggest that over the four months of no rain during the 2000 dry season at least more than 224 times the amount of Mg was deposited on the mine road separating RP2 from RP4 by the water carts, than the entire following wet season of rain (taking into account run-off).

The magnitude of the relative input to rain decreases dramatically for the stockpile scenario due to the rain being able to cover the entire stockpile surface and slopes compared to the relatively limited coverage of the sprinkler system on the water carts (refer to Figure 6.10a). Still, if the small stockpile region in the NCWP from the 1999 aerial photograph had existed in the following year, then in the single month of August it would have received over 40 times the amount of Mg from the water carts than it would have from the entire 2000/2001 wet season of rainfall.

Table 6.7 also highlights a significant concentration effect in regards to dust suppression water input. This occurs on three levels. Firstly, within the stockpile system, for instance, the August total Mg input from dust suppression water to the small section of stockpile in the first scenario is equivalent to 30% of the amount of Mg deposited to the entire RUM waste and LGO stockpile system by the 2000/2001 wet season rainfall. Alternatively, by the estimations of Table 6.7, some 1.64 times the total amount of Mg deposited to the RUM waste and LGO stockpiles by the 2000/2001 wet season was concentrated onto that single section of mine road in Figure 6.10(b) by dust suppression water application in the four months leading up to that wet season.

Secondly, concentration occurs on a level shown above, whereby dust suppression water is localised to the path taken by the water cart upon the Surface Platform of the stockpile, where as rainfall falls relatively evenly across all of the stockpile. Thirdly, concentration occurs relative to rainfall in that dust suppression water application does not involve a volume of water that would allow for any significant penetration into the platform surface, nor does it allow for any significant run-off. The result is a thin layer of wetted surface exposed to evaporation, and therefore the potential for dust suppression water to precipitate its mineral contents within a small layer of the surface platform. Rainfall, on the other hand, due to both volume and the duration of delivery, has a far greater potential to penetrate the stockpile platform surface, despite
significant run-off. Thus, where as rainfall may saturate an entire surface Platform Horizon (see Chapter 3 for definition), dust suppression water may be localised at the very surface of the Platform Horizon, with penetration probably limited to the first few millimetres.

The fact that dust suppression water contributions to the stockpile will be limited to the upper layers of small localised areas of roads and surface platforms within the stockpile system means that the actual input to the system may be governed by certain external influences. Most of these revolve around rainfall. For instance, during the dry season dust suppression water contribution will be allowed to accumulate at the surface, but during the monsoon, the consistent relatively large volume afternoon rain events will work to dilute and/or push out the morning dust suppression water contribution on a regular basis. The question then arises, how much of the dust suppression water contribution during the dry season, actually survives the following wet season? More studies need to be undertaken to answer such a question, however one would expect that much of the dry season dust suppression water contribution to a stockpile surface platform would be either washed away with run-off with the onset of the first wet season rains or taken back into solution and transported with that rainwater that penetrates the platform. In other words, during the wet season, at least part of the dry season dust suppression water contribution will be redistributed or lost to run-off.

This is particularly interesting due to the fact that pulses of certain elements are observed in some mine water bodies at RUM at the start of the wet season (Jones and Hughes, 1999), including the increase in concentration of some elements in RP2 during October-November highlighted above (6.3.2). Such ‘first flush’ signatures are not uncommon phenomena in mines around the world, and in most cases are easily explained by oxidation processes that have occurred during the dryer periods or left over precipitates from the previous rainfall period (Gzyland and Banks, 2007, Harris et al. 203, Younger, 2002). In natural settings of tropical climate catchments around the world, the ‘first flush’ is a well known event and in Kakadu National Park fish kills have been observed as a result (Jones, pers. comm., 2006). However, the examples in Table 6.7 combined with the localisation effect described above, suggest
that at RUM a build up of dust suppression water contribution (precipitate) in the dry season is probably a significant contributor to the content of the ‘first flush’.

Exactly how much dry season dust suppression water contributes to the first flush is another question, and one not answered here. However, if one considers the fact that the 2.4kg of uranium delivered to the scenario involving the road of Figure 6.10(b) in the four dry months of 2000 is equivalent to approximately 24 tonnes of the waste grade schist sample studied in Chapter 4 (112ppm U), or that the 756.4kg of SO$_4^{2-}$ delivered to the road in this scenario is equivalent to over 3000 tonnes of the Jones and Hughes (1999) waste material (0.021% S), then dry season dust suppression water input may be a significant contributor to the first flush at RUM. The calculations suggest that it will be important for Mg, SO$_4^{2-}$, and Ca$^{2+}$, apart from U$^{6+}$ and Mn$^{2+}$, but not necessarily for K$^+$, Na$^+$ and NO$_3^-$, and it would seem not at all for Cl$^-$. 

6.6 CONCLUSIONS

The hypothesis has been proven correct and for the first time, dust suppression water has been recognised as an important source for chemical input to the stockpile system at RUM. Despite the orders of magnitude greater volume of solution supplied by rainfall and the complete stockpile coverage that rainfall has been assumed to have, the orders of magnitude higher concentrations of ions in dust suppression water mean that it is a significant contributor of ions to RUM stockpile system and mine waters. At a local level, such as old road bases and working platforms, and current working roads and platforms, for some particular ions, dust suppression water is a much greater contributor of ions than rainfall and important component of the ‘first flush’ of ions from the stockpiles at the start of the wet season. This is obviously particularly the case for trace elements such as U$^{6+}$, where it is in most cases the only measurable supplier. Specifically, dust suppression water is a significant contributor to input into the stockpile system in comparison to rainfall for the major ions Mg$^{2+}$, SO$_4^{2-}$ and Ca$^{2+}$, and importantly for the cation U$^{6+}$. On a local scale, such as the main haul road, it far outweighs rainfall as an input of chemical components for all major ions measured except for Cl$^-$. 

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This study has resulted in good understanding of the chemistry of dust suppression water, and since dust suppression water is sourced from RP2, also a good understanding of the chemistry of RUM’s central retention pond. Mg$^{2+}$ and SO$_4^{2-}$ dominate the RP2 water, and to a lesser extent so does HCO$_3^-$, Na$^+$ and Ca$^{2+}$, with U$^{6+}$ and Mn$^{2+}$ being the most significant trace elements by far. A significant seasonal trend has been delineated in RP2 chemistry, whereby at the start of the wet season (October to December) there is a dramatic increase in the concentration of most major and minor chemical species. This can be correlated directly to the run-off associated with the start of wet season rains, the ‘first flush’, and the beginning of input to RP2 from other water bodies around the mine, including Sump98, as well as increases from P3. In fact it has been shown here that the concentration of various ions in RP2 are largely controlled by certain inputs or a combination of inputs and the amount of water RP2 holds at any one point in time.

More important than this however, this study has delineated the causes of a major long term trend towards increased concentrations of species such SO$_4^{2-}$ and U$^{6+}$ in RP2, a trend that has been of obvious concern for environmental managers at Ranger. All of these causes stem from two factors, a major increase in the rate of extraction of waste and LGO material from the mine between 1995/96 to 2001 and the deepening of P3 into fresh, yet to be oxidised material of higher ore grades. This resulted in two new stockpiles being created (the WWP and the NWP), RP4 being filled in by un-oxidised LGO, a significant increase in the relative amount of LGO material being dumped compared to previous, and a significant increase in the amount of ore in the ore stockpiles. It also meant that a new input of waste and LGO influenced water was introduced to RP2, and the relatively long undisturbed input, RP4, became enriched in elements from the weathering of large quantities of freshly mined rock.

It is difficult to predict whether such increases in concentrations of ions in RP2 will continue into the future; stockpile weathering rates may settle, particularly if mining rates also decrease. If dust suppression water is as a significant contributor as it seems to the chemical input to stockpile surface platforms at Ranger, and the concentration of elements such as U continue to increase in RP2, then at some point in time ERA may have to find another source for dust suppression water. One option would be
RP1. It is interesting to note that in 1997, U concentrations in dust suppression water were orders of magnitude less than they are now.

This study has resulted in tangible estimations of input from precipitation for each month of the entire wet seasons of 1999/2000 through to 2001/2002. Importantly, in doing so, this study has established a method by which future estimations of bulk chemical input from precipitation can be made, and thus will aid in any future large scale 'system' studies of the final landform at Ranger.
CHAPTER 7

CHARACTERISING THE CHEMISTRY OF MINE WATERS – STOCKPILE OUTPUT

7.1 INTRODUCTION

The single purpose of this particular part of the study is to identify and characterise the mine waters collected for this research that may have influence from the waste and LGO stockpiles of RUM. In doing so, a better understanding of the relationship between the chemistry of certain mine waters and the geology of the stockpiles can be achieved. In other words, this part of the study aims to understand the hydrogeochemistry of the ‘output’ of the stockpile system.

7.2 METHODS

The precise methods involved in this part of the research, from water collection procedures through to analytical chemistry, have been detailed in Chapter 2 and hence this chapter should be referred to for more information. Analytical chemistry techniques included IC for major anions, ICPOES for major cations and ICPMS for trace elements. The general chemical parameters of pH, eh, EC, DO and temperature were measured in the field with the appropriate electrodes and meters. Total alkalinity was calculated from in-field alkalinity titrations. Given a total pH range of between 4.85 and 8.49 (disregarding a single ARD sample), with most waters falling within pH 6-8, total alkalinity was assumed to be best approximated as the concentration of HCO₃⁻ in solution and thus calculated accordingly.

A total of 46 water samples from waters found inside the RUM operating lease were collected over 5 expeditions, the first of which, in November/December 1999, was simply to test procedures. The following four expeditions entailed the end of the 1999/2000 wet season (April 2000 – R100series samples), the 2000 dry season
(August 2000 – RW200 series samples), the start of the 2000/2001 wet season
(November 2000 – RW300 series samples) and just after the finish of the 2001/2002
wet season (May 2002 – RW400 series). The April 2000 collections and the
November 2000 collections were part of a joint collection project, whereby S-isotopes
from various waters associated and not associated with the mine were determined for
a S-budget study by Kilby (2001). As such, the R100 series and R200 series water
chemistry results have been previously published, although not significantly studied

The geochemical modelling package PHREEQC-2.13.2-1727 from the United States
Geological Survey was used to investigate speciation of the dominant elements in
solution. In one instance the historical record of mine water chemistry at RUM was
used to investigate a particular issue (refer to section 7.4.3). The problems associated
with the Ranger water chemistry data have been previously outlined in Chapter 2.

7.3 RESULTS

All analytical chemistry results for all of the waters collected from within the RUM
mining lease are tabled in Appendices 8 to 11, in order of sample number. This
includes a description of each sample as well as comments, the date of collection
(Appendix 8), the in-field parameters, HCO₃⁻ (Appendix 9), all major anions and
cations (Appendix 10), and all of the 36 trace elements analysed (Appendix 11).
Figure 2.1 and Table 2.2 in Chapter 2 detail the locations of these samples.

It should be noted that P was only analysed by ICPMS. It is thus included in the trace
element results of Appendix 11. Only for mine water samples collected during the last
expedition to RUM was P analysed by ICPOES (sample series 400). Not one of the
400-series samples contained P above the detection limit for P on the ICPOES. This is
not surprising, due to the low solubility of its inorganic compounds P is normally
found in solution in natural waters in concentrations no more than a tenth of a mg/L
(Hem, 1985). P is expressed here as total P, although it is probably in its highest
oxidation state (P⁵⁺) within the species H₂PO₄⁻ and HPO₄²⁻, given that apart from a
single sample the range of pH is within the stability fields of these two solute species
(see Hem, 1985).
Of the N-based species, only $\text{NO}_3^-$ has been measured in this study. $\text{NO}_2^-$ is seldom present in water in concentrations that affect the ionic balance (Hem, 1985). In surface waters N-species are normally oxidised so that ammonium ($\text{NH}_4^+$) would be transformed to $\text{NO}_3^-$, although in some ground waters reduced N species may be significant (see Hem, 1985).

In Appendix 10 all major ions are expressed in terms of mg/L and all trace elements in $\mu$g/L. It should be noted that a result of a zero value refers to a result that was below the detection limits of the analytical instrument for that particular species. In other words, if the element could not be detected by the analytical instrument it was not assumed to be present at any particular concentration, as is sometimes done in industry by presenting a concentration equal to half of the detection limit in analytical results (pers. comm., Klessa, 2006). All detection limits are given in the appropriate section of Chapter 2.

The in-field parameters of $\text{eh}$ and $\text{EC}$ for the samples from the procedural development and testing expedition, samples W1, W2a and b, W3 and W4 are treated with suspicion and considered not reliable for any further statistical analysis or comment due to the use of a different set of probes that yielded indifferent results.

Duplicate samples have been included in the ion balance test below, however they are not included in any other analysis.

**7.3.1 Accuracy Test – Ion Balance**

As for rainfall in Chapter 5, a cation-anion balance test has been performed on all relevant samples with sufficient analytical chemistry using the formula set out in [5.1]. The numerical results of this test are presented in Appendix 12 along with the sum of major cations including $\text{H}^+$ (in meq/L), the sum of major anions (in meq/L) the sum of major cations and anions (in meq/L) and the total sum of all species analysed (in mg/L). Note that samples are grouped according to their location within the mine, with ground waters towards the bottom of the table.
The ion balance has been based on major cations (including H\(^+\)) and anions only. This has been done due to the uncertainty of the exact complexes formed by some of the trace elements, the possibility that some of these elements may have been in solid microcrystalline compound phases that passed through the 0.45\(\mu\)m filter in the un-acidified samples, and because the addition of all of the trace elements to the sum of the major cations and anions is insignificant. Included in Appendix 12 is an equivalent summation of the major cations and anions (including H\(^+\)) with the addition of charged trace elements in significant concentrations, which includes Al\(^{3+}\), Fe\(^{3+}\), Co\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\), Rb\(^+\), Sr\(^{2+}\), Ba\(^{2+}\) and U\(^{6+}\). The oxidation states used for the trace elements are those that the elements are most likely to be present as, within the pH ranges of this study, if present as non-associated metals. It is acknowledged that this will not be the case, for example U will most likely exist as the uranyl (UO\(_2^{2+}\)) ion. However, this is a sufficient approximation to see the insignificant change in the equivalent sum of ions if trace elements were to be added. It should be noted that P\(^{5+}\) is not included in the addition since it is probably present as the H\(_2\)PO\(_4^-\) and HPO\(_4^{2-}\) anions and hence will have been measured as part of total alkalinity and thus accommodated within the HCO\(_3^-\) value. For the same reason it is not included in the major anion summation.

Anions were not analysed in all of the samples from the first expedition (W-series), nor for the portion of an ERA Environmental Department sample analysed for cations and trace elements in this study (sample RW326 – MB bore), hence these have been discarded from the cation-anion balance and are treated with caution from here in. They still may be important in the overall analysis of mine water chemistry for comparison purposes. Anions were also not analysed in the sample of the RUM process water (RW218), which was sampled specifically for the S study by Kilby (2001) and so is also not included here. Once again this sample is only used in the following study for reference, it is not used in any statistical analysis.

No alkalinity titrations were performed on samples RW212, RW213, RW215 and RW315 due to the lack of sample volume collected combined with the importance of having three aliquots of sufficient volume for analytical chemistry procedures. Sample RW213 represents a dewatering bore for P#1, a water that is not entirely necessary for this study and so it has been discarded from the ion balance. However
the other three samples have been included in the analysis as they are all important to this study, particularly RW215. In all except RW215 the addition of HCO₃⁻ would not have significantly affected the balance result. Sample RW212 is a sample of the LGO sump and other samples from the LGO sump have HCO₃⁻ equivalent concentrations of no more than 1.47% of the sum of major anions. Likewise, sample RW315 was collected only a few metres downstream of sample RW316, which has a HCO₃⁻ equivalent concentration of only 1.55% of the sum of major anions.

Figure 7.1(a) is a summary of the results of the ion balance test showing the proportion of samples within given ranges of percentage of the sum of cations and anions. The less than 2% range represents Hem’s (1985) suggested ideal margin of accuracy allowed for waters of moderate concentration (250-1000mg/L). The 2-5% range incorporates the UNEP/WHO limits established for ion balances on ground water analyses (5%) (Steel, 1996). The 5-10% range incorporates the UNEP/WHO limits established for ion balances on surface water analyses.

Figure 7.1(a) shows that 95% of the chemical analyses of the RUM mine waters have ion balances that fall within the UNEP/WHO range for surface waters, with 33% falling within Hems (1985) ideal 2% range. Only two samples fall outside the 10% cut-off, sample RW216 and RW403. Sample RW216, a ground water sample, one of a few bores sampled by hand, has an ion balance of over 57% and so this sample has been discarded from further analysis. Sample RW403, is also a groundwater sample but is close to the suggested range with an ion balance of 10.68%. This sample will not be discarded for analysis, instead just flagged for caution. Two other groundwater samples are to be considered with caution from here in, samples RW310 and RW319, both with ion balances just outside the range allowed for groundwater samples (8.1% and 5.69% respectively). Figure 7.1(b) displays the linear relationship between major cation sum and major anion sum after sample RW216 has been discarded. The R² of 0.9835 equates to a relationship not far from the ideal.
Figure 7.1: Cation anion balance test results (a) Percentage of samples with results within various ranges of acceptance. See text for details. (b) Correlation between Major cation summations and major anion summations.
This ion balance is only a test of the data and should not be taken as proof that the analyses are absolutely correct. This is particularly the case for the waters in this study, of which the majority are completely dominated by two to three ions (see below) and thus in such samples the ion balance can sometimes be a test only of the analyses of these dominating ions.

7.4 CHEMICAL CHARACTERISATION – IN FIELD PARAMETERS

7.4.1 Temperature

In situ temperature measurements for all of the waters sampled ranged from 23°C for the dry season sample of the second bund on Corridor Creek (RW205) to 36.1°C for the start of wet season sample of Sump98 (RW318). However, RW205 was a definitive outlier, and without this sample the average temperature for the waters collected here was 30.8°C with a standard deviation of 2 (disregarding duplicates). There was no relationship found between the temperature of water and the sample site, nor between the temperature of the water and the season in which it was sampled. There was also no correlation found between temperature and the concentration of any element in solution, other factors were far too dominant in determining changes in water chemistry.

7.4.2 Electrical Conductivity

In-field electrical conductivity (EC) measurements ranged from a low of 82.2 µS/cm³ for the second bund on Corridor Creek to a high of 4720 µS/cm³ for the water sampled from a pond collecting leachate from the western stockpile. The average of 34 EC measurements for this study was 1534.6 µS/cm³, with a median of 1131 µS/cm³ (standard deviation of 186 units), disregarding duplicates. The EC of the groundwater samples ranged from 394 µS/cm³ for both OB23 and OB24 on the western side of the mine to 3610 µS/cm³ for an open bore hole on the WWP. The average of 10 EC measurements from ground water samples was 1807.7 µS/cm³ with
a median of 2580 μS/cm³ and for the 24 surface water samples the average EC was 1420.8μS/cm³ with a median of 1005μS/cm³.

7.4.3 eh – pH Reliability

As already noted in Chapter 2, not all of the in-field eh measurements taken for this can be regarded as reliable. A good example of this is a simple comparison of the eh-pH conditions measured in this study to that of generally accepted eh-pH conditions in natural waters in Figure 7.2. Whilst groundwater eh-pH measurements from this study seem to match the generally accepted eh-pH conditions for groundwater, and the only two rainfall eh measurements are close to that expected of rainfall, the surface water eh measurements seem to skew from what would be expected. The surface water eh conditions seem more akin to what would be expected for oxygen poor environments, such as groundwater, and far from what seems to be normally expected for mine waters. Whilst some of the surface waters analysed were relatively stagnant, some were collected from running streams, hence it is more likely that the eh measurements in this study are in error rather than the waters being unique examples.
Figure 7.2: The eh-pH characteristics of the RUM mine waters in comparison to the stability field of natural waters in eh-pH space. See text for further details. The eh-pH diagram is that of the popularly published diagram from Blatt et al (1980) with additional data from Middleton et al (1960).

7.4.4 pH

The average in situ pH of 35 water samples was 6.58, the median 6.64 (standard deviation of 0.19 pH units). The average pH for the 11 groundwater samples was 6.8, the median 6.6, and the average for the 24 surface water samples was slightly lower at 6.48, the median 6.6.
Most of the RUM mine waters were relatively neutral, however 9 of the 35 samples (some 25.7%) fell outside the neutral pH 6-8 range. The 5 samples with lower pH were all samples very close to a stockpile leachate source or were a leachate source themselves, evidence that acid producing weathering reactions are probably occurring in the stockpiles (see Chapter 8). The low pH samples included two start of wet season samples from the Grand Canyon, catching run-off and leachate from the CWP and NWP (RW308 [pH 5.04] and RW325 [pH 4.85]), two start of wet season samples from a small stream seeping from the WWP (RW305 [pH 5.26] and RW316 [pH 5.18]), an end of wet season sample from a pond receiving leachate from the NWP (RW405 [pH 4.82]), and the sample of the seep from the excavation into the WWP in the 2000 dry season (RW215 [pH 2.97]). The latter sample is the most definitive representation of what conditions may be like inside the stockpiles, at least in some regions, and the activity of free H⁺ in this sample was almost 2 orders of magnitude greater than any other sample collected, strengthening the argument that acidic conditions can be produced within the Ranger Uranium stockpiles.

The three alkaline samples consisted of an early wet season RP2 sample (RW312 - pH 8.38), a dry season sample of Sump98 (RW208 - pH 8.49) and the sample taken from the drainage water on top of the SWP at the end of the 1999/2000 dry season (RW114 – pH 8.49). Whilst it is difficult to speculate on exactly why these samples have high pH, they are to some degree related, in that sump98 can receive RP2 water at times, depending on the pumping regime, and the SWP stockpile drainage had been pumped via sump98.

### 7.5 CHEMICAL CHARACTERISATION – COMPOSITION

#### 7.5.1 Dominant Major Element Chemistry

##### 7.5.1.1 MgSO₄ Solutions

Figure 7.3(a) is a plot of the concentration of all the major ions in mM/L, within each RUM mine water sample, both surface water and groundwater. Different coloured lines join the concentrations of each species in each sample together so that a line of concentration is formed for each species through all of the samples.
The chart reveals that the ions Mg$^{2+}$ and SO$_4^{2-}$ are the most dominant ions in almost all of the Ranger mine waters, and as such most of the Ranger mine waters sampled in this study can be described as MgSO$_4$ waters. Further to this, almost all of the waters have a Mg/ SO$_4$ ratio of close to 1.0, proving that it is the MgSO$_4$ salt dominating the Ranger mine water chemistry.

Only six samples differ markedly from this, samples R102, R105, RW205, RW303, RW310 and to an extent RW402, having concentrations of Mg and SO$_4$ much lower than all of the other samples, and except for RW402, having Mg/ SO$_4$ equivalent ratios far greater than 1.0. The first two of these samples are from water bodies that, for most of the time, receive no direct input from the stockpiles. R102 is from RP1, a potential release pond (depending on water quality and only during the wet season) situated at the end of a catchment that includes the WWP, tailings dam (not currently being used for depositing tailings) and output from the western wetland filter system. R105 and RW205 are from the second bund downstream along Corridor Creek, a creek on the eastern side of the mine (see Figure 2.1). This bund did not receive any input of water sourced directly from the stockpiles, water only reached the bund after being filtered through a primary bund upstream (pers. comm. Jones, 2000). The bund was also well vegetated at the time of sampling. Sample RW402 was also sampled from the Corridor Creek catchment, further upstream from the bund in which R105 and RW205 were sampled from, in the first receiving cell of a man-made wetland filter. The wetland filter was built between the R200 and R400 sampling expeditions, and so this structure was not present when samples R105 and RW205 were taken.
Figure 7.3: Concentration of major elements and ions in RUM mine waters, (a) with dominant ions and (b) without dominant ions, the latter to show greater detail. See text for further details.
Samples RW303 and RW310 represent samples from the observation bores OB23 and OB24 respectively, the most western of all bores sampled, located to the north of the western edge of the WWP (refer to Figure 2.1). The fact that all six of the samples with a much lower MgSO$_4$ concentration than the rest of the sample set are also the furthest from any potential stockpile source is strong evidence that the concentration of MgSO$_4$ can be used as an indicator of proximity to an exposed Ranger rock source, and hence an indicator of mine influence in waters surrounding the mine.

7.5.1.2 Mixed Solutions and Bicarbonate

Rather than MgSO$_4$ waters, RW303 and RW310 can best be described as mixed solutions with significant amounts of Na$^+$, Ca$^{2+}$, Mg$^{2+}$, HCO$_3^-$ and to an extent Cl$^-$. The dominance of HCO$_3^-$ in samples RW303 and RW310 can be seen in Figure 7.3(a). Figure 7.3(b) plots the concentrations of major ions (in Moles) just as in Figure 7.3(a) but with Mg and SO$_4$ disregarded. Figure 7.3(b) reveals that HCO$_3^-$ is a significant ion in all of the groundwater samples, as well as in samples RW208, RW406, R114 and R115. This is consistent with normal ground water chemical compositions (Hem, 1985). The tendency for groundwater to have higher HCO$_3^-$ than the surface waters can be due to a number of factors including leaching of carbonate soil sources into the groundwater reservoir, weathering of carbonate in rocks, lower proportions of complexing ions that allow for the precipitation of CO$_3^{2-}$ minerals (in this case Mg) and processes that release CO$_2$ into the groundwater reservoir such as reduction of SO$_4^{2-}$, generally a bacteria mediated process (Hem, 1985).

Of the high bicarbonate surface waters, samples R114 and R115 are from the SWP. Sample R114 was sampled from a drain created in the top of the stockpile, where water originally from a Pit#3 dewatering bore, DW3A (situated between RP2 and Pit#3), was being pumped through in a mine water management trial (Pers. comm. Jones, 2000). However, observations in the field suggest that this water never reached the end of the drain, instead it sunk through a void into the SWP and broke through near to the toe of the stockpile approximately 20 metres away, an obvious example of tunnelling as would be expected in the SWP according to the stockpile structural maps produced in Chapter 3.
Sample R115 was collected from a small pond that had formed at the toe of the SWP and which was in receipt of the stockpile toe seepage. The sample was taken as close as possible to the observed seepage that seemed to be a result of the water infiltrating the base of the drain on top of the stockpile. Thus, the high concentrations of HCO$_3^-$ in both R114 and R115 may be a result of their apparent origin from bore DW3A. It is important to note that bore DW3A resides in carbonate (pers. comm. Hughes, 2002), and confirmed by recent geotechnical diamond drilling in the area (pers. comm. Coffey, 2006). However, it must also be pointed out that observations during this study and the stockpile geology estimations made in Chapter 4, suggest that the SWP holds by far the majority of the carbonate mined from Pit#1. Thus, it is possible that the SWP may produce leachate with higher HCO$_3^-$ concentrations anyway. Apart from HCO$_3^-$ and Mg$^+$SO$_4^-$, samples R114 and R115 do not contain any other major ions of any comparable significance.

RW208 and RW406, the remaining samples with high HCO$_3^-$, represent Sump98 in the 2000 dry season and after the end of the 2001/02 wet season respectively. These samples also contained significant amounts of Ca$^{2+}$ and Na$^+$ compared to other samples. It is shown in Figure 7.3(b) that these two ions have similar significance in the ground water samples, but only for those from the western side of the waste and LGO stockpiles, representing bores OB23, OB24, Bore23552, OB44, MB and OBWWP. Importantly, RW208 and RW406, although surface water, are also from the western side of the stockpiles within the same area as Bore23552 and OB44. It is difficult to understand exactly why this relationship occurs, however this will be discussed later.

It should be noted that in all of the ground water samples $P^{5+}$ and Si concentrations are relatively high compared to other samples. Since $P^{5+}$ will be in solution in the form of either the H$_2$PO$_4^-$ or HPO$_4^{2-}$ anions then it will be contributing slightly to the HCO$_3^-$ result for these samples, given that it is obtained by a total alkalinity titration (see Chapter 2). The pH of both R114 and RW208 is 8.49, which falls close to the first dissociation step for the silicate ion, H$_3$SiO$_4^-$, in the pH range of 9.41 to 9.91 (Hem, 1985, based on Sillen and Martell [1964] data). According to Hem (1985), no more than 10% of the total dissolved Si may be in the form of the silicate ion between pH 8.41 and pH 8.91. During an alkalinity titration the silicate ion will be converted
to silicic acid, Si(OH)₄ (H₄SiO₄), the most common form of Si in solution (Hem, 1985). Thus it is possible that a small amount of H₅SiO₄⁻ may also be contributing to the HCO₃⁻ result in the high HCO₃⁻ samples.

Compared to other ions and disregarding the Mg+SO₄ dominance, Figure 7.3(b) shows that Ca²⁺ is of significance in samples RW211 to RW407 on the chart, as well as sample RW405. Samples RW211 and RW407 are from the LGO sump and the GC site respectively, both of which receive water directly from the CWP. Sample RW405 is from the small pond that collected leachate and run-off from the NWP during the 2001/02 wet season.

**7.5.2 The Behaviour of Other Major Species**

Figure 7.3(b) reveals a definitive increase in Si and Cl⁻ in the groundwater samples on the far right hand side of the chart, from sample RW303 to sample RW403. This parallels the pattern observed for Ca²⁺ and Na⁺ in the groundwater samples. All of these samples are from bores on the western side of the stockpiles, either within or north of the WWP. The other groundwater samples comparatively lacking in Si and Cl⁻ (as well as Ca²⁺ and Na⁺) are from the P#3 dewatering bore near RP2 (bore DW3a).

K⁺ also increases in the groundwater samples of the right hand side of the chart, however for K⁺ the increase begins at sample RW319, negating the observation bores OB23 and OB24. The difference between the samples is once again geographical, with the other bores being either further to the east of OB23 and OB24 (refer to Figure 2.1), and closer to a corner of the stockpiles where the WWP meets the NCWP (samples RW319, RW320 and RW401), or actually within the WWP itself (samples RW324 and RW403). Si is also prominent in samples RW215 and RW405, although in the vicinity of only 0.5 mM/L concentration in both. It remains relatively consistent at around 0.1-0.25 mM/L in all other samples except those of the bund on Corridor Creek (RW105 and RW205) and that of RP1 (R102), where it is relatively close to disappearing below analytical detection limits. As has already been explained, these three samples are the furthest geographically from having any direct input of water from the stockpiles and mine.
Slight increases in Cl' occur in samples RW208 and to a lesser extent RW406 and RW405, however all of these increases represent concentrations less than 0.42 mM/L. K' slightly increases in these three samples also, although on a much smaller scale. The former two samples are also characterised by significant increases in Na', Ca^2+ and HCO_3-. It is worth noting that the water bodies represented by samples RW208 and RW406 (Sump98 and r2sed respectively) are directly adjacent each other and at times water is transferred between the two (own observations of pumping regime), so it is not surprising that these two samples should hold some similar chemical characteristics at certain times of the year.

Little NO_3^- is evident in the groundwater samples, below detection limit results being common. N may still be present in these groundwaters, but in the reduced form only (NH_4^+). If anaerobic conditions have existed anywhere within the groundwater flowpath, denitrification processes (bacteria mediated) may have played a part in NO_3^- loss. However NO_3^- does tend to increase in many of the surface water samples, a string of samples within the chart of Figure 7.3(b) from RW211 to RW316 and again in samples RW408, RW405 and RW215. It is particularly high relative to other elements in samples RW315 and RW316, both from the same small stream draining from the northern wall of the WWP into Sump98 at the start of the 2000/2001 wet season.

7.5.3 Dominant Trace Element Chemistry

7.5.3.1 Uranium

Figure 7.4(a) is the same type of chart as those in Figure 7.2, except that it displays the concentration of trace elements (in μg/L). Not surprisingly, U^6+ can be stated as being the most dominant trace element in solution in the RUM mine waters. It is most dominant in samples RW308, RW315, RW316, RW208, RW408 and RW405, with concentrations of 11.814mg/L to 97.405mg/L. These concentrations were some 32.5 to 126.7 times the concentration by weight of the next most abundant trace element in the corresponding samples.
U$^{6+}$ loses its dominance completely in samples R114, R115, RW325, RW323, R105, R205, R102 and all of the groundwater samples. These samples include those from the SWP, (R114 and R115), RP1 (R102), the second bund on Corridor Creek, the creek on the eastern side of the mine (R105 and RW205), a single sample from the GC water body (RW325) and a single sample of run-off collected from the run-off channel on the WWP (site WWP – sample RW322). Uranium is most mobile in its oxidised state U$^{6+}$ (Hem, 1985) and so a lack of sufficient oxygen to maintain it in this state may be the cause of lower U in mine site groundwaters. U can also be attenuated by adsorption to clays and Fe-oxides (Langmuir, 1997) and so this may also be an issue in the ground, where water may interact with wall rock or precipitates on the walls of groundwater flow pathways, such as fractures and faults.

7.5.3.2 Manganese

Figure 7.4 shows that the only other trace element that can be classified as being dominant at Ranger is Mn. This is clearly the case in all of the RP2 water samples (see also Chapter 6) (RW110, RW207, RW217, RW312, RW404), however it actually dominates over U$^{6+}$ in samples R115, RW325 and the groundwater sample RW403. Unlike U, Mn is most mobile in its reduced state (Mn$^{2+}$) and so a lack of oxygen will favour its presence in solution over U$^{6+}$. Therefore, it maybe that strong reducing conditions existed in the water bodies represented by R115, RW325 and RW403 at the time of sampling. This could well be the case for the large manhole style bore extending to the bottom of the WWP (RW403), but it would seem unlikely for the other two samples, where water was observed flowing from the SWP (R115), and early wet season rains had probably already impacted on the relatively organic free Grand Canyon pond (RW325). The fact that U$^{6+}$ concentrations were still relatively high in both RW403 and RW325 suggests that a rich Mn source may be a more likely determinant of the Mn dominance than redox conditions alone. This is particularly the case for the SWP toe seep (R115), which was being driven by tunnelling inflow from a drain on the top of the stockpile. Water sampled from the drain above (R114), considered to be the more oxidative of the two, had only 2µg/L Mn compared to 4071µg/L for the sample from the toe drain (R115), yet had only half the concentration of U$^{6+}$ and similar concentrations of other elements.
Figure 7.4: Trace element concentrations in RUM mine waters. (a) Dominant elements (b) close-up of A with the y-axis limited to 1000 ug/L concentrations and U excluded. See text for further details.
7.5.3.3 Outlier Sample RW215

Sample RW215, a sample of leachate from a submerged Platform Horizon, collected from excavation E1 (Figure 2.8) in the year 2000 dry season, is very different from all other samples in terms of its dominant trace element chemistry, with Al$^{3+}$ and Fe$^{2+/3+}$ also being dominant trace elements along with U$^{6+}$. The sample contains 6.524mg/L of Al$^{3+}$, some 18.4 times the Al$^{3+}$ concentration of sample RW308, the sample with the next highest analytical result for Al$^{3+}$. Fe$^{2+/3+}$ is also extraordinarily high in this sample compared to most other samples, being 3.278mg/L. However, a similar amount of Fe$^{2+/3+}$ was found in sample RW325, where it is the only other dominant trace element with Mn. The significant amounts of trace metals in sample RW215 compared to other samples can be explained simply by the orders of magnitude higher H$^+$ ion activity (pH = 2.97) within the sample and the resultant positive effect on metal and mineral solubility. Such a low pH is well within the range of aluminosilicate solubility, allowing such a solution to begin to completely breakdown such dominant minerals as chlorite (see details on chlorite solubility ion Chapter 8), and hold ions such as Al in solution.

7.5.4 Behaviour of Other Trace Elements

Figure 7.4(b) is Figure 7.4(a) with a y-axis limit of 1000µg/L, and thus allowing for the viewing of trace element behaviour at the lower levels of concentrations. There are a number of patterns worth noting. The highest concentrations of Cu$^{2+}$ (263-983µg/L), Co$^{2+}$ (38-190µg/L) and Ni (59-240µg/L) were found in samples RW308, RW315, RW316, and RW215. All these samples have low pH (<pH5.3), the probable reason for the abundance of the transition elements in solution. Cu$^{2+}$, Co$^{2+}$ and Ni are almost completely absent from the ground water samples.

At lower concentration levels Fe$^{2+/3+}$ seems to be associated with samples RW208, RW205, RW211 and RW212 as well as all of the groundwater samples, but particularly the two western bores closest to Sump98, samples RW319 and RW320 (ranging from 276-619µg/L for all samples). Mn$^{2+}$ is associated in most waters at the lower concentrations.
The highest concentrations of Zn$^{2+}$ are found in all of the bores on the western side of the stockpiles as well as RW215 (WWP Leachate – 377μg/L) and RW325 (GC – 781μg/L). Al$^{3+}$ is most abundant in samples RW308 (LGO Sump – 354μg/L), RW312 (the start of the 2000/01 wet season RP2 sample - 149μg/L) and RW115 (SWP - 70μg/L). Sr is most abundant in the western stockpile groundwater samples, but particularly those bores closest to and in the WWP (RW319-RW403 on the chart in Figure 7.4(b), and in RW325, RW405, RW208, RW406 and RW312 (109-556μg/L).

Mo is abundant in all RP2 samples (17-98μg/L) and V shows one single spike in sample RW405 (78μg/L). Y has two spikes of concentration, samples RW405 (149μg/L), and RW408 (remnant RP4 - 50μg/L)).

### 7.6 CHEMICAL CHARACTERISATION - ASSOCIATIONS

Multivariate analysis, both statistical linear correlation testing and graphical interpretation of scatterplots, was used to examine relationships between the elements analysed in the Ranger Mine waters. This was achieved for all waters combined and for the individual sub-groups of ground waters and surface waters.

#### 7.6.1 Chemical relationships in all waters (surface water and groundwater)

As Figure 7.3 has already shown, the most obvious bivariate linear correlation in the Ranger mine waters sampled in this study is that of Mg and SO$_4$ (Figure 7.5) with a correlation coefficient of 0.97 and a slope of close to 1 ($y = 1.0446x + 0.0028$) when compared in Moles. Thus the Mg v SO$_4$ relationship already discussed in Chapter 6 for RP2 water, also occurs for all mine waters across the entire mine site. This relationship suggests that chemical reactions involving the release of Mg$^{2+}$ and SO$_4^{2-}$ into solution, as well as the affinity these ions have for each other and the lack of
affinity they have for the solid phase once in solution, are the most important contributors to Ranger mine water chemistry.

![Graph showing the relationship between Mg and SO₄ in the RUM mine waters sampled from this study.](image)

**Figure 7.5:** Relationship between Mg and SO₄ in the RUM mine waters sampled from this study.

There are few other relationships as strong as that of MgSO₄, although as is expected, the chalcophile transition elements Cu⁺², Co⁺² and Ni, behave very similarly in solution, mainly due to a pH control on their solubility as discussed above, but also because it is likely that these metals will be associated via related sulfide phase source minerals. The correlation coefficients for Co⁺² v Ni, Co⁺² v Cu⁺², and Cu⁺² v Ni in the waters analyses for this study were 0.996, 0.948 and 0.961 respectively.

When present, the light rare earths La and Ce show excellent correlation (correlation coefficient of 0.956). This is not necessarily surprising given the similar chemical properties of all of the rare earths, particularly since Ce is the most similar rare earth to La in terms of atomic number and ionic radius. In geological materials Y is a trace element that is always associated with the rare earths (the heavy rare earths in particular) due to its tendency to form a 3⁺ ion (as do the REEs [except for Eu]) as well as having an ionic radius similar to Ho (Gill, 1996). Although not quite linear, Y also shows good correlation with La and Ce (correlation coefficient of 0.952 [with Ce] and 0.847 [La]) in the Ranger mine waters.
Interestingly, just as in the geochemical analysis of the Ranger waste and low grade ore, Y continues to show good correlation with U$^{6+}$ in the mine water (Correlation coefficient of 0.895). This means that some correlation also exists between U$^{6+}$ and the other REEs analysed (La and Ce) and suggests that the possibility that REEs are associated with the ore metal in the Ranger rocks, as tentatively suggested by Nash and Frishman (1983), continues into the waters leaching from the rocks. Ce has also been recognised as being associated with U$^{6+}$ in the sandstone uranium deposits of the western US (see Hem, 1985).

It should be noted that Y has long been known to be a relatively common constituent of natural waters, at least in ground waters across the USA (Wedepohl, 1978), and so its presence in the Ranger mine water, considering that it is associated with the deposit, should not be surprising.

Conversely however, the most significantly correlated metal to U$^{6+}$ in the Ranger rocks, Pb, does not correlate with U at all in the mine waters. This reflects the difference in chemistry between the two elements. Pb is relatively immobile in natural waters, mainly due to the low solubility of the hydroxy carbonates that it tends to complex with (Hem and Duram, 1973, Hem 1976b, 1985). On the other hand, in natural waters U$^{6+}$ exists as the highly oxidised uranyl ion (UO$_2^{2+}$), which readily forms more soluble complexes with common anions, in particular that with the bicarbonate anion, such as UO$_2$(HCO$_3$)$_2$ (Langmuir, 1997), but also with SO$_4^{2-}$, as seems to be occurring here (see below). Pb$^{2+}$ behaves most similar to its chalcophile transition ‘cousins’ already mentioned, with correlation coefficients of 0.953 with Co$^{2+}$, 0.945 with Ni and 0.861 with Cu$^{2+}$.

The two commonly associated alkali earths, Sr$^{2+}$ and Ca$^{2+}$ and to a lesser extent Sr$^{2+}$ and K, are also well correlated in the Ranger mine waters, although a few outliers degrade the correlation coefficient. Sr$^{2+}$ is commonly found replacing Ca$^{2+}$ and K$^+$ in feldspars (Deer et al. 1992) and the association in the mine waters probably reflects this association with the weathering of the feldspar containing HWS schists and the unaltered pegmatite, the most notable potential sources. However, geochemistry of the Ranger rocks suggests that the carbonates are also a good Ca+Sr source (see
Chapter 4). Sr\(^{2+}\) is a common constituent of limestone, again due to its affinity with Ca\(^{2+}\) (Hem, 1985, see also Deer et al. 1992).

Another more obvious positive correlation is that of Na\(^+\) and Cl\(^-\), which show good graphical correlation in the mine waters analysed here, although again, a few outliers degrade the correlation coefficient. NaCl is one of the more common salts in natural waters, including that of the incident rainfall to the Ranger mine site (see Chapter 5).

### 7.6.2 Differences in Element Associations between Groundwater and Surface Water

In terms of element correlations, there is no definitive distinction between groundwater and surface water in the Ranger mine waters sampled. There is some hint that P and Si may be positively correlated more so in the ground water than in the surface water, but the relationship is week. There also may be positive correlations between V and Ce, Pb\(^{2+}\) and Zn\(^{2+}\), Co\(^{2+}\) and Zn\(^{2+}\), and Sc and Y in the surface water that do not exist in the groundwater, but again these relationships are week and cannot be regarded as definitive surface water characteristics.

### 7.6.3 Electrical Conductivity and Modelling its Relationship with Chemistry

Given the dominance of the Mg\(^{2+}\) and SO\(_4^{2-}\) ions, it should not be surprising that these two ions are the main ions responsible for measured electrical conductance (EC) in all of the RUM mine waters. This is shown by the strong relationship between EC and Mg\(^{2+}\) + SO\(_4^{2-}\) that exists within the set of mine waters analysed here (Figure 7.6). The relationship is not linear, however the Mg\(^{2+}\) and SO\(_4^{2-}\) concentrations could easily be predicted from EC measurements in the surface waters of this study by a simple second degree polynomial, as has been done for SO\(_4^{2-}\) in Figure 7.7.
Figure 7.6: The relationship between $\text{Mg}^{2+} + \text{SO}_4^{2-}$ and EC in the RUM mine waters sampled for this study, disregarding sample RW215 for which EC was not measured. Note that the independent variable is the concentration of Mg and SO$_4$ to show their influence on EC.

Figure 7.7: The relationship between SO$_4^{2-}$ and EC for the RUM mine waters (surface waters only) sampled in this study, modelled to a simple second degree polynomial (equation displayed on chart). Note that the independent variable is EC as the intention here is to try to use EC to predict SO$_4$ concentrations. See text for further details.
The EC \( v \) \( \text{Mg}^{2+} \) or \( \text{SO}_4^{2-} \) relationship in the groundwaters is not that simple, due to samples OB44 and r2sed (proximal to each other geographically – refer to Figure 2.1) having slightly lower concentrations for their respective measured EC values, and thus fall below the predicted concentrations using a second degree polynomial. Using a quadratic on the groundwater samples would solve this problem, however there are too few samples in the dataset to be certain of the applicability of a quadratic equation for predictive use. A quadratic would also have improved variance slightly on the surface water samples, however the increase in accuracy would be too small to justify the added complexity.

Whether such polynomials can be used in all of the RUM surface waters is another question. Historical chemistry data for RP4 and RP2 (refer to Figure 2.1) was accessed via RUM’s environmental department, the EC \( v \) \( \text{SO}_4^{2-} \) relationship for both data sets are displayed in the bivariate plots of Figure 7.8, and 7.9 respectively.

![Figure 7.8](image)

**Figure 7.8:** The relationship between EC and \( \text{SO}_4 \) in RP4 from the historical mine water database (1980-1999). See text for further details.
As is shown, the trend in the EC v SO$_4^{2-}$ relationship of the RP4 dataset (Figure 7.8) is similar to that of the data from this research, in that there is a slight bend so that a second degree polynomial equation best explains the relationship. This is not the case for RP2 (Figure 7.9), where there seems to be two trends, both easily represented by straight lines, although the upper steeper trend, where SO$_4^{2-}$ values tend to be much higher, is not a strong one. A closer examination of the upper trend in the chart of Figure 7.9 reveals that data represent two specific recent sampling periods, October through to early December in 1999 and June through to the end of August, 2000. This anomaly in SO$_4^{2-}$ concentrations in RP2 has been previously identified in Chapter 6. However, it is important to point out here that despite the SO$_4^{2-}$ anomaly in RP2 remaining unresolved, the two August 2000 samples of RP2 analysed for this study suggests that, at least for the August 2000 period, the high SO$_4^{2-}$ concentrations of the ERA data are due to error. If the SO$_4^{2-}$ concentrations of samples RW207 and RW217 from this study are used, then they would fit comfortably into the trend set by the rest of the data in Figure 7.9. The fact that Mg also seems to increase with SO$_4^{2-}$ in the 1999 period (refer to Figure 6.3) is the reason for caution in disregarding the high SO$_4^{2-}$ outliers.
Other elements that also show some positive relationship with EC in the chemistry from this study include $K^+$, $Ca^{2+}$, $Cl^-$ and $Si$ although for the latter three the relationship only exists in the surface waters. When present the trace elements, $Se$, $Ce$ and $Ba^{2+}$ also have some correlation with EC in the surface waters.

In the past, EC has been used as an indicator for $U^{6+}$ concentration in mine surface waters by the RUM environmental department (Jones, pers. comm. 2001). The data from this study does not support such a use for EC measurements. Figure 7.10 shows that the 2000 dry season LGO sump samples (RW211 and RW212), the 2000 dry season Sump98 sample (RW208), both the start of the 2000/01 wet season and end of the 2001/02 wet season 'Grand Canyon' samples (RW325 and RW407 respectively), the as well as the r2sed sample of May 2002 (RW406) have $U^{6+}$ concentrations too low to correspond with the positive trend between EC and $U^{6+}$ that seems to occur in the rest of the data set.

![Figure 7.10: Relationship between EC and $U^{6+}$ in the RUM mine waters (surface waters only) sampled for this study. See text for further details.](image-url)
7.6.4 The Effect of pH on Solubility

Due to the dominance of near neutral conditions in the samples collected there are few elements that show any clear pH influence as it is beyond such relatively ‘neutral’ conditions that mineral solubilities are most affected. EC and hence Mg and SO$_4$ have no definitive correlation with pH.

Figure 7.11: The relationship between pH and the chalcophile elements Co (a), Ni (b) and Cu (c) in the RUM mine waters (surface waters only) sampled for this study.
Figure 7.12: A comparison of the relationship between U and pH for all the mine waters sampled in this study with the solubility curve for Schoepite (Empirical formula $= [(\text{UO}_2)_8\text{O}_2(\text{OH})_{12-12}(\text{H}_2\text{O})]$ at 25 degrees celsius and 1 bar total pressure as a function of pH and PCO$_2 = 0$ and 10(-2) bar from Langmuir, 1997.
The chalcophile metals Co\(^{2+}\), Ni and Cu\(^{2+}\) are the only three elements that show a distinct increase in concentration in waters of lower pH (Figure 7.11(a-c)), but for the surface waters only. According to the results from this analysis, the increase in solubility for all three of these elements occurs in the Ranger mine surface waters around pH 5-6.

Although there is no distinct pH control on U\(^{6+}\) concentration, the U\(^{6+}\) concentration data does comply with typical U-mineral solubility curves. Figure 7.12 is a mineral solubility curve for schoepite \(((\text{UO}_2)_8\text{O}_2(\text{OH})_{12}(\text{H}_2\text{O})_{12})\) taken from Langmuir (1997) with the RUM mine water data from this research overlaying it. Although not fitting precisely with the calculated solubility curves, particularly considering that the partial pressure of CO\(_2\) for surface waters will be that of the atmosphere at \(\approx 10^{-3.5}\) bar and thus falling between the two curves in the chart, and considering that the RUM mine waters are some 5°C above the conditions for the calculated curves, it can still be said that there is general agreement between the data from this study and the solubility curves for schoepite. It is important to note here that the solubility of schoepite may be important at RUM, due to the fact that metaschoepite \(((\text{UO}_2)_8\text{O}_2(\text{OH})_{12}(\text{H}_2\text{O})_{10})\), its first step dehydration product, has been identified in this study in evaporative precipitates in stockpile drainage channels (see Chapter 8).

7.7 THE PROPORTION OF MgSO\(_4\) AND THE Mg/SO\(_4\) RATIO AS INDICATORS OF A RANGER MINERAL WASTE SOURCE

Figure 7.13 shows the average proportion MgSO\(_4\) (in percent eq/L) to all other major ions for each sample site of the RUM mine waters analysed in this research and their relative geographical location within the mine. Figure 7.14 is the same as Figure 7.13, except that it displays the Mg/SO\(_4\) ratio (eq/L) for each sample rather than the proportion of MgSO\(_4\). Together both Figure 7.13 and Figure 7.14 show that within the waste rock and low grade ore stockpiles, water bodies and streams are commonly close to or above 90% MgSO\(_4\) and have Mg/SO\(_4\) ratios very close to 1.0. However as one moves away from the stockpiles, streams and water bodies become less dominated by MgSO\(_4\) and the Mg/SO\(_4\) ratios move away from 1.0, mostly towards higher values (a depletion of SO\(_4\)). For example, water samples from the Grand
Canyon, in the middle of the NCWP and CWP, average 95% MgSO₄ and have an average Mg/SO₄ ratio of 1.0, run-off on top of the WWP is 90% MgSO₄ and has a Mg/SO₄ ratio of 1.1, further to the east however, downstream of Corridor Creek in the second bund, MgSO₄ accounts for only 53% of the major ions on average and the water has an average Mg/SO₄ ratio of 6.4.
The results also show that the proportion of $\text{MgSO}_4$ and/or the equivalent $\text{Mg}/\text{SO}_4$ ratio (eq/L) within the Ranger mine waters are a better indicator of the strength of a Ranger mineral waste source than any other trace metal or commonly used indicator such as EC. This may be less effective for groundwater where reducing conditions may effect the concentrations of $\text{SO}_4$ in solution, however the $\text{MgSO}_4$ salt is far less affected by changes in chemical conditions such as redox and pH than most of the trace metals, including uranium, and so is more effective than the trace metals as a mineral waste source indicator.

Figure 7.14: $\text{Mg}/\text{SO}_4$ ratio map showing the average $\text{Mg}/\text{SO}_4$ ratio (in eq/L) for each RUM mine water sampling site in this study. Note the CCMBL site has been broken up into its two individual samples to show the difference between the wet season and dry season. See text for further details.
The water samples from the RP2 dewatering bore DW3A (samples R118 and RW209) are an example of this. The proportion of MgSO₄ to major ions in the RP2 dewatering bore has changed only slightly from that of RP2, from an average of 90% to 85%, but is still strongly indicating a dominant mineral waste source where as the ore metal, U, has almost completely lost waste rock source signature, falling from over 6600μg/L to 15-106μg/L. The equivalent Mg/SO₄ ratios in the DW3a bores show that SO₄ has been relatively depleted only slightly with ratios moving from 0.9 in RP2 to 1.2 in DW3a. It should be noted that S isotope studies of Ranger mine waters have also shown very little change in the source of SO₄ from RP2 to DW3a (Lech et al. in press).

RP1 is another good example of the Mg/SO₄ ratio being able to be used to identify a mineral waste source. The RP1 water body, a final release pond for Ranger mine water, was found to have only 17μg/L U and 6μg/L Mn, as well as relatively low concentrations of major ions, yet MgSO₄ accounted for 72% of the major ions in solution (eq/L) and the Mg/SO₄ ratio was 1.5. This indicates that while the metals have been attenuated, either in Coonjimba Creek or through the main wetland filter system, RP1 is still definitively a Ranger mine water, although with some depletion of SO₄.

Further evidence that the proportion of MgSO₄ is a direct indication of influence from the Ranger mineral waste is the fact that a sample of process water, not presented in this study but which can be found in Kilby (2001) and Lech et al. (in press) has MgSO₄ accounting for some 95% of major ions with a Mg/SO₄ ratio, only 1% greater than many of the samples from the Grand Canyon and from the leachate pond water from the NWP. It should be noted that the addition of H₂SO₄ in the leaching process has significantly reduced the Mg/SO₄ ratio in process water to 0.72.

In the groundwater, there is evidence for a MgSO₄ halo on the western side of the mine, with a sharp decrease in mineral waste influence west of the Coonjimba Creek line. Observation bore No.44 (OB44), on the eastern side of Conjimba Creek and closest to the CWP and the sump collecting leachate from the WWP (Sump98), is some 83% MgSO₄ (average) with a Mg/SO₄ ratio of 0.9, where as across the creek to the east, observation bore No.24 (OB24) is only 24% MgSO₄ with a Mg/SO₄ ratio of
122. It could be argued that OB24 has no mineral waste influence at all, but further to the east even still, the proportion of MgSO₄ continues to decrease. Observation bore No.23 (OB23), to the east of OB24 and further from the mineral waste source, is only 12% MgSO₄ with a Mg/SO₄ ratio as high as 151.

Figures 7.13 and 7.14 also show that a lack of water flow from the stockpiles causes a seasonal difference in the % MgSO₄ and the Mg/SO₄ ratio in some locations as has been highlighted for the CCMBL location. A lack of a mineral waste source in the dry season decreased the proportion of MgSO₄ at the CCMBL from 64% to 42%. This decrease in MgSO₄ along with the relatively stagnant dry season water body favouring reducing conditions and a subsequent loss of SO₄ to the sediment interface, has meant that the dry season sample has a much larger Mg/SO₄ ratio of 10.8 compared to the end of the previous wet season of 1.9.

**7.8 SPECIATION**

An investigation into probable speciation within the waters collected for this study was conducted using the geochemical modelling software PHREEQCi, version 2.13 from the USGS. Due to the general nature of the speciation investigation, not all elements were included in the analysis, just the major ions, Mg²⁺, Ca²⁺, K⁺, Na⁺, SO₄²⁻, Cl⁻, HCO₃ and NO₃, and the trace elements U, Mn²⁺, Ba²⁺, Sr²⁺, Ni, and Cu²⁺. In-field parameters were used, including the in-field temperature measurement, and due to the error associated with the eh measurements in this study, an approximate standard pc was derived from the eh-pH stability diagram for natural waters (in Figure 7.2 above) and general conversions to pc such as those found in Stumm and Morgan (1996), being 4 for groundwater and 10 for surface water. The potential errors associated with the assumed pc conditions are acknowledged, however the study was only of a very general nature and not intended to produce accurate concentrations of species, rather relative abundances.

Basically, the geochemical modelling confirmed that Mg and SO₄²⁻ dominate those waters most influenced by interaction with Ranger mineral waste. In such waters, which may be slightly acidic, most of the major cations exist in solution either as
individual ions or with $\text{SO}_4^{2-}$ as a salt. This seems to be the case for Mg, Ca, K, Na, Ba, Cu, Mn, Ni, and Sr. However, in these same waters U is most commonly speciated with $\text{SO}_4^{2-}$ as the uranyl ion either as $\text{UO}_2\text{SO}_4$ or $\text{UO}_2(\text{SO}_4)_2^{2-}$, but is also commonly associated with the carbonate species, in particular as $\text{UO}_2\text{CO}_3$, and $\text{UO}_2(\text{CO}_3)_2^{2-}$. U-hydroxide species also seem like they will be common in those waters most influenced by waste rock interaction, in particular the species $\text{UO}_2\text{OH}^+$ and $(\text{UO}_2)_2(\text{OH})_2^{2+}$. Not surprisingly for the waste rock influenced surface waters, the major carbonate species modelled in solution is $\text{HCO}_3^-$. As the waters become less influenced by interaction with RUM's mineral waste, speciation modelling suggests that carbonate anions take over from $\text{SO}_4^{2-}$ as the most common anion partner for cations. This is particularly the case for groundwater where $\text{Ba}^{2+}$, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{Mn}^{2+}$, $\text{Na}^+$, $\text{Sr}^{2+}$, Ni, and $\text{U}^{6+}$ are dominated by speciation with various anions of $\text{CO}_3^-$. Even Mg in the groundwater is predominantly either a free cation or in the complex $\text{MgHCO}_3^-$. $\text{K}^+$, on the other hand, is still associated with $\text{SO}_4^{2-}$ in the groundwater and many elements still show some preference to no complexation at all.

7.9 CONCLUSIONS

This study has shown that output waters from the stockpile system can be generalised as acidic to slightly acidic MgSO$_4$ solutions of around 31°C. The MgSO$_4$ complex completely dominates the solutions, representing over 90% of all ions in those solutions with direct stockpile influence and being the main determinant of EC. In fact, the MgSO$_4$ complex is so indicative of stockpile influence in these waters that proximity to a $\text{Mg}^{2+}/\text{SO}_4^{2-}$ molecular ratio of 1.0 can be used as a measure of proximity to a stockpile source or an indicator of stockpile influence compared to other sources. Due to the tendency for the MgSO$_4$ complex to remain in solution, the $\text{Mg}^{2+}/\text{SO}_4^{2-}$ ratio may even be a better indicator of stockpile influence than U or even EC. Away from the stockpiles, Mg$^{2+}$ tends to dominate mine waters.
Stockpile output at the surface is also characterised by the trace elements $U^{5+}$ and $\text{Mn}^{2+}$, although $\text{Mn}^{2+}$ seems to vary depending on location around the stockpiles. $U^{5+}$ concentrations can be high, as high as 97.4mg/L were recorded in stockpile influenced water. $\text{Co}^{2+}$, $\text{Ni}$ and $\text{Cu}^{2+}$ are correlated to pH, and become abundant in low pH surface water samples direct from the stockpiles, probably indicating the oxidation of sulphides.

Different chemistries ensure that the best $U^{5+}$ related element in the rock of the stockpiles, $\text{Pb}^{2+}$, is no longer correlated to $U^{5+}$ in the output waters. $\text{Y}$, $\text{Ce}$, and $\text{La}$ show reasonable correlation with $U^{6+}$, the former a potential ore related element in the Ranger rocks (see Chapter 4). The commonly associated alkali earths, $\text{Sr}^{2+}$ and $\text{Ca}^{2+}$ and to a lesser extent $\text{Sr}^{2+}$ and $\text{K}^{+}$ show good correlation in stockpile output waters, all being associated with carbonates and feldspars from the stockpiles (see chapter 4). Although there is not enough data to prove beyond doubt with water chemistry alone, the $U$ v pH relationship in the output waters resembles the solubility curves of $U^{5+}$ minerals such as Schoepite, suggesting that such secondary minerals may play a key role in the stockpile hydro-geochemistry system.

This study has also shown some distinctive regional influence within the stockpiles. The most obvious regional influence is that of the western side of the stockpiles having greater concentrations of $\text{HCO}_3^-$, $\text{Ca}^{2+}$, $\text{Na}^+$, $\text{Si}$, $\text{Cl}$ and $\text{K}^+$ than those sampled from the eastern and southern sides of the stockpiles. This probably reflects differences in geology.

Groundwaters from the stockpile system can be classified as mixed solutions rather than $\text{MgSO}_4$ solutions. Groundwaters proximal to the stockpiles can be differentiated from the surface waters by their larger concentrations of $\text{HCO}_3^-$, probably due to the combination of $\text{SO}_4^{2-}$ reduction, leaching of carbonate from soils and rocks, and lower proportions of complexing ions that allow for the precipitation of $\text{CO}_3^{2-}$-minerals. $U^{6+}$ is less abundant in the groundwaters than in the surface waters, most probably due to reductive conditions and attenuation to Fe-oxide and clays along the groundwater flow path.
Speciation modelling of the stockpile influenced output water shows that most of the major cations exist in solution either as individual ions or with $SO_4^{2-}$ as a salt. $U^{6+}$ is most commonly speciated with $SO_4^{2-}$ as the uranyl ion either as $UO_2SO_4$ or $UO_2(SO_4)_2^{2-}$, but is also commonly associated with the carbonate species, in particular as $UO_2CO_3$, and $UO_2(CO_3)_2^{2-}$. U-hydroxide species also seem like they will be common in those waters most influenced by waste rock interaction, in particular the species $UO_2OH^+$ and $(UO_2)_2(OH)_2^{2+}$. Not surprisingly for the waste rock influenced surface waters, the major carbonate species modelled in solution is $HCO_3^-$. 

As the waters become less influenced by interaction with RUM’s mineral waste, speciation modelling suggests that carbonate anions take over from $SO_4^{2-}$ as the most common anion partner for cations. This is particularly the case for groundwater where $Ba^{2+}$, $Ca^{2+}$, $Mg^{2+}$, $Mn^{2+}$, $Na^+$, $Sr^{2+}$, $Ni$, and $U^+$ are dominated by speciation with various anions of $CO_3^-$. Even Mg in the groundwater is predominantly either a free cation or in the complex $MgHCO_3^-$.
CHAPTER 8

WEATHERING OF THE STOCKPILES AND THEIR CONTRIBUTION TO THE HYDRO-GEOCHEMICAL SYSTEM

8.1 INTRODUCTION

So far this thesis has compartmentalised the stockpile system and investigated each part in turn; the structure and fabric of the stockpiles and how this may affect the flow of water through them; the geological, mineralogical and geochemical composition of the stockpiles; the chemical composition of the major input to the stockpiles, the northern territory’s rainfall; the chemical composition of a secondary but still very important input to the stockpiles, dust suppression water and finally; the geochemical composition of the input water once it has passed through or over the stockpiles, that is the geochemistry of the mine waters.

The final part of the study is to re-focus back into the stockpiles, to attempt to decipher how the stockpiles are weathering and identify the key components in the weathering process. In effect this is an examination of how the stockpile interface changes the chemistry of the input water into the chemistry of the mine waters. Specifically, it is the role of this part of the study to identify the mineral-water interactions driving and controlling the chemistry of the output water.

To do this, this chapter discusses observations made on weathering at the surface of the stockpiles before identifying the key chemical components in the mine waters that are being derived from stockpile weathering. Using these results as well as results and conclusions from previous chapters, this part of the study will then investigate and assess the possible controls on hydro-geochemistry.
8.2 METHODS

All methodology for this chapter is presented in Chapter 2. However, in brief the methods used here include diurnal temperature measurements using a mobile temperature sensor and digital display unit, calculation of a weathering enrichment factor for each mine water sample using Cl as a conservative tracer, a detailed analysis of the historical mine water database, SEM of salt precipitates both from site and some precipitated in the lab.

8.3 CONDITIONS FOR WEATHERING

8.3.1 Weathering Conditions inside the Stockpile: Temperature and Moisture Content

There has been no direct observation made during this research on the internal temperature of the RUM stockpiles and so this remains unknown. Once again, it is argued here that to do this and to end up with precise and meaningful results is very difficult, and even questionable for a fully operational stockpile system. The instrumentation required would need to be set up during the construction of the stockpiles. This instrumentation would not only have to survive the stockpile construction process, but also be set up in a way so that the internal structure and geology of the stockpiles was not changed to accommodate the instrumentation. On top of these problems is the fact that, as has been proven in the previous parts of this research (Chapters 3 and 4 in particular), in a heterogeneous free standing stockpile system such as that of RUM, the number of measurement sites needed to have good representation of the stockpiles is prohibitive both because of cost and because of practicality issues in an operational stockpile system.

The temperatures of waters emanating from the RUM stockpiles ranged between 27 and 34°C. Maximum rock surface temperatures experienced at the surface of the stockpiles were measured as high as 54°C (see below). Maximum ambient air temperatures in Jabiru range from approximately 38-39°C in the wet season to 33-
34°C in the dry. It is difficult to know if any of these temperatures can act as a guide for internal stockpile temperatures.

Most studies that have attempted to monitor temperatures and moisture content inside stockpiles tend to be focused on stockpiles with definitive ARD issues. In such stockpiles the intensive oxidation, an exothermic process, generates heat, which in turn draws in cooler air, setting up a local convection cell, and thus ensuring a continuous feed of oxygen for the oxidation process. It has been envisaged by some, like ANSTO’s Sulfide Solutions group (Garvie, 2003) that such convection cells are intensive enough to ‘suck’ cooler air from outside the stockpiles, in particular through the relatively unconsolidated and uncompacted batter slopes. In theory, such a stockpile scale convective system will have an infinite supply of oxygen and thus will enable the oxidation process to continue until the supply of reactants is exhausted. Such a system can generate relatively high internal stockpile temperatures so that conditions of weathering are far from what would be considered a low temperature surface environment.

Bacteria may also aid in accelerating oxidation (Perkins et al. 1995), and hence potentially increase temperatures, however whilst there should be little doubt that micro-organisms are active in the RUM stockpiles, it is questionable if they are a dominating process.

The structure and hydrology of the stockpiles will also affect the temperatures experienced inside the stockpiles. For example, areas of oxidation in the stockpiles that are frequently flushed during the wet season by fresh ‘incoming’ rain water may be periodically cooled as a result and hence not reach the temperatures that would otherwise have been reached. Areas of long term or at least seasonal saturation will inhibit the amount of exothermic oxidation reactions, and thus stabilise temperatures at lower levels. However, those areas that are blocked off from the large scale inundation of water during the wet season may receive just enough moisture to ensure that an efficient oxidation process is established and therefore may experience higher temperatures than elsewhere in the stockpiles.
There is no evidence for stockpile-scale saturation of the RUM stockpiles as has been modelled by hydrological and geotechnical engineering consultants, not even during the record breaking uninterrupted rainfall days of the 2006/2007 wet season where 813mm was recorded at the mine in 3 days. The water level in a lone stockpile monitoring bore only recently constructed in the centre of the CWP responded to those three days of rain by an increase of only a few metres. The level was already at the bottom of the stockpile, poised within a layer of laterite (Logan, 2007), just as Chapter 3 predicted. Personal observations of the drilling of that particular bore also confirmed the existence of restricted areas of saturation in perched water tables associated with horizons of high clay content, again as Chapter 3 predicted. It has also been proven that it is possible for some areas, most probably submerged clay-pans on Platform Horizons, to be able to retain conditions of saturation or near saturation at least, well into the dry season (observed in this study some 3 months after the last rains of the wet season – refer to Chapter 3).

The observations presented in chapter 3 show that throughout the wet season the base of the CWP is completely saturated up to a level that corresponds with the upper surface of the clay dominated base of the stockpile. This base is a result of the first few years of mining where predominantly it was the weathering profile of the deposits that was excavated. It is also the region of the stockpiles where compaction is greatest due to a combination of experiencing the greatest tensile stresses at the bottom of the stockpile, consistently small grain size, relatively low mineral strength of the dominating clay minerals and the amount of time the material has had to settle and compact. The result is a high matrix potential and an ability of the region to retain water, compared to the less compacted material above it. It must also be recognised that the water levels measured in the CWP throughout the dry season probably also signify intrusion of the underlying water table, having been pushed up into the stockpiles by the increased head pressure (hydrostatic) imposed on the local water table by the stockpiles.
In other parts of the stockpiles it was evident that despite no physical sign of saturation, increased moisture content (an inherent dampness to fresh excavations into stockpile walls) had penetrated into the mineral matrix of some of the schists, allowing cobble-sized rock specimens to be broken open like “a soft cake of soap” literally.

In summary then, conditions for weathering inside the stockpiles will vary depending on spatial location. In regions of compaction with finer grain size and high clay content conditions will be wetter and for longer periods of time. Where saturation is long term, that is semi-permanent (until the stockpiles are removed) like for example the base of the stockpiles, conditions may favour a reductive environment for most of the time. In regions such as perched water tables, where extent of saturation may vary between the wet season and the dry season, conditions of weathering will fluctuate between reductive and oxidative respectively. As compaction increases towards the base of the large stockpiles, so too will moisture content, due to matrix potential, as well as the length of time this moisture will remain post wet season. It may be possible that further into the lower centre sections of the stockpile, in regions that are not the subject of sectional or tunnel style flushing events, moisture content may reach optimum levels for oxidation for long periods of time. It is in these regions that the highest internal stockpile temperatures may be reached, that is if sulfide content is sufficient to generate the required heat, and in small areas, it probably is (see discussion below).

Some sections of the stockpiles will experience frequent flushing, such as sloped Platform Horizons where incoming water is deflected and diverted towards their adjoining buried ramps (see Chapter 3). Areas where tunnelling is occurring will also experience the frequent flushing during the wet season. In these areas, periodic cooling will accompany each flushing event. These areas are the key areas for the transport of materials and weathering products from the stockpiles. Weathered surfaces may be periodically flushed clean so that fresh surfaces can be exposed to the periods of oxidation between flushing events.
Most importantly, it is envisaged here, based on research and observations, that weathering conditions in the RUM stockpiles do not extend to a stockpile scale. That there is no stockpile-scale saturation of the stockpiles during the wet season as is currently modelled by engineering consultants and used at RUM, and there are probably no stockpile-sized convection cells operating either. In some areas in some stockpiles temperatures may be elevated compared to other areas due to higher average sulfide concentrations per cubic area and the associated heat generation from the increased amount of exothermic sulfide oxidation reactions.

Due to the structure of the RUM stockpiles, and the nature of the Northern Territory's top end climate and rainfall pattern, weathering conditions in the RUM waste and LGO stockpiles probably vary, both spatially and through time. These conditions can be discussed in a very approximate sense, based on the hydrological nature of the structures and materials observed, but are yet to be known.

8.3.2 Weathering Conditions at the Surface

A number of experiments were initiated to ascertain the temperatures at which reactions were occurring at the stockpile surface and the nature and speed of physical weathering of rocks at the surface. However these experiments were met with limited success. Despite this, some important observations were made.

8.3.2.1 Temperature

A digital thermometer with a mobile temperature sensor was used to measure temperatures near to the rock surface of a specimen of chloritised dolerite on the SWP in April, August and November of 2000, details of which can be found in chapter 2. Figure 8.1 shows that during the wet season temperatures on rocks surfaces on top of the Ranger Uranium Mine stockpiles can reach as high as 54°C with daily maximums consistently above 50°C, and overnight temperatures decrease to as low as 22°C. During the dry season, despite the lack of rain, the increased distance from the sun ensures temperatures are slightly lower than in the wet, hovering around 45°C for daily maximums, but up to 50°C on occasions, and hovering around 16°C to 20°C for daily minimums.
These are important observations, because it is known that there is an order of magnitude increase in reaction rates when moving from 25°C to 55°C (Lasaga, 1994). This means that weathering reactions occurring at the surface of the RUM stockpiles are occurring much quicker than expected. It also means that laboratory experiments that are aimed at understanding weathering at the surface of the RUM stockpiles, or indeed anywhere in the Northern Territory, will need to incorporate these higher temperatures if they are to accurately portray the conditions for weathering in such systems. This may be particularly important for RUM because unpublished research suggests that changing reaction temperatures from 25°C to 40°C does significantly increase uranium solubility over time (Carpenter, 2000).
It is also important to consider that maximum rock surface temperatures on the stockpile surfaces are being reached in the start and end of the wet seasons, when water is introduced into the system on a relatively regular basis, but in brief periods of convective storm activity. These storms tend to, more often than not, introduce the water onto the surface of the stockpiles in the late afternoon between 3 and 6pm (see Chapter 5). This water does three things. Firstly it can wash away any oxidation products or surface precipitates that have built up on the surface, leaving behind fresh surfaces for oxidation and any other reactions to take place. Secondly, it quickly reduces the temperature of the surfaces undergoing weathering, potentially enhancing physical weathering of surface layers due to thermal adjustment. This was witnessed in April 2000 when within the first 20 minutes of an afternoon storm event, the temperature at the surface of the dolerite dropped from its maximum temperature for the 24 hour monitoring period of over 50°C to near to its minimum of under 25°C.

Thirdly, the rainfall from the convective storm introduces moisture to the surface and the immediate sub-surface to enhance or even ensure oxidation processes taking place during the following period of heating. It has recently been shown by Leon (2004) that moisture content is a crucial factor in the efficiency of oxidation processes such as the oxidation of sulfides and the generation of acidity. In experiments by Leon (2004) an ideal moisture content was achieved whereby oxidation and thus chemical weathering was maximised. The ideal conditions tended to be around 25% saturation (from 4 given conditions of 95%, 70%, 25% and 0.1% saturation).

30cm deep test holes dug into the SWP during the start and end of the wet season proved that whilst the surface of the SWP is completely dried out before the inevitable oncoming rainfall event, the immediate subsurface is not, it remains damp. Moisture contents were not taken, however it would not be unreasonable to suggest that the most immediate subsurface, where rock matter has broken down and formed a relatively inorganic course soil horizon (see Chapter 3), may be a perfect environment for weathering. During the wet season this zone is repeatedly flushed, dried and heated to temperatures close to surface maximums, but never dried completely so that the ideal moisture content for weathering may be maintained for longer and at high temperatures. Of course, when the monsoon is active, these zones will be saturated or
close to saturated often, as well as being flushed, and will therefore be host to completely different weathering conditions, more towards a reductive environment. During the dry season, these zones were observed to be completely dry, and thus a zone of oxidation.

8.3.2.2 Observations of Physical Weathering

A rock weathering experiment was set up on top of the SWP to monitor the progression of the physical breakdown of different waste rock types over time. The rocks selected represented the full spectrum of rocks found throughout the RUM waste rock stockpile system. A total of 19 rocks were selected and placed in an open enclosure made by stringing miners tape around 4 star picks to form a rectangle. After the initial set up, in April 2000, the rocks were measured and photographed from different angles to record their primary condition. During each consecutive expedition the rocks were photographed from similar angles to see if any changes had occurred. However, movement of some of these rocks between the time of the second last and last expedition to RUM rendered the experiment scientifically invalid and so this experiment has not been included in this study. Prior to this very few of the rocks showed any significant sign of breakdown, and it was obvious that more time was needed for the experiment to achieve any significant results. That being said a number of observations were made that are important to note here.

The rock that showed the most signs of physical break-down was the chlorite muscovite quartz schist. This schist had begun to separate along foliation on the upper more exposed surface, to the point where the upper layers were no longer attached to the rock. This was different to the more competent and less schistose darker green chlorite quartz (± sericite) schist which showed no signs of physical weathering at all. This was a little unexpected, since it was hypothesised that the more chlorite rich rocks would weather more quickly. However, it would seem that rock structure may be more important than bulk geochemistry, the more schistose rock allowing more water to penetrate more deeply into the rock in a shorter period of time. This has separated the upper layers and increased total surface area so that the weathering rate of the rock was enhanced.
The rock with the second most signs of physical weathering was a relatively competent chloritised dolerite. Once again it was the structure of the rock that was the most important for the increased visible breakdown. Small pieces of rock had begun to fall away around the edges of the main rock, all related to small fractures. Elsewhere in the stockpiles, this rock showed the most distinctive signs of physical breakdown where it tended to disintegrate in situ into a pile of small blocks with in some cases onion skin type weathering occurring (Figure 8.2). This experiment however, suggests that the distinctive nature of the dolerite weathering may only give the impression that it is the fastest to physically break-down on the stockpiles, and that some of the schists may be just as quick to break-down. Whatever the case there is very little dolerite in Pit#3 and so the dolerite rock is unique to stockpiles constructed pre-1996 (end of mining Pit#1). It is also important to note here that since inherent fracturing and structure seems to be very important to the rate of rock weathering on the surface of the stockpiles, proximity to blasting during mining and the relative response to this blasting of each rock type will also be a factor to the rate of physical breakdown of rocks on stockpile surfaces.

Figure 8.2: A classic example of the distinctive dolerite weathering at the surface of the stockpiles, block fragmenting and onion skin weathering products. Location – SWP.
Other rock types showed very few signs of weathering. This may not mean that they are not weathering at all. The carbonate for instance, will probably not show any noticeable signs of physical weathering in such a short period of time, however at the rock surface water-rock interaction will be slowly dissolving carbonate minerals during the wet season. Over time weathering of the carbonate rocks would be best observed through changes to specimen volume and weight. A reddish/brown tinge on the surface of most of the carbonate rocks that had been exposed to any significant period of time is good evidence of Fe staining from Fe-bearing dolomite weathering.

8.4 ASSESSING THE CONTRIBUTION OF STOCKPILE WEATHERING TO THE CONCENTRATION OF DIFFERENT IONS IN THE RUM MINE WATERS USING CL⁻ AS A CONSERVATIVE TRACER

Due to the fact that the flow path of the RUM mine waters through the stockpiles is relatively unknown, and given the complexity of the stockpile fabric, (refer to Chapter 3), the total surface area for weathering reactions and the time for which such reactions have had to take place cannot be estimated. Thus the precise amount of weathering that has taken place in the stockpiles and the total amount of soluble product this has contributed to the RUM mine waters cannot be known. A further barrier to such knowledge is the fact that most of the RUM mine waters are subject to some degree of mixing with each other, due to the pumping regime within the water management practices of the RUM environmental department, a necessity often simply to control site-wide volumes (for example see the year 2000 water balance for RP2 – Figure 6.4).

That being said, it is possible to gain an understanding into what proportion of the ions and elements in solution within the RUM mine waters may be from sources such as weathering of the stockpiles, relative to rainfall. To do this, ratios of major ions to Cl⁻ (eq/L) in the mine waters are used here against the same ratios in the rainfall. Thus it is assumed that Cl⁻ is a conservative tracer, being the most conservative ion along the flow path between rainfall and the water that has been sampled. This is based on what is generally known about the chemistry of Cl⁻, that Cl⁻ does not significantly
enter into oxidation or reduction reactions, does not form any important solute complexes with other ions unless Cl- concentrations are extremely high, does not form salts of low solubility, is not significantly absorbed on mineral surfaces and is not active in many key biochemical roles (Hem, 1985). Ratios of Cl⁻ (eq/L), notably Ca²⁺+Mg²⁺/ Cl⁻, Na⁺+K⁺/ Cl⁻ and HCO₃⁻/ Cl⁻, have been used previously to estimate the proportion of solutes added to water by mineral weathering relative to cyclic salts sourced from rainfall (Mackay et al., 1988; Herczerg et al., 2001, White and Wasson, 2004).

Rather than using these common weathering ratios, only single ion to Cl⁻ ratios are used here, due to the dominance of Mg above, and to gain an indication as to the contribution of weathering to each individual element in solution. To simplify the results of the analysis, a single value has been created for each ion within each water sample that represents the amount of times each ion has been enriched over its concentration in rainfall. In effect this value is an enrichment factor and has been calculated by:

\[
EF_i = \frac{(X_i/Cl^-_{sample})}{(X_i/Cl^-_{rain})} \quad [1]
\]

Where X = concentration of ion ‘i’ and all concentrations are in eq/L. The Cl⁻ concentration for rainfall used here is the mean concentration of Cl⁻ in the rainfall samples collected for this study (refer to Table 5.1), disregarding the three samples enriched in Cl⁻ (refer to Figure 5.11). The three enriched samples were disregarded due to the fact such enrichment only occurs in the SOWS rains on an inconsistent basis, and as such is not representative of the entire wet season rain Cl⁻ concentrations. Leaving these samples out works to increase the average ion/ Cl⁻ ratios in the rainfall (i.e. increases the denominator in [1]) and hence minimises the EF value for each ion. In other words the EF values given here are conservative.

NO₃⁻ has been calculated differently due to the large and consistent difference between NO₃⁻ concentrations in the SOWS rains and all other rainfall (refer to Chapter 5). Thus the NO₃⁻/Cl⁻ rain for all those samples collected at the start of the wet season (labelled 300-series) is the mean NO₃⁻/Cl⁻ ratio for the SOWS rains only,
where as for the rest of the samples it is the mean NO$_3$ / Cl$^-$ ratio for the EOWS rains only.

Figure 8.3 displays the EF for each sample, in the same sequence as that of Figure 7.3. Note that in Figure 8.3 an EF above 1.0 signifies enrichment of the ion relative to rainfall and an EF below 1.0 signifies a loss of the ion relative to rainfall. The dashed line in Figure 8.3 is the Cl$_{sample}$/Cl$_{rain}$ ratio for each sample, effectively a measure of the amount of concentration that has occurred through evaporation for each water sample. It should be recognised that the evaporation enrichment value is in no way related to the EF because evaporation is inherently accounted for in the EF calculation of [1].

It is important here to highlight the fact that at RUM, the EF calculation will not necessarily be a relative measure of the influence of only the waste and LGO stockpiles in most of the mine waters due to mixing. RP2 receives water from P3 as well as run-off from the mine area, including possible influence from the ore grade stockpiles. Other than direct rainfall input, P3 water will have been sourced from run-off from directly around the pit as well as waters percolating from the wall rock, and may also include some ore influence. It is possible that P3 may also, at times, receive water from the NWP. Sump98 may receive water from RP2 at times, just as RP2 sometimes receives water from Sump98.

However, for some of the waters collected for this research it can be assumed that, other than rainfall, a waste and LGO stockpile source, is the only other influence. These waters are those of the GC water body (RW325 and RW407), the LGO sump (RW211, RW212 and RW308), the WWP run-off channel sample (RW323), the two samples of a small stream emanating from the WWP (RW315 and RW316), the NWP leachate pond sample (RW405), the RP4 sample (RW408) and the submerged platform leachate (RW215).
Figure 8.3 shows that Mg$^{2+}$ and SO$_4^{2-}$ are the most enriched ions in the RUM mine waters relative to rainfall, being orders of magnitude more enriched than the other major ions. That is except for those samples of the bund on Corridor Creek (CCMBL - RW105 and RW205) and the two bores, OB23 and OB24, north of the western edge of the WWP (RW303 and RW310). In these samples it seems that Mg has a greatly reduced EF and that SO$_4^{2-}$ is almost completely sourced from rainfall in the bund water and in fact depleted in the two observation bores. The latter may be an indication of sulphate reduction, but both are definitely an indication of a significantly reduced influence from mineral waste. The waters most enriched in Mg and SO$_4^{2-}$...
includes samples from the LGO Sump (RW211 and RW212) and the sample from the drainage collection pond of the NWP (RW405). This is consistent with the assumption made above, that these waters are some of those with the most direct influence from a stockpile weathering source with the least amount of potential mixing from other water bodies.

\[ \text{Ca}^{2+} \text{ and } \text{HCO}_3^- \text{ also have relatively high EFs throughout the entire data set, although generally present in an order of magnitude less concentration than } \text{Mg and } \text{SO}_4^{2-}. \]  

Therefore, it can be stated that after Mg and \( \text{SO}_4^{2-} \), \( \text{Ca}^{2+} \) and \( \text{HCO}_3^- \) are the next most abundant ions produced from weathering of the RUM rocks. The highest EFs for Ca are once again samples RW405, RW211 and RW212, the same samples containing the highest enrichment of Mg and \( \text{SO}_4^{2-} \), and further proof that the EFs are representative of waste and LGO weathering. Like Mg and \( \text{SO}_4^{2-} \), \( \text{Ca}^{2+} \) EF values fall significantly for the two CCMBL samples to the point where a large proportion of the \( \text{Ca}^{2+} \) concentration can be explained by a simple rainfall source.

\[ \text{HCO}_3^- \text{ EF values are generally high for all groundwater samples, but this is not uncommon for groundwaters (Hem, 1985). The highest concentrations of } \text{HCO}_3^- \text{ in the RUM mine waters occurs in the samples from the SWP (R114 and R115) and from the EOWS and dry season samples of the bore DW3a (RW118 and RW209), a dewatering bore between RP2 and P#3. The enrichment in DW3a is caused by a direct carbonate source influence; the very purpose of the bore was to dewater a known carbonate aquifer transferring water seeping from RP2 into the southern walls of Pit#3. The SWP samples are also influenced by the same source, as they do originate from DW3a, however it should also be considered that almost all of the waste grade carbonates mined from P1 have been concentrated in the SWP area near to the site at which the SWP water samples were collected (see Chapter 4). The pH of the waters in both of these samples is further proof of the } \text{HCO}_3^- \text{ enrichment, DW3a has the highest pH for all of the groundwater samples (pH 7.32 to pH 7.89), and the pH of 8.49 for sample R114 is the highest of all of the surface waters.} \]
An interesting situation occurs in the CCMBL samples (RW105 and RW205), where HCO$_3^-$ EF increases at the same time as Mg$^{2+}$, Ca$^{2+}$, SO$_4^{2-}$ and K$^+$ EFs decrease significantly. The simplest explanation for this is a lack of ion supply from stockpile weathering due to the pond’s distance from such a source, coupled with a proximal HCO$_3^-$ soil source. Concretions of CaCO$_3$ material (calcrete) were observed in dry stream beds within the vicinity of CCMBL (see Kilby, 2001) suggesting that a soil source of CO$_3^{2-}$ does exist for this water body. The CCMBL is the furthest water body sampled in this study from a direct stockpile source. However, it is also possible that bacteria induced SO$_4^{2-}$ reduction is occurring in the CCMBL, which is well vegetated with marshes and does not flow or even receive any water during dry periods.

It would seem that Na$^+$ and K$^+$ are the least enriched major ions in the RUM mine waters relative to rainfall, with K$^+$ being less enriched than Na$^+$ in most samples. In fact in almost all of the groundwater samples K$^+$ seems to have been lost and for most of the surface waters K$^+$ concentrations can almost be explained entirely by rainfall input. In Chapter 4 it was shown that most of the K$^+$ in the unweathered RUM waste and LGO material resides in muscovite and related minerals, such as illite and sericite, which are relatively resistant to weathering, hence the relative lack of K$^+$ from stockpile weathering in the RUM mine waters. Figure 4.13(a-b) shows that Na is not in any significant proportions in the waste and LGO material, mostly below 0.25% or 2500ppm and thus a lack of source is the mostly likely explanation for the low Na EF values.

The EFs for NO$_3^-$ mostly fall under or near to 1, suggesting that most NO$_3^-$, when present, is sourced from rainfall. This is particularly the case for the SOWS samples of November 2000, whereby the highest NO3- EFs correspond to samples collected from shallow streams soon after major rainfall events (sample’s RW315, RW316 and RW323 were all sampled during a significant rainfall period lasting 5 days, beginning with a 20mm event in the 24 hours prior to 23/11/00 and ending with a 47mm event in the 24 hours previous to 27/11/00). The higher concentrations of NO3- in the dry season and end of 2001/02 wet season samples are difficult to explain. They may be a factor of the method by which they were calculated (see above) but such concentrations may also suggest that biologically mediated nitrification processes are at work in the more stagnant ponds when the wet season has completely finished (the
400-series samples were collected after the cessation of the wet season, where as the 100-series samples were collected during the last rains of the wet season) and during the dry season. As already mentioned, NO₃⁻ is absent from most of the groundwaters, a possible consequence of reduction or denitrification processes. The only clear conclusion that can be made by the NO₃⁻/Cl⁻ ratios here is that further investigations are needed into the high NO₃⁻ concentrations of the dry periods, particularly for the sample with the highest EF for NO₃⁻, that of the low pH leachate from the submerged Platform Horizon near the WWP. What should be clear from the ion/Cl⁻ ratios is that the stockpiles are the definitive influence on RUM mine water chemistry.

8.5 CHLORITE WEATHERING – THE DOMINANT CHEMICAL REACTION IN THE RUM WASTE AND LGO STOCKPILES AND A MAJOR CONTRIBUTOR TO RUM MINE WATER CHEMISTRY

The dominant chemistry in the RUM mine water can be explained by the weathering of the most dominant rock type in the waste and LGO stockpiles, the quartz chlorite ± muscovite schist. Mineralogical investigations of the quartz chlorite ± muscovite schist (see Chapter 4) show that this schist is almost completely altered to chlorite with two major chemical varieties, a Mg-Al variety and a Fe-Mg variety, the former being the most common. However, chlorite alteration in the Ranger ore bodies has been pervasive, and almost all non-carbonate rocks mined from the two open cut pits to date have undergone some degree of chlorite alteration.

Importantly, much of this chlorite is in the form of a cryptocrystalline matrix that is too small for individual mineral identification by chemistry under a 4μm EMPA x-ray beam (see Chapter 4). Therefore chlorite’s domination of the mineral weathering influence on solution chemistry within the RUM mine waters due to its abundance is compounded greatly by the fact that per unit area, chlorite also has the largest potential surface area available for weathering compared to all other minerals in the primary waste rock. Such surface area potential is ensured in the stockpiles due to the combined effect of the inherent weak strength of the schist and its resultant break-up during blasting, digging, trucking and dumping. This probably ensures a plentiful
supply of clay sized chlorite in the finest fractions of the stockpiles and surface platforms ready for weathering.

Although technically not the same rock, and not exposed to the same conditions as that of a stockpile, the weathering of the quartz chlorite schist has been previously studied in detail at Koongara (Sverjensky, 1992, Murakami et al.. 1996). Sverjensky (1992) found by comparing geochemical modelling to groundwater chemistry that almost all groundwaters of the Koongara deposit, shallow through to deep, were controlled by the weathering of Mg-rich chlorite and muscovite minerals in the schist to kaolinite in the weathering profile. According to Sverjensky (1992) modelling of the Koongara groundwater chemistry suggested that all waters had evolved through weathering reactions such as

\[
\text{chlorite} \rightarrow \text{kaolinite}
\]

\[
\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10} (\text{OH})_8 + 10\text{H}^+ = \text{Al}_2\text{Si}_2\text{O}_5 (\text{OH})_4 + 5\text{Mg}^{2+} + \text{SiO}_2 + 7\text{H}_2\text{O} \quad [2]
\]

and

\[
\text{sericite} \rightarrow \text{kaolinite}
\]

\[
2\text{KAl}_3\text{Si}_3\text{O}_{10} (\text{OH})_2 + 2\text{H}^+ = 3\text{Al}_2\text{Si}_2\text{O}_5 (\text{OH})_4 + 2\text{K}^+ \quad [3]
\]

This is an end-product reaction set, with the result being the introduction of Mg$^{2+}$, K$^+$ and Si into solution. Even if the weathering of the Fe-rich chlorite is considered along with the Mg-rich chlorite above, the element mix released to solution would not be significantly different, since Fe would quickly precipitate from the oxidising environment. This is precisely what has occurred in both the Ranger weathering profile (Milnes, 1988 and Bernal, 2003) and the Koongara weathering profile (Murakami et al.. 1996) where Mg has been leached by solution and Fe has been consumed by the formation of ferrihydrite, goethite and hematite.

Whilst the RUM mine waters, including most of the groundwater, have considerably higher concentrations of K$^+$ than the Koongara ground water compositions (in Sverjensky, 1992), the Mg/K ratios in the RUM mine waters are up to an order of magnitude higher in some cases. This may be an indication of the immature state of weathering in the stockpiles, where the weathering of the more conservative
muscovite type minerals has not progressed to any significant degree, at least to the extent of the Koongara weathering profile, and thus has not contributed significantly to the relative concentration of elements in solution exiting the stockpiles. Such a comparative should be expected with Koongara, where weathering time may be measured in millions of years, or at least tens of thousands of years compared to the maximum of 22 years (as of 2002, the final sampling expedition to RUM) for the unweathered rock placed on the RUM waste and LGO stockpiles.

In support of such a conclusion is the fact that the deeper Koongara groundwater in contact with the relatively unweathered schists had Mg/K ratios over three times that of the shallow groundwater in contact with the weathering profile (Sverjensky, 1992). Also in support of this and the subsequent dominance of Mg\(^{2+}\) in mine waters is the result of a limited experiment by Wells et al. (2001) on the kinetic dissolution of a single sample of pulverised quartz chlorite schist from RUM, where it was noted that the release of ions into solution were particularly rapid for Mg\(^{2+}\). Within the RUM waste and LGO stockpiles the dominance of Mg\(^{2+}\) in solution may be enhanced significantly by the fact that the largest proportion of the chloritised schist is often made up of a ubiquitous cryptocrystalline matrix and veins of chloritic material dominated almost completely by Mg-Al chlorite over Fe-Mg chlorite (see chapter 4), in other words a larger source stock of Mg\(^{2+}\) than if only Mg-Fe chlorite dominated.

In the RUM mine waters the only sample that seems to have K\(^+\) sourced from anything other than rainfall (according to the EF values above) is RW405, that of the NWP leachate collection pond. This sample also has a high Si concentration relative to other surface waters at RUM, second only to RW215, the sample collected from the submerged platform. The NWP has been predicted here (see Chapter 4) to consist mostly of UMS schist and apart from its base, is made up almost entirely of un-oxidised material from below the Ranger No. 3 weathering profile, but more importantly, in a zone of significantly increased occurrences of pyrite. A relatively low pH (pH 4.82) coupled with an extremely high SO\(_4\)\(^{2-}\) concentration suggests that the schists in the NWP may have had relatively high average pyrite content upon placement in the stockpile. Fresh sulfides were observed in the area within P3 where the material in question had originated from (see Figure 4.21). As a result of the subsequent increased acid production by larger amounts of pyrite weathering.
(discussed further below), the NWP may have an increased ability to weather the muscovite minerals (mostly likely dominated by the extremely fine grained sericite – see chapter 4) and maintain the excess ions in solution. This in turn results in sample RW405 containing more of the product from reaction [3]. It is even possible that the rocks of the NWP have much larger proportions of the sub-microscopic sericite/illite material, given that they come from one of the most altered regions of the pit, the SW corner, although this is probably of minimal, if any, influence.

Whilst the chemistry of the RUM mine water may be indicative of the initial weathering of Mg-Al chlorite towards kaolinite, it does not provide information as to the progression of this weathering. The evolution of chlorite weathering has been well studied (Herbillon and Makumbi, 1975, Eggleton and Banfield, 1985, Proust et al., 1987, Buurman et al., 1988, Murakami et al. 1996, Carnicellie et al., 1997, Giorgetti et al., 2000 and Aspandiar and Eggleton, 2002). At Ranger, Bernal (2003) suggests a number of interim steps for chlorite weathering in the weathering profile of P3 depending on the chlorite’s initial composition (Fe-rich or Mg-rich). Mg-rich chlorite (chlinoclore) weathers to vermiculite before kaolinite via a chlorite/vermiculite interlayered structure (see also Herbillon and Makumbi, 1975, Carnicellie et al., 1997, Giorgetti et al., 2000 and Aspandiar and Eggleton, 2002) where as Fe-rich chlorite (chamosite) weathers to smectite before kaolinite via a chlorite/smectite interlayered structure. Others also suggest that smectite occurs as a weathering product within the chlorite weathering process, although at a final stage between vermiculite and kaolinite (Herbillon and Makumbi, 1975, Proust et al., 1987 and Buurman et al., 1988), including Milnes (1988) for the RUM waste and LGO stockpiles. Milnes also finds smectite in the weathering profile of Ranger No.1, however, von Gunten et al. (1996) found no smectite beneath 6 metres in the Ranger No.3. weathering profile.

Murakami et al. (1996) make no mention of a smectite interim step for Koongara, which would need to gain Na⁺ or Ca⁺, identifying smectite in only one sample of 14 at Koongara and concluding that if smectite is related to chlorite weathering at Koongara, it is only short lived. Hence, Murakami et al. (1996) believe the evidence at Koongara proves that both Mg-rich and Fe-rich chlorite varieties weather to vermiculite with the Fe-rich varieties losing only minor amounts of Mg and the
composition of the vermiculite also having no relationship with the initial chlorite composition, as had been previously suggested by Ross and Kodama (1976 in Murakami et al. 1996).

XRD of samples from a limited amount of drilling into the stockpiles by Riley et al. (1993) found only one sample that contained smectite (10% of sample), at 4 metres depth in the NCWP, and did not find vermiculite. However, Milnes (1988) found that both smectite and vermiculite were prominent clay minerals in trenches and gullies of early stockpile surfaces.

Five samples of suspended sediment in run-off from the WWP and a single sample of particulate matter in leachate from the WWP, collected on 0.45\(\mu\)m filter paper by staff of EWL Sciences Pty. Ltd. for a study external to this, were analysed by XRD for this thesis. Standard procedures for identifying clay minerals by XRD as outlined in the Methods Chapter, were undertaken, the resulting XRD traces are provided in Appendix 13. The XRD traces show that quartz, chlorite, kaolinite and muscovite/illite are the primary phases in this particulate matter. The absence of smectite is definitive and whilst the presence of small amounts of Mg-vermiculite could not be ruled out, it was definitely not present in any significant quantity.

The XRD study of particulate matter in water samples from the WWP performed here are far too limited in their extent for any conclusions to be made from them alone. The kaolinite may not be the result of weathering within the stockpile, instead simply a mineral from the Ranger weathering profile introduced to the stockpile through dumping, a conclusion also made by Riley et al. (1993) in regards to smectite. Clays were observed here to be prominent features of all surfaces of all stockpiles with surface platforms (see Chapter 3), some of this will be brought in by mine vehicles traversing clay dominated surfaces of the access roads to the mine and stockpile areas (own observations).
That being said, the amount of Mg that is being leached from the stockpiles dominated by the quartz chlorite schist (re-sample RW405 and recent work by Puhalovich et al., 2002) suggest that the Mg-Al chlorite is well on its way towards alteration to kaolinite. Vermiculite should be present in the stockpiles within areas dominated by the chloritised schist. Based on work by others (Milnes, 1988 and Riley et al. 1993), it would seem that smectite is also present in the stockpiles, however it is believed that further work needs to be achieved in order to determine its abundance, and whether it is primarily from chlorite weathering or from remnant feldspars from other lithology, including the HWS schist. Because of its shrink-swell property with changing hydration state the abundance of smectite may be important to closure and rehabilitation considerations at RUM, particularly considering that a 50-50 mix of locally sourced weathered material to primary rock is planned for the store and release cover system on the current final landform design (Hollingsworth, 2006).

8.6 SULFIDES - THE PRIMARY SOURCE OF SO₄ IN THE RUM MINE WATERS

Rainfall will introduce SO₄²⁻ to the RUM mine waters and their catchments (Chapter 5 and 6 –see Table 6.5, see also further discussion below) however, the SO₄²⁻/Cl⁻ ratios above suggest that very little of the SO₄²⁻ in the RUM mine waters influenced by the stockpiles can be accounted for by rainfall input alone; for instance according to the SO₄²⁻/Cl⁻ ratios as little as 0.17% of SO₄ in sample RW405 has been sourced from rainfall.

Another potential source of SO₄ is from the S prill stockpile, the raw S source for the RUM acid plant. There is some visual evidence that run-off from the S stockpile enters a culvert beneath the main mine access road into RP2, however the potential contamination of RP2 seems limited compared to water input from other sources, and even if this did occur, it does not explain the extent of S dominance throughout all of the RUM mine waters. Although there is also some evidence of dispersion of the S prill from a combination of transport via tyres on trucks and other mining equipment, as well as some limited wind transport, the limited amount and extent cannot explain the SO₄ dominance across the entire site.
Recent $\delta^{34}S$ isotope studies on some of the RP2 samples by Lech et al. (in press, see also Kilby, 2001), samples also analysed chemically for this study, are inconclusive as to the influence of S-prill on RP2. The S34 values for RP2 waters were however somewhat closer to the values received for samples of sulfides collected from various parts of the Ranger waste rock stockpiles, and thus point to a Ranger rock sulfide source.

It was shown in chapter 4, that average S concentrations of the Ranger rocks, according to studies made to date, are relatively low. However, recent observations made in Pit#3 revealed that there are localisations of increased sulfide concentrations within the deposit, and importantly these can occur in the waste. The western wall of Pit#3 for instance is a definitive sulfide ‘hot spot’ where waste grade chert, carbonate and schist has a high content of visible sulfides, mainly chalcopyrite and pyrite (see chapter 4 for further detail). This seems to be related to a structural control on fluids containing the S, as well as the carbonate dissolution process that has been postulated as part of the ore formation process. Chalcopyrite is associated with carbonate veins in the alleged replacement chert, as well as on the walls of large vughs in the carbonate and carbonate coated vughs in the chert. In some circumstances, this chalcopyrite can be relatively massive and pod-like. In the same zone, where tectonically mobilised metasediments have been pushed up against the basement Nanambu gneissic complex, pyrite is common in the schists infilling fractures and coating foliation surfaces.

Higher sulfide concentrations have also been observed in waste schist within ore zones. This is particularly the case where graphite is present, and is probably indicative of the generally reductive environment near to ore formation, an environment necessary to precipitate the uraninite minerals and argued to be the main trigger for mineralisation. Due to the close proximity of this material to ore, and the nature of the grade control methods currently in practice at RUM (see discussion below), some of this material will not enter the waste grade stockpiles. However, it is just as likely, and for the same reasons as above, that some of the ore material with a probability of a higher sulfide content will enter the waste grade stockpiles. Thus,
there are areas within the waste and low grade ore stockpiles that contain relatively high concentrations of sulfides that can in turn contribute large quantities of SO4 to any water that interacts with them.

Importantly however, SEM studies of schists with as low as 0.023% SO3 show that sulfides, whilst not visible in hand specimen are still not uncommon. In such samples pyrite is the primary sulfide and is found disseminated throughout but mainly within cleavage partings of chloritised mica (see Figures 4.7 and 4.8). There is little doubt that although high concentrations of chalcopyrite occurs in some localities with the Ranger deposits, pyrite is the most common sulfide ion overall (see Table 4.7 and Table 4.8).

Considering the RUM waste and LGO stockpile system as a whole, given that high grade material has a greater probability of containing pyrite than low grade material (see chapter 4), it can therefore be concluded that the higher grades of LGO rock are larger contributors of SO42- to the RUM mine waters than waste grade material per unit volume. Given that there is more material of grade 2 and above than there is waste grade (grade 1) (as of January 2007 - Dunstone, 2007), the LGO material will also be the largest absolute contributor to SO4 in the RUM mine waters.

Based on the S content of the primary grade 3 composite sample of P#3 rock (which actually only contained schist and pegmatite according to geologist descriptions) (Jones and Hughes, 1999) and the calculated maximum pyrite content of Table 4.7, a 100 tonne load of grade three primary rock from P#3 (approximating a RUM haulage vehicle load for a CAT 777 truck) may introduce some 70kg of S as pyrite to a stockpile. Thus a single RUM truck load of grade 3 material can produce a maximum of 200kg of SO42-, or approximately 56,000 litres of leachate with the same SO42- concentration as that of sample RW405, the leachate from the NWP; that is 3744.7mg/L SO42-. Alternatively, a single truck load of grade 3 material from Pit#3 can produce some 447800 litres of RP2 water at the end of the wet season (using April 2001 figures from this study).
It should be very clear from this evidence, that the most important source for the dominating $SO_4^{2-}$ ion in the RUM mine waters is the weathering of sulfides in the RUM waste and LGO stockpiles. As is discussed below, there is another source that adds complexity to the issue, however despite this, it is the weathering of the sulfides, in particular the pyrite in the quartz chlorite mica schists, both on fracture surfaces, foliation planes, and disseminated throughout cleavage partings in the chloritised mica laths, that is the primary $SO_4^{2-}$ source for Ranger mine water.

8.7 ACID PRODUCTION – DOES IT PLAY A ROLE IN DISSOLUTION DYNAMICS, MINERAL WEATHERING AND THE GENERATION OF SOLUTE FROM RUM WASTE AND LGO STOCKPILES?

8.7.1 Acid Production and RUM

This study has reinforced the already well known view, at least among those within ERA, ERISS and associated researchers, that $SO_4$, along with Mg, is by far the most dominant ion in the RUM mine waters. This study and the recent work by Lech et al. (in press, also in Kilby, 2001) has also shown that where the MgSCU ion is dominant at RUM, pyrite in the RUM rocks, and thus stockpile, is the most likely source.

To extract the S from pyrite into solution, the pyrite in the rock must first be oxidised, whereby the pyrite becomes catalysed into aqueous ferrous Fe (FeII) and $SO_4$. At its most basic, pyrite oxidation can be conceptualised by the following reaction:

$$2FeS_2(s) + 7O_2(g) + 2H_2O(l) \rightarrow 2Fe^{2+}(aq) + 4SO_4^{2-}(aq) + 4H^+(aq) \quad [4]$$
where the end result is the production of free $H^+$ ions via the formation of the strong acid, $H_2SO_4$. However, close to the reaction site the FeII from reaction [4] is quickly oxidised to ferric Fe (FeIII) and much more acidity from free $H^+$ can subsequently be produced by the following 2 follow-on reactions:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \quad [5]$$

$$FeS_2(s) + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{3+} + 2SO_4^{2-} + 16H^+ \quad [6]$$

where FeIII forms an hydroxide or begins oxidising more pyrite.

In other words, the oxidation of pyrite to release $SO_4$ into solution produces considerable amounts of acidity. As is well known, this acidity will work to increase the dissolution rate of those minerals directly adjacent the oxidising pyrite and then, if not consumed in buffering reactions, will enhance the solubility of those metals released by dissolution, as well as those released by the oxidation of the pyrite itself.

So, if $SO_4$ is the most dominant ion in the mine waters of RUM, and it has been proven that the S is derived almost entirely from sulfides in the Ranger rocks, then it follows that acid produced by sulfide oxidation is a fundamental process within the RUM waste and LGO stockpiles and potentially one of the driving forces behind mineral weathering and solute generation within them. The question is, is there any direct evidence that acid generation in the RUM waste and LGO stockpiles, other than the dominance of sulfide derived $SO_4$ in the mine waters, occurs on a scale larger than that of the mineral-water interface?.

In general, it is this question that seems to have lead ERA and associated researchers to conclude that acid generation is not an issue at RUM, since the most direct evidence for it, acid mine or acid rock drainage (AMD or ARD respectively), does not occur in the stockpiles. However, in clear contrast this research shows there is in fact acidic drainage occurring in certain areas of the RUM stockpile. Drainage sampled from the NWP (sample RW405) had an in situ recorded pH of 4.82, drainage from the WWP had an in situ pH of 5.18-5.26, and a single seepage sample from a fresh excavation into a grade 1 stockpile on the western side of the CWP had a pH of 2.9. In
2002, an internal consultant report also found similar pH drainage at the NWP (Puhalovich et al. 2002), and yet still there was no conclusion of acidic drainage being a potential issue at RUM.

So then, why has there been a local perception that acidic drainage does not occur at RUM when only two seasons of water sampling in this research revealed that it does? It is believed here that there are two main reasons for this. Firstly, the extensive ERA mine water monitoring regime is biased towards retention pond waters and downstream monitoring stations. Such waters will not give accurate representation of the chemical conditions in drainage at the stockpile interface, factors such as groundwater input, direct rainfall input, evapo-concentration, lake ‘turnover’, algal growth, oxygenation, redox and temperature will ‘cloud’ the signatures of rock-water interaction and mineral weathering kinetics and solubility in the stockpiles. To complicate interpretation even further, the RUM pond waters are affected by mixing by the water management pumping regime between ponds and other waters, effectively blending pond signatures. Thus, by the time a sample of water is collected from a pond, it is far from representative of stockpile drainage at all, and in the case of RUM, has mostly become neutral to slightly alkaline (for example see chapter 6 in regards to RP2 chemistry and see Figure 8.5 below). Therefore, although it is not the purpose of this study to advise on environmental management strategies at RUM, it must be concluded here that the RUM water monitoring sampling regime is inherently inadequate, as it does not give any warning of potential environmental problems that may be occurring in the stockpiles.

The second reason why there is a perception at ERA that ARD does not occur at RUM is a lack of understanding of how ‘acid’ a water must be before it signifies that acid generation has occurred. This perception is probably built on hearsay from worst case scenarios, where the pH recorded in stockpile drainage streams (not retention ponds) has been extremely low. It is true, such extreme conditions do not seem to be occurring at RUM, at least not extensively as far as recorded data is concerned (the pH of 2.9 recorded for this study is very low), however it is argued here that this does not equate to a conclusion of an absence of significant acid generation in the stockpiles.
The in-stream stockpile drainage pH recorded in this study for a number of locations of near to and below pH 5 is a sign that acid generation is an important weathering mechanism in the RUM stockpiles. It shows that in some of the stockpiles, or in some locations within the stockpiles, the net reaction product is one of acid rather than neutral or alkaline. It thus shows that the oxidation of sulfides is an important factor in generating the pH conditions of some stockpile drainage streams, and it shows that early and fast reacting carbonate minerals that could buffer such acidity almost immediately are either too slow in reacting or their volume is too small to counter the acid production from sulfide oxidation.

This does not mean that buffering reactions are not occurring; indeed it is argued here that the volume of acid production in certain stockpiles at RUM is actually being masked by buffering reactions, so that drainage stream pH is not a true representation of the amount of sulfide oxidation, acid production and overall mineral weathering of the stockpiles.

Based on reactivity, the main mineral groups existing in the primary Ranger rocks, disregarding secondary minerals, that have the potential to be acid buffering in the stockpiles are the carbonates (magnesite, dolomite, calcite), chlorites (throughout all rocks), amphiboles (from the amphibole rock), feldspars (from the pegmatite and some Hanging Wall Sequence Schists) and biotite (partly preserved in the schists in some places). Table 8.1 is a general representation of relative reactivity for many of the major rock forming minerals, including the five stated for RUM, at pH 5. As Table 8.1 shows, the four silicate groups identified for RUM are generally considered less than half reactive as the carbonates at a pH not too dissimilar to some of the stockpile drainage measured in this study. Also, apart from chlorite, which has pervaded all of the Ranger rocks, the total relative volumes of the rocks containing the silicates highlighted above are probably too small to be considered as even minor contributors to the acid buffering capacity of the RUM stockpiles.

Geologically, the carbonates are mostly restricted to the Lower Mine Sequence, a sequence that current mining does not target. As a result the amount of carbonate in the waste and LGO stockpiles is limited and as has been shown in Chapter 4, when it has been mined in the past (Pit#1) it has been stockpiled separately to a large extent.
Thus the carbonates probably do not have a large potential for buffering acidity at all locations within the RUM stockpiles. In any regards, the fact that drainage pH in this study was measured to be near to and less than pH 5, suggests that even if carbonates are buffering acid production, the reactions are in not enough volume to adequately neutralise acidity in the particular stockpile drainage in question.

<table>
<thead>
<tr>
<th>MINERAL GROUP</th>
<th>TYPICAL MINERALS</th>
<th>RELATIVE REACTIVITY AT pH 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolving</td>
<td>Calcite, aragonite, dolomite, magnesite, brucite</td>
<td>1.0</td>
</tr>
<tr>
<td>Fast weathering</td>
<td>Anorthite, nepheline, olivine, garnet, jadeite, leucite, spodumene, diopside, wollastonite</td>
<td>0.6</td>
</tr>
<tr>
<td>Intermediate weathering</td>
<td>epidote, zoisite, enstatite, hypersthene, augite, hedenbergite, hornblende, glaucophane, tremolite, actinolite, anthophyllite, serpentine, chrysotile, talc, chlorite, biotite</td>
<td>0.4</td>
</tr>
<tr>
<td>Slow weathering</td>
<td>albite, oligoclase, labradorite, montmorillonite, vermiculite, gibbsite, kaolinite</td>
<td>0.02</td>
</tr>
<tr>
<td>Very slow weathering</td>
<td>K-feldspars, muscovite</td>
<td>0.01</td>
</tr>
<tr>
<td>Inert</td>
<td>Quartz, rutile, zircon</td>
<td>0.004</td>
</tr>
</tbody>
</table>

Table 8.1: Relative reactivity of major rock forming minerals at pH 5. Taken from Mills (2007) based on data from Kwong (1993a, 1993b) and Sverdrup (1990). Note, minerals observed in the RUM rocks have been highlighted in bold type.
This leaves chlorite as the sole mineral for large scale buffering potential in the RUM stockpiles, which it is. As Chapter 4 has clearly shown, chlorite is by far the dominant mineral in the Ranger deposits, pervasive throughout all rock types, but particularly in the UMS, where it has replaced all fero-magnesian minerals and has been introduced via fluids as an extremely fine grained (sub 4μm) matrix infill. In some parts of the HWS chlorite has replaced large volumes of amphibolite, most pegmatite in Pit#3 has been completely chloritised and there is even a rock type, the Massive Chlorite rock, which consists almost entirely of fine grained chlorite.

Figures 4.7, 4.8, and 4.21 and the related discussion from Chapter 4 show that sulfides can be found in veins, as smears along foliation plains, disseminated in the cleavage planes of chloritised mica, and pyrite is particularly more common in the intensely chloritised zones near to the ore body. Thus, chlorite is one of the first minerals to come into contact with any acid produced by pyrite oxidation. It has already been shown above that chlorite is a significant contributor to the Mg$^{2+}$ content of the Ranger mine waters, and so there is little doubt that mineral-water interaction with chlorite is occurring on a large scale.

In a major study on the dissolution kinetics of chlorite, through experimental work and a review of available data, Lowsen et al. (2005) and Lowsen et al. (2007) found that the chlorite dissolution rate is highly pH dependant. Figure 8.4 shows that the chlorite dissolution rate was found to be an order of magnitude higher for a pH of 3 and 4 compared to a pH of 7-10 (Figure 8.4a). Thus, chlorite weathering in the stockpiles will be far greater under acidic conditions than under alkaline conditions. Importantly, in Lowsen et al.’s (2005) chlorite dissolution v pH graph (Figure 8.4b), there is a noticeable potential increase at pH 4.5, despite the smooth curve that has been drawn through the data. Such pH is very close to those measured in the low pH stockpile drainage found in this study and that of Puhalovich et al. (2002). Given this, it is argued here that significant acid generation is occurring in some parts of the RUM waste and LGO stockpile system, but that this acidity is being buffered by chlorite dissolution, which is controlling the pH of streams draining from such regions to pH 4-5.
It is important to note here that it has been suggested that an in-stream pH range of between pH 4 and pH 5 is merely caused by the influx of early wet season low pH rainfall (pers. comm. Jones, 2005). However sample RW405 was taken at the end of the wet season where the pH of rainfall is more towards a pH of 6 (See chapter 5). Also, the start of wet season low pH samples of the WWP drainage (samples RW315 and RW316) and the GC (RW325 and RW407) are all associated with extremely high relative ionic concentrations, including high concentrations of Mg\(2^{+}\), SO\(4^{2-}\) and trace metals such as U. It has been shown that rainfall is not a source for trace metals (see Chapter 5) and for the samples specified, enrichment factor calculations prove that rainfall is an insignificant source of Mg\(2^{+}\), SO\(4^{2-}\) and Ca\(2^{+}\).

Although not given credence here due to its uncontrolled nature, it also worth pointing out that a small test of rainfall pH after contact with the stockpile surfaces, whereby the pH of small pools of water formed during a rainfall event on the surface of the WWP was measured using a H\(^+\) selective ion probe (see Chapter 2), suggested that the slightly acidic rainwater at the start of the wet season was quickly buffered by stockpile surface fines, from a pH close to 4 to a pH close to 5.8-6.0. Whatever the case, it should be clear that low pH stream drainage is not caused by low pH rainfall at RUM.

Proof that conditions are more acidic within the stockpiles than they are in drainage running from them, is the pH 2.97 of sample RW215, a remnant waterlogged depression in a submerged Platform Horizon within a waste rock grade stockpile. This sample probably represents a locale void of significant chlorite, such as a clay filled former pond on a surface platform, where internal acidic drainage had not had the chance to react with significant amounts of fine grained chlorite on its way out of the stockpile. Lower U content in this water sample compared to those of other less acidic samples probably relates to the uranium content of the source rocks, as is explained below, but could also be related to the lack of interaction this water has had with other minerals since its interaction with the sulfides. The extremely high Fe content of sample RW215 along with the observed Fe-coloured sludge (probably Fe oxyhydroxides and hydroxides) is also evidence of the relative close proximity of this water to oxidising pyrite.
Figure 8.4: (a) A low resolution plot of the relationship between the dissolution rate of chlorite and pH. Line A is a linear least squares regression line for results at pH 3 and 4, while line B is a linear least squares regression line for results at pH 7 and 10. Taken from Lowsen et al. (2007) (b) the chlorite dissolution rate as a function of pH using data from their own experiments (Lowsen et al. 2005) and data from Ross (1967), Kodama and Schnitzler (1973), Sverdup (1990), May (1995), Rochelle et al. (1996), Hamer et al. (2003), Brandt et al. (2003) and Gustafsson and Puigdomenech (2003). Taken from Lowsen et al. (2005)
8.7.2 Evidence of Acid Generation from the Historical Mine Water Database

It has been proven above that the pH signature of acid induced weathering within the RUM waste and LGO stockpiles is actually only a moderately low pH related to the dissolution kinetics of chlorite, of around pH 4 to pH 5. Given this, a complete historical mine water chemistry analysis was undertaken using the RUM Environmental Department’s water chemistry database, some 25 years of water monitoring data, to ascertain if there is more direct evidence than just the samples from this research of acid generation within the RUM stockpiles. All methods for this study have been outlined in Chapter 2, however it is important to point out here that waters from RP1 and RP2 were discarded from the study due to their ambiguous nature in terms of their source, as has already been outlined above and in Chapter 6. The data selected for the study represents the complete period of water monitoring from 1981 to 2005.

This is the first time such a study has been undertaken at RUM, short term water chemistry history of over one to two years seems to be examined relatively regularly, but complete historical studies have never been undertaken on the entire database.

Figure 8.5 is a bivariate plot showing the relationship between U and pH in the RUM historical mine water database filtered to the specifications described in Chapter 2. There are many important trends in the data displayed in Figure 8.5 however the most pertinent for the question to be answered here is the fact that there is a definitive set of samples that have a pH less than 6.0, with a not insignificant amount having a pH around and lower than pH 5.

A closer examination of the data reveals the periods of time and the water types concerned included the LGO Sump from 1987 to 1991 (pH as low as 4.1), Sump 98, RP1SED and the VLGCRC around 1999 (as low as 4.8), RP1SED again in 2000 and
2002 (as low as approximately pH 3.5 in 2002), single study seepage and run-off samples from the WWP and NWP (as low as pH 3.5 but generally around 4.2-5.2) in 2002, and the SSLR and run-off from the CWP (Skylab) from 2002 to 2006 (as low as approx. pH 4.4 for SSLR, but generally around pH 5-6).

**Figure 8.5:** Bivariate Fit of log(U) by pH for all surface waters represented in the Ranger Uranium Mine historical mine water database (See Chapter 2 for details)
All of the water samples with a pH lower than pH 6 represent water bodies that are in receivership of water direct from the stockpiles or are themselves run-off or leachate direct from the stockpiles. Most of the other data points in the region above pH 6 are pond waters with either little direct stockpile drainage input or that have been influenced by large amounts of water mixing from the RUM water management pumping regime, and therefore are not necessarily representative of a stockpile pH signature.

Hence, since moderately low pH drainage is a sign that acid generation by sulfide oxidation has been an important chemical process in the source stockpile, then Figure 8.5 confirms what the water chemistry from this research (Chapter 7 and above) indicates, that acid generation is far more significant in the RUM stockpiles than previously thought. Not only is it occurring, but it has been occurring since 3rd February 1987, as witnessed by the chemistry of the LGO sump, and is thus not limited to rock from any one ore body (another theory often suggested by some at ERA [personal communication, Jones, 2005]). A bias towards pond waters and downstream monitoring stations, instead of actual stockpile drainage, as well as a misconception of what signifies the presence of acid generation at RUM, has lead ERA and associated researchers into false conclusions on the subject.

It is important to point out here that Figure 8.5 also highlights the fact that there is a distinctive relationship between pH (the amount of acid generated), U concentration and the type of drainage within the RUM historical mine water chemistry. Figure 8.6 displays this relationship in more detail, whereby there is a specific log-linear increase in U concentration as pH decreases, but there are orders of magnitude increases in U concentration in LGO seepage drainage compared to LGO run-off and in LGO run-off compared to waste-grade seepage drainage. In other words, the amount of uraninite dissolution occurring in the stockpiles seems to be more related to the amount of uraninite available for reaction rather than the amount of acidity generated by the oxidation of sulphides. However, this may not be entirely true, since it is known from the study of the stockpiles in Chapter 4, that there is a general increase in sulphide content with grade.
Figure 8.6: Bivariate Fit of log(U) by pH at pH ≤6.0. The black, green and blue lines represent the log linear relationship for both run-off and seepage samples from LGO stockpiles, the seepage samples from LGO stockpiles and the run-off samples from LGO stockpiles respectively, and the pink line represents the log linear relationship for seepage samples from the waste rock grade SWP at sampling point VLGCRC. The VLGCRC outliers that are positioned within the blue run-off related samples were not included in the regression analysis for the VLGCRC data. Closer inspection of these samples suggests that they are actually incorrectly labelled VLGCRC02 samples, due to the concentrations of ions and the date of sampling.
8.8 THE IMPORTANCE OF EPSOMITE/HEXAHYDRITE TO RUM MINE WATER CHEMISTRY

Figure 7.3 shows that not only do Mg$^{2+}$ and SO$_4^{2-}$ totally dominate the chemistry of almost all of the waters collected, but the concentration lines of both species are almost identical in their value and pattern. The bivariate scatterplot of Mg$^{2+}$ v SO$_4^{2-}$ (mM/L) in Figure 7.5, confirms close to a 1:1 concentration ratio between these two ions for the entire dataset, with an $R^2$ of 0.9732.

This is significant, because it suggests either a similar source of equal proportion upon dissolution for these two ions, or an equilibrium position within mine waters has occurred over time. The latter of these scenarios is considered here unlikely because samples such as RW315 and RW316, which represent a small stream of water emanating from the toe of the WWP and thus having no time to equilibrate in a large holding pond, already have, for all intent and purposes, a 1:1 Mg$^{2+}$/SO$_4^{2-}$ ratio, being 1.092 and 0.987 respectively. Thus it is the first scenario that is more likely and the similar source is clear.

Epsomite (MgSO$_4$.7H$_2$O) has been identified as being a prominent salt around the RUM stockpiles and around the banks of evaporating water bodies (Milnes, 1988). The salt was observed during this research as being common along the edges of roads in the mine area, on stockpile surface platforms, around evaporating seepage points from the toes of stockpiles and on the banks of mine water bodies. XRD analysis in the lab identified these salts as hexahydrite (MgSO$_4$.6H$_2$O), the next step after epsomite in the paragenesis of sulphates in evaporative sequences (Spencer, 2000). Experimental studies show that with increasing temperature the orthorhombic heptahydrite, epsomite, easily loses the seventh unbonded water molecule (all other water molecules are bonded to a metal ion) and changes to the monoclinic hexahydrite (Jambor et al. 2002). A decrease in relative humidity or water activity will also push epsomite towards hexahydrite (Keller et al. 1986a, Jambor et al. 2002). Thus it is possible that the hexahydrite identification by XRD here is a result of transformation in the lab under low humidity (compared to the tropical savanna climate at RUM). However, it is just as likely that high temperatures at the mineral
surface on road bases and surface platforms combined with decreasing relative humidity at RUM as the dry season progresses also causes this change (samples collected for analysis were from the start of the 2002 dry season).

There is little doubt that Mg$^{2+}$ is sourced predominantly from the weathering of chlorite and SO$_4^{2-}$ from the weathering of sulfides, however the 1:1 relationship between these two ions here suggest that the formation of epsomite/hexahydrite is determining their relative abundances in solution within mine waters, in other words epsomite/hexahydrite is probably a significant interim phase between the weathering of Mg from chlorite and S from sulfides and the departure of these ions from the stockpiles (in solution).

The precipitation of metal sulphate salts in mines is a well-known phenomenon (see review by Jambor et al. 2000), in fact even the Greek and Roman civilisations were well aware of their existence in mines, their relationship with the deterioration of the metal ores and their potential environmental impact on wildlife (Jambor et al. 2000). The dissolution of metal-sulphate salts during storm run-off events has been found to cause initial increases in the concentrations of dissolved metals even as stream discharges increase (see Dagenhart, 1980 in Jambor et al. 2000). More important for RUM is the fact that elsewhere the dissolution of sulphates that have accumulated at base-metal waste sites during the dry season, have been noted to cause sharp hydro-geochemical responses following the first wet season rains (Keith and Runnells, 1998, and Keith et al., 1999). The result is cyclical changes in metal and sulphate concentrations (Dagenhart, 1980 in Jambor et al. 2000) and cyclical changes in associated metal/metal ratios (for example Zn/Cu – see Alpers et al. 1994). Figure 6.3 in Chapter 6 shows that this is precisely what is experienced at RUM, with cyclical changes occurring in most of those ions analysed in the environmental monitoring regime, including Mg$^{2+}$ and SO$_4^{2-}$.

It is envisaged here that at RUM, as the rains stop in March-early May and the dry season begins, the ‘drying out’ of the stockpiles also begins. This starts at the pavement like surfaces of the stockpile platforms and progresses through to small water bodies, the banks of larger bodies and eventually to within the stockpiles themselves, starting with the more exposed, less compacted outer slopes. At every
stage during this evaporation process, where water has been during the previous wet season metal-sulphate salts will precipitate. Within the stockpiles, the fragile salts will be protected just as they are in underground mines (Jambor et al. 2000) and hence, come the wet season, there will be a ready supply of highly soluble epsomite/hexahydrite to enter into solution and eventually RUM mine waters.

8.9 THE POTENTIAL IMPORTANCE OF URANYL OXYHYDROXIDES AND/OR SULPHATE SALTS AS A TEMPORARY MINERAL SINK FOR URANIUM IN RUM MINE WATERS

Many of the concentrations of what should be white epsomite/hexahydrite are tinged with a bright yellow surface (see for instance the precipitate in the clay pan of Figure 3.5a). A single sample of this material was selected for identification by XRD (an evaporated seepage drain running into Sump98 at the end of the 2001/2002 wet season, the same drainage as RW315 and RW316 were collected from when running at the start of the 2000/2001 wet season). This sample, along with two other samples (from the surface of the WWP and from around the edge of the NWP leachate pond - where water sample RW405 was collected) were analysed by EMPA.

Results of the XRD analysis (XRD trace in Appendix 14) allowed for the tentative identification of the U-mineral as metashoepite, an oxyhydroxide with the uncertain formula of \((\text{UO}_2)_8\text{O}_2(\text{OH})_{12}(\text{H}_2\text{O})_{10}\) (Finch and Murakami, 1999). Whilst this is the closest matching mineral for the unidentified peaks in the trace (which were few), a combination of the U-mineral being in extremely small relative proportions and the ‘swamping’ effect of hexahydrite suggests caution should be taken with this identification, too many peaks may be hidden behind those of hexahydrite and the background.
SEM and EMPA analysis of these samples revealed that extremely small crystals of U-minerals (<4-20μm diam.) strewn across the surface of the hexahydrite (Figure 8.7) were responsible for the pale yellow tinge to the hexahydrite under the naked eye. However EMPA analysis was also inconclusive as to which uranium mineral this was. A considerable amount of S and Mg was present in each analysis, however much of this could have been due to contamination by hexahydrite, some of the U-minerals were smaller than the EMPA beam width, and it was suspected that many were too thin for beam penetration not to include some of the hexahydrite beneath. In fact on a few occasions the beam destroyed the mineral being analysed before the analysis was
complete. This resulted in large variations in the analytical sums, something that is not uncommon for such fragile minerals. EMPA results were inconsistent in regards to proportions of Mg\(^{2+}\), SO\(_4^{2-}\) and U\(^{6+}\), which is considered here to be potentially representative of varying amounts of contamination.

That being said the minerals were still secondary uranium minerals and U-sulphates are still a likely candidate given the ions that had been detected in the EMPA. Despite there being very little known about the crystal chemistry of the U-sulphate minerals, it is known that they play a major role in controlling the concentration of uranium in mine-drainage waters as well as the distribution of uranium around such sites (Brugger et al. 2003, Finch and Murakami, 1999). The most likely candidate here is Mg-zippeite, first recognised as part of the zippeite group by Frondel et al. (1976) and recently redefined by Brugger et al. (2003) as Mg(H\(_2\)O)\(_{3.5}\)(UO\(_2\))\(_2\)(SO\(_4\))O\(_2\), since this mineral contains all of the ions identified by EMPA, whether from contamination or not.

Apart from Eh-pH conditions, uranium speciation in solution at the surface will also depend predominantly on the concentration of the favoured anions, the dominant and most stable of which are CO\(_3^{2-}\) species and SO\(_4^{2-}\) (Suzuki and Banfield, 1999). Figure 8.8 is a pH v oxygen fugacity diagram for carbonate and sulphate bearing waters at 25°C (note that the RUM waters are around 30°C). As can be seen for waters that contain both anions in significant proportions, uranyl sulphate species predominate in more acidic conditions and in near neutral to alkaline conditions uranyl carbonates are dominant. At RUM many of the surface waters, particularly the leachate, have U\(^{6+}\) and SO\(_4^{2-}\) concentrations in close proximity to the model in Figure 8.8, however, HCO\(_3^-\) concentration is an order of magnitude less in the RUM samples. Although many of the in-field pH measurements for water samples of this study favour the uranyl carbonates, sample RW405, thought here to best represent a ponded evaporating leachate water, has a pH well within the uranyl sulphate boundary (approximately below pH 6).
Also in favour of the mineral being uranyl sulphates are the results of the approximate speciation modelling performed in Chapter 7, where uranyl sulphates were modelled to be the dominant complex of U in solution. However, it also seems from synthesis experiments on the uranyl sulphates that a slow decrease in solution pH is needed for the precipitation of the zippeite group minerals and if this does not occur then oxyhydroxides will tend to form (see Finch and Murakami, 1999).

Figure 8.8: pH v oxygen fugacity diagram for carbonate and sulphate bearing waters at 25°C, from Brugger (2003). See text for further details.

Metaschoepite forms in ambient air through slow dehydration of schoepite \([\text{[UO}_2\text{O}_6\text{O}_2(\text{OH})_{12}\text{(H}_2\text{O})_{12}}]\) via the loss of two water molecules although it is also the favoured direct precipitate over schoepite at higher temperatures, 50°C compared to 25°C for schoepite (Finch and Murakami, 1999, see also Archer and Rard, 1998). Although the normal in-field temperature measured for RUM mine waters in this study was approximately 30°C, during the final stages of evaporation, mineral formation temperatures would be higher, possibly more towards the 50°C for metaschoepite direct precipitation. After all, temperatures of surface sediments on

Maximum diurnal temperatures of dolerite rock surfaces on the SWP of RUM clearly show that temperatures at rock surfaces within the waste rock stockpiles of consistently exceed 50°C in the summer months (refer to Figure 8.1). This is strong evidence to suggest that formation temperatures of minerals forming as ‘last gasp’ precipitates in soon to be evaporated solution films on rocks and in depressions are more likely to be far above 25°C.

It is obvious that a detailed study of U-mineral precipitates from leachate and run-off waters from the RUM waste and LGO stockpiles in conjunction with extensive geochemical modelling of the responsible waters is necessary to understand these minerals. This is beyond the scope of this particular project. Whatever the case, it should be clear that these minerals are acting as a temporary store of U⁶⁺, and due to their relative fragility, are probably responsible for the cyclic pulses of U observed in water bodies at the start of the wet season. Uranyl oxyhydroxide species have lower solubilities than uranyl sulphates, however this may not matter at the surface at the start of the wet, with rainfall pH as low as 3.6 and rarely greater than 4.5 (see Chapter 5), and a temperature upon first contact, potentially as high as 50°C.

8.10 THE RECYCLING OF IONS AT RANGER THROUGH DUST SUPPRESSION WATER

Table 6.7 in Chapter 6 and the accompanying discussion identifies dust suppression water as a significant input of ions and elements to localised areas of the surface platforms and access roads of the RUM waste and LGO stockpiles. Through a build up of deposits on surface platforms and access roads from evaporated dust suppression water during the dry season, it has been concluded here that dust suppression is a substantial contributor to phenomena such as the ‘first flush’ of ions into RUM mine water bodies at the start of the wet season.
Even during the wet season, dust suppression water will contribute to a small degree to rainfall run-off chemistry, and potentially even work to change the chemistry of water entering the stockpile around working areas of the stockpile system where dust suppression water is being utilised. If this is the case, then since dust suppression water is sourced from RP2, which in turn receives water from most areas of the mine, including the waste and LGO stockpiles, the ore stockpiles and P#3 (see Chapter 6), then dust suppression water is the link for a recycling of ions and elements through the RUM stockpile system.

Dust suppression water, as a solution, will be reacting with fine grained minerals on the stockpile surface, although this will not be to the extent as rainfall due to rainfall being more dilute, having lower pH, and being delivered in far greater volumes. However, the key to the importance of dust suppression water to ionic contribution to the stockpile system is its own chemistry and that the thin layer of water is quickly evaporated so to form a dry deposit at the surface.

To test what type of deposit may be formed by dust suppression water, a small portion of a collection of RP2 water was evaporated in a petri dish in the lab at room temperature (approximately 25°C) beneath a closed range hood, both to aid with evaporation and to protect the sample from foreign contaminants. The sample was collected from RP2 at the same time as the dust suppression water sample RW404 (05/05/2002), at the end of the 2001/02 wet season, and so represents solution chemistry not too dissimilar to that sample. At this time the dry season had already begun.

Examination of the resulting precipitate under a normal microscope revealed a translucent white film with small orange/yellow concentrations on top of it in places. A scraping of this material incorporating the orange/yellow mineral was prepared for XRD on a low background holder (see Chapter 2). Analysis of the XRD trace (Appendix 15) revealed that the ubiquitous translucent white precipitate was hexahydrite. Other phases were difficult to identify in the sample due to their relative low abundance in comparison to the hexahydrite, and thus the ‘swamping’ effect of its trace. Using the XRD trace mineral identification software ‘Eva’, the most common
mineral suggested for the vacant peaks, amongst other U-minerals, was Lanthinite (U₆O₇(OH)₂O), a uranyl oxyhydroxide.

These results are significant in that both these types of minerals, epsomite/hexahydrite and uranyl oxyhydroxides, were also identified in the precipitates of the evaporated waste and LGO stockpile leachate (above). It must be understood that this result does not in any way suggest that dust suppression water is responsible for the minerals of the leachate precipitate. However, it does prove that dust suppression water is precipitating the same epsomite/hexahydrite and uranyl mineral (such as uranyl oxyhydroxides) mix as the waters that have reacted with the RUM waste and LGO, directly onto the stockpiles. It is thus adding to the already formed store of readily solubilised minerals in the stockpiles. Further however, since the dust suppression water precipitates will be concentrated in particular areas of surface platforms and access roads, and will build up during the dry season (Chapter 6), they have the potential to be a dominant source of ions and elements for the ‘first flush’ chemical pulse to mine waters in some areas.

Importantly, this is evidence that dust suppression water is a crucial link in the recycling of ions and elements in the RUM waste and LGO stockpile ‘system’. Epsomite/hexahydrite seems to be acting as a control on the chemistry of RUM mine waters, along with uranyl oxyhydroxides and uranyl sulphates for the concentrations of U⁶⁺. Then, via RP2 and dust suppression water, the RUM mine waters are delivering these same minerals back to the stockpile surfaces.
8.11 CONCLUSION

This study has shown that $\text{Mg}^{2+}$, $\text{SO}_4^{2-}$, $\text{Ca}^{2+}$, $\text{CO}_3^{2-}$ (in the form of $\text{HCO}_3^-$ in solution) and $\text{U}^{6+}$ are the main chemical components being extracted from the RUM waste and LGO stockpiles by weathering. There are orders of magnitude more $\text{Mg}^{2+}$ and $\text{SO}_4^{2-}$ than any other ions, which reflect the solubility of $\text{MgSO}_4$ and the dominance of chlorite and sulfides in the weathering process.

The weathering of the dominant rock type, the quartz chlorite ± mica schist, can explain much of the chemistry observed, however, the abundant $\text{SO}_4^{2-}$ is being derived from sulfides, predominantly pyrite. The generation of acid locally by sulphide oxidation is a fundamental process within the RUM waste and LGO stockpiles and one of the driving forces behind mineral weathering and solute generation within them. Importantly, and counter to popular belief at RUM, the production of low pH drainage by sulfide oxidation (acid rock drainage) is not a recent phenomenon, it has been occurring since early 1987. A bias towards pond waters and down-stream monitoring stations, instead of actual stockpile drainage, a misconception of what signifies the presence of acid generation at RUM, and a mistaken belief that lower pH drainage is due to rainfall has lead ERA and associated researchers into false conclusions on the subject previously.

Where chlorite is present, its dissolution buffers the acidity produced by sulphide oxidation to around pH 4-5. Where chlorite is not present, there is potential for localised regions within the stockpiles to be pushed to a pH of at least pH 2.9-3.0. In areas of increased sulphide oxidation mica minerals such as muscovite and/or fine grained sericite/illite are also being broken down and releasing $\text{K}^+$ into solution. Otherwise $\text{K}^+$ in the RUM mine waters can be explained entirely by a rainfall source. Carbonate dissolution is also an important part of the RUM stockpile hydrogeochemical system, explaining the net enrichment of $\text{Ca}^{2+}$ and $\text{HCO}_3^-$ in waters that have interacted with the stockpiles. Where present, carbonates will act as an early buffer to acidity produced from sulfide oxidation reactions.
Secondary minerals are controlling the solution chemistry to a large extent. Although the original source of the Mg\(^{2+}\) and SO\(_4^{2-}\) in solution is that of chlorite and pyrite respectively, the 1:1 molecular ratio between these two ions in all waters related to the stockpiles proves that epsomite/hexahydrite is acting as a temporary interim step for Mg\(^{2+}\) and SO\(_4^{2-}\), between being weathered out of the original mineral and being released from the stockpiles into solution. This is probably the case for many other ions and trace elements, whereby the precipitation of secondary minerals at the end of the dry season, both internally and externally on the stockpiles, provides a store of readily available soluble salts for the start of the next wet season. Observations on top of the stockpiles certainly prove that this is the case not only for MgSO\(_4\) but also for U\(^{6+}\), the latter most probably in the form of uranyl oxyhydroxides and sulphates species.

The dust suppression water is also a significant contributor to the ‘first flush’ of ions into RUM mine water bodies at the start of the wet season because it also is responsible for local concentrations of both epsomite/hexahydrite and uranyl oxyhydroxides and sulphates. Dust suppression water is thus a crucial link in the recycling of ions and elements in the RUM waste and LGO stockpile ‘system’, helping to re-concentrate ions in the RUM mine waters and if continued will increase the salinity and concentration of U in the mine waters.

No direct measurements of internal weathering conditions were taken inside the stockpiles, such as temperature or moisture content, and so this remains relatively unknown. However, measurements of rock surface temperature suggest that reaction rates on the surface of the stockpiles will be at least an order of magnitude greater than at normally considered low temperature environments of 25°C. Such temperatures also increase the solubility of U over time and together with observations of the 30cm sub-surface layer, the surface and direct-subsurface are probably important places of weathering for the stockpile system as a whole.

There is also no evidence for stockpile-scale saturation of the RUM stockpiles as has been modelled by hydrological and geotechnical engineering consultants, not even during the record breaking uninterrupted rainfall days of the 2006/2007 wet season where 813mm was recorded at the mine in 3 days.
CHAPTER 9

CONCLUSION AND SUMMARY

9.1 CONCLUSION

Since each of the chapters in this thesis has been a separate study in itself, with its own related hypotheses, goals and conclusions, there have already been numerous conclusions made and outlined. It is not the purpose of this conclusions chapter to repeat these, for each of the separate goals outlined in the introduction the conclusions can be found in the corresponding study and chapter and these should be referred to.

The main question to be answered here is has the general hypothesis been proven or not? That is, has treating the stockpiles as a complete ‘system’ increased the understanding and potential for prediction of the hydro-geochemistry of the stockpiles? Also has this research proven that it is possible to understand operational stockpiles and their hydro-geochemistry with simple and direct in situ on-site observations with no need for expensive and difficult experimentation or waiting for mine closure to examine the de-construction of the stockpiles?

The answer to both questions is yes. It should be clear from this thesis that the major error in the prediction of stockpile hydrology and thus stockpile stability during the wet season at RUM was due to the fact that the engineering model did not take into account the complexities introduced into the structure and fabric of the stockpile by the formational processes (construction techniques) and stockpile geology (differing rock types and their locations within the stockpile system) and ultimately how this effected the movement of water through the stockpiles. It should be clear that such an oversight will also cause problems for water balance models that divide water beneath the stockpiles entirely on pre-stockpile topography, particularly in cases such as RUM where the stockpiles are built on a drainage divide. It should be clear that predicting the chemistry
of mine waters is futile without full consideration of the chemistry and volume of all inputs, including anthropogenic inputs such as dust suppression water, the mineralogy and mineral chemistry of the constituent rocks, where these rocks are located in the stockpiles (the geology of the stockpiles - which includes examining the mining history and assessing grade control measures in the case of RUM), and how this water may have flowed through and thus interacted with the stockpiles. Treating the stockpiles as a 'system' has revealed complexity but also revealed pattern in this complexity and allowed understanding of where predictions and assumptions can be made and where they cannot.

This research has shown that it is not necessary to set up large scale expensive (sometimes in the millions of dollars) stockpile scale experiments to understand the hydro-geochemistry of the stockpiles. Unless these experiments are set up so that the stockpile precisely mimics the real stockpile's structure, geology and environment, then the results are not valid anyway. Observations made during stockpile deconstruction, often after mine closure, are fine for studying stockpile structure in general, but not for mapping the exact stockpile structure of existing operational stockpiles. Apart from internal temperature measurements and exact measurements of internal moisture content, this thesis is an example of how most information needed to understand the hydro-geochemistry of a stockpile system can be gathered during full mine operations and within an operational stockpile environment.

It could be argued that it was not necessary to include in this thesis an examination of the sources of the chemical components of the rainfall (majority of Chapter 5), nor was it necessary to provide a detailed description of the regional geology and geology of the Ranger deposit (included in Chapter 4). It is true that both of these additions do not increase the understanding of the hydro-geochemistry of the stockpiles.

However, the examination into the source of the rainfall chemistry and the geology of the deposit does provide a much greater context and develops a wider understanding that these stockpiles are landforms exposed and weathering in a natural environment. After-all the rocks and minerals making up the stockpiles may have been re-deposited in the last
two decades, but their chemistry and mineralogy, ultimately key components of the RUM stockpile hydro-geochemical system, are the result of processes that occurred 1.6-1.8 billion years ago. The study on rainfall chemistry provides context for the unique environmental climatic setting that these stockpiles are exposed to, rainfall with a pH of 3.6 at the start for the wet season, rainfall that switches from terrestrial to oceanic chemistry and that can dump over 800mm in 3 days onto the stockpiles.

To illustrate how important the climatic context is to conceptualising and understanding the stockpile ‘system’ at RUM, the rainfall season has been used below to summarise the RUM stockpile ‘system’.

9.2 THE RANGER URANIUM MINE WASTE ROCK STOCKPILE SYSTEM: A SEASON BY SEASON SUMMARY

9.2.1 The Dry Season

As the dry season of the ‘top end’ extends into what would be late winter in southern Australia, the relatively consistent and strong (in comparison to the wet season) easterly trade wind flow continues to bring in dryer air over the RUM waste and LGO stockpiles. By this time, one would expect that a large pile of unconsolidated rock material would be relatively dry throughout; that the zone of saturation that existed as a hydrological mound through the centre of the stockpile, had withdrawn to its base, just as engineers had predicted. However, the RUM waste and LGO stockpiles are not that simple, their hydrological characteristics are more in line with stratified soils and therefore the basic engineering concepts applied to them, for both geotechnical stability and water management reasons at the mine, are fundamentally flawed.

The RUM stockpiles are an intricate set of repeating structures that, not unlike any other geological depositional sequence on earth, are a direct result of the physical characteristics of the constituent materials and the way in which they were deposited. Due to the techniques utilised at RUM for building free standing stockpiles, the RUM
stockpiles are characterised by Extension Lens layers, Lift Mound layers and Platform Horizons. Overprinting this in some areas are major differences in material type for different layers, in particular layers of clay from mining the laterite compared to layers of primary rock from mining deeper sections of each pit. There is even evidence that individual lenses within the Extension Lens layers can randomly alternate between lenses of primary rock and lenses of lateritic clays.

Due to this inherent structure in the RUM stockpiles, air that is entering the relatively porous stockpile batter slopes in the dry season does not have easy access to all parts of the stockpile. Air flow is restricted only to favourable structures, such as the large regions of Extension Lenses made from primary rock. Stacking of Platform Horizons ensures that circulation of air is inhibited to a large extent in the vertical direction. It follows that large stockpile scale convection 'hot' cells set up by sulfide oxidation are not probable in the RUM stockpiles. Rather, oxidation will be regional, established in pockets of the stockpiles where conditions are favourable, or it will be limited or slowed by an inadequate oxygen supply.

The particular structure of the RUM stockpiles also means that whilst some areas of the stockpiles will have dried by the end of the dry season, the clay dominated layers will still be moist and in some restricted areas, even saturated. This is particularly the case at the base of the stockpiles where much of the laterite overlying the deposits was dumped during early mining of both deposits, but it also applies to elevated clay layers where perched water tables will, and do, form.

Where water is trapped well into the dry season rock-water interaction will still be taking place. In the compacted submerged Platform Horizons for instance, silt to gravel sized crushed primary rock may still be reacting with water under saturated to field capacity conditions. The high matric potentials of the finer grain material means water remains and protection from air flow prevents it from being evaporated. If sulfides are present in such regions, the extended time factor may aid in the development of acidic solution
chemistry. It was in a solution like this, that the lowest mine water pH ever recorded at RUM was found.

At the surface of the stockpile, there is very little moisture left by the end of the dry season. Diurnal temperatures of rock surfaces range from a maximum of 54°C during the day to 22°C at night. Although it is very rare to have a rainfall event in the dry season, in areas of the stockpiles where dumping activity or transport is taking place, such as working surface platforms and haul roads, a significant contribution to future stockpile drainage chemistry is being made by dust suppression activities and the re-distribution onto the stockpiles of RP2 water.

The concentration of the various ions in the dust suppression water supply, RP2, is governed by a number of factors, including what was introduced from stockpiles from the previous wet season, the particular strategy of the water management dry season pumping regime (and so input from P#3 or Sump98 for instance), chemical conditions such as pH and evapo-concentration. Whatever the case, by the late dry season dust suppression activities have deposited significant amounts of Mg$^{2+}$, SO$_4^{2-}$, U$^{6+}$ and Mn$^{2+}$ in small concentrated areas of the stockpile system, in particular the main access roads and haul roads where dust suppression is most needed. Further, the dust suppression water evaporites are concentrated in the first few millimetres of the access roads and Platform Horizons, ready for reaction with the first rains of the oncoming wet season. On a local basis dust suppression water is far more significant as a contributor of Mg$^{2+}$ and SO$_4^{2-}$ to the RUM stockpile system than rainfall, and in fact, apart from potential dust movements, is the only external input of the environmentally significant trace elements of U$^{6+}$ and Mn$^{2+}$ to the entire stockpile system.
9.2.2 The Transition

By October-November the ITCZ has begun its movement towards the northern Australian continent, signifying the beginning of the transition. The easterly trade winds have faltered, and the wind direction swings to the north, but with no consistency and no strength. A convective cell now sits directly over RUM for almost the entire period, and the haze of smoke from the ‘burn-off’, which was being transported away during the dry season, now simply hangs in the convection cell. The NOy, sulfur products and assorted organics and gases produced by the burning vegetation begin to rise up through the cell, but have nowhere to go. They are trapped by an atmospheric inversion that develops above the boundary layer at this time of year.

The northerly switch for the incoming air has brought moisture, and thus eventually rain from local convective thunderstorms. The build up of compounds in the atmosphere from the continued, mostly anthropogenic burning is stripped out of the rain column and clouds by the sporadic transition rain storms. The result is rain enriched in SO\(_4^{2-}\), NO\(_3^-\), and organic acid anions, which in turn also creates natural acid rain (pH as low as 3.6-3.7). The chemistry of the transition rains is not consistent; a strong terrestrial signature is sometimes evident in the form of increased Ca\(^{2+}\) and Cl\(^-\).

The first of these rains are not large in volume, nor are they extensive, so not only do these rains not tend to generate significant amounts of run-off, if at all, but a single event may only fall on a part of the stockpile system. The natural acid rain is buffered to more normal rainfall pH (approx. pH 5.8) within minutes of hitting the surface of the stockpiles.

By late November to late December however, well into the transition, RUM mine waters are receiving the start of the wet season ‘first flush’. This ion ‘pulse’ is generated by three factors; firstly the relatively quick dissolution reactions occurring when the incoming extremely dilute and relatively acidic rainfall interacts with the fresh supply of silt to sand sized crushed rock dumped on the stockpiles over the dry season, particularly in regards
to the working platforms and access roads; secondly, the supply of secondary precipitates on protected rock surfaces throughout the near surface regions of the stockpiles that had been left over from the previous wet season’s weathering; and finally the readily available and easily solubilised dust suppression water evaporites that had been repeatedly applied to the stockpiles throughout the dry season. Out of all of the ions in the RUM mine waters affected by the ‘first flush’ it is U that seems to be the most influenced.

In the very first rains of the wet season, depressions in active working platforms accumulate salts, which become part of the first pulse when rain volume is enough to produce run-off drainage. If these platforms become buried at this time due to the construction of a lift, they become submerged pockets of higher grade material, ready to be solubilised by the oncoming monsoon.

In most of the stockpile system at RUM, the compacted fine grained surface Platform Horizons may not allow much of the transition rains past them, the application rate may be too high and total volume too low. However this is not the case for the SWP, where the ripped surface and Extension Lens structure allows rain water to infiltrate and begin to re-open and re-establish water flow pathways. Some of these pathways are short tunnels direct from the surface to basal outflow channels. Even so, short sporadic rainfall events means that seepage flow and thus solute transport from stockpiles is also inconsistent in the transition and the continual precipitation of secondary minerals along fluid pathways is an important process governing the seepage chemistry.

At the surface of the stockpiles weathering is beginning to intensify. Rock surface temperatures reach over 50°C, where reaction rates are at least an order of magnitude greater than at room temperature (25°C). Then, within a matter of minutes a rainfall event can remove weathering products from weathering surfaces and reduce the surface temperature to under 25°C. At the surface, weathering conditions are in constant flux, from saturation, near saturation and flush to dry.
9.2.3 The 'Wet'

As the wet season matures, rainfall events become more frequent and dump greater volumes of water on the stockpiles. A short period of NW wind direction signifies the dominance of the monsoon system which pushes the local convective system to the east. Due to the increased volume and regularity of rainfall, the atmospheric ion store is ‘washed out’ so that wet season rains are relatively low in ion concentrations compared to the transition or start of wet season rains and definitively more consistent.

The regularity of the wet season rains reduces maximum temperatures on rock surfaces on the stockpiles to below 50°C. Although large volumes of rain are now being dumped almost daily onto the stockpile system, still no hydrological head develops in the stockpile due to the inherent internal stockpile structure. The CWP has become a series of perched water tables and diversion platforms between drainage layers, so that water saturates zones of high matric potential, such as Platform Horizons and clay layers, and mostly passes though Extension Lens layers and Lift Mound layers, if dominated by primary rock. The saturated Platform Horizons also act as diversion levels, where water is diverted by gravity towards the buried access ramps, and from there towards various exit points. In effect the slopes on Platform Horizons and access ramps within the RUM stockpile system work to divert water towards RP2, the mine’s central retention pond. However, not all Platform Horizons are sloped towards RP2, and Platform horizons do not cover the entire stockpile system. This means that water flow pathways will divert water to other sides of the stockpile system, such as across the drainage divide that cuts beneath the CWP to the west into the Coonjimba Creek catchment. Water balance models based on surface hydrology cannot predict such variation.

As the wet season progresses water flow paths in the stockpiles become relatively ‘clean’ as weathering products and solute are consistently and regularly washed away from reaction sites. Thus, at this time of year, drainage from the stockpiles will be at its greatest, but will be diluted compared to both the start and end of the wet season.
In the walls aside the flow paths moisture content increases to optimum levels for oxidation of sulfides. Moisture firstly infiltrates the fine grained matrix, a matrix not dissimilar to the matrix of a conglomerate, where silt to gravel sized grains liberated in the blasting, digging, transport and dumping process are packed around cobble and sometimes boulder sized rocks. In this matrix there is potential for more sulphide reaction surfaces to be present, due to both the liberation of sulphide from the rock and the possibility that long held Fe-oxide weathering skins observed on pyrite, that would otherwise provide protection from the oxidation, have been broken and shattered.

In the quartz chlorite ± mica schist existing in the layer, moisture infiltrates foliation and fracture planes and from there begins to infiltrate the sub 4 micron chlorite/sericite matrix. Although sulfides exist in the chlorite matrix and in cleavage partings of mica minerals, there is no need for water to penetrate that far. A large proportion of sulfides inhabit foliation and fracture surfaces as thin smears (in foliation planes) and thin coatings of botryoidal like masses (on irregular fracture surfaces).

At the sulfide-water interface, oxidation of the sulfide coupled with the precipitation of Fe-hydroxides produces excess H⁺. In the foliation and fracture planes this acidified solution may be able to move short distances (rock scale) without being buffered or significantly diluted. However, elsewhere the ubiquitous and sub-microscopic nature of the chlorite ensures that the acidic solution produced at the sulphide water interface does not travel far before being buffered by the dissolution of chlorite, and in many circumstances this may be occurring at the same reaction site (for all intent and purposes — adjacent mineral). Often, but particularly in the higher grade rocks, uraninite will also not be too far away, for instance it also will reside on fracture surfaces, and in quartz and the ubiquitous chlorite matrix of the rock and any acidification will certainly increase the dissolution of uraninite. The end result is a concentrated solution dominated by MgSO₄ and other SO₄²⁻ salts, such as UO₂SO₄ or UO₂(SO₄)₂²⁻. Carbonate may also become an important ion for U⁶⁺ complexation in solution, with such species as UO₂CO₃, and UO₂(CO₃)₂²⁻.
These solutions or resulting secondary mineral precipitates, will remain in such areas of the stockpiles until water flow pathways move to include them (through blockage of existing pathways for instance) or the area becomes saturated, in which case the solution will slowly move off and transport the solute from the stockpiles into the mine water. The acidity of the exiting solution should be diluted as it enters higher volume water flow paths on its way out of the stockpiles, but if not it will remain around pH 4.5-6 due to the chlorite dissolution-pH relationship. It should be noted that even in these areas and even in this period, flows will still flux according to rainfall events, and so it is probable that rather than salts staying in solution around reaction sites, they will actually deposit as highly soluble minerals, and then continue to solubilise and precipitate as they make their way out of the stockpile. In other words, the dissolution of secondary minerals such as epsomite \([\text{MgSO}_4\cdot 7\text{H}_2\text{O}]\), haxahydrite \([\text{MgSO}_4\cdot 6\text{H}_2\text{O}]\), schoepite \([\text{UO}_2\text{O}_2(\text{OH})_2](\text{H}_2\text{O})_{12}\), metaschoepite \([\text{UO}_2\text{O}_2(\text{OH})_{12}(\text{H}_2\text{O})_{10}]\), Mg-zippeite \([\text{Mg}(\text{H}_2\text{O})_{3.5}\text{UO}_2\text{O}_2(\text{SO}_4\text{O}_2)]\) will be just as important to mine water chemistry as is the weathering of primary minerals.

In areas of higher sulfide content, and thus greater acid production, such as the early NWP, seepage water will still be at a higher pH than it reached in the region of oxidation (approx. pH 2.5-3), again being buffered by chlorite dissolution to around pH 4.5-5.5. However such drainage will be distinguished from other drainage regions by a silicate and sericite/muscovite weathering signature, much lower Mg/K ratios and comparatively higher Si content. \(\text{U}^{6+}\) in such seepage can reach in excess of 100,000µg/L and metals such as \(\text{Cu}^{2+}\), \(\text{Co}^{2+}\) and \(\text{Ni}\) are present in higher concentrations than elsewhere, probably a signature of the high sulphide content. If these regions remain saturated or close to saturated for long periods of time and the water does not actually move out, it is possible that they may become areas of reduction, where trace elements such as \(\text{Mn}^{2+}\), which favour such environments, begin to dominate over \(\text{U}^{6+}\) species.
9.2.4 End of Wet Season

By April/May, the ITCZ has begun moving north. The more regular easterly trade winds begin to re-establish. The last rains of the wet season have slightly elevated concentrations of ions in them compared to those rains of the monsoon period due to lower rainfall frequency, easterly terrestrial sources and early dry season burning practices.

The stockpiles have begun to dry up, water flow pathways decrease in number and thus so too do drainage and seepage points from the stockpiles. When it does rain, and the water flows through the former wet season flow paths, it picks up with it solute from easily solubilised secondary minerals that have precipitated along the flow path walls. Seepages will continue to drain the stockpiles some time after the last rainfall event, these will commonly be relatively highly concentrated solutions and often moderately acidic (pH 4.8-6).

Rock surface temperatures remain similar to those of the wet season although start of wet season like maximum temperatures do occur. Moisture is drawn out of all surfaces and as it evaporates secondary mineral precipitates are left behind, the white efflorescence of epsomite/hexahydrite and the yellow surface tinge of uranium sulphates and oxyhydroxides. These precipitates, which are a common sight around the base of the stockpiles in April May, are generally washed away by the final one or two rainfall events of the season. Inside the stockpiles, much of the secondary mineral volume has not been washed away by the last non-penetrative rains, and so this will be left behind ready for the next transition, some 7 months away.
9.2.5 Many Seasons Before

It is difficult to comprehend, but intrinsic to the waste and low grade ore stockpile system at RUM is a sequence of events that began to occur some 1.8 billion years ago, if age dating of rocks has been correct. Taking one of the most popular geological interpretations, it was at this time that some 4km of sandstone, along with inter-layered volcanic sequences, was unconformably deposited on top of a group of metamorphosed intra-continental basal sediments. Some tens of millions of years after (1737 ± 20Ma) diagenitic brines from the sandstone began to interact with the metasedimentary basement, the unconformity had potentially become a focal point for a flow driven by the geothermal gradient. At various points along a major regional structural lineament this slightly acidic oxidised brine was allowed to mix with another reduced fluid, probably from below, in pre-structurally prepared ground. More movement within a complex of structures, particularly close to the unconformity contact, allowed for large scale mineral deposition from the 150-200°C fluid mixing zone. The pervasive wall rock alteration was extensive, extending some 300m at least from the ore zone, and ensuring that almost every single rock that has been and is still being mined from the RUM ore bodies is completely dominated by chlorite, the alteration mineral.

Thus, it was geological events and circumstances that occurred and existed some 1.7 to 1.8 billion years ago that ensured that chlorite dissolution dynamics would be fundamental to the RUM mine water chemistry; that the oxidation of pyrite and the subsequent production of acidity, particularly in higher grade rocks where reduction of the oxidised fluid was more extensive, would insure such dissolution took place, would make the RUM mine waters MgSO₄ solutions and consequently set-up the recycling of MgSO₄ and U back into the stockpiles via dust suppression activities.
REFERENCES


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Garvie, A.M. (2002) Characterisation of soils overburden and tailings, Short Course on Practical Monitoring for Improved Environmental Management in Mining. Australian Centre for Mining Environmental Research, Queanbeyan NSW.


APPENDICES

APPENDIX 1

Detection Limits for Water Analysis by Ion Chromatography

Detection limit for all major anions analysed for all samples except for sulphate:

- Flourine (F) = 0.02mg/L
- Chloride (Cl\(^-\)) = 1mg/L
- Nitrate (NO\(_3\)) = 0.05mg/L
- Bromide (Br) = 0.02mg/L

Detection limits for sulphate (SO\(_4^{2-}\)) by sample (mg/L)

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APPENDIX 2

Detection Limits for Water Analysis by Inductively Coupled Plasma Atomic Emission Spectrometry

Detection limit for all major cations analysed for all samples:

- Magnesium (Mg$^{2+}$) = 0.0016mg/L
- Calcium (Ca$^{2+}$) = 0.020mg/L
- Sodium (Na$^{+}$) = 0.0109mg/L
- Potassium (K$^{+}$) = 0.0205mg/L
- Silica (Si) = 0.0170mg/L

APPENDIX 3

Detection Limits for Water Analysis by Inductively Coupled Plasma Mass Spectrometry

The standard suite of elements analysed by ICPMS included, in order of molecular weight, P, Sc, V, Cr, Fe, Mn, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Cs, Ba, La, Ce, Hf, Au, Hg, Ti, Pb, Bi, Ra, Th and U.

The Fresh Water Ecology laboratory at the University of Canberra chooses to quote a detection limit for all elements of 1µg/L regardless of ICPMS manufacturer claims. If a trace peak was detectable above background but calculation of the peak still resulted in a concentration below 1µg/L, then either ‘tr’ was used or the concentration was quoted as being 0.5µg/L and the sample was flagged.
### APPENDIX 4

Detection Limits for Geochemical Analysis by X-Ray Fluorescence

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**XRF TRACE ELEMENTS**  
*(Determined on fused disc)*

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APPENDIX 5

Detection Limits for Geochemical Analysis By Inductively Coupled Plasma Mass Spectrometry Digest

ICP-MS TRACE ELEMENTS

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<td>Sm</td>
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</tr>
<tr>
<td>Sn</td>
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<tr>
<td>Sr</td>
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<td>Tm</td>
<td>0.01 ppm</td>
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<tr>
<td>U</td>
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<td>Y</td>
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<tr>
<td>Yb</td>
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</tr>
<tr>
<td>Zr</td>
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### APPENDIX 6

**Results of Geochemical Analysis of Major Ions in Rocks by X-Ray Fluorescence**

<table>
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<th>Sample Number and Rock Type</th>
<th>AI&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>CaO</th>
<th>Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;T</th>
<th>K&lt;sub&gt;2&lt;/sub&gt;O</th>
<th>MgO</th>
<th>MnO</th>
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<tr>
<td>RR215B - light green pegmatite</td>
<td>21.625</td>
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<td>1.281</td>
<td>6.433</td>
<td>1.503</td>
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<tr>
<td>RR129 - soapy dark green chlorite schist</td>
<td>18.055</td>
<td>1.4</td>
<td>12.523</td>
<td>0.012</td>
<td>20.424</td>
<td>0.029</td>
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<tr>
<td>RR770 - dark green pegmatite</td>
<td>21.076</td>
<td>0.659</td>
<td>5.094</td>
<td>0.124</td>
<td>28.53</td>
<td>0.024</td>
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<tr>
<td>RR 787 - skylab greenschist</td>
<td>14.915</td>
<td>0.01</td>
<td>3.287</td>
<td>2.118</td>
<td>10.434</td>
<td>0.011</td>
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<tr>
<td>RR128 - grey slatey schist</td>
<td>16.537</td>
<td>0.18</td>
<td>6.022</td>
<td>2.117</td>
<td>7.89</td>
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<td>A1 - dark green soapy schist with red all over</td>
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<td>0.892</td>
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<td>A7 - unknown</td>
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<td>0.174</td>
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<td>3.035</td>
<td>2.387</td>
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<tr>
<td>A4 - sulphides in quartz</td>
<td>16.47</td>
<td>0.225</td>
<td>19.043</td>
<td>0.002</td>
<td>17.284</td>
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<td>A14 - The funny quartz/green rock?</td>
<td>12.047</td>
<td>0.277</td>
<td>3.048</td>
<td>0.999</td>
<td>6.998</td>
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<td>A13 - carbonate with green tinge through it</td>
<td>1.962</td>
<td>0.683</td>
<td>5.952</td>
<td>0.004</td>
<td>43.586</td>
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<tr>
<td>A12 - Dolerite</td>
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<td>16.143</td>
<td>0.691</td>
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<td>A3 - Green rock with quartz through it</td>
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<td>0.142</td>
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<td>0.005</td>
<td>1.248</td>
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<td>A9 - schist</td>
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<td>A18 - weathered rock below the surface?</td>
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<td>1.89</td>
<td>3.76</td>
<td>3.945</td>
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<td>0.247</td>
<td>2.727</td>
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<tr>
<td>A16 - fresh A14</td>
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<td>0.32</td>
<td>7.839</td>
<td>0.376</td>
<td>12.515</td>
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<td>A15 - Dolerite</td>
<td>16.168</td>
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<td>17.459</td>
<td>0.034</td>
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<tr>
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### Appendix 6 Continued..

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<th>Sample Number and Rock Type</th>
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<th>P2O5 XRF %</th>
<th>SiO2 XRF %</th>
<th>SO3 XRF %</th>
<th>TiO2 XRF %</th>
<th>MLOI Calculate</th>
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</thead>
<tbody>
<tr>
<td>RR215B - light green pegmatite</td>
<td>-0.01</td>
<td>0.4</td>
<td>62.804</td>
<td>-0.005</td>
<td>-0.005</td>
<td>5.263</td>
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<tr>
<td>RR129 - soapy dark green chlorite schist</td>
<td>0.033</td>
<td>1.099</td>
<td>35.16</td>
<td>0.018</td>
<td>0.82</td>
<td>10.174</td>
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<td>RR770 - dark green pegmatite</td>
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<td>0.506</td>
<td>30.429</td>
<td>0.011</td>
<td>0.009</td>
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<td>0.011</td>
<td>60.734</td>
<td>0.01</td>
<td>0.27</td>
<td>8.074</td>
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<tr>
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<td>-0.01</td>
<td>0.155</td>
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<td>0.491</td>
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<td>0.259</td>
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<td>5.934</td>
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<td>0</td>
<td>11.087</td>
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<td>94.099</td>
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429
APPENDIX 7

Results of Geochemical Analysis of Trace Elements in Rocks by X-Ray Fluorescence and Inductively Coupled Plasma Mass Spectrometry

X-ray Fluorescence

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<th>Cr XRF ppm</th>
<th>Cu XRF ppm</th>
<th>F XRF ppm</th>
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<td>5</td>
<td>593</td>
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<tr>
<td>RR129 - soapy dark green chlorite schist</td>
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<td>268</td>
<td>-1</td>
<td>1219</td>
</tr>
<tr>
<td>RR770 - dark green pegmatite</td>
<td>294</td>
<td>26</td>
<td>3</td>
<td>1700</td>
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<td>RR 787 - skylab greenschist</td>
<td>85</td>
<td>23</td>
<td>-1</td>
<td>689</td>
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<td>RR128 - grey slatey schist</td>
<td>74</td>
<td>47</td>
<td>9</td>
<td>505</td>
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<td>A1- dark green soapy schist with red all over</td>
<td>128</td>
<td>12</td>
<td>15</td>
<td>845</td>
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<tr>
<td>A2 - soil SWP</td>
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<td>22</td>
<td>900</td>
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<td>A8 - Schist</td>
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<td>4459</td>
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<td>1</td>
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<td>4</td>
<td>258</td>
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<td>A17 - chert</td>
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<td>17</td>
<td>519</td>
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<td>A16 - fresh A14</td>
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<td>5</td>
<td>811</td>
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<td>A15 - Dolerite</td>
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<td>187</td>
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<td>1051</td>
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Appendix 7 Continued..

X-ray Fluorescence

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<td>RR129 - soapy dark green chlorite schist</td>
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<td>185</td>
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<td>RR770 - dark green pegmatite</td>
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<td>142</td>
<td>91</td>
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<tr>
<td>RR 787 - skylab greenschist</td>
<td>93</td>
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<td>58</td>
<td>42</td>
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<tr>
<td>RR128 - grey slatey schist</td>
<td>6</td>
<td>13</td>
<td>55</td>
<td>44</td>
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<td>A1 - dark green soapy schist with red all over</td>
<td>112</td>
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<td>157</td>
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<td>158</td>
<td>140.8</td>
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<td>A8 - Schist</td>
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<td>22</td>
<td>111</td>
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<td>A7 - unknown</td>
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<td>187</td>
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<td>A5 - schist</td>
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<td>68</td>
<td>29</td>
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<td>A4 - sulphides in quartz</td>
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<td>140</td>
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<td>14</td>
<td>13.6</td>
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<tr>
<td>A12 - Dolerite</td>
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<td>6</td>
<td>34</td>
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<td>A3 - Green rock with quartz through it</td>
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<td>181</td>
<td>23.6</td>
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<td>155</td>
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<td>A17 - chert</td>
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<td>36</td>
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<tr>
<td>A16 - fresh A14</td>
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<td>11</td>
<td>213</td>
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<td>355</td>
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Appendix 7 Continued..

Inductively Coupled Plasma Mass Spectrometry

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<th>Bi</th>
<th>Ce</th>
<th>Cs</th>
<th>Ga</th>
<th>Hf</th>
<th>La</th>
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<tr>
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<td>444</td>
<td>0.2</td>
<td>1.51</td>
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<tr>
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<td>4</td>
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<td>2.49</td>
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<td>76.6</td>
<td>0.1</td>
<td>0.89</td>
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<td>RR 787 - skylab greenschist</td>
<td>1.6</td>
<td>33</td>
<td>-0.1</td>
<td>3.67</td>
<td>3.4</td>
<td>42.5</td>
<td>6.1</td>
<td>3.52</td>
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<td>54.75</td>
<td>1.24</td>
<td>26.4</td>
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Appendix 7 Continued..

Inductively Coupled Plasma Mass Spectrometry

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<th>Nb ppm</th>
<th>Nd ppm</th>
<th>Pb ppm</th>
<th>Pr ppm</th>
<th>Rb ppm</th>
<th>Sn ppm</th>
<th>Sr ppm</th>
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<td>-3</td>
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Appendix 7 Continued..

## Inductively Coupled Plasma Mass Spectrometry

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<th>U (ppm)</th>
<th>Y (ppm)</th>
<th>Zr (ppm)</th>
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# APPENDIX 8

Table of Site Descriptions, Details and Sampling Dates for Mine Waters of Ranger Uranium Mine sampled and analysed for this research

<table>
<thead>
<tr>
<th>Field No.</th>
<th>Site description</th>
<th>Comments</th>
<th>Sam. Date</th>
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<tr>
<td>W1</td>
<td>SWP</td>
<td>Bottom of waste-rock W1</td>
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<tr>
<td>W2a</td>
<td>Ore</td>
<td>Direct drainage from High grade stock pile</td>
<td>2/12/1999</td>
</tr>
<tr>
<td>W2b</td>
<td>Ore</td>
<td>Drainage near creek/station drop HGSP</td>
<td>2/12/1999</td>
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<td>W3</td>
<td>LGO Sump 1</td>
<td>Up-welling pond at bottom of laterite stockpile</td>
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<td>W4</td>
<td>LGO Sump 2</td>
<td>Creek running into RP2 from laterite stockpile.</td>
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<td>R102</td>
<td>RP1</td>
<td>Near the spillway near road</td>
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<td>R105</td>
<td>CCMBL</td>
<td>2nd from the Tailings. Raining</td>
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<td>R110</td>
<td>CC</td>
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<td>R114</td>
<td>SWP</td>
<td>Top of waste-rock</td>
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<td>R115</td>
<td>SWP</td>
<td>Bottom of waste-rock</td>
<td>19/04/2000</td>
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<tr>
<td>R118</td>
<td>DW3A</td>
<td>DW3A, Dewatering bore between RP2 and P3</td>
<td>21/04/2000</td>
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<td>RW205</td>
<td>CCMBL</td>
<td>1m less water than April</td>
<td>5/08/2000</td>
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<tr>
<td>RW206</td>
<td>CCMBL</td>
<td>Duplicate of RW205. 5 filters used for these two samples</td>
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<tr>
<td>RW207</td>
<td>RP2</td>
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<td>5/08/2000</td>
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<tr>
<td>RW208</td>
<td>Sump98</td>
<td>NW corner of Eastern pool.</td>
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<tr>
<td>RW210</td>
<td>DW3A</td>
<td>Duplicate of RW209</td>
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<td>RW211</td>
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<td>RW212</td>
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<td>75cm&lt;April water level. 50cm from shoreline</td>
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<td>P1DWB</td>
<td>Dewatering bore for P1 near CC</td>
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<td>ARD leachate from platform horizon WWP</td>
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<td>OB30</td>
<td>Using the white manual bailer.. 9.2metres depth</td>
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<tr>
<td>RW217</td>
<td>RP2</td>
<td>After fill from pumping from Pit3. 8 days after first sampling.</td>
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<tr>
<td>RW218</td>
<td>Process Water</td>
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<td>LGO sump away from stockpile</td>
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<tr>
<td>RW310</td>
<td>OB24</td>
<td>OB24, observation bore, WWP influence</td>
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### Appendix 8 Continued

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<th>Field No.</th>
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<td>DW3A</td>
<td>10 minutes pumped before sampling</td>
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<tr>
<td>RW314</td>
<td>DW3A</td>
<td>Duplicate of RW313. 10 minutes pumped before sampling</td>
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<td>RW315</td>
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<td>Waste-rock trickle A, the second sample taken here. Upstream, definitely coming from the waste-rock pile itself.</td>
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<td>RW318</td>
<td>Sump98</td>
<td>Exact same sampling location as before</td>
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<td>RW319</td>
<td>Bore23552</td>
<td>WWP. Smelt H2S coming from this capped bore</td>
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<td>RW323</td>
<td>WWP 2</td>
<td>WWP runoff channel. After storm</td>
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<td>RW324</td>
<td>OBWWP</td>
<td>Unused observation bore WWP. Lots of dead insects in it, and next to the manhole bore</td>
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<td>GC</td>
<td>Grand Canyon, CWP influence</td>
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<td>MB</td>
<td>ERA sample of main bore on WWP</td>
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**APPENDIX 9**

*In-field Chemical Parameter Measurements for Mine Waters of Ranger Uranium Mine*

Note: $\text{HCO}_3^-$ has been calculated from in-field alkalinity titrations.

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APPENDIX 10

Analytical Chemistry Results (IC and ICPAES) for Major Ions (mg/L) in Mine Waters of Ranger Uranium Mine

Note: All anions were analysed by IC and cations and total S were analysed by ICPAES. All concentrations are in mg/L.

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APPENDIX 11

Analytical Chemistry Results (ICPMS) for Trace Elements (µg/L) in Mine Waters of Ranger Uranium Mine

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APPENDIX 13

X-Ray Diffraction Analysis of Five Samples of Suspended Sediment in Runoff from the Western Waste-rock Pile

Sample: CASD81132

PRE-TREATMENT

GLYCOL

+ 350°C

+ 550°C
Sample: CARD81133

Sample: CARD81131

447
Sample: CARD81136

PRE-TREATMENT

Kaolinite/Chlorite
Muscovite
Quartz

Kaolinite/Chlorite
Muscovite

+350°C

+ 550°C

Chlorite
Chlorite
Chlorite
APPENDIX 15

Trace of XRD analysis of precipitate of RP2 water - U-mineral identified = Lanthinite.