The Application of Sm-Nd and Rb-Sr Isotopic Systematics
to Ore Deposits

by

Roland Maas

Thesis submitted for the degree of
DOCTOR OF PHILOSOPHY

THE AUSTRALIAN NATIONAL UNIVERSITY
November, 1987
Statement

The analytical data, interpretations and conclusions presented in this thesis are my own unless otherwise acknowledged. The work is based on research carried out at the Research School of Earth Sciences between March, 1984 and October, 1987. The XRF and neutron activation analyses were performed by BW Chappell and his assistants at the Department of Geology, Australian National University.

Roland Maas
Acknowledgements

I am indebted to the ANU and RSES for providing the financial and technical support that made this project possible. I am grateful to my supervisors MT McCulloch and IH Campbell whose enthusiasm, support and advice were most important for me throughout this thesis work.

My thanks go to Bruce Chappell (XRF and INAA analyses), Nick Ware (electron probe analyses), Mike Shelley and Ross Taylor (ICP) and to the many people who provided help and advice: Suresh Bhargava, Mick Bower, Maury Cowan, Joan Cowley, Ross Freeman, Les Kinsley, Elmer Kiss, Robyn Maier, Keith Massey, Derek Millar, Richard Rudowski, Norm Schram, Mike Shelley and Liz Webber.

I appreciate the support from the following mining companies who provided access to their field facilities, leases and drill core material: Kidd Creek Mines Ltd., Queensland Mines Ltd., Pancontinental Mining Ltd., Denison Pty. Ltd. and Ranger Uranium Mines. I am particularly grateful to mine geologist C Kendall who provided excellent sample material from the Ranger pit. I thank RW Page, RS Needham, LAI Wyborn and BI Cruikshank (Bureau of Mineral Resources) for the use of samples and analytical data.

My work benefitted from collaboration with AR Wilde (Monash University) whose support and interest in our joint project on the East Alligator Rivers uranium deposits was invaluable. I also thank NHS Oliver for exchange of ideas and manuscripts during work on Mary Kathleen. Throughout the course of this study I benefitted from discussions with WM McDonough, DR Nelson, J Hergt, MT McCulloch, IH Campbell, RW Page, LAI Wyborn, PK Zeitler, G Corlett, M Honda, T Esat, JR Richards, J Walshe and SS Sun.

Finally, I would like to thank my fellow postgraduate students at RSES for enthusiasm, sarcasm, soccer and squash skills, Friday evenings and great field trips.
Abstract

Reliable information on the age of mineralization and the source of ore metals is essential to models of ore genesis and the formulation of exploration strategies. Recently, Sm-Nd isotope systematics have been added to the isotopic techniques used to obtain such information. This thesis examines the feasibility of combined Sm-Nd and Rb-Sr isotopic studies in case studies on six important Archean to Proterozoic ore deposits in Australia and Canada.

The Kidd Creek Cu-Zn mine, Ontario, one of the world's largest volcanogenic massive sulfide deposits, is hosted by intensely altered felsic volcanics and interpreted to be of syngenegetic origin. This is confirmed by a Sm-Nd isochron age on whole rocks from the alteration zone and on stratiform ores, which is indistinguishable within the quoted errors from a precise U-Pb zircon age for the felsic volcanics. This agreement suggests that Sm-Nd dating may be useful in the dating of hydrothermal alteration events associated with ore deposits, provided rare earth elements were sufficiently mobile to generate a large spread in Sm/Nd ratios. Comparison with the younger Rb-Sr age of the samples indicates the greater robustness of the Sm-Nd isotope systems during post-mineralization metasomatic alteration. Initial 143Nd/144Nd ratios in the ores are used to infer the importance of the host volcanics as a base metal source.

Rare earth element-uranium mineralization at Mary Kathleen U mine, Queensland, is controversial in terms of timing of ore deposition and the source of uranium and rare earths. Published U-Pb data are confirmed by a Sm-Nd mineral-whole rock isochron which indicates that ore formed about 200-250 Ma after emplacement of a nearby U-rich A-type granite previously considered the major metal and fluid source for the mineralization. However, Nd isotope systematics nevertheless indicate a genetic link between the granite and the ore; the preferred interpretation being that present-day ore was formed during metamorphic-hydrothermal remobilization of an older contact-metasomatic protore.

Sm-Nd isotope dating of primary ores and uraninites from the Nabarlek, Jabiluka and Koongarra unconformity-type uranium deposits in the Northern Territory indicates a narrow range of ages scattered around ~1600 Ma, in agreement with Rb-Sr data on rocks from the alteration zones at Nabarlek and Jabiluka. In combination with initial Nd-Sr isotopic data, the Sm-Nd age constraints are used to argue for a post-unconformity origin of mineralization with ore fluids and uranium being derived predominantly from the volcano-sedimentary rocks above the unconformity rather than the metamorphic Late Archean-Lower Proterozoic basement as was suggested previously. In contrast, neither Sm-Nd data nor geological relationships unambiguously define the age of mineralization at Ranger. However, initial Nd-Sr isotope ratios are consistent with a pre-unconformity age as suggested by published U-Pb data; this interpretation would require substantial modifications to current models for the origin of unconformity-type U deposits.

It is concluded that Sm-Nd isotope systematics have considerable potential in the study of ore deposits and are particularly useful in terrains with a long and complex history. The greater robustness against post-ore disturbance compared to the Rb-Sr and U-Pb
systems is an additional benefit.

High precision measurements of stable isotope ratios in Gd, Sm and Nd from Northern Territory unconformity-type U ores reveal anomalies whose distribution and relative magnitudes are consistent with an origin from U fission. Calculated thermal neutron fluences and fission yield partitioning indicate spontaneous fission of $^{238}\text{U}$ plus variable but generally small amounts of thermal neutron fission of $^{235}\text{U}$ as the causes of the anomalies. A method is presented which is used to remove the (small) effects of U fission in measured $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratios and which allows their utilization in geochronological studies.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>STATEMENT</th>
<th>ACKNOWLEDGEMENTS</th>
<th>ABSTRACT</th>
<th>TABLE OF CONTENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>PART I. Sm-Nd AND Rb-Sr ISOPOPE SYSTEMATICS OF ORE DEPOSITS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>The Problem</td>
<td>Aims</td>
<td>Thesis Organization</td>
</tr>
<tr>
<td>CHAPTER 1. Rb-Sr ISOTOPE STUDIES OF ORE DEPOSITS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1 Mobility of Rb and Sr in hydrothermal systems</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.2 $^{87}\text{Sr}/^{86}\text{Sr}$ as a tracer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.3 Rb-Sr dating of mineralizations</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4 Sr isotopic tracing of cations in ore-forming solutions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHAPTER 2. BEHAVIOUR OF THE RARE EARTH ELEMENTS DURING FLUID-ROCK INTERACTIONS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.2 REE solubility</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.3 Immobility versus mobility of REE in altered rocks</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.4 REE in ore-forming hydrothermal systems</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5 REE in hydrothermal solutions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHAPTER 3. Sm-Nd ISOTOPE STUDIES OF ORE DEPOSITS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1 Introduction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.2 Earlier studies</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3 Case studies</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3.1 Kidd Creek volcanogenic massive sulfide deposit</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3.1.1 Introduction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3.1.2 Results: Sm-Nd isotopes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3.1.3 Rb-Sr isotopes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3.1.4 Initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratios</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3.1.5 Conclusions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3.2 Mary Kathleen uranium - REE deposit</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3.2.1 Introduction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3.2.2 REE, U and Th concentrations</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3.2.3 Isotopic results: U-REE mineralization</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3.2.4 Sm-Nd isotopic evidence for two periods of skarn formation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3.2.5 The origin of U-REE mineralization</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3.2.6 Conclusions</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.3.3 Unconformity-type uranium deposits

3.3.3.1 Introduction

3.3.3.2 ARUF uranium deposits: common features and genetic models

3.3.3.3 Nabarlek

3.3.3.5 Jabiluka

3.3.3.6 Koongarra

3.3.3.7 Ranger

3.3.3.8 Conclusions

3.4 Sm-Nd isotope systematics in economic geology

REFERENCES

APPENDIX 1a. Sm-Nd and Rb-Sr dating of an Archean massive sulfide deposit: Kidd Creek, Ontario
(co-authored with MT McCulloch, IH Campbell and P Coad, published in GEOLOGY, 14, 585-588, 1986)

APPENDIX 1b. Sm-Nd and Rb-Sr isotopic data for Kidd Creek massive sulfide ores

APPENDIX 2. Sm-Nd isotope systematics in uranium rare-earth element mineralization at the Mary Kathöen uranium mine, Queensland
(co-authored with MT McCulloch, IH Campbell and RW Page, in press, ECONOMIC GEOLOGY, 82, 1987)

APPENDIX 3a Nd-Sr isotope constraints on the age and origin of unconformity-type uranium deposits in the Alligator Rivers Uranium Field, Northern Territory, Australia
(co-authored with MT McCulloch, submitted to Contrib. Miner. Petrol.)

APPENDIX 3b REE concentrations in Nabarlek U ores and in standard rocks analysed by ICP

PART II. Gd, Sm AND Nd ISOTOPIC ANOMALIES IN U ORES AND URANINITES FROM THE NABARLEK, JABILUKA, KOONGARRA AND RANGER URANIUM DEPOSITS
(co-authored with MT McCulloch, to be submitted to Isotope Geoscience)

APPENDIX 4 Correction for uranium fission in Nd isotopic data
Part 1

The application of Sm-Nd and Rb-Sr isotope systematics to ore deposits
INTRODUCTION

The Problem

Ore deposits have formed in the upper parts of the crust since the Early Archean. They are generated by common geological processes such as magmatic, metamorphic, sedimentary processes and fluid-rock interactions. In most cases these processes will not produce a mineralization that would be called economic. A combination of favourable circumstances is required to maximize the concentration of a few valuable elements. The study of ore deposits aims at identifying these critical factors and to construct genetic models for ore genesis based on these findings.

Isotopic studies play an important part in the investigation of ore-forming processes. The variations in stable isotope abundances of the elements H, C, O and S in rocks, minerals and fluid inclusion waters associated with ore deposits can provide valuable information about temperature and other physico-chemical conditions during ore deposition. In addition, they can be utilized to identify the source(s) and evolution of the ore-bearing fluids (Ohmoto and Rye, 1979; Taylor, 1979; Hall, 1974 and references therein).

The other group of isotopic systems, the parent-daughter isotope systems or radiogenic isotopes, allows the dating of ore-forming events. Accurate data on the timing of ore deposition are of critical importance in the understanding of fossil ore deposits; models based on inaccurate age information may be misleading. It is often possible to accurately determine the relative timing of the various depositional stages preserved in a deposit by detailed petrological and structural studies. Further, the absolute age may be inferred from the relationship of the deposit to associated dated magmatic, metamorphic, sedimentary and/or tectonic features. In many cases, however, absolute age estimates from these methods give inconclusive or not sufficiently precise results, in particular in terrains with a long, complex geological history. It is therefore desirable to obtain more reliable absolute ages by direct radiometric dating of the mineralization.

K-Ar, U-Pb and Pb model age dating have been used in economic geology for more than 30 years. Pb isotopic compositions are also used extensively as tracers of Pb provenance in base metal deposits and many other types (see reviews by Doe and Stacey, 1974; Doe and Zartman, 1979). More recently these methods have been joined by the Ar-Ar method (Kesler et al., 1981; York et al., 1981; Hudson and Dallmeyer, 1982; Sutter et al., 1983; Kerrich and Watson, 1984; Zentilli and Reynolds, 1985; McMaster et al., 1987; Bray et al., 1987; Hanes et al., 1987) and the Rb-Sr and Sm-Nd methods.

Aims

This thesis presents the results of an investigation on the feasibility of Sm-Nd dating and Nd isotopic tracing as applied to ore deposits. The deposits chosen, the Kidd Creek volcanogenic Cu-Zn deposit in Ontario, the Mary Kathleen U-REE deposit in NW Queensland, and the four large unconformity-type U deposits Jabiluka, Nabarlek, Ranger and Koongarra in the Northern Territory, were selected on the basis of demonstrated REE mobility during ore deposition and the availability of geochronological data on ore deposition.
obtained by other methods.

The following are the major goals of this study:

(1) Obtain Sm-Nd isochron dates or model ages on the time of REE fractionation in the ore and/or associated wall-rock alteration and assess its relevance to ore formation.

(2) If possible, compare the results with Rb-Sr data obtained on the same samples to evaluate the relative sensitivity of the two systems to hydrothermal and other thermal events during and after ore deposition.

(3) Compare the results of the Sm-Nd and Rb-Sr analyses with other published radiometric data.

(4) Use initial $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in ore minerals or whole rocks to constrain possible sources of Nd and Sr, i.e. sources of metallic components in the ore-forming fluid.

(5) Integrate the isotopic data with existing geologic and geochemical data and evaluate their contribution to genetic models of ore deposition.

Thesis organization

To achieve concise but adequate treatment of the results and concentrate on the aims listed above, detailed geological descriptions, analytical details and results are not given in this thesis; the reader is referred to appendices 1-3. Instead, I will summarize the findings of these studies and highlight the most significant conclusions in order to best evaluate the potential of Sm-Nd isotopic studies on ore deposits.

Chapter 1 reviews briefly previous Rb-Sr isotopic work on ore deposits to demonstrate both its potential and its limitations. In Chapter 2, I discuss the available information on the mobility of the rare earth elements in fluid-rock interactions both in non-mineralizing and mineralizing settings, with emphasis on the implications for Sm-Nd isotopic studies of ore deposits. Chapter 3 presents summaries of case studies on six important ore deposits followed by an evaluation of the potential and limitations of Sm-Nd isotopic studies in economic geology. Appendices 1-3 contain three papers (one published, one in press, one submitted) on the results of this thesis; additional data not included in the papers are given in appendix 1b and 3b.

In Part 2 of the thesis I will discuss the significance of isotopic anomalies found in Nd, Sm and Gd extracted from high-grade U ores from Nabarlek, Jabiluka, Koongarra and Ranger. These anomalies are compared to those found in the natural nuclear reactor at Oklo and in lunar soils.
CHAPTER 1. Rb-Sr ISOTOPE STUDIES OF ORE DEPOSITS

1.1 Mobility of Rb and Sr in hydrothermal systems

Rb and Sr are two of the more mobile trace elements, a fact long recognized in Rb-Sr dating and trace element studies of altered igneous rocks. This mobility combined with the availability of high precision isotopic analysis makes $^{87}\text{Sr}/^{86}\text{Sr}$ an ideal cation tracer in many types of fluid-rock systems. Among the many examples, Sr isotopic studies are used to model diagenetic reactions in seafloor sediments (e.g. Hawkesworth and Elderfield, 1978; Gieskes et al., 1987), and to date authigenic carbonate deposits (e.g. Ludwig et al., 1987) and the age of dolomitization (Vahrenkamp et al., 1986) using high resolution seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curves (e.g. Burke et al., 1982; DePaolo and Ingram, 1985). The amount of seawater circulated through mid ocean ridge hydrothermal systems has been estimated using the Sr isotopic composition of the exiting solution (e.g. Albarède et al., 1981; Spooner et al., 1977).

In alteration halos around ore deposits, Rb and Sr are often found to be very mobile, for example in Archean massive sulfide deposits (Campbell et al., 1984), porphyry Cu deposits (Taylor and Fryer, 1980), Archean Au lode deposits (Ludden et al., 1984) and U deposits (Binns et al., 1980a). Depending on the Rb-Sr contents of the phases affected by the hydrothermal alteration, and those in the secondary alteration minerals, both depletions and enrichments of Rb and Sr are observed, which may change Rb/Sr ratios considerably. Hydrothermal fluids involved in these fluid-rock interactions at elevated temperatures show strong increases in their Rb-Sr concentrations as illustrated in Table 1-1.

<table>
<thead>
<tr>
<th>Table 1-1 Rb and Sr concentrations in surface and hydrothermal waters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rb (ppm)</strong></td>
</tr>
<tr>
<td>rivers$^1$</td>
</tr>
<tr>
<td>ocean$^1$</td>
</tr>
<tr>
<td>EPR 21°N$^2$</td>
</tr>
<tr>
<td>Guaymas Basin$^2$</td>
</tr>
<tr>
<td>oilfield brines$^3$</td>
</tr>
<tr>
<td>fluid inclusions$^4$</td>
</tr>
<tr>
<td>fluid inclusions$^5$</td>
</tr>
<tr>
<td>fluid inclusions$^6$</td>
</tr>
</tbody>
</table>


Hot (300-350°C) hydrothermal solutions at mid ocean ridge systems are up to 30 times richer in Rb than unmodified seawater while Sr concentrations remain more or less constant. Hydrothermal springs from sediment-covered ridge segments in the Guaymas Basin leach...
Rb and Sr from the sediments they traverse generating a 60-fold increase in Rb and a 3-fold increase in Sr. Fluid inclusion waters from a variety of ore deposits generally carry considerable Sr abundances at highly variable Rb concentrations. Brines, i.e. solutions with more than 10 wt % total dissolved solids, may carry from 7 to 3000 ppm Sr and typically have very low Rb/Sr ratios. These figures show that Sr is very mobile in hydrothermal fluids which suggests that the Rb-Sr isotopic system could be a useful tool in the study of ore deposits.

1.2 87Sr/86Sr as a tracer

If the Sr isotopic composition is to be used as a tracer for the provenance of cations in hydrothermal solutions, it is necessary to consider possible processes by which hydrothermal fluids acquire their 87Sr/86Sr and their sensitivity to subsequent reequilibration with rocks along their fluid pathway.

During fluid-rock contact, chemical components, in this case Sr or Sr isotopes, may be transferred from the rock to the fluid by diffusion processes, i.e. isotopic exchange. For example, such a mechanism is assumed in equations for the calculation of fluid/rock ratios because it provides a plausible mechanism for rapid isotopic equilibration. The other main mechanism for transfer of Sr isotopes is dissolution of the rock, either congruent or incongruent. Sr isotopic transfer by this mechanism would strongly depend on the relative stabilities of the rock's mineral phases and the nature of possible secondary minerals; variations in Sr concentration and 87Sr/86Sr in the fluids would be modelled best by reaction path models (Berndt et al., 1986). In the case of incongruent dissolution, the Sr transferred to the fluid could be in gross isotopic disequilibrium with the host rock, in particular in the case of very old rocks that have developed large differences in the Sr isotopic composition of their constituent minerals, or in rocks with minerals of widely differing solubilities such as shale with a carbonate component (Bofinger et al., 1968). Further, radiogenic 87Sr could be preferentially removed from Rb-rich phases such as biotite (Clauer, 1981). Obviously, incongruent dissolution would seriously affect any inferences on Sr sources if the measured fluid Sr isotopic compositions are interpreted assuming fluid - whole rock equilibration.

Stettler and Allegre (1978) addressed this problem in a study of fresh rainwaters and thermal waters from the geothermal region of the Cantal in France. They found that Sr isotopic equilibration between freshly fallen rainwater and underlying volcanic rock was completed within a very short time. By itself this would not necessarily prove congruent equilibration because the volcanic rocks underlying the area are very young with only small differences in 87Sr/86Sr between their constituent minerals. However, Rb/Sr and K/Rb ratios in the rainwater closely mimic those in the local volcanics implying an overall control on fluid composition by more or less congruent dissolution of the major silicate phases in the rocks as suggested by Garrels (1967), Helgeson (1971), Petrovic et al. (1976) and Garrels and Mackenzie (1967). Thermal waters from the area represent blends of surface water and deep-seated waters derived from the granitic-metamorphic basement underlying the volcanics; alternatively, deep-seated waters may have been the only component in the thermal waters but partially equilibrated with the volcanics during ascent. Stettler and Allegre
conclude that overall the fluids acquire a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio corresponding to the average Sr isotope composition of the rocks along their fluid path. Under elevated temperatures, equilibration appears to be slower enabling the basement signature to be partially preserved. Alternatively, this may be due to rapid fluid ascent which could have prevented more extensive equilibration with the volcanic wall rocks.

A very good example of more or less complete isotopic equilibration between fluid and whole rock is a study on deep mine waters in Canada by McNutt et al. (1984). They showed that brines tapped by the mining operations originated in 'pockets' isolated from one another over long periods of time. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the mine waters were distinctly different from one another. In one example, two isotopically distinct pockets occurred within the same mine only separated by a fault zone. Fluids and surrounding Precambrian host rocks of a given mine were close to Sr isotopic equilibrium suggesting extensive congruent fluid-rock reactions. Hydrothermal fluids derived from any of these mines would therefore accurately record the average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the source. In contrast, brines from the Michigan basin apparently did not achieve complete Sr isotopic equilibrium with their host rocks (McNutt et al., 1987)

It is probably not possible to conclusively decide whether a fluid equilibrated by congruent or incongruent dissolution and in most cases a tentative decision has to be made.

The sensitivity of a hydrothermal fluid to preserve its chemical and Sr isotopic identity depends on many factors including the Sr contents of the fluid and the rocks along the fluid path, the fluid chemistry and temperature, and the solubility of the wallrock minerals. Another important parameter is the kind of fluid flow. Slow flow through porous rock will be more efficient in terms of recurrent chemical reequilibration than fast flow though fractures. Norman and Landis (1983) argue that Sr isotopes should be as efficient as a tracer as oxygen isotopes because the $\text{Sr}_{\text{fluid}}/\text{Sr}_{\text{rock}}$ ratio is close to unity for many hydrothermal fluids, comparable to the $\text{O}_{\text{fluid}}/\text{O}_{\text{rock}}$ ratio. They suggest that the kinetics of Sr equilibration and reequilibration should therefore be roughly analogous to those of oxygen isotopes.

1.3 Rb-Sr dating of mineralizations

Early Rb-Sr isotopic work on ore deposits utilized whole rock and mineral isotopic age determinations on igneous bodies related to mineralization or model ages on hydrothermally altered equivalents (e.g. Turek, 1966; Brooks, 1966). In recent years, ore material has been dated directly using gangue minerals (Ausburn and Kish, 1986), sulfides (Lange et al., 1983) and fluid inclusions (Shepherd and Darbyshire, 1981; Horn et al., 1986). In addition, glauconite dating has been used extensively to determine the age of ore-related brine migration during formation of Mississippi-Valley-type Pb-Zn deposits (e.g. Stein and Kish, 1985). A model age approach was used by Ruiz et al. (1984) who argued that in many hydrothermal deposits, Sr is essentially derived from the wallrocks and their average $^{87}\text{Sr}/^{86}\text{Sr}$ was preserved in Rb-free gangue minerals such as calcite. If the wallrocks develop with high Rb/Sr until the present, the difference $\Delta^{87}\text{Sr}/^{86}\text{Sr}$ between average gangue and average wallrocks is proportional to the age of mineralization. Despite problems with the determination of reasonable means for wallrock $^{87}\text{Sr}/^{86}\text{Sr}$ and Rb/Sr ratios required in the
age calculation, model ages for three ore deposits, the Late Precambrian White Pine sediment-hosted Cu deposit in Michigan, the Hercynian granite-related Panasquiera Sn-Wo deposit in Portugal, and the Tertiary shale-hosted Pb-Zn veins of Parral, Mexico, agreed well with ages obtained by other methods.

1.4 Sr isotopic tracing of cations in ore-bearing solutions

Reesman (1968) and Hedge (1974) evaluated the usefulness of the Sr isotopic tracer by analysing Sr-rich gangue minerals in hydrothermal veins from a number of deposits and found that the Sr isotopic composition of gangue phases and wallrocks were broadly comparable, implying an origin of the Sr predominantly by local lateral secretion. They concluded that Sr isotopic tracing was probably not very useful in ore deposit studies.

In contrast, many more recent studies have shown considerable differences in Sr isotope ratios between ore and gangue minerals, and the immediate wallrocks. In some cases such as the monzonite-related Pasto Bueno tungsten deposit in Peru, hydrothermal ore-forming solutions must have travelled for several kilometers without Sr isotopic reequilibration with the wallrocks (Norman and Landis, 1983).

Attempts to use Sr isotopes as tracers are particularly useful in deposits which carry Sr-rich Ca and Ba minerals such calcite, gypsum anhydrite, barite and fluorite as major ore or gangue minerals because of the very similar geochemical behaviour of Sr, Ca and Ba. In these cases, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is a direct tracer of Ca and Ba sources. Several studies of barite deposits (Barbieri et al., 1984; Kesler and Jones, 1981; Kesler et al., 1985) and fluorite deposits (Barbieri et al., 1977; Kesler et al., 1983; Brookins et al., 1971; Norman and Segalstad, 1978) have utilized this relationship. Other attempts to use the Sr isotopic tracer include studies on Mississippi-Valley-type Pb-Zn deposits (Kessen et al., 1981; Chauduri et al., 1983; Lange et al., 1983) and similar deposits at Pine Point (Medford et al., 1983), skarn deposits (Langmuir et al., 1985), massive sulfide deposits (Farrell and Holland, 1983; Whitford et al., 1986), the Ivigtut cryolite ore (Blaxland, 1976), epithermal Au mineralization (Ausburn and Kish, 1986; Kerrich, 1987), Mo-U-base metal vein mineralization in Colorado (Dickin et al., 1986), Archean Au lodes (King et al., 1986; King and Kerrich, 1987), Kiruna apatite-magnetite ore (Kogarko et al., 1986), Cyprus-type Cu deposits (Chapman and Spooner, 1977), monzonite-related Wo mineralization (Norman and Landis, 1983), porphyry Cu-associated wallrock alteration (Taylor and Fryer, 1983b) and a possible metamorphosed Proterozoic equivalent (Yngström et al., 1986). Further, Sr isotopes have been used extensively in the study and correlation of oilfield brines (Chauduri, 1978; Sunwall and Pushkar, 1979; Starinsky et al., 1983; Steuber et al., 1984).

It is obvious from these examples and those in the previous section that Rb-Sr dating and Sr isotopic tracing are applicable to a wide range of ore types and materials. Its versatility gives this method a considerable potential in economic geology. However, with the exception of two examples, all quoted case studies have dealt with unmetamorphosed Phanerozoic deposits where Rb-Sr isotopic systems can be assumed to be essentially undisturbed. Metamorphic overprinting coupled with large age corrections would probably seriously impair the usefulness of the method in Proterozoic and Archean ore deposits.
Because of its demonstrably greater robustness Sm-Nd isotope systematics could be more useful in such cases than Rb-Sr systematics; the behaviour of both methods is compared in the case studies summarized in chapter 3.

The rare earth elements (REE) are widely used by petrogenetic researchers for igneous, sedimentary and metamorphic rocks (see reviews by Kurz, 1976; Albee and Albee, 1978; Hudson, 1984; Taylor and McLennan, 1988). This is based on their unique geochemical behaviour as a group (Moorbath, 1964) and their demonstrated immobility during many geologic interactions. In contrast, the utilization of REE and related elements systematics in the petrogenesis of natural rocks relies on their mobility in some geologic interactions.

This chapter attempts to briefly summarize current knowledge of REE mobility in magmas operating under upper crustal conditions such as submarine volcanism, metamorphism, and hydrothermal alteration. It will concentrate largely on studies involving such hydrothermal systems as data for REE mobility during diagnostic and weathering are not immediately relevant to hydrothermal ore deposits, the subject of this work.

2.1. LREE mobility

A first order feature of LREE is their extremely low solubility in aqueous solution (Sillitoe and Marill, 1964; Turner and Whitefield, 1973) which is reflected by their low concentrations in natural waters. Table 1 lists typical concentrations of Nd as a representative of the LREE in various natural waters compared with typical seamounts.

<table>
<thead>
<tr>
<th>Water Type</th>
<th>Nd (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seamount</td>
<td>2.7</td>
</tr>
<tr>
<td>River</td>
<td>5.169</td>
</tr>
<tr>
<td>Marine</td>
<td>1.482</td>
</tr>
</tbody>
</table>

Source: Silver and Groves (1987); and this review.

Flynn et al. (1984), Goldstein and Aronson (1987)

While Nd is generally present in the early stage Sr contrasts of natural brines are orders of magnitude higher, reflecting its much greater solubility. Of course, REE concentrations in natural waters are in part determined by removal (precipitation and adsorption onto clay surfaces (Moosbeier, 1973) and scavenging by settling particles in both marine (Ellis, 1985) and riverine systems (Flynn et al., 1984; Ussellis-Goldfarb et al., 1984; Goldstein and Dymek, 1977), which mechanisms are responsible for the REE underrepresentation by seawater relative to their mobility set by the solubilities of their many idealized hydrothermal ore deposits (see also Humphris, 1984). Nevertheless, both experimental data (Flynn and Bustin, 1979;
CHAPTER 2. BEHAVIOUR OF THE RARE EARTH ELEMENTS
DURING FLUID-ROCK INTERACTION

2.1 Introduction

The rare earth elements (REE) are widely used as petrogenetic tracers for igneous, sedimentary and metamorphic rocks (see reviews by Hanson, 1978, 1980; Allègre and Minster, 1978; Henderson, 1984a; Taylor and McLennan, 1985). This is based on their unique geochemical behaviour as a group (Henderson, 1984b) and their demonstrated immobility during many fluid-rock interactions. In contrast, the utilization of REE and Sm-Nd isotopic systematics in ore petrogenetic studies relies on their mobility in ore-forming fluid-rock interactions.

This chapter attempts to briefly summarize current knowledge of REE mobility in processes operating under upper crustal conditions such as submarine weathering, diagenesis, metamorphism and hydrothermal alteration. I will concentrate largely on studies dealing with hydrothermal systems as data on REE mobility during diagenesis and weathering are not immediately relevant to hydrothermal ore deposits, the subject of this thesis.

2.2 REE solubility

A first order feature of REE is their extremely low solubility in aqueous solutions (Sillén and Martell, 1964; Turner and Whitfield, 1979) which is reflected by their low concentrations in natural waters. Table 1 lists typical concentrations of Nd as a representative of the LREE in various natural waters compared with typical Sr abundances.

Table 2-1. Nd and Sr concentrations in natural surface waters

<table>
<thead>
<tr>
<th></th>
<th>Nd (pg/g)</th>
<th>Sr (ng/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>seawater</td>
<td>2-7</td>
<td>7600</td>
</tr>
<tr>
<td>river + lake water</td>
<td>5-3100</td>
<td>80</td>
</tr>
<tr>
<td>(mean =100) 1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Sources: Elderfield and Greaves (1982) and refs. therein; Hoyle et al. (1984); 1 Goldstein and Jacobsen (1985).

While Nd is generally present in the pg/g range, Sr contents of natural waters are orders of magnitude higher, reflecting its much greater solubility. Of course, REE concentrations in natural waters are in part determined by removal mechanisms such as adsorption onto clays (Roaldset, 1973) and scavenging by settling particles in both oceanic (Klinkhammer et al., 1983; Aplin, 1984; deBaar et al., 1985; Elderfield and Greaves, 1982) and riverine environs (Hoyle et al., 1984; Upstill-Goddard et al., 1986; Goldstein and Jacobsen, 1987). Such mechanisms are responsible for the REE undersaturation in seawater relative to their solubility set by the solubilities of their most likely insoluble salts (see also Humphris, 1984). Nevertheless, both experimental data (Flynn and Burnham, 1978;
Zielinski and Frey, 1974; Cullers et al., 1973) and data on hydrothermal fluids reacted with rocks (Michard and Albarède, 1986; Piepgras and Wasserburg, 1985) point to an extremely low effective REE solubility.

2.3 Immobility versus mobility of REE in altered rocks

Given this low REE solubility, one would not expect any changes in REE patterns of rocks undergoing hydrothermal alteration. This is borne out by many studies in particular on the REE geochemistry of oceanic basalts, either fossil in ophiolites or recovered from the seafloor (Dungan et al., 1983; Frey et al., 1968; Kay and Senechal, 1976; Philpotts et al., 1969; Smewing and Potts, 1976). Similar results were obtained for volcanics and other rock types with metamorphic grades ranging from zeolite facies to amphibolite facies (Humphris et al., 1978; Herrmann et al., 1974; Muecke et al., 1979). Furthermore, experiments in which basaltic material was reacted with hot seawater at water/rock ratios up to 120 and temperatures from 150-350°C (Menzies et al., 1979) and 500-600°C (Hajash, 1984) produced none or very minor changes in the REE patterns of the basalt despite complete alteration to a clay assemblage in some cases.

In contrast, other studies have found REE to be mobile under a wide range of conditions. Again most studies concentrated on hydrothermally altered mafic and ultramafic rocks (Dostal et al., 1980, Fowler et al., 1983; Frey et al., 1974, Hellman and Henderson, 1977; Hellman et al., 1979; Nyström, 1984, Ludden and Thompson, 1979, Menzies et al., 1977; Thompson, 1973; Wood et al., 1976; Floyd, 1977; Kerrich et al., 1987), but REE mobility was also demonstrated in intermediate to felsic volcanics (Jones, 1981; Baker and deGroot, 1983), granites (Alderton et al., 1980; Baker, 1985; this study, see appendices 2 and 3a), sediments (Zielinski, 1985) and gneisses (Vocke et al., 1987).

Several different types of REE mobility can be distinguished as illustrated in Fig. 2-1.

Fig. 2-1: Different types of REE mobility as found in crustal rocks displayed on standard chondrite-normalized REE diagrams. A, differential REE mobility affecting either the light or the heavy rare earths, rarely both. B, differential mobility affecting only Ce and/or Eu. Ce and Eu may occur in variable oxidation states while the other REE are trivalent (Henderson, 1984b). Once they have changed their oxidation states, their geochemical behaviour is different from that of the trivalent REE which can cause anomalies in an otherwise smooth REE pattern. C, bulk REE enrichment or -depletion may be caused by real REE addition or removal, respectively, but in most cases the apparent changes are due to volume changes in the rock.
Differential mobility is demonstrated in many studies. For example, LREE enrichment involving predominantly La, Ce, Pr and Nd is common in altered basalts (Frey et al., 1974; Ludden and Thompson, 1979) while HREE are usually less mobile. Anomalous behaviour of Eu during fluid-rock interactions is also quite common (Jahn and Sun, 1977; Sun and Nesbitt, 1978; Hellman et al., 1979; Nyström, 1984; Alderton et al., 1980). Ce anomalies are generally restricted to the marine environment where they are a prominent feature of seawater (Elderfield and Greaves, 1982), ferromanganese nodules and hydrothermal-hydrogenous sediments and crusts (Elderfield et al., 1981a; Elderfield and Greaves, 1981; Robertson and Fleet, 1976; Piper and Graef, 1974) and some submarine basalts exposed to submarine weathering (Ludden and Thompson, 1979; Bonnot-Courtois, 1980; Masuda and Nagasawa, 1975; Menzies et al., 1977; Seifert et al., 1985; Patocka, 1987). Ce anomalies have also been reported for subaerial lavas in East Africa (Jones, 1981) and there are some indications for anomalous Ce behaviour in continental ground- and surface waters (Lei et al., 1986; Goldstein and Jacobsen, 1987). The anomalous Ce signature of some marine sediments may be transferred to the mantle in subduction zones and may reappear in island arc lavas (Heming and Rankin, 1979; Hole et al., 1984).

Bulk REE changes can often be explained by volume changes due to leaching of major components (leading to bulk REE enrichment) or dilution with REE-poor material such as water, carbonate, quartz etc. (bulk REE depletion). This type of apparent REE mobility is very common (Hellman et al., 1979; Dickin and Jones, 1983; Ludden et al., 1982; Dostal and Strong, 1983; Lesher et al., 1986; Landrus and Ikramuddin, 1986) and has also been observed in experiment (Menzies et al., 1979). True bulk REE removal is probably rare; a well documented case is reported in Staudigel and Hart (1983).

The interpretation of REE behaviour in hydrothermal fluid-rock interactions is greatly hampered by a general lack of knowledge about REE partitioning between minerals and aqueous solutions or about their aqueous geochemistry at elevated temperature and pressure. Empirically, however, a few factors have been found to be of critical importance for REE behaviour in most if not all cases of fluid-rock interactions. These are:

a) the water to rock ratio
b) the physico-chemical properties of the alteration fluid
c) the nature of the primary and secondary phases and the REE partitioning between them and the fluid.

To a) If REE are as insoluble as indicated by their low abundances in natural waters, large quantities of water will be required to effect any changes in the rock (w/r ratio of ca. 10^5, McCulloch et al., 1980; Michard et al., 1983). Seafloor basalts with extended exposure to seawater (several 10^6 years) have contact with virtually unlimited amounts of seawater and consequently inherit the typical negative Ce anomaly of seawater (Ludden and Thompson, 1979; Bonnot-Courtois, 1980; Robertson and Fleet, 1976). In contrast, similar basalts from within layer 2 of the ocean floor have more or less pristine REE patterns, conceivably due to
the restricted amount of seawater penetrating the volcanic pile (Staudigel and Hart, 1983; Menzies et al., 1977).

To b) It is a well established fact that REE solubility is increased by complexing ligands such as various carbonate species, hydroxide, chloride, fluoride and phosphate ions. Non-particulate REE in seawater (Goldberg et al., 1963) and many hydrothermal fluids are thought to be largely present in complexed form (Kosterin, 1959). REE complexing in seawater is borne out by experimental data on major complexing species (e.g. Cantrell and Byrne, 1987; Turner et al., 1981). Other factors such as pH and Fe content may also be of importance (e.g. Goldstein and Jacobsen, 1985; Keasler and Loveland, 1982; Hoyle et al., 1984). In general, complex stabilities for REE increase from La to Lu, i.e. HREE are generally thought to be more stable in solution than LREE. Chloride-REE complexes seem to be an important exception (Flynn and Burnham, 1978). Hydrothermal solutions rich in potential complexing ligands are likely to be more efficient in extracting REE from the rock and transporting REE than solutions poor in these species.

Anomalous behaviour of Eu and Ce is caused by their ability to exist in two oxidation states. In contrast to their trivalent neighboring REE, Eu$^{3+}$ may be reduced to Eu$^{2+}$ while Ce$^{3+}$ can be oxidized to Ce$^{4+}$. Under surface temperatures, Eu is dominantly Eu$^{3+}$ and would not be expected to show anomalous behaviour. The ubiquitous negative Eu anomalies of many sediments are therefore probably inherited from their magmatic (in general granitic) precursors. Thermodynamic calculations by Sverjensky (1984a) indicate a strong temperature dependence of the Eu$^{3+}$/Eu$^{2+}$ ratio. With increasing pH and temperature in the interval 25-400°C, Eu$^{2+}$ becomes more stable in aqueous fluids and should be the dominant Eu species above about 250°C. While pressure effects are small relative to the temperature effect, independent redox buffering (e.g. the SO$_4$/H$_2$S ratio) is another critical parameter (Möller, 1983).

The oxidation of Ce is almost completely restricted to the marine environment with a few exceptions (see above). At typical pH values around 8, marine Eh values between -0.1 to 0.6 V readily produce Ce$^{4+}$ (Addy, 1979) which is scavenged strongly by settling particles leaving the seawater Ce depleted (Möller, 1983; deBaar et al., 1985). Lowering of pH would act to increase Ce$^{3+}$ relative to Ce$^{4+}$ (deBaar et al., 1985). In most hydrothermal environments, however, oxygen fugacities are too low to allow anomalous Ce behaviour.

To c) The site of the REE before fluid-rock interaction, its stability during the process, and the secondary phases that might develop exert a great influence on REE behaviour. For example, the basalt - seawater hydrothermal experiments by Menzies et al. (1979) and Hajash (1984) did not significantly change the REE patterns of the starting material, despite complete destruction of the igneous mineralogy in the charges; obviously the secondary phase assemblage took up the REE quantitatively. A natural example of this effect is a recent mid-ocean ridge basalt altered at high temperatures which recrystallized in greenschist facies but preserved its igneous REE pattern as indicated by comparison with related unaltered MORB glasses (Ludden and Thompson, 1979). Apparently, metamorphic - hydrothermal mineral assemblages formed under very low grade conditions (zeolite facies, prehnite -
Fig. 2-2: REE patterns of common secondary phases produced in a wide range of rock types undergoing low- to medium temperature (ambient to ca. 400°C) hydrothermal alteration. Note generally high REE abundances in chlorites and epidotes; these alteration phases may take up REE released from primary minerals quantitatively, thus making REE immobile on a whole rock scale. REE patterns may vary significantly depending on the REE released from primary phases. Secondary calcite (except for the calcite in E) and laumontite (a zeolite) have very low REE contents and commonly 'dilute' the rare earths (similar to quartz and the zeolite group in general, Wood et al., 1976). Samples shown in E have high to very high REE and display no Eu anomalies; they are from fractures of a high-REE, plagioclase-rich granite without Eu anomaly. Sources: Copeland et al. (1971); Baker and deGroot (1983); Baker (1985); Kerrich et al. (1987); Alderton et al. (1980); Dickin and Jones (1983); Hellman et al. (1979); Nyström (1984); Kamineni (1986). Normalizing values are chondritic abundances given in Evensen et al. (1978) multiplied by 1.5.
pumpellyite facies) are less efficient in retaining REE than low-grade assemblages formed under greenschist facies conditions (containing e.g. chlorite, epidote, actinolite, sphene). This picture emerges from a number of studies on metabasalts which have shown that the higher grade rocks have REE patterns more akin to their presumed igneous precursors than the lower grade rocks (Herrmann et al., 1974; Frey et al., 1968; Dickin and Jones, 1983; Dungan et al., 1983; Menzies et al., 1977; Nyström, 1984; Wood et al., 1976). Fig. 2-2 shows REE patterns measured in alteration phases formed under very low and low grade conditions.

2.4 REE in ore-forming hydrothermal systems

In the last years interest in REE distributions in ores and their associated gangue- and alteration assemblages has increased strongly. Some of the basic principles of REE systematics in the study of hydrothermal systems are reviewed in Möller (1983). REE patterns in ore minerals such as fluorites (Möller et al., 1976a,b; Grappin et al., 1979; Strong et al., 1984; Ekambaran et al., 1986; Parekh and Möller, 1981; Muecke and Clarke, 1981; Jebrak et al., 1985; Marchand et al., 1976; Gundlach et al., 1976; Norman and Segalstad, 1978), calcites (Möller et al., 1979, 1984; Graf, 1984), apatites (Parák, 1973, 1985; Fleischer, 1983; Gerasimovskiy and Mineyev, 1981; Helvaci, 1984), magnesite (Morteani et al., 1981, 1982), tourmaline (King et al., 1986), anhydrites (Zhuk-Pochekutov et al., 1987) and uraninites (Rao, 1967; Sankaran et al., 1970; Shude, 1984; Fryer and Taylor, 1987) have been used to evaluate the origin of the ore-forming solutions and processes operative during transport and mineral precipitation. Similarly, REE have been used extensively as tracers in the study of banded iron formations (Fryer et al., 1979; Appel, 1983) and hydrothermal and hydrogenous seafloor deposits (Piper, 1974; Piper et al., 1975; Courtois and Clauer, 1980; Elderfield and Greaves, 1981; Elderfield et al., 1981 a, b; Aplin, 1984). This is based on the variability in geological settings and physico-chemical conditions found among hydrothermal ore deposits which in many cases produces highly variable REE distributions. In fact, the whole range of ore deposits from magmatic (e.g. carbonatites and alkaline rocks, Semenov, 1979) to sedimentary-hydrogenous (BIF or oceanic ferromanganese nodules) is characterized by a multitude of unusual rare earth patterns rarely encountered in unmineralized rocks. Figs. 2-3 and 2-4 illustrate this point with some examples from the literature and this work. Other examples can be found in Taylor and Fryer (1982, 1983a).

Variability in REE patterns is found in altered wallrocks and even more so in ore and gangue minerals. This is caused by variable combinations of differential REE mobility in the altered zone, introduction and/or removal of REE by the alteration/ore-forming fluids, and differential precipitation of REE from the fluids into the various solids, i.e. the same processes that control REE mobility in non-mineralized environments. However, the effects of hydrothermal fluid-rock interaction on wallrocks of ore deposits are in many cases greater than they are for non-mineralizing systems, conceivably due to the generally large amounts of fluids involved with resultant intensive alteration (large w/r ratio, Campbell et al., 1984).
Fig. 2-3 Chondrite-normalized REE patterns in a variety of ore deposits. Sources: Appel (1983); Kerrich and Fryer (1979); Drysdall et al. (1984)

and high abundances of potential complexing ligands for the REE which would enhance their mobility (Taylor and Fryer, 1983a). Furthermore, in some deposits conditions of ore formation are such that preferential deposition of the REE is favoured, mostly in
Fig. 2-4. Data sources: Graf (1977); Maas et al. (in press, see appendix 2); McLennan and Taylor (1979). Numbers in upper left hand corner in lowermost diagram represent U concentrations in the samples (after McLennan and Taylor, 1979).

Geochemical association with some other elements such as U (McLennan and Taylor, 1979; Roberts and Hudson, 1983; Staatz, 1978; Cathelineau, 1987), Th-Zr-Nb etc. (the so-called granitophile suite, Taylor and Fryer, 1983a; Drysdall et al., 1984; Staatz et al., 1972) or Fe (e.g. Qiu Yuzhuo et al., 1983; Tu Guangzhi et al., 1985).
2.5 REE in hydrothermal solutions

Information on REE concentrations in hydrothermal fluids is scarce. Michard and Albarède (1986) presented REE data for hot (300-350°C) hydrothermal solutions exiting on the East Pacific Rise (13°N and 21°N) as well as for continental hot springs in Tibet and Bulgaria (Fig. 2-5).

Fig. 2-5: REE abundances in hydrothermal fluids and some associated hydrothermal ocean-floor deposits. Note REE in fluids are multiplied by 10^4. A, Hydrothermal fluids sampled at the East Pacific Rise at 13° and 21°N, compared with cogenetic anhydrite (13°N) and Sm-Nd isotope dilution data for fluids from EPR 21°N (P&W 1985). Anhydrite and fluids from 13°N have similar εNd distinctly below εNd for local MORB. B, chondrite-normalized REE abundances in mid ocean ridge basalt from EPR 13°N and two hydrothermal sediments from the Red Sea deeps. C, chondrite-normalized REE contents in hot spring waters from Tibet and Bulgaria; D, as in C but normalized to shale (PAAS, Taylor and McLennan, 1985). Sources: Michard et al. (1983), Michard and Albarède (1986), Piepgras and Wasserburg (1985), Courtois and Treuil (1977)
REE patterns of fluids from the East Pacific Rise are drastically different from REE patterns in local ocean floor basalts which is interpreted to be a function of the metamorphic mineralogy at depth (likely to consist of quartz, albite, epidote, chlorite, actinolite and sphene) which acts as a buffer for REE released from the primary igneous phases (Michard et al., 1983; Sverjensky, 1984b). REE concentrations in the hydrothermal fluids are lower than in the basalt by a factor of $10^5$ and are therefore unimportant for both MORB and seawater REE budgets. Nevertheless, they appear to control the REE geochemistry of some hydrothermal ridge crest sediments with matching REE patterns (see Fig.2-4). REE data on most Archean and some Early Proterozoic banded iron formations indicate that the hydrothermal REE component may have been much more important at that time (Fryer et al., 1979).

REE abundances in continental hot springs are even lower than in the submarine examples (e.g. 10-60 pg/g Nd). Their shale-normalized REE patterns are flat to HREE-enriched depending on their alkalinity, i.e. the degree of REE complexing with (OH)$^-$ and carbonate species (Fig.2-4). Similar absolute REE concentrations were found in cold springs from Vals les Bains (France) but REE patterns are strongly HREE-enriched relative to shale reflecting the considerably higher degree of carbonate complexing (in this case bicarbonate, Michard et al., 1987).

Considerably higher REE concentrations were measured in fluid inclusion waters from the Copper Flat porphyry copper deposit in New Mexico (Baron et al., 1984). The fluids were highly LREE-enriched with La ranging from 1 to 100 ppm and HREE from 10-100 ppb. Novgorodova et al. (1984) quote REE abundances in Au-associated quartz between 0 and 1.6 ppm Ce; as the quartz lattice is assumed to reject REE and the studied samples were carefully screened to avoid mineral inclusions, the authors contend that the results reflect the REE contents in fluid inclusion and their daughter crystals. Consequently, if the large dilution by SiO$_2$ is considered, rather high fluid REE contents are obtained. Chondrite-normalized REE patterns are characterized by flat LREE patterns with strongly sloping HREE abundances and negative Ce anomalies of variable size; while Lu correlates with Cl$^-$ content, Au and LREE show anticorrelations with Cl$^-$. Norman and Mearns (1986) report 0.8-5 ppm Nd and 0.3-2.1 ppm Sm from fluid inclusions in miiarolytic quartz found in the Mo-mineralized Drammen Granite, Oslo paleorift. The Sm/Nd ratios suggest highly LREE-enriched patterns in these inclusion waters. Norman and Mearns also report the first Nd isotopic data on pure fluid inclusion liquids: inclusions formed at 800-650°C apparently preserve the isotopic signature of the granite melt (positive initial $\varepsilon_{Nd}$) while fluids extracted from lower temperature inclusions show some evidence of mixing with fluids derived from surrounding Precambrian gneisses. Even after normalization for salinity differences, these fluid inclusion liquids still carry 100-1000 times more REE than the most REE-enriched hydrothermal solutions from the EPR submarine hot springs.

Of course, these few examples do not necessarily imply that all mineralizing solutions are high in REE. Nevertheless, the cases where REE are high encourage the use of REE and Nd isotopes as tracers of metal provenance, fluid pathways and ore deposition.
CHAPTER 3. Sm-Nd ISOTOPE STUDIES OF ORE DEPOSITS

3.1 Introduction

For the purpose of Sm-Nd dating, one important requirement is a sufficiently wide spread in Sm/Nd ratios within a suite of rocks and/or minerals characterized by coeval REE (Sm-Nd) fractionation. This represents one of the major drawbacks in Sm-Nd whole rock dating of many rock types as Sm-Nd fractionation is often small leading to large errors in isochron ages and initial ratios. In contrast, many ore deposits possess a wide range in Sm/Nd ratios as can be seen in Figs.2-3 and 2-4. Fig.3-1 shows a compilation of the Sm/Nd ranges in 14 different ore deposits compared to the range found in common felsic and mafic-ultramafic rocks and their minerals. It is obvious that many ore deposits should in principle allow precise Sm-Nd dating if other prerequisites of the dating method are met.


In cases where excessive data scatter or an insufficient spread in Sm/Nd ratios make isochron dating impossible, a $\varepsilon_{Nd}$ versus time diagram may be used if the Sm/Nd ratios in the ore samples are very different from those in the country or host rocks. Assuming the Nd in the ore originated in these source rocks, the intersect of the time-$\varepsilon_{Nd}$ trajectories of the ore with those of the source rock should give a good indication of the time of REE fractionation, i.e. ore deposition (Fig.3-2). For definitions of $\varepsilon_{Nd}$ and other isotopic expressions see appendices 1 and 2.
Fig. 3.2: Principle of the $\varepsilon_{\text{Nd}}$ versus time diagram as applied to the dating of ore samples having high Sm/Nd ratios. In this plot, the isotopic evolution of a model earth mantle reservoir CHUR is represented by the horizontal line intersecting the y-axis at $\varepsilon_{\text{Nd}}=0$. The typical isotopic evolution of a crustal segment from which ore might be extracted is also shown. The line labelled 'model depleted mantle' represents the more realistic isotopic evolution path of mantle from which continental crust has been extracted. Assume 2 ore deposits with extremely high Sm/Nd ratios formed within the same crustal segment. Using their measured present-day isotopic compositions and Sm/Nd ratios, the times $T_1$ and $T_2$ may be calculated. Assuming no significant changes in Sm/Nd ratios after initial mineralization, $T_1$ and $T_2$ represent the times of ore formation in the deposits. Applications of this diagram can be found in appendices 2 and 3.

In analogy to Sr and Pb isotopes, the utilization of $^{143}\text{Nd}/^{144}\text{Nd}$ variations in hydrothermal minerals and ores to infer the sources of REE and other cations in the hydrothermal solution is based on the assumption that the hydrothermal solution and metal source rocks in contact with it equilibrate their Nd isotopic compositions. Considering the generally much lower solubility of REE as compared to that of e.g. Sr, and the often large proportions of a rock's REE budget that reside in resistant accessory phases, one might expect problems with Nd isotopic disequilibrium between fluid and whole rock. Unfortunately, very little is known about Nd isotopic systematics in hydrothermal systems. In one of the few studies on Nd isotopic variations in hydrothermal solutions, Piepgras and Wasserburg (1985) observed that $\varepsilon_{\text{Nd}}$ values in hydrothermal solutions from vent fields on the East Pacific Rise are lower than those of local ocean floor basalt. This cannot be explained by dilution of the hydrothermal fluid with fresh seawater but must be caused by recharge of the hydrothermal system through ridge sediments having lower $\varepsilon_{\text{Nd}}$ than the basalts. These findings have been confirmed by Michard and Albarède (1986) and imply rather rapid Nd isotopic equilibration between fluids and isotopically distinct rocks under these conditions. Hydrothermal minerals precipitated at the ridge are isotopically identical to their parent solution (Michard and Albarède, 1986; Tatsumoto et al., 1985). Until more detailed data on Nd isotopic systematics in hydrothermal solutions become available, any assumptions of Nd isotopic fluid-rock equilibrium will remain speculative.
3.2 Earlier studies

To date, only few studies reported Sm-Nd isotope data on ore deposits and minerals. Fryer and Taylor (1984) obtained a three-point isochron on pitchblende separates from the Collins Bay unconformity-type U deposit in the Athabasca region of Saskatchewan, Canada. The age of 1281±80 Ma (1σ) is consistent with $^{207}\text{Pb}/^{206}\text{Pb}$ model ages obtained from the same samples and isotopic data for primary U mineralization at other unconformity-type U deposits in the region (see Bray et al., 1987). Another two pitchblende separates with Pb model ages of 410 and 470 Ma were colinear with one of the 1281 Ma samples giving a younger isochron age of 334±0.2 Ma. This age is interpreted as the time of minor U redistribution and secondary mineralization; similar U-Pb ages for secondary mineralization are known from other deposits. Initial Nd isotope ratios for the pitchblendes suggest an origin of the U-bearing fluids in normal Lower to Mid Proterozoic country rocks without the need for remobilization of older U mineralization. Although the value of these radiometric data for assigning an age to primary U deposition at Collins Bay has been questioned on statistical grounds (Ludwig, 1985; see reply by Fryer and Taylor, 1985) the study nevertheless demonstrates the potential of Sm-Nd dating for the study of ore deposits.

Chemyshev et al. (1986) report Nd, Sr and Pb isotope data on two Jurassic Sn deposits in the USSR. Fluorites associated with one of the deposits yield an isochron age of 167±12 Ma which agrees with K-Ar ages on coexisting muscovite. Variations in age-corrected Nd and Sr isotope data on scheelites, fluorites and carbonates reflect variable degrees of mixing of magmatic fluids having relatively radiogenic $\varepsilon_{\text{Nd}}$ (+2.9 and -1) with fluids derived from surrounding older crust.

An interesting study on the North Pennine English fluorite deposits was presented by Halliday et al. (1986). Like many sediment-hosted mineralized veins in Central Europe, these were commonly assumed to be related to late-stage magmatic-hydrothermal activity of hidden Late Hercynian granites. However, K-Ar evidence and a 206±9 Ma fluid inclusion Rb-Sr isochron on material from the Great Sulphur Vein point to a younger, Mesozoic age of mineralization. This is supported by Sm-Nd isotopic data on fluorites which cannot be traced to any reasonable source unless the mineralization is indeed younger than Permian. If a post-Permian age is assumed, the most likely source of REE in the fluorite veins would be basinal brines derived from the host Late-Paleozoic sediments.

Nd and Sr isotopic variations together with oxygen isotope systematics of hydrothermal minerals were used to characterize the sources of dissolved cations and fluids throughout the three stages of vein-type mineralization at the 278 Ma Mt. Carbine tin-tungsten deposit in Northern Queensland, Australia (Higgins et al., 1987). Initial Nd and Sr isotope ratios in apatites, fluorites and chlorites lie on or close to a straight mixing line between a 280 Ma high-level granite and the host Mid-Paleozoic metasediments. This suggests binary mixing of fluids derived from these two endmember source rocks. The straight mixing relationship implies similar Sr/Nd ratios in the two fluid types. As Sr/Nd ratios in fluids were probably much larger than Sr/Nd in either rock type, extensive water-rock reaction during
mineralization was either limited or did not significantly affect the relative elemental concentrations in the fluids as this would result in strongly curved mixing arrays. Inferred δ¹⁸O of fluids in the early high-temperature stage of mineralization suggest granite-derived magmatic fluids mixed with isotopically evolved (high δ¹⁸O) cooler sedimentary fluids. During later stages, evolved sedimentary and low δ¹⁸O meteoric waters became more important. Due to their high W concentrations, magmatic fluids must have supplied the bulk of the tungsten before the magmatic fluid pressure regime collapsed to give way to invading sedimentary and meteoric waters.

3.3 Case studies

In the following I summarize relevant geologic, geochemical and isotopical characteristics of six ore deposits of Late Archean to Mid-Proterozoic age from Canada and Australia. The Canadian example is the Kidd Creek Cu-Zn mine, one of the largest known volcanogenic massive sulfide deposits. The Mary Kathleen U-REE mine in Queensland and the four large unconformity-type U deposits Nabarlek, Jabiluka, Koongarra and Ranger in the East Alligator River Uranium Field in the Northern Territory represent two contrasting types of U deposits in Australia.

3.2.1 Kidd Creek volcanogenic Cu-Zn mine

3.2.1.1 Introduction

The Kidd Creek ore bodies are hosted by ca. 2700 Ma old felsic volcanics and related marine sediments of the Abitibi greenstone belt near Timmins, Ontario. Although of unusually large size, the nature of its ore and the geological setting of Kidd Creek are typical of many volcanogenic massive sulfide deposits in the Abitibi belt and elsewhere (Franklin et al., 1981). Key features, such as their predominant stratiform nature and their ubiquitous association with submarine felsic volcanics, are generally interpreted to indicate a syngenetic origin of these deposits. Throughout the Abitibi belt the volcanics have undergone some seawater alteration and were recrystallized under prehnite-pumpellyite facies conditions (200-300°C) (Beaty and Taylor, 1982). At Kidd Creek the orebodies are underlain by extremely altered volcanics and volcaniclastics. They represent the exit zone of a large seafloor hydrothermal circulation system responsible for metal accumulation on the seafloor and within the uppermost part of the alteration zone, the so-called stringer zone.

In addition to significant changes in major and trace element contents, Campbell et al. (1984) observed distinct changes in REE patterns going from weakly altered footwall volcanics outside the alteration zone into strongly altered equivalents within the alteration zone and the massive ore. Typical REE patterns found in rocks along this traverse are shown in Fig. 3-3.

Campbell and coworkers attribute this variation to strong REE mobility during hydrothermal alteration associated with ore deposition, in particular mobility of the LREE and less so the MREE. These elements were leached from the highly altered volcanics in the stringer zone and partly redeposited in a metasomatic chlorite-rich zone immediately below
The alteration produced a suite of rocks with a large range in Sm/Nd ratios favourable for Sm-Nd dating. If REE fractionation was coincident with ore deposition, as suggested by Campbell et al. (1984), the Sm-Nd systems should record the age of mineralization.

Fig. 3-3: Chondrite-normalized REE abundances in variably altered felsic volcanics and massive sulfide ores from Kidd Creek. A, typical REE patterns in weakly altered volcanics outside the alteration zone (weakly altered, 204H), strongly altered volcanics in the stringer zone (600-11, 204 Z11) and chlorite schist (a completely chloritized tuff, 600-2). Note that strongly altered rocks are both depleted and enriched in LREE but invariably depleted in Eu relative to 204H. B, Cu-Zn ores with variable Cu/Zn ratios. The REE are probably located in hydrothermal and/or detrital silicates and sulfates as sulfides have very low REE abundances. Note absence of negative Eu anomalies in the ores which may be related to the preferential leaching of Eu in the alteration zone.

3.3.1.2 Results: Sm-Nd isotopes

16 whole rock samples from the footwall volcanic sequence representing the entire range from weakly altered volcanics to intensively altered stringer zone rocks and massive ores, were analysed for Sm-Nd and Rb-Sr isotopes. The results are given in appendix 1a. In addition, 6 new analyses for massive sulfide ore samples from various parts of the orebody have been included (appendix 1b). Both sets of data are shown in Figs. 3-4 and 3-5. All ages and initial ratios are quoted on the 95% confidence level and were calculated using a modified version of McIntyre et al. (1966).

The 16 samples analysed initially comprise 4 weakly altered felsic volcanics (WFV), 10 altered felsic volcanics (AFV) and 2 massive sulfide ores. AFV and ores define a Sm-Nd isochron with some excess scatter (MSWD=4.7) and an age of 2670±40 Ma (appendix 1a).
Fig. 3-4: Sm-Nd isochron plots for Kidd Creek samples. A, all samples including weakly altered felsic volcanics from outside the alteration zone (WFV), variably altered felsic volcanics (AFV) and massive sulfide ores. Note the small range in Sm/Nd ratios displayed by WFV compared to the wide dispersion in Sm/Nd observed in AFV and ores. The age of 2682±47 Ma is calculated after rejection of one outlier and is slightly older than the Sm-Nd age given in appendix 1 due to the incorporation of five new data points representing massive sulfide ores. B, massive sulfide ores only. The age of 2774±140 Ma is calculated for 7 out of 8 samples.

WFV fall on or close to this isochron (Fig.3-4). This age may be compared to the chrono-stratigraphic framework provided by precise U-Pb zircon dating of volcanic marker units within the volcano-sedimentary sequence in the Timmins area: Age limits on ore deposition are set by a 2717±4 Ma age for rhyolites immediately underlying ore at Kidd Creek and a 2703±3 Ma age for stratigraphically younger felsic volcanics (Nunes and Pyke, 1981). If the ore is syngenetic, it should have formed very close to 2717 Ma. The 2670±40
Ma age is somewhat younger than this age but overlaps with the 2703 Ma datum. It is, however, indistinguishable from the 2640±60 Ma Pb-Pb isochron age for Kidd Creek sulfides reported by Bugnon et al. (1979). Although some of the ore appears to be spatially related to a break in volcanic activity marked by argillic sedimentation and a regional paraconformity (Walker et al., 1975; Nunes and Pyke, 1981), it is unlikely that ore deposition was significantly younger than 2717±4 Ma as the 2703 Ma old horizon is separated from the mine volcanics by several thousand meters of volcanics. It is concluded that the 2670±40 Ma Sm-Nd age as well as the Pb-Pb age slightly underestimate the age of mineralization. The small difference between the Sm-Nd datum and the 2717 Ma zircon age is tentatively interpreted to reflect post-depositional isotopic disturbance of some of the samples rather than a separate event unrelated to ore deposition. Of course, bias introduced by correlated scatter in initial $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ ratios can not be ruled out but is considered unimportant.

Recalculation of the isochron age including 5 of the 6 new analyses slightly increases the scatter (MSWD=6.2) and the Sm-Nd age to 2682±47 (model 3) with an initial ratio corresponding to $\varepsilon_{\text{Nd}} = 1.7\pm0.3$. The excluded data point (Cu ore 7871) has a highly imprecise Sm/Nd ratio and is an obvious outlier (Fig.3-4A).

Regression of the ore samples alone, again excluding 7871, yields a moderately well-fitted (MSWD=4.2) isochron with a model 3 age of 2774±140 Ma (Fig.3-4B), within errors of both the zircon age and the 2682±47 Ma Sm-Nd age. The updated Sm-Nd age of 2682±47 Ma is based on 17 samples and is identical within analytical errors to the 2717±4 Ma U-Pb zircon age. Although not entirely satisfactory considering the 100 Ma age range obtained for the various data subsets, the pooled results demonstrate the potential of Sm-Nd dating of highly altered ore zone material. Low temperature alteration, which is recorded by the Rb-Sr results, had only minor effects on the Sm-Nd systems.

### 3.3.1.3 Rb-Sr isotopes

The Rb-Sr data for the 16 samples analysed initially define an isochron (MSWD=5.25) with a model 3 age of 2576±26 Ma and an initial $^{87}\text{Sr}/^{86}\text{Sr}_i = 0.7047\pm24$ (Fig.3-5). Inclusion of the new analyses (appendix 1b) increases scatter and $^{87}\text{Sr}/^{86}\text{Sr}_i$ and decreases the age by some 50 Ma. In Fig.3-5A the isochron age has been calculated using two of the new analyses. Regression of 6 massive sulfide samples (excluding outlier Zn ore 7875) which form a poorly fitted isochron (MSWD=32.3), yields a model 2 age of 2365±114 Ma with $^{87}\text{Sr}/^{86}\text{Sr}_i = 0.7094\pm7$ (Fig.3-5B). These data suggest that the Rb-Sr of AFV and ore as well as WFV have been disturbed after the hydrothermal event that fractionated REE. Rb-Sr whole rock ages between 2400-2600 Ma in demonstrably older igneous rocks are common in the Abitibi greenstone belt and are attributed to low-temperature metasomatic alteration by some workers. Recent work on the rhyolites and ultramafic rocks at Kidd Creek indicates two prominent alteration events separated by a deformation event (Schandl and Wicks, 1987). The first event is represented by early albition of plagioclase (high pH fluid), silicification, carbonitization, followed by sericitization (low pH fluid) and chloritization. The second event is represented by carbonate alteration.
Fig. 3-5: Rb-Sr isochron plots for Kidd Creek samples. Symbols like in Fig. 2-4. A, all samples (WFV sample 204G with high Rb/Sr ratio beyond right hand margin). The isochron age of 2530±26 Ma was calculated for 18 out of 22 samples and is somewhat lower than the age given in appendix 1 due to incorporation of two new ore samples. B, massive sulfide samples only. The isochron age of 2365±115 Ma is calculated after rejection of one outlier.

Primary fluid inclusions (T\text{hom} = 136°C) indicate low temperatures during the second alteration. Schandl and Wicks (1987) do not comment on the relations between these alteration events and mineralization but the alteration mechanisms described from the first alteration event are similar to those associated with ore deposition (Walker et al., 1975). If processes such as the second, low-temperature alteration were responsible for the young
Rb-Sr ages at Kidd Creek they have been highly efficient in homogenizing Sr isotopes within a large rock volume comprising volcanics inside and outside the alteration zone to generate the relatively well-fitted 2576 Ma isochron. This does not necessarily imply that Sr was redistributed on the same scale but rather that rock subvolumes within the affected terrain may have equilibrated extensively with large amounts of a fluid of rather constant Sr isotopic composition. Within the massive ores isotopic homogenization appears to have been less efficient as indicated by the higher MSWD for the massive sulfides isochron. This may be a function of the relatively lower porosity in the fine-grained ore compared to the fractured and brecciated volcanics.

3.3.1.4 Initial $^{143}$Nd/$^{144}$Nd ratios

The initial ratio of $\varepsilon_{\text{Nd}}(2682) = 1.7 \pm 0.3$ for AFV and sulfide ores lies within the range of the WFV samples ($\varepsilon_{\text{Nd}}$ at $2682 \text{ Ma } = +1.1 \text{ to } +2.4$) which are considered equivalent to the felsic volcanics prior to the ore-forming hydrothermal activity. This similarity implies that the footwall volcanics were homogenous with respect to their Nd isotopic ratios and/or that any fluid-derived Nd added to the altered rocks and deposited in the ores was isotopically similar to that in the mine volcanics (WFV). This would suggest a local origin of the REE in the fluids within the most altered part of the footwall volcanics below the orebodies. Such a model is supported by a Nd mass balance and is consistent with the REE redistribution model by Campbell et al. (1984). By inference this would imply that a large part of the base metals was also derived from the footwall volcanics, in accord with common concepts about the genesis of volcanogenic massive sulfide deposits.

This point deserves some attention as Beaty et al. (1980) found a highly unusual increase in $\delta^{18}O$ across the alteration zone as well as a distinct $\delta^{18}O$ peak in the altered footwall volcanics some 60 m below the stratiform ore. The variation in $^{18}O/^{16}O$ is complex in detail and suggests hydrothermal alteration involved both normal seawater and an unusual, high- $\delta^{18}O$ fluid ascending from depth. Beaty et al. (1980) considered three plausible sources for this deep-seated fluid: seawater enriched in $^{18}O$ through 1) evaporation or 2) exchange with high- $\delta^{18}O$ country rocks, or 3) metamorphic water, all atypical for volcanogenic massive sulfide deposits (Beaty and Taylor, 1982). The authors speculate that the unusual fluid characteristics may be related to the exceptionally large size of the Kidd Creek mineralization.

The Nd isotopic data presented here do little to clarify this interesting observation. If the deep-seated fluids have transported and precipitated isotopically distinct Nd, it is probably masked by locally-derived Nd and can not be detected in the present sampling. The Sr initial isotopic ratios are considered artifacts of isotopic rehomogenization and therefore unsuitable as tracers of fluid isotopic composition.

Interestingly, initial $\varepsilon_{\text{Nd}}$ values in AFV, WFV and stratiform ore are only marginally lower than the range of $2.6 \pm 0.8$ observed for mantle-derived material across the whole Abitibi belt (Machado et al., 1986). This suggests that remelting of significantly older granitoid basement ($\geq 2940 \text{ Ma }$, Gariépy et al., 1984) which is inferred to underlie parts of the Abitibi Belt, played a limited, if any role in the petrogenesis of the mineralized felsic
volcanics.

3.3.1.5 Conclusions

Sm-Nd isotopic analyses of stratiform massive sulfide ores and variably altered felsic volcanics from the underlying hydrothermal alteration zone define an isochron with an age of 2682±47 Ma. Within the precision of the data, this age is indistinguishable from the 2717± Ma U-Pb zircon age for the footwall rhyolites which is believed to represent the most reliable estimate of the time of syngenetic ore deposition. Massive sulfide samples alone define a model 3 age of 2774±140 Ma. This result demonstrates that the REE redistribution associated with ore-forming hydrothermal alteration at Kidd Creek can be used to directly determine the age of the ore.

The Rb-Sr isochron age for the same samples is some 100 Ma, that for the massive sulfide ores ca. 300 Ma younger than their Sm-Nd age. This is attributed to low-temperature metasomatic alteration affecting rocks both within and outside the alteration zone. Initial $^{87}\text{Sr}/^{86}\text{Sr}$ are considered artifacts of isotopic rehomogenization during the metasomatic alteration. The effects of younger alteration(s) on Sm-Nd isotopic systems appears to have been minor but may be responsible for some of the observed scatter.

Initial $\varepsilon_{\text{Nd}}$ values for the altered volcanics calculated at 2717 Ma vary between +0.8 and +2.4 (mean 1.7±0.5, 1 s.d.), those for the massive sulfide ores between +0.7 and +3.1 (mean 2.1±0.8). This range is similar to the range found in weakly altered felsic volcanics outside the alteration zone (+1.4 to +2.7, mean 2.0±0.6). The isotopic similarity indicates that the footwall volcanics were isotopically homogenous and/or that hydrothermal alteration did not change Nd isotope ratios in the altered rocks. This would be expected if the fluids were low in REE or, more likely, if REE in the fluids were predominantly derived from the footwall volcanic sequence. Because base metals are more soluble than REE this would imply that a large part of the Cu, Zn and Fe were also derived from this sequence.

The present data set does not contribute much towards the identification of the source of an unusual deep-seated high-$\delta^{18}\text{O}$ fluids that was involved in hydrothermal alteration of mine volcanics. The Nd isotopic compositions in the stratiform ore appear entirely dominated by Nd derived from the underlying volcanics. If the high-$\delta^{18}\text{O}$ source enriched the fluid in isotopically distinct Nd, it can not be detected with the available sampling and resolution.
3.3.2 Mary Kathleen U-REE mine

3.3.2.1 Introduction

The Mary Kathleen mine in the Mt. Isa Inlier of NW Queensland represents a rather rare class of uranium deposit and is considered the main example of the so-called 'contact-metasomatic type' in the classifications by Dahlkamp (1978) and Nash et al. (1981). Uraninite ore of average grade of ca. 0.1 wt% $\text{U}_3\text{O}_8$ is disseminated in a dense mass comprising predominantly allanite, a Ce-Fe$^{2+}$ epidote, and F-apatite; this assemblage replaces an earlier garnet-diopside assemblage which forms part of extensive outcrops of massive exoskarn in the Mary Kathleen Syncline (see Fig.1 in appendix 2). The exoskarn assemblages formed within calcisilicates and impure marbles of the 1780-1740 Ma Corella Formation before the onset of major deformation and regional amphibolite facies metamorphism (1620-1500 Ma). Their regional distribution suggests they are related to intrusion of the nearby Burstall Granite and associated rhyolitic dikes. U ore at Mary Kathleen and many other occurrences in the area is always associated with allanite-rich alteration of primary garnet-pyroxene skarn; this led most workers prior to 1983 to suggest a genetic relationship between intrusion of the U-rich granite and the dikes, high-temperature exoskarn, and subsequent lower-temperature alteration of the skarn by granite-derived U-REE-rich fluids - the contact-metasomatic model. This model was questioned when Page (1983) reported U-Pb isotope data which indicate a ca. 200 Ma age difference between the Burstall Granite (1730 Ma) and U mineralization (1550±15 Ma). Furthermore, while the granite showed clear signs of metamorphic recrystallization and minor deformation, the uraninite-bearing allanite-apatite orebody appeared to be undeformed. Page (1983) concluded that U mineralization in its present form could not be directly linked to the pre-metamorphic granite but rather formed during regional metamorphism. These findings were essentially confirmed by detailed field and petrological studies of skarn-host rock relationships (Oliver et al., 1986).

To check the U-Pb age of uraninite by Page (1983) and to further study the complex relationships of skarn and U ore, a REE and Sm-Nd isotopic study of the ore deposit and related skarns was initiated using samples provided by R.W.Page. Details about the geology, sample locations, analytical procedures and the analytical results are summarized in appendix 2.

3.3.2.2 REE, U and Th concentrations

Hawkins (1975) noted a correlation of U and REE, in particular the LREE, which reflects the tendency of uraninite to be concentrated in the most allanite-rich parts of the skarn alteration zones. Fig.3-6 shows REE patterns for high-grade ore whole rocks and some of its constituent minerals.
The three whole rocks studied have more or less identical patterns while the minerals show some variability. The strongly LREE-enriched pattern for allanite was to be expected while the fractionated patterns for apatite and sphene suggest strong LREE enrichment in the ore-forming hydrothermal solutions. The same conclusion can be drawn from the LREE-enrichment in uraninite. The uraninite fluorite-type lattice would be expected to possess a crystallochemical preference for the HREE (Ho); the chondrite-normalized Nd maximum therefore requires either a high LREE/HREE ratio in the fluid or very efficient solution complexing of the HREE.

U concentrations in the ore whole rocks are between 0.5 - 0.83 wt% with Th/U ratios of 0.14-0.55, distinctly lower than in the skarn and other country rocks which have Th/U of 1-7.8, but much higher than the exceedingly low values found in low-temperature sedimentary- and in unconformity-type U ores.

REE patterns in non-skarn metasediments and various skarn lithologies are shown in Fig.3-7. Compared to the rather uniform shale-like REE patterns in their sedimentary precursors, the skarns show variable degrees of REE redistribution which is strongest in the pervasively garnetized samples, the massive skarns. There appears to be a trend of LREE depletion and HREE enrichment in the skarns which is most probably mineralogically controlled by replacement of the primary mineralogy with garnet and pyroxene. Available data on mineral REE abundances (see Fig.2c and Table 2b in appendix 2) suggest that skarn garnets are considerably higher in REE, in particular HREE, than coexisting clinopyroxenes.
Fig. 3-7: Chondrite-normalized REE patterns for Corella Formation metasediments (stippled band) and examples of the two major skarn lithologies. REE patterns of metasediments are very similar to average post-Archean shale while the skarns show variable degrees of REE redistribution. Changes in REE patterns during transformation from sediment to skarn are controlled by the degree of replacement of primary phases and the fluid/rock ratio: A, banded skarns with generally minor REE mobility (with the exception of LREE-enriched 5013); B, massive skarns with pervasive garnetization. Note the lack of negative Eu anomalies in the massive skarns.

and HREE retention or even addition would be expected during garnetization while LREE would be retained less efficiently. Given the considerable volumes of garnetized Corella Formation metasediments, large amounts of LREE may have been released. An obvious complementary LREE sink would be the allanite-rich U ore with its strong LREE-enrichment. However, alternative LREE reservoirs (such as skarn 5013 J1 with strong LREE enrichment, Fig.4, appendix 2) may not have been adequately covered by the sampling. U contents in non-mineralized metasediments and skarn are uniformly low at 1-6ppm, in agreement with data obtained by other workers.

REE patterns in the Burstall Granite and related dikes show evidence of considerable REE mobility. Weakly altered granite and dike samples possess REE patterns typical of many granites with fractionated LREE, a negative Eu anomaly which deepens in the course
of differentiation, and a rather flat pattern for the HREE (Fig.3-8). Based on petrological and geochemical criteria, Abeysinghe et al. (1984) classified the Burstall Granite as a fractionated A-type granite.

![Chondrite-normalized REE patterns in weakly altered Burstall Granite and related rhyolite dikes](image)

Fig.3-8: Chondrite-normalized REE patterns in weakly altered Burstall Granite and related rhyolite dikes (open squares and crosses, respectively), and albitized Burstall Granite (closed symbols).

Two highly albitized granite samples show strong depletion of the LREE relative to the less altered samples with development of a conspicuous Ce excess over neighboring REE (Fig.3-8). Similar REE mobility, but without anomalous Ce behaviour, has been reported for albitized granites in Nigeria (Bowden and Whitley, 1974), Sweden (Baker, 1985) and France (Cathelineau, 1987), the latter example being accompanied by vein-type U mineralization. U concentrations in the altered granites are, however, within the range observed in the less altered granite. Again, LREE may have been released to migrating hydrothermal fluids but whether or not there is a relationship between REE mobility in the country rocks and LREE accumulation in the Mary Kathleen orebody, can only be decided on the basis of isotopic evidence for the timing of REE fractionation.

### 3.3.2.3 Isotopic results: U-REE mineralization

To determine the age of U-REE mineralization at Mary Kathleen, 3 whole rock ores and 16 mineral separates from two of the ores have been analysed for Sm-Nd isotopes. Rb-Sr isotopic analyses were performed for the whole rocks and three of the mineral separates. The samples for which Rb-Sr data are available have Rb/Sr ratios close to zero; they display no isochron relationship but have variable initial \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios between 0.7191-0.7262 (calculated at 1470 Ma, see below). The significance of this variation is ambiguous because of possible effects of a cryptic thermal event, dated at around 1200 Ma, on the Rb-Sr isotopic systems in skarn throughout the Mary Kathleen area (Page, 1983). In contrast, the Sm-Nd data for the ores and mineral separates define a moderately well fitted isochron (MSWD=4.9) with a model 3 age of 1472±40 Ma and an initial ratio corresponding to \(E_{\text{Nd}} = -9.5±0.7\) (Fig.3-9). This would suggest the age of REE fractionation in the U-REE
Mary Kathleen U-REE ore : Sm-Nd

1472±40 Ma
IR = 0.50945±2

gt

cpx

K9447
gt res

ur

sph

all,wr

t47Sm/144Nd

Fig.3-9 Sm-Nd isochron plot showing data points for U-ore whole rocks and 16 mineral separates. These data points have been used to calculate the 1472±40 Ma isochron age. Clinopyroxene and garnet separates from pre-ore skarn plot distinctly above the isochron. Skarn K9447 and a leach-residue pair of a third skarn garnet separate are contaminated by ore allanite. Abbreviations: all, allanite; wr, whole rock; ap, apatite; sph, sphene; ur, uraninite; gt, garnet; cpx, clinopyroxene; gt res and gt lea, garnet residue and garnet leach.

ore is some 78±55 Ma younger than deposition of uraninite at 1550±15 Ma (Page, 1983). This apparent age discrepancy is not considered a real difference in crystallization ages but probably reflects some variability in initial $^{143}$Nd/$^{144}$Nd ratios and/or post-crystallization disturbance, particularly between allanite and uraninite which show ubiquitous reaction zones along mutual grain contacts (see appendix 2 for further discussion). This is supported by the MSWD>1 which indicates some scatter beyond analytical uncertainties, i.e. geological scatter. The 1472 Ma Sm-Nd age is therefore regarded as a minimum age for deposition of uraninite and contemporaneous allanite and strongly supports the conclusion by Page (1983) that U-REE mineralization in its present form can not be directly related to the intrusion of the A-type Burstall Granite and associated metasomatism, but rather formed during regional metamorphism.

This interpretation is consistent with observations by Oliver et al. (1986) who report a spatial association of mineralization with structural and alteration features clearly formed during or after the major $S_2$ deformational event. $S_2$ axial-planar cleavage and small scale folds are superimposed on the granite-related skarn and formed under peak and/or near-peak amphibolite facies metamorphic conditions. According to these authors, intensive metamorphic hydrothermal activity, concentrated onto zones of tectonically increased permeability within and adjacent to older skarn and metadolerite bodies, is responsible for
widespread alteration (ca. 300-500°C) in these zones. Oliver et al. (1986) suggest U-REE mineralization was formed during this period of structurally enhanced circulation of hot, highly saline metamorphic fluids within the (pre-S$_2$) skarn pod that hosts the Mary Kathleen orebody.

3.3.2.4 Sm-Nd isotopic evidence for two periods of skarn formation

In their model, Oliver et al. (1986) distinguish two generations of metasomatites in the Mary Kathleen Syncline, an older, granite-related skarn generation of clearly pre-S$_2$ age, and a younger, syn- to post-S$_2$ generation similar in mineralogy to the older skarn. While the older generation is widespread and makes up the bulk of the exposed skarn in the area, the younger generation metasomatites are confined to zones of structurally enhanced metamorphic fluid flow around and partially within older skarn and metadolerite bodies. A garnet-bearing vein cutting the ore in the Mary Kathleen pit may represent this younger generation although the model does not predict the relative timing of mineralization and the younger skarn generation apart from their mutual syn- to post-S$_2$ age.

Because of its close spatial association with U mineralization it is important to assess the timing of skarn-forming metasomatism independently. Fig.3-10 shows Sm-Nd isotopic data for two skarn lithologies, a banded skarn developed in calcisilicate sediments, and a massive skarn from the vicinity of the S$_2$ Mary Kathleen Shear and minor U-REE mineralization. Five of six adjacent ca. 5-8 mm thick slabs representing the compositional banding of the calcisilicate skarn define a well-fitted isochron (MSWD=1.72) with an age of 1766±80 Ma and initial $^{143}$Nd/$^{144}$Nd ratio corresponding to $\varepsilon_{Nd}=-3.4\pm1.1$. This age is indistinguishable from the 1730 Ma U-Pb zircon age of Burstall Granite magmatism; considering the field relations, this date is regarded as evidence in favor of a syn-granite origin for the banded skarn and, by inference, the bulk of skarn in the area including the massive garnet-pyroxene skarn surrounding the Mary Kathleen ore. In contrast, the massive skarn 0832 yields a mineral-whole rock age of 1557±40 Ma with $\varepsilon_{Nd}(1557)=-6.1\pm0.7$, distinctly younger than the age of the banded skarn but identical to the U-Pb age of Mary Kathleen uraninites. If this age is not merely the result of isotopic resetting of an earlier skarn but the product of renewed metasomatism and skarn formation, it strongly supports the model put forward by Oliver et al. (1986). An origin of the 0832 age by solid state closed-system isotopic resetting in a hypothetical garnet-cpx-feldspar proto skarn is unlikely because $\varepsilon_{Nd}(1557)$ would be expected to be between -3 to -1 instead of -6.1, assuming a reasonable, pre-1557 Ma, Sm-Nd budget controlled by garnet and feldspar with $^{147}$Sm/$^{144}$Nd=0.2. The 1557±40 Ma age is therefore regarded as the time of renewed metasomatism possibly equivalent to the younger generation skarn-forming event of Oliver et al. (1986). The similarity of this and the U-Pb uraninite age suggests that both the metasomatism which formed massive skarn 0832 and U-REE ore deposition occurred within overlapping stages of regional metamorphism.
3.3.2.5 The origin of U-REE mineralization

$^{143}\text{Nd}/^{144}\text{Nd}$ initial ratios in the ore and associated country rocks may be used to make inferences about the sources of the large quantities of LREE accumulated in the orebody. Fig. 3-11 shows that the initial isotopic composition in the ore is less radiogenic than any of the measured country rock types for most of the time since intrusion of the granite and initiation of the skarn-forming metasomatism. A change of the time of ore-deposition from 1472 Ma to the more appropriate 1550 Ma would not change this conclusion. There is some overlap in $\varepsilon_{\text{Nd}}(T)$ values between the ore and the most LREE-enriched skarns until about 1650 Ma but at the time of ore formation, ore is clearly isotopically distinct from the country
rocks. This precludes direct derivation of REE from the country rocks during ore formation, assuming that our analyses cover the entire range of potential REE source rocks in the Mary Kathleen area. If country rocks are not the source, what is the origin of Nd in the ore?

Fig.3-11 Age-corrected $\varepsilon_{\text{Nd}}$ versus time diagram showing the isotopic evolution paths of Mary Kathleen U-REE ore and typical country rocks in the time interval 1730 - 1300 Ma. The dark box in the centre represents the range in initial $\varepsilon_{\text{Nd}}$ values in Burstall Granite, Corella Formation metasediments and skarn at the time of granite emplacement. The lines extending from the box back in time towards the chondritic mantle (CHUR) and depleted mantle (DM) evolution lines define the model isotopic evolution band of crustal precursors to the granite and metasediments (numbers in parentheses are typical $^{147}\text{Sm}/^{144}\text{Nd}$ ratios). The cross-hatched box labelled U-REE ore indicates the initial $\varepsilon_{\text{Nd}}$ value derived from the Sm-Nd isochron in Fig.3-9.

Fig.3-11 depicts the Nd isotopic evolution required in a hypothetical REE source rock which fractionated from the normal upper crustal evolution trend in the Mary Kathleen area at ≈1730 Ma. The average $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of this source depends on the starting point $\varepsilon_{\text{Nd}}(1730)$ chosen; if a $\varepsilon_{\text{Nd}}(1730)$ in the middle of the observed range of country rock initial ratios is used, an estimate for the model source $^{147}\text{Sm}/^{144}\text{Nd}$ of 0.037±0.012 is found. This is somewhat higher than $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of the U-REE ore but distinctly lower than the $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of any measured country rock. Two alternative sources appear possible, both capable of providing the required amounts of U and REE characterized by a lower
initial $^{143}$Nd/$^{144}$Nd ratio than that typical of the country rocks. These are (1) REE-U-rich accessory phases with strong LREE-enrichment (i.e low Sm/Nd) such as monazite and allanite, and (2) a U-LREE protore at or near the site of the present orebody with element abundances and ratios similar to those in the present orebody.

Accessory phases may contain a considerable proportion of their host rock's U-REE budget and have been considered potential sources for many U deposits, in particular those associated with granites (see e.g. Bowie and Watson, 1981 and companion articles; Cuney and Friedrich, 1987). Although these accessory phases are generally regarded as highly resistant during weathering and other low-temperature processes, some have been shown to be unstable under higher temperature conditions, especially in the presence of metamorphic fluids (see appendix 2 for references). To become a viable source of LREE (and U) with the appropriate Nd isotopic composition, LREE-enriched accessory minerals with an average $^{147}$Sm/$^{144}$Nd ratio of less than about 0.04, present in trace abundances in the granite, metasediments and skarn would have to age for $\approx$200 Ma before extraction of REE and U by the ore-forming fluids. Mass balance considerations suggest that a volume of just a few km$^3$ would carry enough accessory-held LREE and U to be an adequate U-REE source. On the other hand, it is unlikely that accessory-derived Nd in the fluids would escape contamination by 'normal' more radiogenic Nd derived from the major rock forming minerals; it is difficult to imagine a process capable of selectively extracting REE and U from resistant accessory phases while not affecting the relatively less resistant major rock forming minerals. While it may be quite possible to generate unusually U-REE-rich fluids due to accessory mineral destruction, the accessory isotopic signature would not survive unless accessory-derived Nd comprises an overwhelming part of the system's Nd and/or is transported rapidly through fractures.

In contrast, an origin of the U-REE ore by in situ remobilization of a nearby LREE-U protore would not only provide suitable quantities of REE and U characterized by suitably unradiogenic $^{143}$Nd/$^{144}$Nd ratio, but would also avoid serious contamination of protore-derived Nd with country-rock Nd. The origin of the hypothetical protore is speculative. A paleo-placer origin would be one possibility but this hypothesis can not explain the occurrence of allanite-uraninite ore in fine-grained banded calcisilicates (e.g. Rita prospect, appendix 2) and the exclusive association with altered skarn. It is therefore argued that the protore was a product of syn-granite U-REE-rich late-stage magmatic activity such as suggested by the proponents of the single-stage contact-metasomatic model for ore formation. Many A-type granites are known to be associated with rare metal mineralization including U and large amounts of highly fractionated REE (Drysdaill et al.,1984; Bowden, 1985). An additional source of LREE in the protore could be garnetized Corella Formation sediments which have been shown to have lost LREE during garnet metasomatism while HREE were retained.

Inheritance of U-REE mineralization from older, possibly skarn-hosted protore would also conveniently explain the exclusive association of ore with hydrothermally altered garnet-rich pre-$S_2$ skarn. Remobilization would conceivably have involved some homogenization of $^{143}$Nd/$^{144}$Nd ratios in protore Nd but it is envisaged that such resetting
effects would not significantly change the average protore Nd isotopic composition if the overall Sm/Nd ratio of the protore was as low or lower as required by the isotopic source modelling in Fig.3-11. In contrast, radiogenic Pb inherited from the U-rich protore must have been quantitatively lost during the remobilization as no trace of it is found in the studied ores (Page, 1983).

3.3.2.6 Conclusions

The results of Sm-Nd isotopic dating of ores and U-REE minerals from the Mary Kathleen mine are consistent with the published U-Pb age of uraninite deposition and recent field observations. The small difference between the 1550±15 Ma U-Pb age and the 1472±40 Ma Sm-Nd isochron age is explained by post-ore disturbance of Sm-Nd isotopic systems due to isotopic exchange between low-Sm/Nd allanite and high-Sm/Nd uraninite. The isotopic evidence suggests that U-REE mineralization at Mary Kathleen in its present form was not directly related to late-stage hydrothermal activity of the nearby U-rich Burstall Granite, but rather formed during regional metamorphic hydrothermal activity some 200 Ma after emplacement of the granite.

The extensive outcrops of calcic exoskarn in the area between the mine and the Burstall Granite are shown isotopically to have formed as a result of at least two periods of metasomatism. The 1766±80 Ma Sm-Nd age of a key skarn lithology, within error of the 1730 Ma U-Pb zircon age for the granitic intrusives, is considered representative of the bulk of the skarn and is consistent with an origin of the skarn from syn-granite metasomatism. This conclusion confirms petrogenetic models of most workers in the area. In contrast, a massive garnet-pyroxene-feldspar skarn lithology from the vicinity of a major fault and minor U-REE mineralization yields a Sm-Nd age of 1557±40 Ma, considerably younger than the other skarn but identical to the U-Pb age for uraninite deposition. This similarity is considered strong evidence for a recent model which predicts renewed hydrothermal activity during regional metamorphism in zones adjacent to and within areas of earlier skarn deposition where permeability was temporarily increased by concurrent tectonism. Among other features, the hydrothermal activity produced garnet-clinopyroxene-rich metasomatites mineralogically similar to earlier skarn and uraninite-allanite mineralization. The 1557±40 Ma age may date this activity.

Nd isotopic data on ore and the various country rock types exposed in the area indicate that at the time of ore deposition, $\varepsilon_{Nd}$ was significantly lower in the ore than in any country rock type measured. REE in the ore could therefore not simply be derived from the surrounding country rocks by processes such as metamorphic-hydrothermal leaching. Simple modeling requires the REE source to have fractionated from a Burstall Granite-type reservoir at ≈1730 Ma with an extremely low Sm/Nd ratio and to have remained isolated from the surrounding rocks for ≈200 Ma until ore formation. The REE extracted from this source into the ore fluids during metamorphism would have had a $\varepsilon_{Nd}$ value comparable to the value determined for the ore. An origin from LREE enriched accessory minerals, although attractive in view of the known large REE and U concentrations and extreme Sm/Nd fractionations in these minerals, is unlikely because mixing of accessory-derived
REE with REE leached from other phases during transport to the orebody would tend to erase the unradiogenic accessory mineral Nd isotopic signature. A model is proposed which involves derivation of LREE and U from a protore which was located very close to the present mineralization and had element contents and ratios similar to those of the present ore. This model is capable of explaining not only the Nd isotopic data - local remobilization would minimize admixture of externally-derived, more radiogenic Nd - but also the ubiquitous association of uraninite-allanite mineralization with hydrothermally altered garnet-rich skarn.

The origin of the protore is speculative but it is argued that it may be derived both from late-stage U-REE-rich hydrothermal activity of the A-type granitic intrusives, and the liberation of LREE from local calcsilicate sediments during syn-granite skarn formation, in particular garnetization.

### 3.3.3 UNCONFORMITY-TYPE URANIUM DEPOSITS

#### 3.3.3.1 Introduction and regional geology

Unconformity-type uranium deposits are vein-type deposits of often large size and high grade characterized by their proximity to a prominent unconformity separating contrasting rock types (see also Nash et al., 1981; Dahlkamp, 1978). They represent one of the world's largest resources of low-cost uranium. Deposits of this type are primarily known from two areas, the Athabasca Basin in Saskatchewan/Canada and the Pine Creek Geosyncline in the Northern Territory/Australia; in both cases the unconformity separates a metamorphosed and deformed Archean to Early Proterozoic basement from essentially undeformed Mid Proterozoic fluviatile sandstones deposited on the peneplanated basement. In the Pine Creek Geosyncline most of the known reserves of unconformity-type uranium are concentrated in the Alligator Rivers Uranium Field (ARUF). Among the numerous U occurrences in this area, four major concentrations have been identified, the Jabiluka and Koongarra deposits and the Ranger and Nabarlek mines. This study presents Nd and Sr isotopic data on these four deposits.

The various ARUF deposits have a broadly similar regional geological setting which is summarized in appendix 3a. Briefly, the unconformity-type uranium deposits are hosted by poly-deformed, amphibolite-facies metasediments of the Lower Cahill Formation comprising dolomitic marbles, semi-pelitic and psammitic schists and some amphibolites which are probably derived from dolerites. At Nabarlek, host rocks are schists and amphibolites of the Myra Falls Metamorphics, commonly thought to be an equivalent of the Cahill Formation. Basement to the metamorphic rocks are Late-Archean gneisses and granitoids of the Nanambu Complex. The most important metamorphic and deformational event, the Top End Orogeny, has reset Rb-Sr and K-Ar ages between 1870-1770 Ma and was followed by emplacement of late - to post-tectonic high level granites (=1780 Ma) and extensive sills of the 1688 Ma Oenpelli Dolerite. Deposition of fluviatile sandstones and interbedded basaltic to rhyolitic volcanics (Nungbalgarri Volcanic Member, NVM) of the Kombolgie Formation at 1648±29 Ma terminated a 150 Ma stable hiatus; they overlie the
metamorphic basement with a marked angular unconformity. Volumetrically minor phonolitic and doleritic dikes postdated the sandstones between 1300-1200 Ma.

3.3.3.2. ARUF uranium deposits: common features and genetic models

Besides sharing a common regional geology, the ARUF uranium deposits show remarkable similarities in their geological setting. The most important of these similarities are:

1. U ore is located in intensively chloritized breccia zones penetrating the folded Cahill Formation/Myra Falls Metamorphics basement just below the unconformity or what must have been within 10 of meters of the unconformity prior to erosion of the sandstone cover. There is no known U mineralization extending into the overlying sandstone although the breccia zones and chloritization do not end at the unconformity (at least in the case of Jabiluka II where the sandstone cover is still partly preserved).

2. Koongarra, Jabiluka and Ranger are stratabound within the Lower Member of the Cahill Formation and are associated with graphitic schists. A conspicuous absence of carbonatic rocks in the mineralized zone and their reappearance outside this zone has been interpreted in terms of a solution collapse origin of the ore-hosting breccia zones. Others have argued for a tectonic origin of the breccias in reverse faults. Nabarlek is hosted by chloritic schists and altered amphibolites; carbonates are not known in this area.

3. There is a striking spatial relationship of mineralization with the unconformity. Koongarra, Jabiluka and Ranger occur within a few kilometers or less of Late Archean basement; Late Archean rocks are not known from the vicinity of Nabarlek.

4. The main primary ore mineral is uraninite; Jabiluka has economic quantities of gold but otherwise uranium is the only element present in economic concentrations. Uraninite occurs in several textural varieties including massive, colloform and disseminated forms which possess crosscutting relationships indicating essentially contemporaneous formation.

Some of these characteristics have also been recognized in the unconformity-type deposits of Saskatchewan where the overall geology is quite similar to that of ARUF. The genetic models proposed by Australian workers for the ARUF deposits are, however, quite different from those proposed for the Canadian deposits. They share the concept of an epigenetic origin of mineralization but the importance of hypogene versus supergene processes is debated. Detailed descriptions of the mineralizations and wallrock alteration features pertinent to the various genetic models are compiled in the proceedings of an 'International Uranium Symposium on Uranium in the Pine Creek Geosyncline' in 1979 (Ferguson and Goleby, 1980) and some more recent references are given in appendix 3a; only brief accounts of some contrasting models will be given here:

1. Ferguson et al. (1980) used the idea of a solution collapse origin for the ore-hosting breccia zones in impure dolomites previously put forward by Eupene et al. (1975) to suggest a model involving adsorption of groundwater-transported uranium onto colluvial accumulations of organic matter and clayey weathering products in karst holes in peneplanated Cahill Formation dolomites. Later, after infilling of the holes and burial of the unconformity, the colluvial clays and the adsorbed U would be remobilized and recrystallized in response to increased temperatures.
(2) Binns et al. (1980b) favour a hypogene origin of the mineralizing hydrothermal solutions with estimated temperatures for fluids responsible for wallrock alteration and mineralization in the range of 300-120°C as derived from stable isotope systematics. In the absence of igneous bodies unequivocally associated with mineralization, they suggest an origin of the hypogene solutions from broad circulatory systems within the basement induced by radiogenic heat build-up in subjacent U-rich granitic rocks.

(3) Based on their fluid inclusion data, Ypma and Fuzikawa (1980) propose an origin of mineralization from mixing of two fluids of contrasting composition. One of these fluids was of low salinity, rich in CO$_2$ and carried the uranium; the other fluid was highly saline and its evolution may have been related to the presence of evaporitic rocks in the Cahill formation. The CO$_2$-rich solutions, probably derived from oxygenated groundwater descending through fractured Kombolgie sandstones, leached U from the basement and stabilized it in the form of uranyl-carbonate complexes. During mixing, changes in pH destabilized the complexes, releasing uranyl ions which were probably deposited by redox reactions involving methane from the reaction of metamorphic graphite with CO$_2$-rich aqueous solution. The elevated temperatures inferred from fluid inclusion and stable isotope data resulted from the geothermal gradient under a substantial cover of Kombolgie Formation sandstones.

Finally, (4), Johnston and Wall (1984) suggest an origin of the ore-hosting breccia zones in reverse fault planes just below the overlying sandstone aided by hydraulic fracturing and dissolution. Surface-derived, oxygenated U-rich solutions circulating in the sandstone entered the basement along these breccia zones where they mixed with more reducing locally-derived solutions causing wall rock alteration and U deposition. Based on supporting fission track data (Koul et al., 1984), they propose that the circulatory system within the Kombolgie cover sequence may have been extremely long-lived. Temperatures at the unconformity exceeded 90-100°C during a period from 1650 Ma to about 650 Ma, which could cause recurrent remobilizations of the U mineralizations and may be an explanation for the wide spread in U-Pb ages for ARUF uraninites (Hills and Richards, 1976).

The model by Johnston and Wall (1984) is in many aspects similar to a widely accepted model proposed for the Saskatchewan unconformity-type U deposits by Hoeve and Sibbald (1978) and Hoeve et al. (1980), the so-called 'diagenetic-hydrothermal model'. This model relies on the observation that U mineralization postdates deposition of the cover sandstone by ~100-150 Ma (Bray et al., 1987). This is consistent with fluid inclusion data which indicate that mineralization took place at ~160-220°C beneath ~3000 m of cover at a relatively advanced stage in the evolution of the Athabasca Basin. The similar initiation dates for U mineralization in several deposits now located along the eastern erosional margin of the Athabasca Sandstone cover may be related to widespread tectonic activity, which produced the necessary fracture permeability in sandstone and basement to allow saline, oxygenated, U-rich diagenetic solution from the sandstone to penetrate the basement (Bray et al., 1987). Reactions between these solutions and the graphite-rich basement rocks would produce reducing solutions rich in CO$_2$ and methane which, upon mixing with fresh diagenetic solutions near the unconformity, would cause deposition of uranium. The high grades found in some unconformity-type U deposits may have developed in a stationary hydrodynamic
regime characterized by continuous replenishment of U-bearing and reductant-bearing solutions. The absence of unusually radiogenic initial Pb isotope ratios suggest that the U was leached from normal rocks and was not derived from older U concentrations. The authors favour altered rocks of the Athabasca Formation as the most plausible source of U.

To aid in understanding the processes responsible for the formation of the ARUF deposits, it was necessary to provide independent radiometric data on the timing of ore deposition to update and/or complement the existing geochronological data base. A combined Sm-Nd and Rb-Sr approach was considered highly promising based on experience by other workers (Fryer and Taylor, 1984; Page et al., 1980; this study). Further, the demonstrated mobility of the REE elements associated with U mineralization in the ARUF uranium deposits (McLennan and Taylor, 1979; see also Fig.2-4) suggested that Nd isotopes could be useful in tracing the origin of REE and, by inference, other metals such as U in the ore-forming solutions.

3.3.3.3 Nabarlek

Nabarlek is distinguished from the other three ARUF deposits by its location ca. 50 km east of the nearest known Archean basement, important lithological differences in country rock types (notably the absence of carbonatic rocks), and the abundance of hematite in ore and alteration halo. The uraninite ore is hosted by complexely folded chlorite- and white mica-rich schists and amphibolite and concentrated in a brecciated part of the Nabarlek Shear where it forms veins, stringers, massive pods and encrustations intimately associated with chlorite. Further details can be found in appendix 3a.

U-Pb isotope studies by Hills and Richards (1976) suggest an age of U mineralization of ca. 900 Ma, based on a 920 Ma upper intercept U-Pb age for uraninites and supporting galena Pb isotopic data. Similarly, Page et al. (1980) found some evidence for a metasomatic event that reset Rb-Sr model ages in altered schists from the orezone between 900 and 1260 Ma ago. However, the majority of samples in a suite of chloritic and sericitic collected within 50 m of ore yielded Sr model ages averaging 1610±40 Ma (1s.d.). Ewers et al. (1983) tentatively interpreted this age as the age of chloritic alteration related to uranium mineralization and suggested that later 'sericitization', perhaps coincident with the ≈900 Ma U-Pb age, may have erased Pb isotopic signatures of the older age.

REE patterns

REE analyses on eleven ore samples are shown in Fig. 3-12. Low grade ores below 3 wt% U have quite variable REE patterns ranging from shale-like with some HREE enrichment via LREE-depleted to convex upward. Although the magnitude of Eu anomalies can not be defined precisely because Gd was not measured, at least two of the samples appear to have negative anomalies comparable in size to shale. All other measured samples with U contents from 12.6 - 64.4 wt% have convex upwards patterns similar to those reported by McLennnan and Taylor (1980). However, there is little systematic variation in La/Yb ratios over an order of magnitude range in U concentrations. Negative Eu anomalies are present in some samples, others have no anomaly. This is somewhat different from
McLennan and Taylor's results who found only one sample without a negative Eu anomaly (on a chondrite-normalized plot). The geochemical behaviour of Eu in aqueous solutions is critically dependent on oxygen fugacity and temperature (see section 2.3). Below ca. 250°C, i.e. at conditions appropriate to ARUF ore deposition, Eu $^{3+}$ should be the dominant Eu species in hydrothermal solutions unless they are unusually reducing. According to Ewers et al. (1983) and Wilde et al. (1986) the ore-forming solutions at Nabarlek were oxidized; any REE transported in these solutions would have the negative Eu anomaly typical of most ARUF rock types (some stratigraphically early metasediments and some of the Late Archean granitoids do not have a negative Eu anomaly, McLennan and Taylor, 1980; AR Wilde, unpublished analyses). This could be different if plagioclase with its typical positive Eu anomaly were preferentially leached by the solutions as suggested by Graf (1977). Indeed, ICP analyses of fluid inclusion waters rich in Ca, Ba and Sr (AR Wilde, unpublished data) suggest that feldspar destruction could have had an important influence on fluid compositions.
**Sm-Nd and Rb-Sr isotope data**

The studied sample suite encompassed a variety of ore forms ranging from intensely chloritized mineralized schists to pure massive uraninite chunks. U contents ranged from 0.46 to 64 wt %. Most of the samples show signs of incipient illite-hematite alteration and a few possess strongly altered domains. In addition to these samples, several chloritized schists and amphibolites from below the ore zone, one HNO₃ leach and three uraninite separates have been analysed.

High precision measurements of all Nd isotope ratios in selected ore samples from Nabarlek indicated the existence of small correlated isotopic anomalies in all stable Nd isotope ratios (up to 3 parts in 10⁴, see part 2 of this thesis). Distribution and relative magnitudes of the anomalies are similar to that expected from addition of small amounts of fissionogenic Nd to normal Nd which causes increases in the critical ¹⁴³Nd/¹⁴⁴Nd ratio by 0.2 - 3 ε-units at the U/Nd ratios involved. Of course, the fissionogenic component Δ₁₄₃ in ¹⁴³Nd/¹⁴⁴Nd can not be measured directly because it is obscured by decay of ¹⁴⁷Sm to ¹⁴³Nd. We have therefore measured Nd isotope ratios in 26 samples from the four ARUF deposits and used the predicted covariation of Δ₁₄₃ and ε₁₄₅ to correct measured ε₁₄₃ for the fission effects (see appendix 3a and part 2 of the thesis). The effect of fission on Sr isotopic ratios would be to increase the ⁸⁷Sr/⁸⁶Sr, but the magnitude of this effect (< 2 ε units at the most) is sufficiently small to be negligible for the purpose of this study.

![Sm-Nd isochron diagram for Nabarlek ores and altered host rocks. The 1616 Ma isochron is calculated for 10 high grade ores (>4wt% U) and 3 uraninite separates (all termed h-g primary ore). Primary high grade sample 4/40 (marked *) is excluded. The remaining ore samples with generally lower U contents are designated "l-g ore" (lower grade ore) and "altered ore" where hematite-illite alteration is particularly strong. The samples labelled "altered rocks" are unmineralized altered schists and amphibolites from the inner halo. The 1125 Ma isochron is calculated for 3 samples; uncertainties of this line are not 95% confidence limits but were estimated from the 2 sigma mean in-run precision of the two extreme data points.](image-url)
Fig. 3.13 shows the Sm-Nd data points for Nabarlek ores and altered host rocks. Ten high grade ores (2-64 wt% U) and the three uraninite separates define an isochron (MSWD=2.9) with a model 2 age of 1616±50 Ma and $\varepsilon_{Nd}= -3.3±0.9$. This age changes only marginally if two highly chloritic, unmineralized wallrocks and the HNO$_3$ leach of one of these are included (see appendix 3a). The age is indistinguishable from the mean Sr model age for chlorite-sericite schists from Nabarlek of 1610±40 Ma and close to the Rb-S isochron age of 1561±17 Ma for hydrothermally altered parts of the Nabarlek Granite some 400 m below the orebody (Page et al., 1980).

The remainder of the samples, mostly of lower grade or unmineralized, plots below the 1616 Ma isochron. The three most unradiogenic samples at $^{147}\text{Sm}/^{144}\text{Nd} > 0.2$ define a well fitted correlation line (MSWD=0.74) whose slope corresponds to an age of 1125±400 Ma, the large uncertainty being caused by the small number of data points and a correspondingly large t multiplier. If the uncertainty is recalculated using the $2\sigma_{\text{mean}}$ errors of the extreme data points, the errors are reduced to ±90 Ma. Although the 1125 Ma age is within the range of Sr model ages for some of the altered host rocks analysed in this study (see below) and those reported by Page et al. (1980), only one of the three samples shows obvious mineralogical changes that could be attributed to alteration and it is this sample which controls the slope of the 1125 Ma line. The low initial ratio of $\varepsilon_{Nd}= -12.2$ would suggest that the Nd present in the 1125 Ma samples was derived from or equilibrated with normal country rocks or low grade U ores rather than the main mineralization which had initial $\varepsilon_{Nd}$ values at that time ranging from +2 to +20. This may indicate that the 1125 Ma line could be a mixing line rather than an isochron.

The potential for age bias in Sm-Nd dating due to mixing was highlighted recently by studies of Cattell et al. (1984), Chauvel et al. (1986) and Gruau et al. (1987) and should not be ignored in a complex setting such as a hydrothermal ore deposit. At Nabarlek, one possible mixing scenario would involve inclusion of non-equilibrated wallrock material in the uranium ore during sampling. Such a mechanism can be ruled out for the present case because the Sm-Nd correlation line is defined by pure uraninites and very high grade ores (associated with little or no chlorite or other gangue material) over the entire range of the data population used to calculate the isochron age. Another possible mechanism would involve mixing of radiogenic Nd (for example derived from older uranium mineralization or other radiogenic sources) and unradiogenic Nd (derived from older crustal sources) at the time of mineralization. In other words, the ore would have been isotopically heterogeneous at this time. To introduce serious bias in the ages deduced from a data array produced in that fashion, the degree of mixing and the Sm/Nd ratio would have to be correlated (a 'zero age isochron'). This possibility seems unlikely for two reasons: first, mixing of isotopically distinct fluids producing correlated $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ on an isochron plot would seem to require a great deal of coincidence in a hydrothermal setting like Nabarlek, and second, the Sm-Nd age is in excellent agreement with Rb-Sr isochron and model ages which, in this case, would be insensitive to mixing. Although some of the scatter on the Sm-Nd isochron may be caused by non-correlated initial isotopic heterogeneities, mixing is
unlikely to have had a serious influence on the Nabarlek Sm-Nd age.

The Rb-Sr data for the very high grade ores do not display an isochron relationship (Fig.3-14a). They cluster at Rb/Sr ratios near zero between $^{87}\text{Sr} / ^{86}\text{Sr} = 0.710-0.714$. Fig.3-14b shows the other samples including three layer silicate-rich high grade ores with high Rb/Sr ratios and all lower grade ores. Regression of 3 low grade ores, 3 altered but unmineralized host rocks and 9 analyses on altered host schists reported by Page et al. (1980) yields a poorly fitted isochron (MSWD = 21.9) with a model 2 age of 1619±30 Ma, $^{87}\text{Sr} / ^{86}\text{Sr} = 0.704±0.003$. Despite the scatter, the calculated errors are small because of the large dispersion in Rb/Sr ratios. Some of this scatter may be caused by differences in initial ratios due to variable Sr isotope reequilibration of the rocks with the alteration fluids. As pointed out by Page et al. (1980), Sr model ages for highly radiogenic samples might be a more suitable approach to extract meaningful age information from such samples. The average Sr model age for five samples of 1592±23 Ma (±1 s.d.) is similar to the 1610±40 Ma model age average by Page et al. (1980) and within error of the 1619±30 Ma isochron age.

![Fig. 3-14 Rb-Sr isochron diagram for Nabarlek samples. A) Low-Rb high grade primary ore. These comprise all those high grade samples por in layer silicates, plus one chloritic ore (#3). A 1620 Ma reference line is shown for comparison. B) Data points shown are for 3 high grade primary ores with high Rb/Sr, one ore that is strongly affected by illite-hematite alteration (94/41.3) plus a white mica/illite separate from this sample (94/41.3 wm) and a hematite separate, 9 low grade ores, 4 altered host rocks (3 with high Rb/Sr shown in large inset in B), and 9 analyses on 7 altered schists from the orezone by Page et al. (1980) (filled circles). Other symbols as in Fig. 3-13. Small inset shows area covered by A; 900 Ma reference line shown for comparison.](image-url)
Another four orezone samples define a well fitted (MSWD = 2.5) isochron with a model 1 age of 880±11 Ma and $^{87}\text{Sr}/^{86}\text{Sr}_i = 0.9215±0.0004$ (Fig.3-14b). This isochron comprises two samples which fall on the 1125±90 Ma Sm-Nd isochron and one which conforms to the 1616 Ma Sm-Nd isochron. The 880 Ma age is similar to the =900 Ma U-Pb age and the Rb-Sr age of the last recorded alteration at Nabarlek (Page et al., 1980). It is therefore considered the most precise estimate for the age of profound (illite-hematite-coffinite-) alteration of primary ores obtained so far.

Other samples below the 1619±30 Ma model 3 line possess Sr model ages between 865 and 1480 Ma (relative to $^{87}\text{Sr}/^{86}\text{Sr}_i = 0.705$). If it is assumed that these samples were all disturbed at = 900 Ma, the range in Sr model ages could be interpreted to reflect variable response to resetting at this time. Alternatively, if initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were heterogeneous and higher than 0.705 (as suggested by the high initial ratio of the 880 Ma isochron), many of the model ages could be too old and their true Sr model ages would be closer to 900 Ma.

In summary, both Sm-Nd data on high grade ores and Rb-Sr data on low grade ores and hydrothermally altered chlorite-white mica-rich schists from the inner alteration halo indicate that hydrothermal alteration (chloritization etc.) and high grade U mineralization were essentially contemporaneous at about 1615 Ma, some 700 Ma earlier than indicated by the U-Pb studies of Hills and Richards (1976). The = 900 Ma U-Pb age may represent the age of U remobilization; this is supported by Rb-Sr ages between 1200-850 Ma which most likely record the time(s) of alteration of the primary ore.

Initial Nd and Sr isotope ratios and implications for ore genesis

The systematic covariation of U and REE found in ARUF U ores (this study, Fig.2-3) could be interpreted to indicate transport of REE and U by the same ore-forming solution (e.g. McLennan and Taylor, 1979; Fryer and Taylor, 1984). On the other hand, uraninite is known to incorporate up to several weight percent REE, in particular high temperature uraninites (Fryer and Taylor, 1987; this study, section 3.3.2). Even the relatively low-temperature uraninites (=200°C) of the ARUF deposits contain up to 3000 ppm total REE and it could be argued that uraninites were merely very efficient scavengers of REE liberated during hydrothermal alteration at the site of ore deposition. In either case Nd isotope ratios would reflect the source material.

Fig. 3-15 shows the Nd and Sr isotope data for those ores which conform to the 1616 Ma Sm-Nd isochron, require minimal age corrections to measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and calculate back to reasonable initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ≥ 0.704, the lowest Sr isotope ratio known from the area. This selection naturally limits the range in initial $\varepsilon_{\text{Nd}}$ but is necessary to ensure that only the purest primary material is used.

Comparison with typical country rocks present in the Nabarlek area indicates some overlap in $\varepsilon_{\text{Nd}}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ of the ores with amphibolites and NVM but the ore field extends to higher $^{87}\text{Sr}/^{86}\text{Sr}$ towards the schist field. In contrast, the Nabarlek Granite is isotopically quite different from the ore. The observed Nd-Sr isotopic variation in the ores can be explained as a result of isotopic buffering in the ore fluids by local schist and amphibolite
host rocks. However, within the resolution of the data it is impossible to exclude the possibility of substantial contributions from either the Oenpelli Dolerite or the NVM volcanics. On the other hand, the Nabarlek Granite which has been considered as a source of U (Ewers et al., 1983), appears a much more unlikely source of Nd and Sr; if the granite was part of the ore-forming hydrothermal system, its Nd-Sr isotopic signature was not preserved during ore deposition. Late Archean basement is not known from Nabarlek; the Nd-Sr data suggest it would be an even more unlikely source than the granite.

![Diagram](image-url)

**Fig. 3-15** Initial $\varepsilon_{\text{Nd}}$ versus initial $^{87}\text{Sr}/^{86}\text{Sr}$ for 9 high grade ores and uraninites from Nabarlek (filled circles). Amph = amphibolites from Nabarlek and Jabiluka I, O.D. = Oenpelli Dolerite, NVM = Nungbalgarri Volcanic Member, schists = schists from Cahill Formation and Myra Falls Metamorphics.

While the isotopic data alone do not allow to distinguish between proximal and distal metal sources, mass balance calculations for the HREE and U clearly require massive influx of fluids carrying HREE and U from sources outside the Nabarlek alteration zone (appendix 3a). If these fluids have come from the Nabarlek Granite or concealed Archean basement, their isotopic signatures must have been overprinted prior to ore deposition. On the other hand, if the ore fluids and at least a major part of the ore components originated above the unconformity, its isotopic signatures would have been dominated by the Kombolgie Sandstone and NVM volcanics, both isotopically similar to Nabarlek host rocks. The isotopic data can be explained more conveniently in terms of this latter model as it requires only minimal changes in fluid Nd-Sr isotope ratios during ore deposition to produce the observed variation.
3.3.3.4 Jabiluka

Jabiluka is one of the largest U deposits in the world; in addition to uranium there are economic quantities of gold and minor PGE. The uraninite ore is stratabound within Cahill Formation schists (partly graphitic) but detailed studies show the ore to be concentrated in several more or less stratiform breccia zones which extend into overlying Kombolgie Sandstone and evidently controlled the distribution of hydrothermal alteration and mineralization. As in all ARUF uranium deposits, chlorite is the predominant gangue mineral. Wallrock alteration is extensive and bears a certain similarity to alteration at Nabarlek, in particular with respect to the change from pre-ore white mica to syn-ore chlorite (Wilde et al., 1987). Ore-related alteration affects overlying sandstones which strongly suggests a post-unconformity age of mineralization. In contrast to Nabarlek, bedded carbonates are present within the host sequence but are only preserved outside the orezone. Within the mineralized zone, their stratigraphic positions are occupied by brecciated 'jasperoid bands' which may represent the silicified residue of former carbonates.

![Sm-Nd isochron plot for Jabiluka uraninites, high grade ore total rocks and chloritized Kombolgie Formation. The 1614 Ma isochron is calculated for 6 uraninite fractions. The short tieline connects total rock W141V2/88 and the mineral separate from the same sample. O186V/241 is uraninite from Kombolgie Fm. Six of the ten uraninite fractions analysed define an isochron (MSWD=3.9) with an age of 1614±67 Ma and initial \( ^{143}\text{Nd}/^{144}\text{Nd} = 0.50941±17 \); the model 3 age for these samples is 1614±132 Ma with identical initial ratio corresponding to \( \varepsilon_{\text{Nd}} = -6.6±3.1 \) (Fig.3-16). The other four uraninite fractions plot below the 1614 Ma isochron and do not form a linear array. The two high grade ore total rocks are isotopically similar to the uraninite fractions separated from them but are displaced to lower Sm/Nd ratio and, in the case of W141V2/88tr, lower \( ^{143}\text{Nd}/^{144}\text{Nd} \). A line between W141V2/88tr and the uraninite separate from this sample has a slope similar to that of the 1614 Ma isochron. We can only speculate as to the reasons for the excess scatter about the 1614 Ma isochron and between the 1614 Ma samples and the rest of the uraninites. It may be caused by variable degrees of isotopic...](image-url)
equilibration between the ore fluids and local wallrocks and/or fluids derived from them if it is assumed that the two were isotopically different. Alternatively, the samples may not all have the same age or they may have experienced variable degrees of recurrent remobilization which has clearly disturbed U-Pb systems in Jabiluka ores and sulfides (Hills and Richards, 1976; Ludwig et al., 1987). Whatever the cause of the scatter, any possible bias would be well covered by the large errors associated with the model 3 age.

Two samples of uraniferous, chloritized Kombolgie Sandstone collected within meters of the unconformity (X141V/65.8, S141S/95.5) have quite variable Sm/Nd ratios and lie close to the 1614 Ma isochron. If it is assumed that chloritization in these rocks was contemporaneous with chloritization in the uranium ores (Wilde et al., 1987), these samples could be used to improve the precision of the ore isochron. The pooled age for the six uraninites plus the two chloritized sandstones is 1645±22 Ma (MSWD=2.96) with εNd = -7.4±1.3, within errors of the uraninites-only isochron age. However, as these data points may represent mixtures of pre-ore Nd and Nd introduced during chlorite metasomatism, we prefer the age obtained using uraninites only.

Comparison with previous geochronological data shows that the 1614±132 Ma age is similar to the 1600±150 Ma age for sulfides extracted from mineralized sample 54955 (DDH S180V/231.7m, Gulson and Mizon, 1980). Their sample was collected close to one of the 1614 Ma samples of this study (S180V/232). Further, the Sm-Nd age is indistinguishable from the 1600±80 Ma (+1s.d.) mean of Rb-Sr model ages on seven altered schists from Jabiluka (Page et al., 1980). This agreement between results from three different isotope systems provides strong evidence for an important hydrothermal event which produced at least part of the uranium mineralization at around 1600 Ma.

However, the relatively large errors of the Sm-Nd age overlap marginally with the U-Pb whole-rock age of 1437±40 Ma by Ludwig et al. (1985). Further, Riley et al. (1980) suggest that Rb-Sr model ages for hydrothermal alteration at Jabiluka could be as young as 1400 Ma if initial Sr isotopic ratios were heterogeneous. Gulson and Mizon (1980) obtained 1380 Ma Pb model ages for sulfides from unmineralized samples. If this age variability reflects real age differences for different parts of the mineralization, it would provide support for models which advocate semi-continuous rather than periodic uranium mineralization (e.g. Ypma and Fuzikawa, 1980; Johnston and Wall, 1984).

On the other hand, both the Sm-Nd and the U-Pb age by Ludwig et al. have the potential for bias. Sample S180V/238 exerts considerable control over the Sm-Nd age; if this sample is excluded from the regression, the Sm-Nd age for the remaining samples could lie anywhere between about 1650 and 1350 Ma. The U-Pb data by Ludwig et al. (1987) show increasing scatter with increasing degrees of discordancy and indicate isotopic disturbance(s) between about 400 to 600 Ma ago. Their data treatment therefore weights the data points according to the degree of discordancy, assuming that the most concordant data points are least disturbed. Although their approach appears adequate, the resultant age may nevertheless be in error if the U-Pb systems have been disturbed not only between 400-600 Ma as suggested by their data array, but also earlier than 600 Ma ago. For example, if it is assumed that the 1280 - 1380 Ma age for uraninites and sulfides (Gulson and Mizon, 1980)
and the =900 Ma age for uraninites (Hills and Richards, 1976) reflect the times of remobilization and partial Pb loss in U ores initially formed at 1614 Ma, a scattered data array as found by Ludwig and coworkers would be expected. The data points would plot in a polygon with edges at 1614 Ma, 1280-1380 Ma, 900 Ma and 400-600 Ma. In such a scenario, even the most concordant data points would give spurious U-Pb ages younger than the true age of mineralization.

Fig.3-17 \( \varepsilon_{\text{Nd}} \) vs. time diagram for Jabiluka uraninites compared with ARUF country rocks. The ore evolution lines end at 1650 Ma, the age of burial of the unconformity and assumed to be a maximum age of ore deposition. The 1614 Ma Sm-Nd and 1437 Ma U-Pb ages are indicated. Signatures: lower stippled area, Archean; cross-hatched, Lower Proterozoic metasediments; dotted, Kombolgie Fm. sandstones; upper stippled band, Nungbalgarri Volcanics.

In Fig.3-17 the Nd isotopic evolution lines for the uraninites are shown on a \( \varepsilon_{\text{Nd}} \) vs. time plot. It is obvious that for ages older than about 1550 Ma the evolution lines for the '1614 Ma' samples intersect those of Cahill Formation schists and other country rocks. In contrast, at 1437 Ma, apparent initial \( \varepsilon_{\text{Nd}} \) for these uraninites are between -4 and +1, significantly higher than any potential source rock at this time. Thus, if it is assumed that the Nd was derived from normal country rocks such as those represented in Fig.3-17, and that the Sm/Nd ratios of these uraninite samples have not been significantly affected by open system behaviour, the samples must be older than 1550 Ma. It is therefore concluded that primary mineralization at Jabiluka II was at around 1600 Ma. However, further (Sm-Nd) work is needed to substantiate the 1614 Ma age.

The remaining four uraninite analyses have intersections with source rock evolution lines which range between 800-1500 Ma. These 'Nd model ages' suggest uraninite separate
O186V/241 from mineralized Kombolgie sandstone and W141V2/88, a breccia ore collected < 20 m below the unconformity may have been formed up to 700 Ma later than the other samples which is consistent with a ~900 Ma U-Pb age for Jabiluka I uraninites reported by Hills and Richards (1976). This would imply that virtually all the (unradiogenic) Nd present in these samples was derived from the country rocks and not remobilized from the older ore, similar to the 1125 Ma ore samples from Nabarlek but quite different from secondary ore at Collins Bay (Fryer and Taylor, 1984) which incorporated highly radiogenic Nd derived from the primary ore.

![Fig. 3-18 Rb-Sr isochron diagram for uraninites from Jabiluka, Koongarra and Ranger. A 1600 Ma reference line is shown for comparison. The dashed tie lines connect the two high grade ore total rocks from Jabiluka and their respective uraninites which have lower $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$. The 4 samples surrounded by a dashed line indicate the range of repeat analyses of sample S180V/232.8. The Rb-Sr data for the Jabiluka uraninites do not show any isochron relationships; most have similar present-day $^{87}\text{Sr}/^{86}\text{Sr}$ around 0.720 at variable Rb/Sr ratios (Fig.3-18). This may be coincidental or it may suggest young Rb-Sr redistribution. Recent disturbance is likely in the case of S180V/232.8 which was analyzed four times with poor reproducibility and has unrealistically low $^{87}\text{Sr}/^{86}\text{Sr}$ (1614 Ma) values. Fig.3-19 shows initial Nd and Sr isotope ratios for Jabiluka uraninites compared to those of country rocks. In contrast to Nabarlek, Late Archean gneisses and Cahill Formation carbonates are present at Jabiluka while amphibolites, although known in the vicinity, were probably much less important as a source for Nd, Sr and U than at Nabarlek where they form a significant proportion of the immediate host rocks. Oenpelli Dolerite is not known in the Jabiluka area. The variation in initial $\varepsilon_{\text{Nd}}$ values is limited because only those samples...
which define the 1614 Ma isochron have been plotted. The data points lie between the fields of Kombolgie Sandstone and Cahill Formation schists which would suggest that the ore fluids acquired their Nd and Sr isotopic compositions from binary mixing of Nd and Sr derived from these two sources. Dissolved bedded carbonates could represent a third source which would have contributed mainly unradiogenic Sr (i.e. $^{87}\text{Sr}/^{86}\text{Sr} < 0.710$); hence the pseudo-binary mixing array in Fig.3-19. It should be noted that Late Archean gneisses appear to be the most unlikely Nd-Sr source rocks present, a situation quite similar to that at Nabarlek.

![Graph showing isotopic compositions of Jabiluka uraninites compared to ARUF country rocks](image)

**Fig.3-19** Initial $\varepsilon_{\text{Nd}}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ for Jabiluka uraninites compared to ARUF country rocks. Fields labelled K-1600 and K-1650 are Koongarra No.2 lens uraninites calculated at 1600 and 1650 Ma, respectively. Abbreviations as in Fig. 3-15.

### 3.3.3.5 Koongarra

Uranium mineralization at Koongarra is hosted by Cahill Formation quartz-chlorite schists and is concentrated in breccia zones which are parallel to the Koongarra Reverse Fault. This fault juxtaposes schists and strongly altered Kombolgie Sandstone implying a post-unconformity age of faulting and thus uranium mineralization. Wallrock alteration is similar to that at Nabarlek but lacks the intense white mica alteration adjacent to the mineralized breccia zone (Wilde et al., 1986); uraninite-brannerite plus magnesian chlorite are the major coexisting phases in the ore. U-Pb and Pb isotope data by Hills and Richards (1976) indicate an age of $\approx 900$ Ma for uraninite formation. However, some analyses with
higher $^{207}\text{Pb}/^{206}\text{Pb}$ apparent ages suggest uranium mineralization predates 900 Ma.

Fig.3-20 Sm-Nd isochron diagram for Koongarra and Ranger uraninites. The correlation lines drawn through some of the data points are visual fits. The numbers in the boxes indicate the ages and initial $\varepsilon_{\text{Nd}}$ values obtained from the correlation lines assuming they represent isochrons. The 420 Ma and the 1270 Ma apparent ages are not considered the real ages of primary mineralization; their high initial ratios would suggest a resetting origin for these isochrons. Alternatively, the linear alignment may be due to mixing or mere coincidence.

The two ore lenses present at Koongarra were sampled in drillcores 87 (No.1 lens) and 94 (No.2 lens). The Sm-Nd data are plotted in Fig.3-20 where the two ore lenses occupy distinct fields, lens No.2 samples having generally lower present-day $^{143}\text{Nd}/^{144}\text{Nd}$ ratios than the No.1 lens samples at overlapping $^{147}\text{Sm}/^{144}\text{Nd}$. Five of the No.1 lens analyses plot close to a correlation line which, if interpreted as an isochron, would have an age of =420 Ma and $\varepsilon_{\text{Nd}}(420 \text{ Ma}) = 65$. As this age is younger than the U-Pb age, it can not be the age primary ore deposition but may date the time of remobilization in parts of the No.1 lens. This is strongly supported by the high initial ratio. Lower intercept ages between 400-600 Ma have been found for the Ranger and Jabiluka ores (Ludwig et al., 1987) and for U-Pb systems in zircons from the Nimbuwah Complex (Page et al., 1980). They are interpreted to suggest a thermal event or regional groundwater activity.

Fig.3-21 shows the analyses in a $\varepsilon_{\text{Nd}}(T)$ vs. time diagram. The sample evolution lines were not extended to ages older than 1650 Ma because the ore locating breccia zone is
younger than the Kombolgie Formation (1650 Ma); an age of 1650 Ma is therefore regarded as a maximum age of uranium mineralization at Koongarra. An obvious conclusion from Fig.3-21 is, that the analyzed samples must be older than 900 Ma because they had $\varepsilon_{Nd}(900)$ exceeding +25. This would imply that both 420 and 900 Ma are times of partial remobilization of an older uranium ore. This is consistent with U-Pb data for three of Hills and Richards's samples which they interpret in terms of Pb inheritance from an older radiogenic Pb reservoir.

Fig.3-21 $\varepsilon_{Nd}$ versus time diagram for Koongarra uraninites compared to ARUF country rocks. The uraninite evolution lines end at 1650 Ma which is assumed to be the maximum age of ore deposition at Koongarra. Signatures as in Fig. 3-17.

While this conclusion appears straightforward regardless of possible resetting effects, the extraction of a reliable and meaningful age for primary mineralization is problematic. The No.1 lens evolution lines do not intersect local country rocks at any time before 1650 Ma. The only exception is sample 87/91.7 which has $\varepsilon_{Nd}(1650) = -9$. However, because of
indications for possible 420 Ma Sm-Nd redistribution for this and four other analyses from No.1 lens, the $\varepsilon_{\text{Nd}}(1650)$ values for these samples are considered artifacts. Three of the No.2 lens samples intersect the evolution band for NVM, Kombolgie Sandstone and Cahill Fm. schists in the interval from 1580 to 1650 Ma. This would imply an age of \approx 1600 Ma for uranium mineralization at Koongarra, provided the samples have developed as closed systems with respect to Sm and Nd. However, the evidence to support this hypothesis is certainly weaker than in the case of Naborlek and Jabiluka, where other dating methods give ages comparable to the Sm-Nd ages of uraninites.

The Rb-Sr isotopic data are shown in Fig.3-18. The data points for the No.1 lens samples scatter strongly between 0.7128 and 0.7197 with no correlation of present-day $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ ratios. This suggests Rb and Sr have been redistributed relatively recently but an age for this redistribution cannot be assigned. As Sr abundances are remarkably constant between 22 and 26 ppm while Rb concentrations vary by a factor of 20, it is likely that Rb was more mobile than Sr. The situation is further complicated by the fact that some of the samples have a HCl-leachable Sr component which is more radiogenic than the HCl-insoluble residue (appendix 3a). No.2 lens analyses are less scattered but again provide no age constraints.

Calculation of initial Nd and Sr ratios for the Koongarra uraninites is hampered by the evidence for young (Phanerozoic) disturbances of both Sm-Nd and Rb-Sr isotope systems at least in the No.1 lens samples, and by the lack of reliable age information. The No.2 lens samples are shown in Fig.3-19 where they are age-corrected for ages of 1600 and 1650 Ma. Obviously any age younger than \approx 1600 Ma would shift the uraninite data points rapidly towards higher $\varepsilon_{\text{Nd}}(T)$ and would generate an unrealistic gap between ore and reasonable Nd and Sr sources. It should be noted that even the No.2 lens samples may have suffered minor isotopic disturbance; nevertheless the data seem to follow the same general mixing relationship as the Jabiluka samples. Cahill Formation schists plus the interbedded carbonates and the volcano-sedimentary rocks above the unconformity appear to be suitable sources of Nd and Sr while the Late Archean basement is again a much more unlikely source.

3.3.3.6 Ranger

Mineralization at Ranger occurs in six high radiation anomalies hosted within Cahill Formation schists over a strike length of 6 km. Anomaly No.1 with pre-production reserves of 53000 tonnes of uranium oxide is currently being mined and has been sampled for this study. While the host rocks at Ranger are similar to those at Jabiluka and Koongarra, uraninite mineralization is generally much finer grained than in the other ARUF deposits. The uranium minerals are predominantly disseminated (\approx 5 \mu m) throughout the coexisting chlorite or form coatings in veinlets and hairline fractures. Similar to Jabiluka and Koongarra, carbonate horizons within the host Cahill Formation appear to be represented by brecciated siliceous bands within the ore zone.

Age relations of mineralization are uncertain apart from a clearly post-metamorphic (post 1800 Ma) origin of mineralization. Possible chloritized and silicified Kombolgie Fm.
sandstones intersected in drillcore at the No.3 orebody are interpreted to suggest a post-unconformity, i.e. syn-Kombolgie age for mineralization (Eupene et al., 1975). In contrast Hills and Richards (1986) and Ludwig et al. (1985, 1987) report U-Pb ages which indicate pre-Kombolgie ages between ~1700 - 1737 Ma for mineralization in both the No.1 and No.3 orebody.

Only six uraninite fractions from Ranger were analyzed because of the difficulty in obtaining suitable ore material for uraninite separation. The samples were collected from Upper Mine Series schists in the pit in December 1986. Fig.3-20 shows the Sm-Nd data in comparison with those for Koongarra uraninites. Three of the Ranger data points define a correlation line with an apparent age of ~1270 Ma and $\varepsilon_{Nd}(T) = +17.7$. As in the case of the 420 Ma line for the Koongarra samples, the high initial ratio of the 1270 Ma isochron would suggest partial remobilization and isotopic resetting of the ore at this time rather than initial mineralization. However, the correlation line could just as well represent a mixing line or result from mere coincidence.

Fig.3-22 $\varepsilon_{Nd}$ versus time diagram for Ranger uraninites compared to ARUF country rocks. Because of the pre-Kombolgie U-Pb ages obtained for this mineralization and its more ambiguous relationship to the unconformity compared with the other ARUF deposits, the uraninite evolution lines were not terminated at 1650 Ma. Signatures as in Fig.3-17.
On a $\varepsilon_{\text{Nd}}$ (T) vs. time plot (Fig.3-22), Nd isotopic evolution trajectories for three of the Ranger uraninites intersect local country rocks at ages younger than 1650 Ma while the other three samples have $\varepsilon_{\text{Nd}}(1650 \text{ Ma}) = 0$, i.e. higher than any country rock. In contrast, at 1737 Ma, the U-Pb age for Ranger ores by Ludwig et al. (1985), all six uraninite Nd trajectories are within the range of local country rocks. If the samples have not been isotopically disturbed since the time of ore deposition, the overlap in $\varepsilon_{\text{Nd}}$ (T) would lend some support to the results of Ludwig and coworkers. However, this does by no means prove a pre-Kombolgie Sm-Nd age for Ranger. For example, extrapolation of Nd isotopic evolution paths to ages older than 1650 Ma would allow some of the Koongarra uraninites as well as primary Nabarlek and Jabiluka uraninites to be older than the unconformity, a conclusion which is clearly inconsistent with the geological evidence for a post-Kombolgie origin of these deposits. In this sense, the Sm-Nd data for Ranger do not provide a unique solution as to the age of primary mineralization.

Fig.3-23 Initial $\varepsilon_{\text{Nd}}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ for Ranger uraninites compared to ARUF country rocks. A) calculated at 1614 Ma assuming Ranger was formed at the same time as Jabiluka. Abbreviations as in Fig.3-16. B) calculated at 1737 Ma, the U-Pb age by Ludwig et al. (1985). Note absence of NVM and KF which did not exist prior to 1650 Ma.
The Rb-Sr data for the Ranger samples scatter between 0.726-0.738 and do not show any isochron relationships (Fig.3-18). Initial Nd and Sr isotopic ratios are shown in Fig.3-23 where they have been recalculated for two ages: a hypothetical 1614 Ma age and the 1737 Ma U-Pb age of Ludwig et al. (1985). Five of the six data points form a linear array from low $\varepsilon_{\text{Nd}} - \text{low}^{87}\text{Sr} / ^{86}\text{Sr}$ to high $\varepsilon_{\text{Nd}} - \text{high}^{87}\text{Sr} / ^{86}\text{Sr}$; sample Ranger I has low $\varepsilon_{\text{Nd}}(T)$ but high $^{87}\text{Sr} / ^{86}\text{Sr} (T)$. Due to the high Sm/Nd ratios in the samples, the arrays for 1614 Ma and 1737 Ma are offset mainly in the $\varepsilon_{\text{Nd}}$ direction as Rb/Sr ratios are generally low with little change in $^{87}\text{Sr} / ^{86}\text{Sr}$ over 120 Ma. The 1737 Ma array can be explained conveniently in terms of mixing between a carbonate-type and a schist-type component (Fig.3-23b). For the Cahill Formation carbonates no initial $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios lower than $= 0.709$ have been found in this work, but Sr isotope data on bedded and vein carbonates from Jabiluka (RW Page, unpublished data) indicate initial $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios in Cahill Formation carbonates could have been as low as $= 0.707$, close to the most unradiogenic $^{87}\text{Sr} / ^{86}\text{Sr}$ value in the uraninites. Sample Ranger I plots in the field for Late Archean gneisses which are known in the immediate vicinity of Ranger No.1. The direction of the Ranger linear array is in marked contrast to the Nd-Sr isotopic characteristics of the Nabarlek and Jabiluka samples which consistently suggest mixing involving important contributions from either amphibolites or NVM/Kombolgie Sandstone-type sources. This would be expected if the 1737 Ma age for Ranger is the true age rather than a post-Kombolgie age because Kombolgie Formation sandstones and NVM volcanics did not exist at that time and amphibolites are unimportant in the Ranger area. The position of the sample array would thus lend support to the 1737 Ma age for U deposition at Ranger.

In contrast, the '1614 Ma' array does not form a meaningful mixing array as one endmember is undefined (Fig.3-23a). The high $\varepsilon_{\text{Nd}} - \text{high}^{87}\text{Sr} / ^{86}\text{Sr}$ data points would require a source with $\varepsilon_{\text{Nd}} > +4$ and $^{87}\text{Sr} / ^{86}\text{Sr} > 0.732$, a highly unusual combination not known in the area. It appears a pre-Kombolgie age for mineralization can explain the Sm-Nd data more conveniently; on this basis we accept the 1737 Ma U-Pb age by Ludwig et al. (1985) as a more likely age of primary mineralization at Ranger.

3.3.3.7 Conclusions

The Sm-Nd data for ARUF uraninites and high grade ores provide several new constraints on the origin of unconformity-type uranium deposits:

(1) primary mineralization at Nabarlek and Jabiluka was contemporaneous at Sm-Nd ages of 1616±50 Ma and 1614±132 Ma respectively. These ages are identical to previously published and new Rb-Sr ages for metasomatic alteration at the two deposits and, in the case of Jabiluka, to a $^{207}\text{Pb} / ^{206}\text{Pb}$ model age for sulfides from a mineralized sample. In contrast, they are older than published U-Pb ages which range from 900 to 1437 Ma. Evaluation of Nd isotopic evolution paths for the uraninites suggests the studied uraninites must be older than 1550 Ma because of unreasonably high initial $\varepsilon_{\text{Nd}}$ obtained for any younger age. This treatment assumes the samples behaved as closed systems with respect to Sm and Nd since the time of crystallization. The general agreement of the Sm-Nd and Rb-Sr data suggests this assumption is reasonable at least for the samples in question;
(2) Parts of the Nabarlek ore were profoundly altered at about 900 Ma, consistent with published U-Pb and Rb-Sr ages for this deposit. However, scattered Sm-Nd isochron and Rb-Sr model ages ranging from $\approx 1200$ to 900 Ma may indicate several alteration events over a prolonged alteration period. At least two uraninites from Jabiluka have Nd 'model ages' (intersections of their Nd isotope evolution trajectories with those of probable source rocks) significantly younger than 1614 Ma. Their ages suggest they may have formed at about 900 Ma, the U-Pb age for Jabiluka uranium mineralization (Hills and Richards, 1976);

(3) The age of mineralization at Koongarra is less well defined because of possible resetting effects long after initial mineralization, but the samples considered to be least disturbed indicate an age close to 1650 Ma, the geological maximum age for ore deposition at Koongarra;

(4) Initial Nd and Sr isotopic ratios for least disturbed ores and uraninites from the three deposits suggest isotopic signatures in the ore-forming fluids were controlled by the local host rocks within the alteration zones, comprising schists and amphibolites at Nabarlek, and schists and possibly interbedded carbonates at Jabiluka and Koongarra. However, mass balance considerations suggest additional sources were important at Nabarlek to account for the large amounts of HREE and U which cannot be derived solely from the altered rock volume. The similarity of the Nd-Sr isotope data in the ores to those in post-unconformity rocks (Kombolgie Sandstone and NVM volcanics) in all three deposits would favour these rocks as sources of much of the uranium and HREE as well as part of the Nd and Sr;

and (5), the isotopic data for Ranger do not allow to independently date the time of mineralization. However, Nd-Sr isotopic systematics in Ranger uraninites are more consistent with the pre-Kombolgie 1737 Ma age of Ludwig et al. (1985) than with a hypothetical post-unconformity 1614 Ma age. For an age of 1737 Ma, the samples would form a linear Nd-Sr isotopic array between local Cahill Formation schists and carbonatic rocks with possible contributions from the Late Archean basement. These sources are entirely consistent with the known age distribution of the rocks which indicate that the post-unconformity rocks were not present at 1737 Ma. It appears more than fortuitous that the Nd-Sr isotopic data should indicate only pre-1650 Ma metal sources in the only deposit with pre-1650 Ma U-Pb ages but suggest important contributions from post-1650 Ma metal sources for those deposits with post-1650 Ma ages.

The Sm-Nd ages for Nabarlek, Jabiluka and possibly for Koongarra indicate a remarkably uniform period of primary uranium mineralization in the entire ARUF region. This suggests the ore-forming processes were widespread, consistent with the abundance of unconformity-type uranium occurrences in ARUF (Needham and Roarty, 1980). A similarly confined range of initiation dates for uranium mineralization has been found for many of the unconformity-type uranium deposits in Saskatchewan (Bray et al., 1987).

Despite some statistical overlap, the 1600 - 1615 Ma age range found for the three deposits is consistent with their post-unconformity age (i.e. later than 1648$\pm$29 Ma, Page et al., 1980) as inferred from their geology, in particular the fact that ore-related alteration
features extend into the overlying sandstone (Gustafson and Curtis, 1983; Wilde et al., 1987). On the other hand, magmatic activity associated with the intrusion of alkaline dikes and dolerites between 1370 and 1200 Ma (Page et al., 1980) appears to clearly post-date the mineralizing period. This relative age sequence suggests uranium mineralization occurred under a substantial cover of Mid Proterozoic sediments and volcanics at a rather advanced stage of basin formation, consistent with paleotemperature and paleopressure estimates in the range of 100-200°C and ≈500 bars (Wilde et al., 1986; Ypma and Fuzikawa, 1980; Walsh, 1986). Similar mineralization conditions have been identified in the Saskatchewan deposits (Hoeve and Sibbald, 1978; Pagel et al., 1980). The deep burial during mineralization removes the need for magmatic or other deep-seated heat sources to drive the ore-forming hydrothermal system (Johnston and Wall, 1984) but by no means disproves possible contributions from such sources. For example, hypogene heat sources have been suggested for Jabiluka by Binns et al. (1980b) and Gustafson and Curtis (1983).

The source(s) the uranium in the ARUF deposits is much debated in the literature. Most authors agree that the generally high U background of the Lower Proterozoic and Late Archean rocks was an important prerequisite for U mineralization in the area (e.g. Needham, 1985). McAndrew and Finlay (1980) suggest disseminated uraninite in Nanambu Complex gneisses as a possible source of U. The U may be incorporated into the mineralized breccia zones either directly via ascending hydrothermal fluids (Binns et al., 1980b), or indirectly after an intermediate erosional step (Ferguson et al., 1980; Crick and Muir, 1980). Ewers et al. (1983) suggest the U-rich Nabarlek Granite as a possible source of U for Nabarlek. In contrast, Johnston and Wall (1984) and Wilde et al. (1986) propose the ore-bearing fluids and therefore at least part of the uranium originated in the rocks above the unconformity.

The post-Kombolgie timing of uranium deposition and initial Nd-Sr isotope data for uraninites from Nabarlek, Jabiluka and possibly also Koongarra would lend support to the latter hypothesis; deep-seated sources such as uranium-rich post-tectonic granites or the Archean basement are neither required nor indicated by the present data. Instead, the Kombolgie Formation and the interbedded volcanics are seen as a more likely source of at least part of the uranium and the enormous quantities of water involved in mineralization (Wilde et al., 1986). Contrary to some workers who discounted the sandstones as a possible source of U on the basis of their low U concentrations, the Kombolgie Formation may in fact represent a favourable U source rock, in particular the interbedded Nungbalgarri Volcanics. Porous volcanic deposits rich in glass have long been recognized as important U sources for many groundwater-related U deposits (Rosholt et al., 1969; Walton et al., 1981; Zielinski, 1982) and the wide distribution and appreciable thickness of the NVM (up to 170 m, Page et al., 1980) would make it an ideal U source for circulating oxygenated ground and formation waters. Indeed, Hoeve and Sibbald (1978) go even further and hypothesise unconformity-type U deposits in Canada may represent a special class of sandstone-type deposits.

Although we do not intend to present a detailed genetic model for ARUF uranium mineralization, a number of points relevant to ore genetic models can be derived from the data discussed in this study. The relatively narrow, post-Kombolgie Sm-Nd age range for
mineralization in the three vein-type ARUF deposits Nabarlek, Jabiluka and Koongarra suggests burial of the unconformity was an important factor in the ore-forming process:

(1) it provided the heat necessary to drive the ore-forming hydrothermal alteration; Ypma and Fuzikawa (1980) suggest it may have also acted as a thermal blanket allowing radiogenic heat build up from the uraniumiferous basement,

(2) the sandstones are a more likely source of the vast quantities of water involved in ore deposition and alteration than the relatively impermeable basement rocks which were previously dehydrated during regional metamorphism,

(3) fluids capable of mobilizing and transporting U as uranyl complexes were oxidized (i.e. in equilibrium with hematite) and therefore must have contained a considerable meteoric component (or interacted with hematite in the sandstone) (Wilde et al., 1986),

(4) the sandstones and in particular the interbedded volcanics would represent a favourable source of U for leaching by circulating hot, oxidized waters,

(5) access of fluids to the reducing (carbonaceous) basement rocks via brecciated parts of reverse faults at the unconformity may have been in response to basinwide faulting which would explain the narrow range of Sm-Nd ages. Bray et al. (1987) have used similar arguments to explain U-Pb ages for the unconformity-type deposits associated with the Athabasca Basin in Saskatchewan.

The origin of uranium mineralization at Ranger I remains unclear in the light of the U-Pb and Sm-Nd isotopic evidence. The pre-Kombolgie age and inferred fluid sources suggest ore deposition at Ranger involved processes that were unique among the known ARUF deposits. Clearly, more work is needed to clarify the relationships between Ranger and the other ARUF uranium deposits.

3.4 Sm-Nd isotope systematics in economic geology

The case studies presented in the previous section allow several generalizations concerning the utilization of Sm-Nd isotope studies on ore deposits:

(1) Sm-Nd isochron dating is a feasible addition to the isotopic dating methods already in use in ore genetic studies. A modified Sm-Nd ‘model age’ approach (chondritic or depleted mantle growth models are replaced by the growth curve of potential local Nd source rocks) appears useful in cases of excessive data scatter and/or limited dispersion in Sm/Nd. However, this method is only useful if Sm/Ndore >> or << Sm/Ndsource. Because of the scarcity of minerals with Sm/Nd ratios much less than average crustal ratios, this approach is limited to ores with high HREE/LREE, e.g. many fluorite deposits, rare element (Zr, Nb, REE etc) mineralizations, some lode Au deposits (Kerrich and Fryer, 1979) and U deposits.

(2) Initial $^{143}$Nd/$^{144}$Nd ratios represent a useful tracer of the sources of metals in the mineralizing fluids. However, wallrock buffering of the Nd isotopic composition is important as repeatedly shown in this study, and has to be taken into account. In this respect, Nd isotopic studies on ore deposits are most promising where potential Nd sources and ore host rocks are isotopically very different from each other. Considering the attainable reproducibility in $\varepsilon_{Nd}$ values (±0.5 - 1 $\varepsilon$ unit, depending on the size of the age correction, assuming no problems with sample homogeneity), at least 3-5 $\varepsilon$ units difference between
sources and host rocks would seem a minimum requirement. As in all isotopic tracer studies, several isotopic systems should be employed.

(3) Even the small number of case studies undertaken for this thesis demonstrates the limits of the Rb-Sr system in deposits with a long geological history. In all cases, Rb-Sr isotope data on ore material failed to provide any age information relevant to primary mineralization. Exceptions are layer silicate-rich ore samples and altered host rocks from Nabarlek and the altered schists from Jabiluka studied by Page et al. (1980). It has been shown that the Sm-Nd systems of the ore minerals studied here invariably behave more predictably than their Rb-Sr systems. This is illustrated in Fig.3-24 for uraninites and high grade ores from the ARUF deposits.

![Graph A](image1)

![Graph B](image2)

**Fig.3-24** Present-day isotopic data for uraninites and high grade uranium ores from ARUF. A) Sm-Nd isotopic compositions. Individual subsets may show effects of partial isotopic resetting but overall the data define a remarkably confined linear array. The 1600 and 1400 Ma isochrons are shown for reference and do not necessarily imply synchronous mineralization of all samples around 1600 Ma. B) Rb-Sr isotopic compositions. Scatter within one deposit and between the deposits is large compared to the Sm-Nd results and isochron relationships are absent.
The Sm-Nd data define a relatively confined array despite demonstrated partial resetting (e.g. Koongarra) and and suggest the overall age of primary mineralization is closer to 1600 Ma than to 1400 Ma (see 3.3.3). In contrast, the Rb-Sr data are much more scattered and it is impossible to extract any meaningful and reliable age information regarding the time of ore deposition. The reasons for the erratic behaviour of the Rb-Sr system on one hand, and the more regular behaviour of the Sm-Nd system on the other hand are unclear but may be related to the greater crystallochemical affinity of U and REE (small ionic radii, high valency) compared to Sr and particularly Rb (large ionic radii, low valency) and the resultant greater sensitivity of the Rb-Sr system to even mild alteration events. The Rb-Sr systems in sulfide-rich samples from Kidd Creek are much better behaved than those of the ARUF uraninites but nevertheless have been strongly affected by mild alteration. In contrast, their Sm-Nd systems show only minor signs of alteration and preserve the age of primary Sm/Nd fractionation associated with ore deposition.

In summary, Sm-Nd isotope studies on ore deposits are applicable to deposits of all ages even in cases where primary assemblages have been affected by later low-temperature hydrothermal alteration or mild thermal events. However, the effects of higher grade metamorphism on Sm-Nd systematics in ores is unexplored. Rb-Sr isotopic studies will be most useful in young (Phanerozoic) deposits that have not been altered but can be used to delineate the timing of alteration events post-dating mineralization.
REFERENCES


Fleischer M (1983) Distribution of the lanthanides and yttrium in apatites from iron ores and its bearing on the genesis of ores of the Kiruna type. Econ Geol, 78, 1007-1010.


Frey FA, Haskin MA, Poetz JA and Haskin LA (1968) Rare earth abundances in some basic rocks. J Geophys Res, 73, 6085-6098.


Govindaraju K (1984) Special Issue, Geostandards Newsletter, 8, appendix 1, 03.
Graf JL, Jr (1977) REE as hydrothermal tracers during the formation of massive sulfide deposits in volcanic rocks. Econ Geol, 72, 527-548.
Gustafson LB and Curtis LW (1983) Post-Kombolgie metasomatism at Jabiluka, Northern Territory, Australia, and its significance in the formation of high-grade uranium mineralization in Lower Proterozoic rocks. Econ Geol, 78, 26-56.
Halliday AN, Shepherd TJ, Dickin AP, MacLaren F and Darbyshire F (1986) Sm-Nd dating and fingerprinting of the North Pennine fluorite deposits. Terra Cognita, 6, 227.
Hanson GN (1978) The application of trace elements to the petrogenesis of igneous rocks of granitic composition. Earth Planet Sci Lett, 38, 26-43.


Jabrak M, Smejkal V and Albert D (1985) Rare earth and isotopic geochemistry of the fluorite-barite vein deposits from the Western Rouergue district (France). Econ Geol, 80, 2030-2034.


Kessen KM, Woodruff MS and Grant NK (1981) Gangue mineral $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios and the origin of Mississippi Valley-type mineralization. Econ Geol, 76, 913-920.


Medford GA, Maxwell RJ and Armstrong RL (1983) $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measurements on sulfides, carbonates, and fluid inclusion from Pine Point, Northwest Territories, Canada: An $^{87}\text{Sr}/^{86}\text{Sr}$ ratio increase accompanying the mineralizing process. Econ Geol, 78, 1375-1378.


Möller P, Parekh PP and Schneider HJ (1976b) The application of Tb/Ca - Tb/La abundance ratios to problems of fluor spar genesis. Miner Depos, 11, 111-116.


Morteani G, Möller P and Schley F (1982) The rare earth element (REE) contents and the origin of the sparry magnesite mineralization of Tux/Lanersbach, Entachen Alm, Spiessnägel, Hochfilzen (Austria) and the lacustrine magnesite deposit of Alani/Kozani (Greece) and Bela Stena (Yugoslavia). Econ Geol, 77, 99-113.


Parák T (1973) Rare earths in the apatite iron ores of Lappland together with some data about the Sr, Th and U content of these ores. Econ Geol, 68, 210-221.

Parák T (1985) Phosphorus in different types of ore, sulfides in the Iron deposits, and the type and origin of ores at Kiruna. Econ Geol, 80, 646-665.


Piper DZ, Veeh HH, Bertrand WG and Chase RL (1975) An iron-rich deposit from the Northeast Pacific. Earth Planet Sci Lett, 26, J14-120.


Reesman RH (1968) Strontium isotopic compositions of gangue minerals from hydrothermal ore deposits. Econ Geol, 63, 731-736.


Roaldset E (1973) Rare earth elements in Quaternary clays of the Numedal area, southern Norway. Lithos, 6, 349-372.


Rosholt JN and Noble DC (1969) Loss of uranium from crystallized silicic volcanic rocks. Earth Planet Sci Lett, 6, 268-270.


Smewing JD and Potts PJ (1976) Rare earth abundances in basalts and metabasalts from the Troodos Massif, Cyprus. Contrib Mineral Petrol, 57, 245-258.


Stettler A and Allègre CJ (1978) \(^{87}\)Rb-\(^{87}\)Sr studies of waters in a geothermal area: the Cantal, France. Earth Planet Sci Lett, 38, 364-372.


Wilde AR et al. (1987) Spatial and temporal distribution of alteration in unconformity-related uranium deposits, Northern Territory, Australia: implications for metal transport and depositional mechanisms (in prep)


Zielinski RA (1982) The mobility of uranium and other trace elements during alteration of rhyolite ash to montmorillonite: a case study in the Troublesome Formation, Colorado, USA. Chem Geol, 35, 185-204


APPENDIX 1

A. Sm-Nd and Rb-Sr dating of an Archean massive sulfide deposit: Kidd Creek, Ontario

Roland Maas, Malcolm T. McCulloch, Ian H. Campbell
and Paul Coad

B. Sm-Nd and Rb-Sr isotopic data for Kidd Creek massive sulfide ores
Sm-Nd and Rb-Sr dating of an Archean massive sulfide deposit: Kidd Creek, Ontario

Roland Maas, Malcolm T. Mc Culloch, Ian H. Campbell
Research School of Earth Sciences, Australian National University, P.O. Box 4, Canberra, A.C.T. 2601, Australia
Paul R. Coad
Kidd Creek Mines, B-2002, Timmins, Ontario P4N 7K1, Canada

ABSTRACT

Highly altered felsic metavolcanics associated with the Kidd Creek, Ontario, Cu-Zn massive sulfide deposit show a large range of Sm-Nd ratios and yield a Sm-Nd isochron of 2674 ± 40 Ma (initial ratio 147Nd/144Nd = 0.57 ± 0.30), which represents the time of rare-earth-element redistribution during intense hydrothermal alteration. That the Sm-Nd age is consistent with age constraints on ore deposition provided by precise U-Pb zircon data indicates contemporaneity of ore deposition, hydrothermal alteration, and rare-earth mobility. The age is therefore interpreted as a minimum age of ore deposition. In contrast, the Rb-Sr age of the altered rocks, as well as the metavolcanic rocks outside the alteration zone, has been reset at 2576 ± 26 Ma, most likely as a result of widespread low-temperature metamorphism unrelated to ore deposition. Our results suggest that Sm-Nd dating could be a useful tool in the study of ore deposits and, potentially, in the study of a wide range of mineralizations.

Initial 147Sm/144Nd(T) values for massive ore, altered felsic volcanics, and their weakly altered precursors are identical, indicating derivation and redistribution of light rare-earth elements within the altered footwall volcanics. These data suggest that the footwall volcanics have also supplied part of the base metals to the stratiform ore.

INTRODUCTION

Rare-earth elements (REE) are immobile under most geologic conditions, but they may become mobile in zones of intense alteration associated with some ore deposits (Graf, 1977; Kerrich and Fryer, 1979). For example, Campbell et al. (1984) reported extreme REE mobility from the large Kidd Creek Cu-Zn massive sulfide deposit in Ontario and suggested that hydrothermal alteration of footwall volcanics during ore formation was responsible for fractionation of REE. We show that Sm-Nd whole-rock dating can be used to determine the time of REE fractionation and to obtain useful information on its relationship to ore deposition. This approach has potential in a variety of ore-forming environments and may be valuable in the study of ore deposits. The Sm-Nd data are compared with Rb-Sr isotopic data to evaluate their relative importance of previous disturbance.

Initial 147Sm/144Nd ratios for altered host rocks and stratiform sulfide ore are used to constrain the source of mobile Nd within the alteration system. This can give information on the source or pathway of the hydrothermal solutions precipitating Nd and can complement data on ore fluid sources obtained from other methods.

GEOL O GIC SETTING AND SAMPLES

The Kidd Creek deposit—one of the world’s largest Cu-Zn mines—is an Archean, volcanics-hosted, massive sulfide deposit (Franklin et al., 1981). It is located in an overturned volcanic-sedimentary sequence near the boundary between Lower and Upper Supergroup of the western part of the Abitibi greenstone belt, 45 km north of Timmins, Ontario. Massive stratiform sulfides occur within rhyolitic volcanioclastics, and they are stratigraphically underlain by a conformable, lobate-shaped blanket of stringer-Cu mineralization located within a crackle-brecciated massive rhyolite (Coard, 1985). The mineralized sequence is sandwiched by pillowd metabasalts (hanging wall), and rhyolitic volcanioclastics and subvolcanic sills of massive rhyolite (footwall), which have a U-Pb zircon age of 2717 ± 4 Ma (Nunes and Pyke, 1981). Several ultramafic and felsic stocks occur in the mine area, but field relations are unclear because of structural complexity and pervasive alteration. Felsic volcanics in the alteration zone associated with the mineralization contain quartz ± chlorite ± sericite ± calcite assemblages typical of many volcanics-hosted, massive sulfide deposits (Walter et al., 1975). There ore-related alteration features contrast with the low-grade assemblages associated with burial metamorphism and include distinct changes in major and trace elements (Campbell et al., 1984) and unusual oxygen isotopic characteristics (Beatty et al., 1980).

Samples for Nd and Sr isotopic analyses were taken from both within and outside the alteration zone to represent the compositional range from nonmineralized, weakly altered volcanics, through altered and highly altered volcanics, to massive chalcocite ore. Weakly altered felsic volcanics (WFV) were collected from massive footwall rhyolites about 300 m below the Cu-stringer ore zone; they are probably geochemically similar to pre-ore mine sequence volcanics (Campbell et al., 1984). Sample locations for altered felsic volcanics (AFV) and massive stratiform Cu ore are shown in Figure 1. Major- and trace-element data for most of the samples are reported in

Figure 1. Left: Schematic geologic map of mine level 2400 ft showing relative position of samples with prefix KC from crosscut 26-600 on 2600-H level (quadrangle). Right: Details of sample locations in crosscut 26-600. Modified after Coad (1984).
Campbell et al. (1984) who demonstrated specular REE mobility within the alteration zone at the stringer zone—massive ore contact. In essence, intense hydrothermal alteration, probably associated with ore formation, produced zones of depletion in light REE and middle REE, as well as zones of light REE enrichment within AFV (Fig. 2). This zoning resulted in a large spread of Sm/Nd ratios in AFV which makes these rocks amenable to Sm-Nd isochron dating. Furthermore, AFV exhibits a wide range in Rb/Sr ratios, which allows precise Rb-Sr dating.

TIME OF RARE-EARTH FRACTIONATION AND ORE DEPOSITION: Sm-Nd ISOTOPES

The Sm-Nd isotopic data (Table 1) show a large range in ($^{143}$Sm/$^{144}$Nd) for AFV and massive ore (0.09 to 0.27) compared to the very limited range in WFV. The most altered AFV from the lower part of the alteration zone have the highest ($^{143}$Sm/$^{144}$Nd) compared to AFV closer to stratiform ore which have values lower than WFV. Massive, stratiform sulfide ore has the lowest ($^{143}$Sm/$^{144}$Nd).

The AFV and ore data define $^{267}$±40 Ma Ma sanite (95% confidence limit (C.L.) model 4, McIntyre et al., 1966) with an initial ratio of $^{147}$Sm/$^{144}$Nd for Kidd Creek sulfide and whole rocks which has been interpreted as the age of sulfide ore deposition (Bugnon et al., 1979). It is, however, somewhat younger than the U-Pb zircon age of $^{271}$±7 Ma for massive sulfides underlying stratiform ore which represents a maximum age for ore deposition (Nunes and Pyke, 1981). A similarly precise U-Pb zircon age of $^{270}$±3 Ma for a rhyolite higher up in the stratigraphic sequence from elsewhere in the Timmins area (Nunes and Pyke, 1981) sets a minimum age for ore formation, which is within error of the Sm-Nd age. It is not clear whether the small difference between the $^{271}$ Ma zircon age and the Sm-Nd age is real or the result of minor disturbance which may be responsible for some of the data scatter seen in Figure 2a. The same process could have disturbed the U-Pb isotopic systems of Kidd Creek whole rocks and resulted in the low Pb-Pb isochron age of the sulfides (Bugnon et al., 1979). Alternatively, the presence of systematic differences in initial ($^{143}$Nd/$^{144}$Nd) could also affect the age. However, without a priori reasons for sample rejection, we accept $^{267}$±40 Ma as a minimum estimate for the time of ore deposition.

uncertainty (see inset Fig. 2a), both age and initial ratio are surprisingly well defined considering the strong alteration of the samples. The age is regarded as the time when REE in AFV and stratiform ore were mobilized and fractionated as a result of hydrothermal alteration (Campbell et al., 1984).

The $^{267}$±40 Ma age is identical within error to the $^{264}$±60 Ma Pb-Pb isochron age for Kidd Creek sulfides and whole rocks which has been interpreted as the age of sulfide ore deposition (Bugnon et al., 1979). It is, however, somewhat younger than the U-Pb zircon age of $^{271}$±4 Ma for massive sulfides underlying stratiform ore which represents a maximum age for ore deposition (Nunes and Pyke, 1981). A similarly precise U-Pb zircon age of $^{270}$±3 Ma for a rhyolite higher up in the stratigraphic sequence from elsewhere in the Timmins area (Nunes and Pyke, 1981) sets a minimum age for ore formation, which is within error of the Sm-Nd age. It is not clear whether the small difference between the $^{271}$ Ma zircon age and the Sm-Nd age is real or the result of minor disturbance which may be responsible for some of the data scatter seen in Figure 2a. The same process could have disturbed the U-Pb isotopic systems of Kidd Creek whole rocks and resulted in the low Pb-Pb isochron age of the sulfides (Bugnon et al., 1979). Alternatively, the presence of systematic differences in initial ($^{143}$Nd/$^{144}$Nd) could also affect the age. However, without a priori reasons for sample rejection, we accept $^{267}$±40 Ma as a minimum estimate for the time of ore deposition.

Table 1. Time and Sm-Nd analytical results for Kidd Creek Phle asleep volcanism and massive sulfide

<table>
<thead>
<tr>
<th>Sample Room</th>
<th>Sm</th>
<th>Nd</th>
<th>Sr</th>
<th>$^{143}$Sm/$^{144}$Nd</th>
<th>$^{147}$Sm/$^{144}$Nd</th>
<th>$^{143}$Nd/$^{144}$Nd</th>
<th>$^{142}$Nd/$^{144}$Nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>206 LA</td>
<td>21.19</td>
<td>129.69</td>
<td>19.75</td>
<td>0.1098</td>
<td>0.510197</td>
<td>-11.87</td>
<td>2.7569</td>
</tr>
<tr>
<td>206 CB</td>
<td>18.95</td>
<td>99.19</td>
<td>14.21</td>
<td>0.1077</td>
<td>0.510250</td>
<td>-22.2</td>
<td>2.7870</td>
</tr>
<tr>
<td>206 W</td>
<td>6.33</td>
<td>29.72</td>
<td>48.39</td>
<td>0.1099</td>
<td>0.510194</td>
<td>-19.84</td>
<td>2.6356</td>
</tr>
<tr>
<td>206 KB</td>
<td>2.19</td>
<td>11.23</td>
<td>26.39</td>
<td>0.1026</td>
<td>0.510272</td>
<td>-19.84</td>
<td>2.6356</td>
</tr>
<tr>
<td>206 GP</td>
<td>3.75</td>
<td>29.72</td>
<td>25.31</td>
<td>0.1157</td>
<td>0.510278</td>
<td>-20.0</td>
<td>2.6356</td>
</tr>
<tr>
<td>206 J</td>
<td>2.59</td>
<td>19.91</td>
<td>25.31</td>
<td>0.1157</td>
<td>0.510278</td>
<td>-20.0</td>
<td>2.6356</td>
</tr>
<tr>
<td>206 K</td>
<td>1.53</td>
<td>8.71</td>
<td>18.51</td>
<td>0.1491</td>
<td>0.510195</td>
<td>-22.2</td>
<td>2.5465</td>
</tr>
<tr>
<td>206 KB</td>
<td>1.53</td>
<td>8.71</td>
<td>18.51</td>
<td>0.1491</td>
<td>0.510195</td>
<td>-22.2</td>
<td>2.5465</td>
</tr>
<tr>
<td>206 KB</td>
<td>2.59</td>
<td>19.91</td>
<td>25.31</td>
<td>0.1157</td>
<td>0.510278</td>
<td>-20.0</td>
<td>2.6356</td>
</tr>
<tr>
<td>206 P</td>
<td>2.59</td>
<td>19.91</td>
<td>25.31</td>
<td>0.1157</td>
<td>0.510278</td>
<td>-20.0</td>
<td>2.6356</td>
</tr>
<tr>
<td>206 W</td>
<td>6.33</td>
<td>29.72</td>
<td>48.39</td>
<td>0.1099</td>
<td>0.510194</td>
<td>-19.84</td>
<td>2.6356</td>
</tr>
<tr>
<td>206 LA</td>
<td>21.19</td>
<td>129.69</td>
<td>19.75</td>
<td>0.1098</td>
<td>0.510197</td>
<td>-11.87</td>
<td>2.7569</td>
</tr>
</tbody>
</table>

Note: Procedures for sample preparation and mass-spectrometry as in Readwood et al. (1985).

Kidd Creek composition normalized to "KCC" (176) at 1.971.

All errors quoted are 2 standard deviations.

The AFV and ore data define $^{267}$±40 Ma for Kidd Creek whole rocks and resulted in the low Pb-Pb isochron age of the sulfides (Bugnon et al., 1979). Alternatively, the presence of systematic differences in initial ($^{143}$Nd/$^{144}$Nd) could also affect the age. However, without a priori reasons for sample rejection, we accept $^{267}$±40 Ma as a minimum estimate for the time of ore deposition.

Figure 2. Chondrite-normalized REE patterns for Kidd Creek massive volcanics, altered volcanic rocks from stringer zone, and stratiform Cu ore, illustrating REE mobility within alteration zone (REE data from Campbell et al., 1984, and unpublished analyses). Normalizing values are those of Evensen et al. (1978) for the rare earth elements (REE).

Solid circles = weakly altered volcanic rocks; squares and diamonds = altered volcanic rocks; stars = stratiform, massive Cu ore.
POST-ORE DISTURBANCE: 
Rb-Sr ISOTOPES

The pooled Rb-Sr isotopic data for AFV, stratiform ore, and WFV (Table 1) define a 2576±26 Ma isochron (95% C.L., model 3) with an initial \( ^{187} \)Rb/\(^{86} \)Sr of 0.7047±0.0024 (Fig. 3b). The pooling of all data appears justified in view of their coincidence on the isochron diagram and only small differences in ages and initial ratios obtained from regressing the data sets for AFV and WFV individually. The significance of the 2576 Ma age is uncertain. Resettling of Rb-Sr isotopic systems between 2600 and 2400 Ma is a common feature throughout most of the Superior province and may be attributed to one or more phases of the Kenoran orogeny (Turek et al., 1982; Davis et al., 1982). Jolly (1978) assigned an age of 2400 to 2600 Ma to Kenoran events that involved north-south compression, emplacement of granitoid igneous, and contact metamorphic overprinting of earlier burial metamorphic assemblages in the volcanics. However, precise U-Pb zircon ages for granitoids cutting deformed metavolcanics in the western part of the Abitibi belt indicate that major metamorphism and tectonism in this area occurred shortly after termination of the volcanic activity and was completed, at least at crustal levels occupied by the metavolcanics, before about 2685 Ma (Pericival and Krogh, 1983); therefore, contact metamorphism is eliminated as the reason for isotopic resetting of Kidd Creek rocks at 2576±26 Ma.

Brooks (1980) suggested widespread low-temperature metamorphism as the process responsible for resetting of the Rb-Sr age of the Chibougamau batholith and surrounding metavolcanics. Similar processes may have been active at Kidd Creek where WFV show signs of low-temperature alteration (Coad, 1985), although AFV may have had a more complex history, as indicated by the trace-element data of Campbell et al. (1984). We propose a two-stage model for Sr isotopic evolution in AFV and ore which involves alteration of initial \(^{87} \)Sr/\(^{86} \)Sr ratios and Rb-Sr redistribution during reaction with hydrothermal solutions and ore deposition, followed by more widespread isotopic resetting during a low-temperature metasomatic event affecting both WFV and AFV. The poorly defined initial \(^{87} \)Sr/\(^{86} \)Sr of 0.7047±0.0024 lies above the range of 0.7011 to 0.7020 for 2400 to 2600 Ma mafic magmatic rocks (Hart and Brooks, 1977) and is probably a consequence of multi-stage isotopic resetting.

\[ \text{ND ISOTOPES AND IMPLICATIONS FOR BASE METAL SOURCES} \]

The origin of base metal sulfides in volcanics-bounding, massive sulfide deposits has long been debated (Franklin et al., 1981). Pooled metal sources include the host volcanosedimentary pile, subvolcanic intrusions, and underlying basement. Isotopic tracing methods using Pb, Sr, and Nd isotopes can help constrain possible metal sources. The isotopic composition of hydrothermal minerals should reflect the isotopic composition of the hydrothermal solution forming the minerals and thereby give direct information about the sources(s) of Pb, Sr, and Nd. In sulfidegenerating systems on the sea floor, the Nd isotopic composition of the hydrothermal solution forming the minerals and therefore give direct information about the sources(s) of Pb, Sr, and Nd. In sulfidegenerating systems on the sea floor, the Nd isotopic composition of the hydrothermal solution forming the minerals and thereby give direct information about the sources(s) of Pb, Sr, and Nd. In sulfidegenerating systems on the sea floor, the Nd isotopic composition of the hydrothermal solution forming the minerals and thereby give direct information about the sources(s) of Pb, Sr, and Nd. In sulfidegenerating systems on the sea floor, the Nd isotopic composition of the hydrothermal solution forming the minerals and thereby give direct information about the sources(s) of Pb, Sr, and Nd. In sulfidegenerating systems on the sea floor, the Nd isotopic composition of the hydrothermal solution forming the minerals and thereby give direct information about the sources(s) of Pb, Sr, and Nd.
10^9 tonnes) could be derived from a source volume of 10^9 km^3, if an average decrease in Nd in AFV from 60 to 19 ppm (Campbell et al., 1984) is used. This volume corresponds to roughly three times the volume of the stringer zone and is clearly smaller than the ~100 km^3 source volume for base metals (using a source/core tonnage ratio of 1 km^2/10^9 tonnes; MacGeehan, 1978). It is easily contained in the upper part of the alteration zone within the footwall volcanics where REE mobility was particularly strong (Campbell et al., 1984). In such a scenario, locally derived Nd would mask any externally derived Nd in the hydrothermal solution, and we would expect to see only the Nd isotopic signature of the footwall volcanics, thought to be represented by WPF.

A possible exception—although at the limit of analytical reproducibility—is sample KC 11 from the stringer zone which has a somewhat lower 143Nd/144Nd ratio of 0.784 (Table 1). It is not clear if KC 11 is anomalous or an expression of isotopic heterogeneity in AFV precursors. If the low 143Nd/144Nd (T) is the result of interaction with the hydrothermal fluid, a fluid source with low, possibly negative 143Nd/144Nd (T) is implied. One possible source having negative 143Nd/144Nd (T) is the granitic basement underlying the Abitibi volcanics, or sediments derived from it. The influence of the basement on the composition of igneous and sedimentary rocks in the greenstone belt has been demonstrated in several studies (Gariepy et al., 1984; Gariepy and Allegr, 1985; Lajoie and Ludden, 1984), but its contribution to base-metal deposition is unknown.

In general, however, our data suggest buffering of the 143Nd/144Nd ratio in the hydrothermal fluid by local footwall volcanics wall rocks. This implies that at least part of the base metals are also derived from these rocks, an implication consistent with results by other workers (Franklin et al., 1981). At the moment we can only speculate on further base metal sources, but there is some indication (Beasy et al., 1980) that isotopic tracers of a deep-seated ore fluid are preserved at deeper levels of the alteration zone. Further work on rocks from that area and other parts of the stratiform orebody will show whether the Nd isotopic tracer is sufficiently sensitive to characterize the origin of this deep-seated fluid and help constrain base-metal sources at Kidd Creek.

CONCLUSIONS

Despite the small difference between zircon and Sm-Nd age, Sm-Nd whole-rock dating appears to have considerable potential in the dating of alteration and mineralization events, provided they were associated with REE mobility efficient enough to produce a suitable spread in Sm/Nd ratios. Although this does not seem to be the case in other, smaller massive sulphide deposits in the Canadian Superior province (Campbell et al., 1984), suitable REE mobility is known from the base metal deposits of New Brunswick, Canada (Geffen, 1977). Detailed Sm-Nd isotopic studies could provide valuable constraints on the time of formation of numerous hydrothermal vein deposits, U deposits (Frey and Taylor, 1984; Maas and others, in prep.), skarn deposits, and other types of mineralization where REE mobility has been demonstrated. The advantage of Sm-Nd dating over Rb-Sr and K-Ar dating is in far greater resistance to isotopic disturbance during subsequent metamorphic overprinting.

The Nd isotopic data indicate that the 143Nd/144Nd ratio of the ore-forming hydrothermal solution at the stringer zone–stratiform ore zone contact was controlled by Nd derived from the WPF. This suggests that part of the base metals in the ore was derived from the host rhyolitic sequence. Further work is in progress to fully evaluate the potential of the Nd isotopic tracer at Kidd Creek and other massive sulphide deposits.

REFERENCES CITED

Beasy, D.W., Taylor, H.P., Jr., and Coad, P.R., 1980. The oxygen isotopic geochronology of the Kidd Creek ore zone: Evidence for a high-degrees re-forming solution and implications regarding the genesis of volcanogenic massive sulphide deposits. EOS (American Geophysical Union Transactions), v. 61, p. 364.


Graf, J.L., Jr., 1977. Rare earth elements at hydrothermal deposits during the formation of massive sulphide deposits in volcanic rocks: Economic Geology, v. 72, p. 527-548.


Manuscript received December 6, 1985 Revised manuscript received March 24, 1986 Manuscript accepted April 7, 1986.
Appendix 1b

Table App1b-1

Sm-Nd and Rb-Sr data for Kidd Creek massive sulfide ores

<table>
<thead>
<tr>
<th>sample</th>
<th>Sm (ppm)</th>
<th>Nd (ppm)</th>
<th>Rb (ppm)</th>
<th>Sr (ppm)</th>
<th>$^{147}\text{Sm}/^{144}\text{Nd}$</th>
<th>$^{143}\text{Nd}/^{144}\text{Nd}$</th>
<th>$\varepsilon_{\text{Nd}}^{2717}$</th>
<th>$\varepsilon_{\text{Nd}}^{2717}$</th>
<th>$^{87}\text{Rb}/^{86}\text{Sr}$</th>
<th>$^{87}\text{Sr}/^{86}\text{Sr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7871</td>
<td>1.9b</td>
<td>9.59</td>
<td>0.44</td>
<td>7.47</td>
<td>0.1212b</td>
<td>0.510411±24</td>
<td>-2.79</td>
<td>-1.7b</td>
<td>0.1699</td>
<td>0.71520±2</td>
</tr>
<tr>
<td>7875</td>
<td>2.17</td>
<td>13.29</td>
<td>0.45</td>
<td>0.81</td>
<td>0.0986</td>
<td>0.510133±28</td>
<td>-33.3</td>
<td>+0.7</td>
<td>1.5954</td>
<td>0.75534±2</td>
</tr>
<tr>
<td>7882</td>
<td>0.94</td>
<td>2.90</td>
<td>---</td>
<td>---</td>
<td>0.1963</td>
<td>0.511974±32</td>
<td>2.7</td>
<td>+2.8</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>7876</td>
<td>0.67</td>
<td>3.82</td>
<td>0.31</td>
<td>1.77</td>
<td>0.1059</td>
<td>0.510383±30</td>
<td>-28.4</td>
<td>+3.1</td>
<td>0.5038</td>
<td>0.72666±2</td>
</tr>
<tr>
<td>Z31</td>
<td>0.16</td>
<td>0.68</td>
<td>0.16</td>
<td>0.45</td>
<td>0.1407</td>
<td>0.510943±50</td>
<td>-17.5</td>
<td>+1.9</td>
<td>1.0478</td>
<td>0.74340±3</td>
</tr>
<tr>
<td>Z32</td>
<td>0.51</td>
<td>2.44</td>
<td>0.39</td>
<td>0.45</td>
<td>0.1272</td>
<td>0.510684±34</td>
<td>-22.5</td>
<td>+1.6</td>
<td>2.3887</td>
<td>0.78994±4</td>
</tr>
</tbody>
</table>

a for calculation of $\varepsilon_{\text{Nd}}^{2717}$ (i.e. at 2717 Ma) see Table 1 in appendix 1

b Sm concentration for sample 7871 has a 2 sigma mean error of ±0.04 ppm i.e. 2.1%;

$^{147}\text{Sm}/^{144}\text{Nd} = 0.1211±0.0026$; thus $\varepsilon_{\text{Nd}}^{2717} = -2.5$ to -0.8
APPENDIX 2

Sm-Nd isotope systematics in uranium rare earth element mineralization at Mary Kathleen uranium mine, Queensland

Roland Maas, Malcolm T. McCulloch, Ian H. Campbell and Rodney W. Page*

Research School of Earth Sciences, Australian National University
PO Box 4, Canberra, ACT 2601, Australia

* Bureau of Mineral Resources, Canberra, ACT 2601, Australia
Abstract

Sm-Nd isotopic and REE geochemical data for U-REE ore of the Mary Kathleen mine and surrounding country rocks reveal a complex history of metasomatic alteration and multi-stage U-REE mineralization in metasedimentary rocks of the host Corella Formation. Widespread high temperature contact metasomatism and skarn formation related to the emplacement of the U-rich, 1730 Ma A-type Burstall Granite produced large volumes of banded calc-silicate skarn. A Sm-Nd age of 1766 ± 80 Ma (2σ) was obtained on skarn produced at the time of granite emplacement. Sm-Nd data on other skarn types, including massive garnet-diopside skarn which hosts the Mary Kathleen mineralization, suggest that most of the skarn formed during this contact alteration event.

The combined Sm-Nd isotopic data for whole rocks and minerals of two high grade ores yield a significantly younger age of 1472 ± 40 Ma (2σ) which is similar to an earlier reported 1550±15 Ma U-Pb age for uraninite. The age discrepancy is considered the result of minor post-crystallization disturbance of the Sm-Nd isotopic systems of ore minerals. These ages indicate that the Mary Kathleen mineralization formed long after emplacement of the 1730 Ma U-rich Burstall Granite and its related metasomatism. Differences between initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of the ore ($\varepsilon_{\text{Nd}} = -9.5$) and the contemporaneous country rocks including the Burstall Granite and the host skarn ($\varepsilon_{\text{Nd}} = -5$ to $-7.5$) at 1470 Ma preclude a simple genetic relationship between them.

The data suggest a regional metamorphic origin for the present mineralization, probably related to structurally-controlled hydrothermal fluid flow around and within massive skarn bodies. The operation of lithological-tectonic control mechanisms on metamorphic fluid circulation has recently been demonstrated for large parts of the Mary Kathleen fold belt, in particular the area affected by massive pre-metamorphic skarn formation and garnetization. This is supported by a 1557 ± 40 Ma Sm-Nd age for complex garnet-pyroxene-feldspar skarn associated with metamorphic-hydrothermal alteration around prominent $D_2/D_3$ deformation and minor REE-U mineralization.

The significantly lower $\varepsilon_{\text{Nd}}$ of the ore relative to the country rocks at the time of ore deposition is consistent with an origin from remobilized older, highly LREE-enriched sources. Although other possibilities cannot be ruled out completely, we consider a 1730 Ma old U-REE skarn protore the most likely source for both LREE and U. Isotopic and mass balance constraints require this protore to be very similar in element contents and ratios to the present mineralization, i.e. it was highly enriched in LREE and had a long history of very low Sm/Nd ratio. The preservation of this protore isotopic signature during formation of the present mineralization involved essentially in situ hydrothermal reworking of the protore without significant additions of externally derived REE.

The results of this study demonstrate that combined REE geochemical and Sm-Nd isotopic studies provide a powerful tool to date U mineralizing events and to trace the origin of REE and U in the ore solutions.
Introduction

The Mary Kathleen uranium rare-earth mine is located in the Proterozoic Mt. Isa Inlier of NW Queensland, Australia. It is the largest of numerous U occurrences known from the area; from 1956 to 1982, about 10000 tonnes of U oxides at a grade of 0.131 precent $U_3O_8$ and about 200000 tonnes of rare earth oxides were extracted (Scott and Scott, 1985).

Considerable controversy exists regarding the timing and origin of mineralization of the Mary Kathleen orebody. This is mainly due to its unusual association with calcic skarn host rocks and to ambiguous metamorphic and deformational overprinting relationships. According to a widely accepted model, the U-REE mineralization was interpreted as a skarn deposit with unusual element association (Derrick, 1977; Cruikshank et al., 1980; Abeysinghe et al., 1984a). These authors considered that magmatic fluids expelled from the nearby Burstall Granite or associated rhyolitic dikes were responsible for widespread metasomatism, skarn formation and ore deposition. An alternative interpretation was offered by Hawkins (1975) who suggested that uranium of primary sedimentary origin had been remobilized to its present form during regional metamorphism. In a recent U-Pb and Rb-Sr isotopic study on the age of magmatism, contact-metasomatism and U mineralization in the Mary Kathleen area, Page (1983) provided geochronological evidence for a ca. 200 Ma hiatus between granite emplacement and uraninite deposition in the Mary Kathleen ore, thus questioning the previously proposed single-stage link between granite intrusion and mineralization. Instead, he suggested that the U ore formed during regional metamorphism. These results were initially challenged by Oliver et al. (1985a) but these workers later reinterpreted their petrographic and structural data in support of a metamorphic origin of mineralization (Oliver et al., 1985b, 1986; Page, 1985).

The present study utilises REE geochemical and Sm-Nd isotopic data to constrain the time of ore formation and to trace the source(s) of the large quantities of REE and U concentrated in the ore using initial initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratios. This approach is based upon the very similar geochemical behaviour of U and REE in many U ore-forming hydrothermal systems. For example, REE data on unconformity-type U deposits in Northern Australia (McLennan and Taylor, 1979) and Canada (Rimsaite, 1977) show a spectacular sympathetic correlation of U and heavy REE. Enrichment of the light REE is known from the Olympic Dam Cu-U-Au deposit (Roberts and Hudson, 1983), and both light- and heavy-REE enrichment is found at Bokan Mts., Alaska (Staatz et al., 1978) and many other U deposits. In a study on the Collins Bay U deposit in Saskatchewan, Fryer and Taylor (1984) were able to obtain Sm-Nd pitchblende ages consistent with the U-Pb geochronology and to place constraints on possible U sources and mechanisms of ore concentration. It was therefore hoped that this approach could help clarify some of the open questions that surround ore deposition at Mary Kathleen.
Geological Setting

Geological descriptions of the deposit and the general area are available from Whittle (1960), Derrick (1977), Page (1983), Scott and Scott (1985) and Oliver et al. (1986); only a brief description will be given here. The deposit is located near the hinge of the Mary Kathleen Syncline in metasomatically altered, polydeformed metasediments and metavolcanics of the Mid-Proterozoic Corella Formation in the eastern part of the Mt. Isa Block (Fig.1). The sequence consists of ca. 2000 m of impure carbonates, sandstones, evaporites and mafic volcanics with a depositional age of 1780 to ca. 1740 Ma (Page, 1983), which have been metamorphosed to amphibolite facies calc-silicate granofels, marble, quartzite, metadolerites etc.. The Corella Formation forms part of the widespread Mary Kathleen Group which overlies a ca. 1875 Ma old granitic-volcanic basement complex to the west and is interpreted as the filling of a deepening intracontinental rift (Blake, 1985). In the Mary Kathleen area, several igneous bodies intrude the Corella Formation, amongst them the Burstall Granite and related rhyolitic dikes. They have U-Pb zircon ages between 1730 and 1740 Ma (Page, 1983) and clearly predate regional metamorphism and deformation. The Burstall Granite and the rhyolitic dikes are both U-rich (7 and 12 ppm average, Cruikshank et al., 1980), and according to Abeysinghe et al.(1984b) have strong geochemical affinities to A-type granites (Collins et al., 1982).

During granite emplacement, large volumes of calcic skarn were formed in the vicinity of the granite, although recent work indicates that not all skarn is of contact-metasomatic origin (Oliver et al., 1986). Derrick (1977) and Oliver et al. (1985a) distinguish two types of granite-related skarn: banded calc-silicate skarn and massive diopside-garnet-scapolite skarn through to massive garnet skarn. The contents of metasomatic garnet in the banded skarns range from virtually nil up to 50 percent suggesting that the amounts of introduced metasomatic fluid were highly variable. While garnet-poor varieties are the product of diffusive, essentially conservative exchange between neighboring bands, garnet-rich varieties and the massive skarns were formed by infiltration metasomatism. These early high-temperature skarns are commonly overprinted to variable degrees by retrograde hydrothermal alteration. All known U-REE mineralization in the area is exclusively associated with the zones of retrogressed skarn.

During regional metamorphism between 1620 and 1500 Ma (Page et al., 1984), the Corella Formation reached peak metamorphic conditions of 600 - 650°C and 3.5 to 4 kb with attendant isoclinal folding and related foliation (D2 in local terminology). The prominent structural feature in the area, the Mary Kathleen Syncline, was formed during this deformation period. Subsequent D3 kinking and faulting sometimes spatially related to the earlier D2 structures occurred under retrograde conditions (Oliver et al., 1986). Late dolerite dikes as young as 1116 ± 12 Ma (Page, 1983) postdate metamorphism.
Host rocks for U-REE mineralization are strongly garnetized skarns derived from at least three precursor lithologies: a cobble conglomerate, calcisilicate granofels, and an igneous rock of probably intermediate composition. Within the orebody, original precursor textures have been largely obliterated. The mineralization forms a steeply dipping, anastomosing network of shoots and dikes set in massive garnetite, cut to the west by the Mary Kathleen Shear. Structural controls on ore location are difficult to establish (Scott and Scott, 1985), but Oliver et al. (1985b) interpret structural relationships of ore shoots and axial plane foliation in the pit as evidence for syn- to post $D_2$ mineralization.

The ore consists of tiny specks of uraninite ($\leq 0.1$ mm) in a decussate mass of allanite and apatite (80 to 95 percent of the ore), with minor amounts of ferrohastingsite, quartz, epidote, sphene, hematite, and stillwellite. Sulfides include chalcopyrite, pyrite, pyrrhotite, and galena characterized by highly radiogenic Pb isotopic compositions (Page, 1983). This ore assemblage exhibits crosscutting and replacement relationships with earlier garnet-pyroxene skarn and garnetite, and relict skarn phases are found in the ore. The whole assemblage is cut by veins containing calcite, sulfides, garnet, pyroxene and prehnite.

Uraninite was the first ore mineral to be deposited and is invariably shelled by a silica sheath when in contact with allanite. Fluid inclusion studies on apatite suggest temperatures of 500 to 200°C during ore formation with considerable salinities (30 - 50 wt% dissolved solids; Kwak, 1986). Later calcite formed from fluids with homogenization temperatures of 120 to 400°C.

**Previous isotopic work**

The only isotopic data directly related to mineralization is from the work of Page (1983). He found a U-Pb age of 1550 ± 15 Ma for uraninite and somewhat younger apparent $^{207}$Pb/$^{206}$Pb ages for allanite ranging from 1490 to 1430 Ma, the latter being similar to Rb-Sr and K-Ar mineral ages of 1450 Ma and younger from a regional study by Richards et al. (1963). The younger ages are interpreted as cooling ages. Rb-Sr data on various lithologies of unmineralized skarn indicate an age of metasomatism in these skarns of around 1200 Ma (Page, 1983).

**Models for ore genesis**

The relationship of U-REE mineralization at Mary Kathleen with granitic magmatism, contact metasomatism and regional metamorphism has been subject of several studies (Whittle, 1960; Cruikshank et al., 1980; Abeyesinghe et al., 1984a). These workers advocate a contact-metasomatic origin of the ore from magmatic REE-U rich fluids derived from the Burstall Granite during a late stage of the skarn-forming metasomatism. A major problem
with this model is the implicit assumption of a late- or post-metamorphic age for the Burstall Granite and the rhyolitic dikes to explain the apparent paucity of deformation in these rocks and the orebody (Oliver et al., 1985a). This contrasts with the U-Pb zircon work of Page (1983) who clearly showed that the intrusives predate metamorphism.

Oliver et al. (1986), in a substantial revision of their earlier interpretations (Oliver et al., 1985a), have now taken proper account of the U-Pb isotopic data and new field evidence by proposing a metamorphic origin of mineralization. In their current model, U-REE mineralization was produced by metamorphic fluids infiltrating the massive skarns through dilational fractures formed in response to competence contrasts between pre-F₂ skarn bodies and adjacent calcisilicate rocks during F₂ and/or F₃ regional deformation. High differential stresses along the margins of these massive garnet skarn pods resulted in enhanced fracture permeability indicated by intensive veining and alteration both along the lateral boundaries and partly within the competent skarn bodies, and in the pressure shadows at their terminations. These zones focussed metamorphic fluid flow generating high fluid/rock ratios in these relatively confined spaces, resulting in conditions favourable for ore deposition. Ore was precipitated in a dense network of fractures possibly as a result of wall rock reactions, as indicated by the replacement of older garnet-pyroxene skarn in the ore zone. This structural setting and the mineralogy of the ore assemblage strongly suggests ore formation under amphibolite facies conditions. The mineralizing metamorphic fluids are thought to have been highly saline possibly owing to evaporite dissolution and/or interaction with scapolite-bearing skarns.

This model can account for both the ca. 200 Ma age difference between Burstall Granite and U mineralization (Page, 1983), and the preservation of medium- to low-temperature assemblages in retrogressed parts of the skarn, as well as low-temperature fluid inclusions in ore minerals, during amphibolite facies metamorphism.

This paper reports REE and other trace element, and Sm-Nd and Rb-Sr isotopic data on the ore, the host skarn, and surrounding country rocks, with three main objectives: (1) to check the 1550 Ma U-Pb uraninite age using the Sm-Nd method, (2) to provide isotopic evidence for skarn remobilization during metamorphism, and (3) to attempt to determine the source of REE and, by inference, U, by using the initial Nd isotopic composition as a tracer.

Samples and Analytical Methods

With the exception of four samples (0716, 0754, 0755, 0756, courtesy of B.I.Cruikshank), all samples used in this study have been collected and were previously studied by Page (1983). Sample locations are shown in Fig.1; for exact locations see Page (1983). For two of the three ore samples taken from the eastern face of the pit in 50 meter intervals (MK 68, MK 69), mineral separates of uraninite, allanite, apatite, sphene, garnet and diopside were prepared after microscopic and electron probe examination of thin sections. In order to avoid contamination of the isodynamic separator with ore minerals,
magnetic separation of allanite, apatite and garnet was carried out in ethanol within a burette strapped to the magnetic separator (McLeod et al., 1985). Uraninite was separated efficiently using a micropipette.

Sm-Nd and Rb-Sr isotopic analyses on whole rocks were carried out on samples fully spiked prior to acid digestion using the methods described in McDonough et al. (1985). Allanite, sphene and garnet were dissolved in pressurized teflon bombs using HF, HClO$_4$ and HCl; uraninite, apatite and diopside were dissolved in open beakers using concentrated HNO$_3$, HCl and HF-HClO$_4$-HCl, respectively. Procedural blanks throughout the course of the study were <0.7 ng Nd and <3 ng Sr using our stock solutions. Rb blank corrections required for low-Rb mineral separates of small sample size were as high as 30% but introduced only minimal errors into calculated initial $^87$Sr/$^86$Sr$_i$, owing to the very small $^87$Rb/$^86$Sr ($\leq 0.01$) in these samples.

REE concentrations in three whole rock ore samples MK 68, 69 and 70 were determined by inductively coupled plasma spectrometry (ICP) after ion exchange separation of the REE. Agreement of ICP and isotope dilution data for Nd is reasonably good (Tables 1b and 2a); we have therefore used isotope dilution data for Sm to construct REE patterns. All other whole rock REE data were obtained by instrumental neutron activation. Sm/Nd ratios measured by this technique are in good agreement with isotope dilution results. The remainder of the geochemical data on whole rocks is by XRF.

REE, U and Th in minerals were measured by electron microprobe using synthetic standards; the reproducibility of REE patterns is estimated to be better than 10 percent for high-REE minerals, but deteriorated to 20-40 percent for REE abundances close to the detection limit (100 to 200 ppm). Even though some minerals, in particular garnet and diopside, had REE abundances at or below the detection limit, it was often possible to constrain the general shape of their REE patterns by the few REE above detection limit and by the maximum values obtained for the other measured REE. With the exception of the garnet separates, Sm/Nd ratios and Nd abundances for single mineral grains were generally within the range of isotope dilution results on small (1-10 mg) bulk samples of the same separates.

REE, U and Th abundances

**U-REE ore**

REE-ICP data for high grade Mary Kathleen U-REE ore (ca. 0.8 percent U, Table 1b, Fig.2a) demonstrate extreme enrichment in light REE with chondrite-normalized (La/Yb)$_n$>1000, a negative Eu anomaly and $\Sigma$REE of ca. 15 weight percent. Strong LREE enrichment appears to extend through most of the orebody down to much lower grades (Scott and Scott, 1985). Th/U ratios show limited scatter and are comparable with the value of 0.2 reported by Scott and Scott (1985) for analyses of 230 samples.
REE patterns for uraninite and the gangue phases allanite, apatite, and sphene are all strongly fractionated (Table 1a, Fig. 2a, b). Allanite, which comprises 80 to 90 percent of the ore, is extremely LREE-enriched with $(\text{La/Yb})_n \geq 10000$. Uraninites have REE patterns roughly similar to those of apatite and sphene with chondrite-normalized abundance maxima between Ce and Nd, but $\Sigma$REE in uraninite can be higher by up to a factor of 10.

The similarities in abundances and distribution of REE in the bulk ore and allanite demonstrate that allanite is the main REE carrier in the ore, with the other phases being responsible for the lower $(\text{La/Yb})_n$ of the ore compared to allanite. Similarly, the negative Eu anomaly in the bulk ore must reflect deficient Eu in the allanite. U is predominantly fixed in uraninite which has generally high abundances of Th, typical for high temperature uraninites. Amongst the other minerals, only allanite with roughly equal proportions of Th and U in the range of <200 to >1000 ppm contributes significantly (5 to 15 percent) to the U budget of the ore.

The two main pre-ore skarn phases, garnet and diopside, occur as relict masses in essentially uraninite-free patches in sample MK69. REE data for these minerals are incomplete as many elements have concentrations below detection limit of the electron probe. Data for the most REE-rich garnets indicate $(\text{La/Gd})_n$ ratios less than unity with flat HREE patterns (Table 1a, Fig. 2c). Absolute abundances in most analysed grains vary in the sequence Gd$\approx$Nd$>\text{Ce}$, in contrast with the sequence Ce$>\text{La}>\text{Nd}>\text{Y}$ reported by Abeysinghe et al. (1984a). REE patterns of diopside, although poorly constrained, appear to be s-shaped with reversals in slope at Gd and Sm (Fig.2c). The slope between Nd and Sm has been inferred from isotope dilution data on the same sample.

Uranium concentrations in garnet are high, amounting to up to 460 ppm, while Th is below detection limit (ca. 200 ppm). Again there are discrepancies between our data and those of Abeysinghe et al. (1984a) who measured 5 to 24 ppm U in garnets using the fission track method. U abundances in diopside are lower than in garnet with only three analyses exceeding 200 ppm.

*Corella Formation metasediments, skarn, and Burstall Granite*

To assess REE mobility in the skarn and its possible relationship to mineralization, REE patterns of several skarn types are compared to Corella Formation non-skarn metasediments. The metasediments, comprising three calc-silicate granofelses and one marble, have REE patterns and U-Th abundances (Table 1b, Fig. 3) very similar to Mt. Isa shales and other Proterozoic shales (Nance and Taylor, 1976). This suggests that they have preserved their sedimentary REE-U-Th geochemistry through metamorphism. Only a few hundred meters north along strike, equivalents of these sediments have been metasomatically altered and garnetized to varying degrees (see Fig.1). In the following section we will therefore use average Mt. Isa shale as representative of pre-skarn sedimentary REE patterns and compare skarn REE patterns to this standard.
Inspection of Figs. 4 and 5 clearly shows that REE were not immobile in the skarns. While the garnet-poor banded calc-silicate skarns studied here show variable but generally minor changes in LREE/HREE ratios on the scale of centimeters (Table 1b, Fig.4), massive skarns show strong REE redistribution (Table 1b, Fig.5). In particular, they show low (La/Lu)n and have no negative Eu anomaly, normally a characteristic of post-Archean sediments (Nance and Taylor, 1976). Th/U ratios are lowered substantially in massive skarn (Th/U ≤ 1.2) compared to a Th/U of around 4 for felsic calc-silicate rocks (Scott and Scott, 1985). It appears that REE, in particular LREE, and Th - U in these skarns were increasingly mobile with increasing degree of metasomatic alteration, i.e. with garnetization. A comparison of U/Yb ratios for non-skarn metasediments, banded skarns and massive skarns shows virtually identical values for the first two groups averaging between 2.3 and 2.5, whereas the massive skarns average at 1.3. Although these numbers are clearly not based on a representative number of samples, it may indicate some U loss relative to the comparatively immobile HREE. Alternatively it could equally well result from HREE enrichment relative to the protoliths. It is tempting to favour the first alternative as it would help to explain the association of U and LREE in the Mary Kathleen ore and its apparent link to garnet skarn. We will further discuss this hypothesis in the section dealing with the Nd isotopic data.

Pronounced LREE mobility was also observed in parts of the Burstall Granite (Table 1b, Fig.6). Although most samples show some chloritization, original magmatic REE distributions appear largely unaffected by metamorphism. However, two samples from the central part of the granite (240A, 240E) show strong REE depletion with (La/Lu)n ratios considerably lower than in the weakly altered granites. Cerium appears to have been less mobile during alteration as it is present in excess amounts in the highly altered samples (Fig.6). Unpublished data show that in addition to LREE, these samples have also lost large amounts of K, Ba, Rb and Fe, concomitant with an increase in Na₂O from ca. 2.5 percent to more than 9 percent. This suggests local albition at the expense of K feldspar and probably biotite. The same style of alteration occurs in other parts of the granite (B.I. Cruikshank, unpublished analyses). Anomalous behaviour of Ce is rare in granites and other acidic igneous rocks undergoing hydrothermal alteration (Humphries, 1984). A possible explanation could be the presence of Ce as Ce⁴⁺ and its preferential uptake by secondary phases (Baker, 1985). The effect of alteration on the U contents appears to have been negligible, since the highly altered granites have U abundances within the same range as the weakly altered Burstall Granite.

Isotopic Results

**U-REE ore and associated skarn**

After examination of their REE patterns on the electron probe, four minerals were chosen for Sm-Nd dating: allanite, apatite, uraninite and sphene. As the REE patterns of the
minerals, in particular uraninite, showed some variation between grains, several concentrates of each sample were analysed to obtain the largest possible dispersion in Sm/Nd ratios. All isochron parameters were calculated using a modified version of McIntyre et al. (1966) and are reported at the 95 percent confidence level.

Mineral separates and their whole rocks from two high grade ores, MK68 and MK69 (Table 2a), yield isochron ages of 1517 ± 70 Ma (model 2, MSWD=2.3) and 1448 ± 55 Ma (model 4, MSWD=4.3) with initial ratios corresponding to $\varepsilon_{Nd} = -8.7 \pm 1.0$ and $-9.7 \pm 1.0$, respectively. If all data for the two samples are pooled (Fig.7), a combined model 4 fit isochron age of 1472 ± 40 Ma with $\varepsilon_{Nd} = -9.5 \pm 0.7$ is obtained (MSWD of model 1 fit = 4.2). The pooling appears justified on the basis of field, mineralogical and geochemical relations and is confirmed by the colinearity of the samples on the isochron plot. The samples have virtually identical mineralogical and chemical compositions, including their REE patterns, and there is every reason to regard them as cogenetic. The third whole rock ore, MK70, is isotopically indistinguishable from MK 68 and MK 69, confirming the isotopic homogeneity of the ore. Nevertheless, it is noted that small differences in initial $^{143}Nd/^{144}Nd$ and/or age appear to exist between minerals from MK68 and MK69. Alternatively, the results could be influenced by variable post-crystallization disturbance. An evaluation of these possibilities will be given later.

**Garnet and diopside**

The Sm-Nd isotopic data for garnet and diopside separates of MK 69 (Table 2b) are also shown in Fig.7. Their structural relationships to the allanite-apatite ore clearly identify these phases as relics of the skarn replaced by the ore assemblage (Whittle, 1960). They should therefore record the Nd isotopic signature of the original skarn and yield important information about its possible role as an ore source.

Three garnet separates, weighing 13 to 81 mg, were handpicked, finely ground and again cleaned by handpicking (to remove allanite impurities) and magnetic separation in alcohol (to remove apatite). Garnet sample 69-5 was leached for 12 hrs in dilute HF in a pressurized teflon bomb to remove further, extremely small impurities. It was assumed that any possible contaminant would dissolve more rapidly than the garnet, which usually took about 80 hrs to dissolve in 10 N HF at 200° C. Subsequently, both residue and leach were spiked and analysed. Diopside 69-1 was separated from a uraninite-poor stringer in MK69 and analysed without further cleaning. Contamination of this separate by unidentified tiny dark grains is estimated to have been <0.1 percent plus about 1 percent of garnet-diopside composites. Contamination was expected to be substantially less in the garnet fractions.

Despite the careful sample preparation, the garnet analyses revealed serious contamination problems. All measured garnet fractions including the HF-leached residue, have $^{147}Sm/^{144}Nd$ ratios lower than about 0.15 (corresponding to Sm/Nd ≤ 0.26; Fig.7), in contrast to electron probe results for single garnet grains from the same mineral separate,
which consistently show Sm/Nd ≥ 0.30 (see Fig. 2c). The Nd concentrations of garnet separates measured by isotope dilution are up to 3 times greater than the highest abundances measured in single garnets but seem to decrease with increasing $^{147}\text{Sm}/^{144}\text{Nd}$. On the other hand, most garnet concentrates plot above the ore isochron with the difference in $^{143}\text{Nd}/^{144}\text{Nd}$ increasing with increasing $^{147}\text{Sm}/^{144}\text{Nd}$. These features suggest that the measured garnet bulk samples lie on a mixing line or lines between pure garnet and a LREE-enriched contaminant, probably allanite. This is supported by the position of garnet-diopside-allanite skarn K9447 in Figure 7. This skarn comes from an unmineralized section of the Mary Kathleen open pit and is believed to be derived from an igneous precursor, possibly of intermediate composition (Scott and Scott, 1985). Allanite comprises only a few percent in this sample, yet it is sufficient to completely control the Sm-Nd isotopic system of the rock and place it on the ore isochron close to allanite.

The diopside analysis does not appear to have any significant contamination; REE abundances are low as expected from the electronprobe analyses. Like most of the garnets, diopside lies above the ore isochron which suggests that the ore evolved from a source having less radiogenic Nd than available in garnet-diopside skarn.

**Rb-Sr data of U-REE ore**

The Rb-Sr isotopic data for ore whole rocks, allanite and apatite are given in Table 2a. Because Rb/Sr ratios are very low, only minimal age corrections of the measured $^{87}\text{Sr}/^{86}\text{Sr}$ are necessary. Initial $^{87}\text{Sr}/^{86}\text{Sr}_i$ in ore whole rocks at 1472 Ma range from 0.7241 to 0.7262, similar to allanite in sample MK69, which has $^{87}\text{Sr}/^{86}\text{Sr}_i$ and a Sr concentration almost identical to whole rock MK69, identifying allanite as the main Sr carrier in the ore. In contrast, apatites from both MK68 and MK69 have distinctly lower $^{87}\text{Sr}/^{86}\text{Sr}_i$ than their whole rocks, indicative of Sr isotopic disequilibrium. Sr isotopic compositions in relict skarn minerals were not measured.

It is not clear whether the isotopic disequilibrium apparent in the apatite-whole rock data reflects a primary feature, i.e. fluctuations in the $^{87}\text{Sr}/^{86}\text{Sr}_i$ of the ore-forming fluid and/or isotopic variations in the replaced skarn material, or if it is the result of post-ore disturbance. Addition of radiogenic Sr from late calcite veins is tentatively discounted as a major reason for the high $^{87}\text{Sr}/^{86}\text{Sr}_i$ in the ore whole rocks, because coexisting allanite is in approximate equilibrium with the ore whole rock. It is more likely that Rb-Sr isotopes in the ore were not completely closed before ca. 1400 Ma, the age of regional cooling below closure temperatures of mica K-Ar and Rb-Sr systems (Richards et al., 1963). Finally, ore Rb-Sr systems may have been affected by the widespread isotopic disturbance of skarn Rb-Sr systems at 1200 Ma. The profound influence of this cryptic 1200 Ma event on the skarn is exemplified by Rb-Sr data on metasomatized cobble conglomerate just north of the Mary Kathleen pit (Page, 1983). Because of these possible ambiguities we will not use the Sr isotopic data in the following discussion.
Corella Formation, skarn, and Burstall Granite

To identify possible source rocks that could have supplied REE to the Mary Kathleen ore, Sm-Nd isotopic compositions were measured in a variety of rock types throughout the Mary Kathleen syncline. The data are given in Table 2b and shown in figures 8 and 9.

Corella Formation metasediments, the Burstall Granite and some of the skarns have similar Sm/Nd ratios and lie close to a 1730 Ma reference isochron (Fig.8). They yield Sm-Nd model ages ($T_{DM}$) ranging between 2160 and 2330 Ma, typical for Mid Proterozoic rocks in Australia (McCulloch and Hensel, 1984). Initial $\varepsilon_{Nd}(1730 \text{ Ma})$ values for the Burstall Granite and the rhyolite dikes have a narrow range from -3.7 to -2.9, and overlap with age-corrected values for the metasediments (see Table 2b). Two analyses of least contaminated mine skarn garnet and the diopside analysis which were shown in Fig.7, are also plotted in Fig.8. They have an $\varepsilon_{Nd}$ range from -6.4 to -4.8 at 1730 Ma, lower than and overlapping some of the skarns (-3.1 to -5.4, Table 2b). At 1472 Ma the mine skarn relicts have $\varepsilon_{Nd}$ values (-6.8 to -7.8) overlapping with the unmineralized skarns (-4.9 to -8.1) and the granitic intrusives (-5.9 to -7.4). In contrast, ore at that time had $\varepsilon_{Nd} = -9.5 \pm 0.7$, clearly lower than the relict skarn phase. This difference is increased if allowance is made for the contamination effects in the garnet mineral separates which would produce artificially low $\varepsilon_{Nd}$ values.

Samples 240A and 240B which represent highly altered Burstall Granite and show evidence of strong REE and trace element mobility, have initial $\varepsilon_{Nd}(1730 \text{ Ma})$ values of -13.2 and -17.7 and high $^{147}\text{Sm}/^{144}\text{Nd}$ ratios, drastically different from less altered Burstall Granite (Fig.8). The low $\varepsilon_{Nd}$ values are difficult to reconcile with their present high $^{147}\text{Sm}/^{144}\text{Nd}$ ratios and indicate a complex alteration history. The time or times of alteration are not well constrained by the data. Tielines of the altered samples with the less altered granite yields ages significantly different (1065 and 477 Ma) from any known alteration event in the area. In contrast, sample 240A has Sr model ages ranging between 1600 and 1400 Ma for reasonable initial ratios (0.71-0.72; data by Page, 1983). This would place the alteration event into the period of regional metamorphism.

Age of skarn formation

The age of metasomatic alteration resulting in the formation of the skarn is of considerable importance to any model of ore formation at Mary Kathleen. Page (1983) presented Rb-Sr evidence for widespread alteration within the skarns at around 1200 Ma. It is not clear from these data whether the studied skarns formed at this time from metasediments or older skarns, or whether the Rb-Sr system records a cryptic resetting event, possibly related to reactivation along faults and/or dolerite dike intrusion (Page, 1983).

To obtain independent age information on the same samples studied by Page (1983), we
have attempted to date skarn formation using Sm-Nd isotopes. This appeared promising as REE data on the skarns suggest considerable REE mobility, at least on the scale of thin slabs a few millimeters in thickness (Fig. 4 and 5). In the case of garnet-poor banded calc-silicate skarn, where petrological and geochemical evidence suggests bimetasomatic diffusive transport across band boundaries, some scatter in initial $^{143}$Nd/$^{144}$Nd ratios would be expected, reflecting precursor isotopic heterogeneities that were not completely erased during metasomatism. The Sm-Nd age of a suite of adjacent thin slabs, however, should, albeit imprecisely, date the time of alteration and fractionation of Sm/Nd ratios.

On the other hand, initial Nd isotopic compositions in metasomatic rocks formed by infiltration such as the massive skarns studied here (Fig. 5), would strongly depend on the infiltrating fluid. Taylor and O'Neil (1977) present evidence for both stable isotope equilibrium and disequilibrium in massive carbonatic and silicate skarn minerals which correlate with changes in the fluid composition. To minimize disequilibrium effects on the Sm-Nd data we have therefore selected a portion of the massive skarn 0832 representing ca. 5 cm$^3$ for mineral separation of garnet, clinopyroxene, and K-feldspar. The results were combined with Sm-Nd data for 4 adjacent thin slabs from the same fist-sized specimen.

The Sm-Nd isotopic data for banded skarn 5013 A and massive skarn 0832 are shown in Fig. 9. Six adjacent thin slabs of banded skarn 5013 A give a model 2 isochron age of 1707 ± 180 Ma with an initial ratio corresponding to $\varepsilon_{\text{Nd}}(T) = -4.3 \pm 2.5$. If A3, which plots substantially below the 1707 Ma isochron, is omitted, a more precise model 1 age of 1766 ± 80 Ma with $\varepsilon_{\text{Nd}}(T) = -3.35 \pm 1.1$ (MSWD=1.72) is obtained. Massive garnet - diopside - feldspar skarn 0832 from the vicinity of the Elaine Dorothy U-REE prospect defines a model 2 isochron with an age of 1582 ± 80 Ma and initial ratio of $\varepsilon_{\text{Nd}} = -5.6 \pm 1.3$ for all four slabs plus the garnet, clinopyroxene and K-feldspar separates. If the most deviant data point, slab A2, is omitted, the fit improves markedly giving a model 3 age of 1557 ± 40 Ma and initial $\varepsilon_{\text{Nd}} = -6.1 \pm 0.7$.

It is clear from these results that REE redistribution in these skarns is substantially older than indicated by their consistent 1200 Ma Rb-Sr ages. Based on the geochemical evidence presented earlier, and the known mobility of REE during skarn-forming metasomatic activity (Martin et al., 1978; Ganzeyev et al., 1983) we conclude that the Sm-Nd ages record the time of skarn formation. The 1766 ± 80 Ma age of banded calc-silicate skarn is consistent with a syn - Burstall Granite (1730 Ma) origin for this skarn lithology, and probably most of the skarn in the Mary Kathleen syncline (Oliver et al., 1986).

In contrast, the younger age for massive skarn from near Elaine Dorothy suggests remobilization of earlier skarn or renewed garnetization during regional metamorphism, as was predicted on the basis of petrographic and structural evidence by Oliver et al. (1986). It should be emphasized, however, that only a minor part of the massive skarn formed at that time as there is compelling field evidence for a pre - kinematic and pre - metamorphic age of the bulk of the massive skarn pods (Oliver et al., 1986). Furthermore, some relict fluid inclusions in garnet from the mine skarn at Mary Kathleen which record fluid temperatures...
of up to 700° C (see fluid inclusion data Abeysinghe et al., 1984a) argue for a granite-related (1730 Ma-) origin of this skarn.

On the other hand, it is interesting to note that the 1557 Ma age for the Elaine Dorothy massive skarn is identical to the 1550 Ma U-Pb age for Mary Kathleen uraninites by Page (1983). Furthermore, the massive and brecciated garnetite masses from which sample 0832 was taken, occur close to mineralized allanite-diopside skarn of the Elaine Dorothy prospect (Scott and Scott, 1985), where medium- to low-temperature assemblages postdating peak metamorphism have been found (N.Oliver, written communication, 1985). However, this does not necessarily imply that the 1557 Ma age dates mineralization in the Elaine Dorothy skarn.

**Discussion**

The most important results of this study may be summarized as follows: (1) a 1472 ± 40 Ma Sm-Nd age for uraninite and associated REE-rich gangue minerals, (2) Sm-Nd ages for two skarn lithologies of 1766 ± 80 Ma and 1557 ± 40 Ma, and (3) the initial $\varepsilon_{Nd}$ of -9.5 ± 0.7 of the U-REE ore which is significantly different from those of contemporaneous host and country rocks.

*Regional metamorphic origin of U-REE mineralization*

The Sm-Nd age of 1472 ± 40 Ma for the U-REE ore is younger than the U-Pb age for uraninites of 1550 ± 15 Ma which has been interpreted as the time of primary crystallization of uraninite (Page, 1983). As mineralization is thought to be accompanied by REE fractionation for a cogenetic set of minerals including uraninite, the Sm-Nd age and the U-Pb age would be expected to coincide; the reason for their disagreement (at the 95 percent confidence limit) is uncertain. This problem appears even more severe if the individual internal isochron ages for MK68 and MK69 are used rather than the pooled age. Although MK68 would then be within error of the U-Pb age, MK69 (1448 ± 55 Ma) would differ even more from the U-Pb age.

Page (1983) suggested, on the basis of apparent $^{207}\text{Pb}/^{206}\text{Pb}$ ages for allanite which are 60 to 150 Ma younger than the uraninite age, and Rb-Sr isotopic evidence for skarn formation around 1200 Ma, that allanite and many other phases of the gangue assemblage may in fact be significantly younger than the uraninite. Supporting evidence for this would come from the paragenetic relationships of uraninite and gangue, which demonstrate that gangue postdates uraninite (Whittle, 1960). However, the Sm-Nd isotopic systems of all analysed uraninite fractions conform to the 1472 Ma isochron. Moreover, the exclusive association of uraninite with allanite-apatite gangue and similarities in their REE geochemistry suggest that they were formed together. If allanite and apatite in the orebody were younger and not cogenetic with uraninite, there would be no reason for the
uraninite-allanite paragenesis so typical for U-REE mineralization throughout the Mary Kathleen area. Significant differences in age and initial ratios between uraninite and gangue are therefore considered unlikely.

A preferable explanation for the differences between the U-Pb uraninite age and younger Sm-Nd isochron age would be different closure temperatures for the two isotope systems and/or post-crystallisation isotopic disturbance. For example, uraninite grains enclosed by allanite are invariably shelled by silica-rich rims (±pyrite) suggesting post-crystallization reactions which could have caused migration of relatively unradiogenic Nd from allanite into uraninite, thus producing the lower Sm-Nd age and some of the scatter beyond analytical uncertainty as indicated by the MSWD values for MK68 and MK69. Furthermore, the variation in $^{87}\text{Sr}/^{86}\text{Sr}_i$ between whole rocks and apatite in ore samples may also suggest some post-crystallization disturbance. For these reasons we conclude that the 1470 Ma Sm-Nd age for the ore represents a minimum age and that ore formation was completed between 1550 Ma, the U-Pb age of the uraninites, and 1470 Ma. The Sm-Nd data confirm the conclusions of Page (1983) of an origin for the U-mineralization during regional metamorphism, ca. 200 Ma after emplacement of the U-rich Burstall Granite and attendant intensive contact-metasomatism.

Evidence for two periods of skarn formation - a genetic link to ore deposition?

Ever since the earliest studies in the area it has been felt that the extensive volumes of skarn found in the Mary Kathleen Syncline were somehow linked to U ore formation (e.g. Whittle, 1960; Hawkins, 1975). In particular Oliver et al. (1986) report evidence for at least two phases of garnetization separated by phases of deformation. They suggest a U-mineralizing mechanism which involves some leaching of earlier uraniferous skarn, and precipitation of ore late during $D_2$ or $D_3$ in favourable structural positions around and within large pre-tectonic skarn bodies. Hydrothermal alteration of pre-tectonic skarn is very common throughout the skarn area where - for reasons outlined earlier - it is conspicuous for its close spatial association with massive skarn and metadolerite bodies. Renewed garnet growth, probably related to hydrothermal reworking of older skarn, is evident from observations of garnet ± pyroxene lenses axial planar to $F_2$ folds in earlier (pre- $F_2$) banded garnet-rich skarn, massive garnet in strain shadows associated with earlier boudinaged massive skarn and garnet-bearing veins cutting uraninite-allanite ore in the Mary Kathleen pit (Oliver et al., 1986). The association of both ore and the new syn-$F_2$ garnet±pyroxene with metamorphic hydrothermal alteration of earlier skarn suggests they formed by similar mechanisms probably during roughly the same temperature interval of retrograde metamorphism. However, some U-REE mineralization appears to have formed at lower temperatures (Elaine Dorothy prospect).

The two Sm-Nd ages for skarn formation found in this study are therefore important as they provide the first isotopic evidence for two separated skarn-forming episodes. As
mentioned earlier, most of the skarn, including banded and massive types such as the garnetite hosting the Mary Kathleen ore, are probably of syn-granite age, i.e. classical contact-metamorphic and contact-metasomatic types. This widespread alteration event is seen as an important step for the preconcentration of U and REE supplied by magmatic and sedimentary sources. In particular, the ubiquitous garnetization of many precursor lithologies could potentially aid the release of LREE from altered rocks while the HREE were quantitatively fixed in newly grown garnet. The garnet structure has a strong affinity for HREE, but lower distribution coefficients for the LREE (Irving and Frey, 1978). In fact, precursor-normalized REE patterns of garnetiferous skarns (Figs. 4 and 5) and REE data for mine skarn garnets (Fig.2) show moderate to strong LREE depletion but relatively unfractonated HREE. Similarly, data on U distribution throughout the area show that regional skarn garnet does not contain more than a few ppm U (Scott and Scott, 1985). Minor amounts of uranium may have been mobilized together with the LREE during the garnetization of sediments and igneous rocks. If large volumes of rock were involved considerable quantities of these elements would be released. Magmatic late-stage fluids would constitute an additional source of U and REE (Derrick, 1977).

An important exception is Fe-rich garnet found within high-grade U ore at Mary Kathleen. Several REE-rich grains measured on the electron probe had several hundred ppm of U. Coexisting clinopyroxenes have similarly elevated U contents. Abeysinghe et al. (1984a) interpreted andraditic garnet of the mine skarn as the main pre-uraninite U-REE carrier with U contents between 5 and 24 ppm, and ΣREE between 400 and 7600 ppm. Although there are distinct differences in trace element contents between the garnet measured in this study and those reported by Abeysinghe et al. (1984a) possibly indicating the presence of different garnet generations (N.H.S. Oliver, written comm., 1987), the general impression is that the mine skarn concentrated REE and U far more than skarn found away from mineralization.

The second skarn-forming metasomatic event at ca. 1550 Ma was recorded in massive, partially brecciated feldspar-bearing garnet - Fe-rich diopside skarn located close to minor U-REE mineralization. Although secondary skarn production may have occurred recurrently during regional metamorphism, the relatively precise age and its agreement with the U-Pb age for uraninite lends support to a close relationship of tectonic-hydrothermal processes leading to mineralization with those processes that produced metamorphic hydrothermal garnet growth.

In the models developed by Abeysinghe et al. (1984a) and Cruikshank et al. (1980) allanite formation from garnet-diopside skarn is described as immediately following garnet formation in an evolving skarn system. Although such processes may have occurred, they are unlikely to have been preserved through metamorphism. The model by Cruikshank et al. (1980) was developed assuming syn-metamorphic granite intrusion and related metasomatism which was geologically reasonable at the time because the intrusives show only minor signs of deformation and metamorphic overprinting (Oliver et al., 1985a) and the
precise U-Pb zircon ages by Page (1983) were not available. The study by Abeysinghe et al. (1984a) implicitly adopts similar assumptions but fails to state them.

Initial $\varepsilon_{Nd}$ values, REE distribution, and the source of U-REE mineralization

Initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratios at the time of ore formation can be used to characterize possible source rocks that could have supplied REE to the ore. As uranium was probably transported by the same hydrothermal ore fluid, this approach should also identify the U source rocks. The comparison of ore and country rocks is conveniently done using a $\varepsilon_{Nd}$ versus time diagram. Fig.10 clearly shows that the mineralization and contemporaneous country rocks including host skarn and Burstall Granite have different $\varepsilon_{Nd}$ values at the time of ore deposition. Consequently these rocks cannot have been the direct source of REE in the ore nor can they have been main aquifers to ore fluid transport if wallrock reactions were important. In particular the massive skarns suspected to constitute a potential LREE-U source do not have the appropriate isotopic composition to be a viable source for ore Nd.

If REE in the ore were ultimately derived from the Burstall Granite and/or Corella Formation sediments, the low $\varepsilon_{Nd}$ in the ore would require a highly unusual, strongly LREE-enriched source, i.e. with a very low Sm/Nd ratio. In such a source, the increase in $^{143}\text{Nd}/^{144}\text{Nd}$ with time would be retarded and its $\varepsilon_{Nd}$ would become more negative with time relative to surrounding country rocks with higher Sm/Nd ratio. Alternatively, a very old upper crustal source (i.e. with average upper crustal $^{147}\text{Sm}/^{144}\text{Nd}$ ratio between 0.10-0.13, Taylor and McLennan, 1985) having a Nd model age around 2500 Ma, could account for the unradiogenic Nd of the ore. However, even the oldest rocks in the eastern part of the Mt. Isa Inlier, exposed in the 1875 Ma Kalkadoon Granite, have Nd model ages that do not exceed 2300 Ma. This does not change in the younger rocks measured in this work such as the Corella Formation or the Burstall Granite; we therefore regard this possibility as improbable.

Instead, we have chosen to examine more closely the possible role of skarn and the granite as ore sources. This is based on field relations and on the REE data, which show a striking pattern of precursor-normalized LREE depletion in massive skarn and altered granite, and strong LREE enrichment in the ore. Although the significance of this observation for ore formation is not clear, it demonstrates that LREE redistribution processes were operative in skarn spatially associated with mineralization.

As mentioned above, only an extremely LREE-enriched source can account for the Nd isotopic composition of the ore if sources substantially older than the skarn and the Burstall Granite are excluded. We can estimate the necessary degree of LREE enrichment, i.e. the LREE pattern of the model source, by calculating the $^{147}\text{Sm}/^{144}\text{Nd}$ ratio necessary to shift $\varepsilon_{Nd}$ from the source value to that of the ore in a given period of time. If we assume an initial value of $\varepsilon_{Nd} = -4$ (equivalent to initial $^{143}\text{Nd}/^{144}\text{Nd} = 0.509394$, an average for Burstall Granite, surrounding metasediments and skarn at 1730 Ma), an end value of $\varepsilon_{Nd} = -9.5 \pm 0.7$ at 1472 ± 40 Ma (equivalent to initial $^{143}\text{Nd}/^{144}\text{Nd} = 0.50945 \pm 2$, the value of the ore at
1472 Ma), and a source evolution spanning 250 Ma, we obtain a present-day
$^{147}\text{Sm}/^{144}\text{Nd}_{\text{model source}} = 0.037 \pm 0.012$ (corresponding to $\text{Sm/Nd} = 0.061 \pm 0.017$). The
calculated Sm/Nd ratio for the model source, which is illustrated in Fig.10, is very similar to
that in the present ore (i.e. has a similar REE pattern, not necessarily similar $\Sigma$REE), but is
drastically different from that of any measured country rock outside the orebody.

The calculations put several constraints on the model source and the ore-forming process
and require: (1) extreme fractionation of REE to form the model source at the time of granite
emplacement and skarn formation; (2) isolation of the model source from Nd isotopic
reequilibration with increasingly more radiogenic country rocks for 200-250 Ma, and (3)
release of REE (and presumably U) from the model source during amphibolite facies
metamorphism and hydrothermal alteration not earlier than ca. 1550 to 1470 Ma. This
requires that REE were recombined from the source into the ore without significant
admixture of more radiogenic Nd from surrounding country rocks.

Additional indications for strong LREE enrichment in the model source come from an
examination of ore mineral REE patterns. For example, a comparison of REE data for Mary
Kathleen apatites with data from the literature clearly shows strong similarities with apatites
from carbonatites and alkalic rocks (Fleischer, 1983) i.e. rocks derived from highly
LREE-enriched magmas. The same relationship is observed for sphene (Fleischer, 1978).
By analogy, strong LREE-enrichment is implied for the hydrothermal fluids from which
these minerals formed. REE partitioning into allanite is less diagnostic because, on the basis
of its mineral chemistry, allanite strongly favours LREE and exhibits often extreme LREE
enrichment in a wide variety of rock types ranging in composition from granitic (Exley,
1980; Gromet and Silver, 1983) to carbonatitic (Kapustin, 1966). A wide range of REE
patterns has been reported for uraninite and pitchblende but there appears to be no general
consistency (Rao, 1967; Sankaran et al., 1970; Shude, 1984). In uraninite, $\text{REE}^{3+}$ and $\text{Ca}^{2+}$
are expected to substitute for $\text{U}^{4+}$ (0.89 Å, Shannon, 1976) in a fluorite type 6-coordinated
site. On this basis, Ho (0.901 Å) and Er (0.89 Å) would be preferentially substituted into the
uraninite lattice; the Nd maximum observed in Mary Kathleen uraninites therefore implies a
high (La/Lu)$_n$ ratio in the ore-forming fluid. Before using the evidence of strong LREE
enrichment in the ore-forming hydrothermal fluid to make inferences about the source rock
REE patterns, we have to keep in mind that LREE-enriched hydrothermal fluids can be
generated from rock sources having no LREE enrichment such as in the case of 300°C vent
fluids on the East Pacific Rise (Michard et al., 1983). Fluid REE patterns obviously do not
necessarily mimic their source but depend critically on phase assemblages during source rock
alteration, availability of complex-forming ligands in solution and on the subsequent fluid
evolution. Nevertheless, if crystal chemical effects on REE distribution in minerals and
available data on REE chloride complexes (Flynn and Burnham, 1978; Graf, 1984 and
references therein), the most likely complexing ligands available in metamorphic fluids
influenced by evaporite dissolution (Oliver et al., 1986; also Kwak, 1986) are considered,
the general impression is that the fluid solute source had above average LREE enrichment.
We conclude that the mineral REE data are consistent with ore derivation from an extremely LREE-enriched source.

Based on these and the geological constraints, only two types of sources appear reasonable. The first are LREE-U-Th-rich accessory phases such as monazite and allanite, which frequently show (La/Lu)_n ratios > 1000 (Exley, 1980) and are disseminated in granite, metasediments and skarn. Alternatively, the present-day ore could have been derived from an older, extremely LREE-enriched U protore, probably located within the skarn.

*Accessory phases as U-REE sources*

Many studies have shown that accessory phases in granitic and sedimentary rocks often concentrate major proportions of the rock's total U, Th and REE (see e.g., Bowie and Watson, 1981 and Pagel, 1982 and companion articles, Stuckless et al., 1977). Although many of these minerals (with the notable exception of uraninite) are often regarded as too insoluble to constitute a viable source of leachable U etc., there are a number of cases where U concentrations could be traced back to accessory phases (Halliday, 1981; Andrade-Ramos and Fraenkel, 1974; Negga et al., 1986). Mechanisms proposed for the release of U and other elements from resistant accessory phases include metamorphic recrystallization (Negga et al., 1986), pervasive microcracking of the host rock (e.g. granites) and redistribution of U and REE within the microcrack planes (Caruso and Simmons, 1985), and crystal weakening due to internal radiation damage which would greatly facilitate leaching of U and REE by even weak epithermal solutions (Petit et al., 1985).

The Nd isotopic constraints on the source for REE in the Mary Kathleen ore require the ore source to be extremely LREE-enriched for at least 200 Ma before it was tapped by the ore-forming metamorphic fluids. As examples of accessory phases possibly involved in U mineralization, we have analysed REE for U-rich accessory phases in the Burstall Granite. As shown earlier, parts of this granite have undergone strong hydrothermal alteration resulting in pronounced LREE loss. The granite must therefore be considered as a potential U-REE source. Typical REE patterns and REE-U-Th concentrations of the four most abundant REE-rich accessory phases in two samples of Burstall Granite are given in Fig.11 and Table 3.

It is clear from Fig.11 that at least two minerals in the granite, the REE-Ca phase and allanite have Sm/Nd ratios low enough to produce Nd isotopic compositions similar to those observed in the ore. Similarly, Oliver (written comm., 1985) reports allanite as a common accessory component from Corella Formation metasediments and skarn in the Mary Kathleen area. Leaching of these minerals could have potentially contributed large quantities of LREE and U to the hydrothermal solutions. Simple mass balance considerations assuming that LREE-enriched accessories such as those in the Burstall Granite hold about half the rock's LREE, indicate that a minimum rock volume on the order of 1km³ of allanite-bearing rock could supply both total U and REE fixed in the orebody, if the system operated at 100
percent extraction and precipitation efficiency. Even if more realistic lower efficiencies are used, source volumes remain surprisingly small.

However, hydrothermal flushing of large volumes of country rock would probably not only attack LREE-enriched accessories but also major minerals such as feldspars, micas, and the various skarn assemblages. REE released from these phases would increase total REE in solution but would also drive the $E_{Nd}$ value of the solution towards the bulk rock value which is not consistent with the measured isotopic ratio in the ore.

Remobilization of older skarn U-REE mineralization

An origin of ore from older, strongly LREE-enriched U protore could meet the Nd isotopic constraints and would be consistent with the observed hydrothermal alteration of massive skarn bodies by tectonically focussed metamorphic fluids. The idea of a protore for the Mary Kathleen mineralization is not new. It was first proposed by Hawkins (1975) who considered a sedimentary pre-concentration, and has been revived by Page (1983). However, the Nd isotopic and REE data allow more definitive constraints to be placed on the nature and location of a protore than was possible with the previously available evidence.

As discussed earlier, strongly LREE-enriched and U-rich phases would be essential components of a protore, but in this case as major constituents to explain the size of the present mineralization. To preserve its unique Nd isotopic composition, reworking of the model protore between 1550 and 1470 Ma must have been essentially conservative, at least with respect to REE. Admixture of more radiogenic, externally derived Nd cannot have been significant. This requires essentially in situ remobilization, only possible if the protore was located within the mine skarn. Most of the mine skarn body consists of barren garnet-pyroxene skarn unsuitable in both REE-U abundances and initial Nd isotope ratios to be an important source of ore components. This is supported by simple mass balance calculations which show that on the order of 100 to 250 times the volume of the present mineralization would have to be reworked to accumulate the LREE and U contents found in the ore. This is clearly unrealistic given the proportions of the mine skarn body (even if erosional loss is allowed for) and the fact that much of the mine skarn body is still largely unaltered primary skarn and cannot have been involved in ore extraction.

The remaining and preferred hypothesis is that the present mineralization is simply the metamorphic equivalent of an older primary skarn deposit which was very similar to the present deposit in both element contents and ratios. Hydrothermal alteration around fractures redistributed and recrystallized much of the previous mineralization and produced the current mineralogy under amphibolite facies conditions. It probably erased any Pb isotopic evidence of the high U/Pb environment that must have existed in the U protore for ca. 200 Ma prior to metamorphism. Such complete removal of radiogenic Pb during hydrothermal reworking of an older U deposit has been observed in some of the unconformity-type U deposits. For example, the Koongarra deposit in the East Alligator River area of Northern Australia
contains ca. 900 Ma old uraninite which plots on the U-Pb concordia curve (Hills and Richards, 1976), yet Sm-Nd data on Koongarra uraninites strongly indicate an age of primary U mineralization of around 1600 Ma (Maas et al., in prep.). These data suggest that reworked U mineralization does not necessarily inherit older radiogenic Pb produced by earlier generations of U minerals which could explain the apparent lack of radiogenic Pb inheritance in Mary Kathleen uraninites.

The ore minerals present now had their U-Pb and Sm-Nd isotopic systems set at the time of metamorphism but the bulk Sm/Nd ratio remained extremely low as before. In the absence of any appreciable pre-1550 Ma Sm/Nd fractionation which would have produced more radiogenic Nd, isotopic reequilibration did not affect the Nd isotopic composition of the bulk ore; in other words, the effect of an increased initial ratio commonly observed for rotated metamorphic isochrons was negligible, thus preserving the unradiogenic initial Nd isotope ratio observed in the ore.

As many aspects of ore deposition are still unknown we cannot comment on the possible mineralogy of the protore and mechanisms of redistribution. However, it is likely that focusing of saline, oxidized metamorphic fluids around and through skarn bodies (Oliver et al., 1986) was of importance. This is supported by the similarity of the U-Pb age for uraninites and the Sm-Nd isochron age for remobilized skarn thought to have formed by such processes.

In an evaluation of the two proposed models we have to rely mostly on our strongest constraint, the Nd isotopic systematics of ore and country rocks. Even though the accessory phase model is appealing and has been considered for many U deposits, we do not regard it to be applicable here as the sole source of U and REE. There may have been some contribution from allanite which is described to be abundant in parts of the primary skarn (N.H.S.Oliver, pers.comm.,1985), but extraction of accessory-held ore constituents from a much larger volume is considered unlikely for the reasons outlined earlier.

The protore model on the other hand does not present these problems and provides a simple explanation for the exclusive association of U-REE mineralization with garnet skarn. In certain aspects, our model incorporates the single-stage contact-metasomatic models proposed by Derrick (1977), Cruikshank et al. (1980) and Abeysinghe et al. (1984a) in that it supports the deposition of a U-REE protore within the primary skarn during syn-Burstall Granite metasomatism. The ultimate source of U and REE is therefore the Burstall Granite and the rhyolitic dikes. In addition, some of the U and LREE may have been derived from the Corella Formation sediments during their widespread garnetization as shown by the REE data. However, the early models did not recognize the reworking of the protore during regional metamorphic hydrothermal activity. This reworking occurred under similar temperature conditions as those inferred for skarn retrogression by Abeysinghe et al. (1984a) and certainly involved dissolution and precipitation of andraditic garnet (Oliver et al., 1986). This similarity of skarn and retrograde metamorphic-hydrothermal assemblages was one of the main reasons for controversial models of ore deposition at Mary Kathleen.
Conclusions

Both U-Pb (Page, 1983) and Sm-Nd dating of ore minerals strongly indicate a regional metamorphic origin of U-REE mineralization at Mary Kathleen. These and additional Sm-Nd data on two key skarn lithologies from the Mary Kathleen syncline rule out the single-stage link between pre-metamorphic A-type granitic intrusives and the mineralization proposed by previous workers. The isotopic data are more consistent with a multi-stage model for ore deposition spanning ca. 200 to 250 Ma.

A syn-Burstall Granite age for most of the skarn exposed in the area is indicated by a 1766 ± 80 Ma Sm-Nd age for banded calc-silicate skarn. REE distributions and initial $^{143}$Nd/$^{144}$Nd ratios in the ore suggest that in the course of exoskarn formation at ca. 1730 Ma, magmatic hydrothermal solutions, probably after extensive interaction with sediments of the surrounding Corella Formation, produced a U-LREE protore very similar in element contents and ratios to the present mineralization at or near the site of the present mineralization.

Ca. 200 to 250 Ma later, during retrograde amphibolite grade regional metamorphism, hot hypersaline metamorphic fluids were circulated around skarn bodies producing volumetrically minor alteration assemblages commonly similar to those formed 200 Ma earlier (Oliver et al., 1986). One of these newly formed skarn-type assemblages which occurs near minor U-REE mineralization, has a Sm-Nd age of 1557 ± 40 Ma, identical with the published U-Pb age for Mary Kathleen uraninites. The U-LREE protore was metamorphosed and experienced some in situ hydrothermal reworking involving loss of radiogenic Pb. The Sm-Nd and U-Pb isotopic systems in the ore minerals were set during this reworking which, on the basis of U-Pb and Sm-Nd isotopic data, occurred between 1550 and 1470 Ma. Initial $^{143}$Nd/$^{144}$Nd ratios in the ore are significantly lower than in surrounding skarn and country rocks, a result of the ca. 200-250 Ma history in the extremely LREE-enriched (low Sm/Nd) environment of the protore. The preservation of this unique isotopic signature is the most important argument against other possible models for ore deposition such as hydrothermal extraction of U and REE from country rocks rich in U-LREE-bearing accessory minerals. This latter model is considered not applicable here because it cannot guarantee that accessory-derived Nd with a $^{143}$Nd/$^{144}$Nd ratio appropriate for the ore would reach the site of ore deposition without significant contamination by common Nd from the surrounding rocks.

The mineralization at Mary Kathleen is essentially the metamorphosed, recrystallized and probably upgraded equivalent of an older, granite-related U-REE mineralization. The inferred U-REE-Th element association in the initial mineralization, and the association with a U-REE rich A-type granite is reminiscent of deposits typically associated with alkaline granitic rocks (Taylor and Fryer, 1983; Drysdall et al., 1984; Bowden, 1985).
Acknowledgments

We wish to thank N.H.S Oliver who provided constructive criticism and helpful comments throughout the course of this study. We also thank J. Philpotts and an anonymous reviewer for their comments on an earlier draft. We are indebted to B.W. Chappell for neutron activation and XRF trace element data and to S.R. Taylor who provided access to ICP facilities. M.G. Shelley assisted with ICP rare earth analyses for some of the most unusual samples he will ever come across. R. Rudowski shared much of the frustration in our attempts to obtain pure garnet separates. We appreciate donation of 4 metasediment samples by B.I. Cruikshank. R.W. Page publishes with the permission of The Director, Bureau of Mineral Resources, Geology and Geophysics, Canberra, Australia. R. Maas was supported by an A.N.U. Ph.D. scholarship.
REFERENCES


--- 1983, Distribution of the lanthanides and yttrium in apatites from iron ores and its bearing on the genesis of ores of the Kiruna type: Econ. Geol., v. 78, p. 1007-1010.


Matheson, R.S. and Searl, R.A., 1956. Mary Kathleen uranium deposit, Mount Isa-Cloncurry district, Queensland, Australia: Econ. Geol., v. 51, p. 528-540.


Oliver, N.H.S., Pearson, P.J. and Holcombe, R.J., 1985a. Chronology of magmatism, skarn formation, and uranium mineralization, Mary Kathleen, Queensland, Australia - a discussion: Econ. Geol., v. 80, p. 513-517.


--- 1985, Chronology of magmatism, skarn formation, and uranium mineralization, Mary Kathleen, Queensland, Australia - a reply: Econ. Geol., v. 80, p. 517-520.


Figure Captions

Fig.1 Simplified geological map of the Mary Kathleen area showing sample locations (after Page, 1983, and Oliver et al., 1985a).

Fig.2 REE abundances in Mary Kathleen U-REE ore, and in relict skarn minerals. (a) REE patterns for whole rock ores MK68, MK69 and MK70 (crosses) and uraninites (open squares) from sample MK69. Extrapolations of uraninite REE abundances between Gd and Yb are based on maximum values for Yb (Table 1a). (b) REE patterns for allanite (oblique crosses), sphene (filled squares) and apatite (open triangles). (c) REE patterns for relict skarn phases garnet (squares) and clinopyroxene (diamonds) extracted from sample MK69. Dashed lines in a-c are tielines joining rare earths below detection limit of the electron probe inferred from probe maximum values or isotope dilution data (ID). Normalizing values are those by Evensen et al. (1978) multiplied by 1.5.

Fig.3 Chondrite-normalized REE abundances for Corella Formation metasediments compared to average Mt.Isa shale (Nance and Taylor, 1976). Lower total REE in the Corella Formation calc-silicate rocks is due to their higher content in REE-deficient carbonatic component. Marble 716 has the lowest REE abundances. REE patterns in metasediments have preserved their shale-type REE patterns through amphibolite grade metamorphism.

Fig.4 REE patterns for banded calc-silicate skarns from the Rita area showing limited REE mobility. Samples were taken parallel to the 5 mm banding defined by alternating microcline-diopside-rich and scapolite-rich layers. The banding is thought to represent a primary sedimentary feature accentuated by metasomatic exchange across layer boundaries. (a) chondrite-normalized; (b) normalized to Mt.Isa shale (see Table 1b), assumed to have a REE distribution similar to the skarn precursors.

Fig.5 REE patterns for massive skarns from the Elaine Dorothy U prospect (0832) and from altered cobble conglomerate near the Mary Kathleen mine (0822), showing severe differential REE mobility. Samples comprise predominantly garnet, clinopyroxene and feldspar. (a) chondrite-normalized; note absence of negative Eu anomaly; (b) normalized to Mt.Isa shale; note relatively flat HREE, excess Eu and strong LREE depletion.

Fig.6 REE patterns for comparatively unaltered Burstall Granite and rhyolitic dikes, and highly altered granite showing strong REE mobility. Note excess Ce in highly altered samples.

Fig.7 Sm-Nd isochron diagram for minerals and whole rocks from MK68 and 69 (open symbols). Whole rock ore MK70 plots close to allanite and the other whole rocks. Filled squares represent analyses of garnet showing variable effects of sample contamination by allanite, details see text. The garnet together with clinopyroxene (cpx) were separated from a 10 cm stringer of relict high-temperature skarn pre-dating the ore in sample MK69. Garnet-diopside-feldspar-allanite skarn K9447 is from the mine skarn (collected by R.W. Page).

Fig.8 Sm-Nd isochron plot showing weakly altered Burstall Granite and rhyolitic dikes, highly altered Burstall Granite, Corella Formation non-skarn metasediments and various skarns (open symbols) and relict skarn minerals from the mine skarn. Two reference lines corresponding to ages of 1472
Ma and 1730 Ma are shown. Dashed lines are tielines between less altered granite and highly altered granite corresponding to ages of 477 Ma (shallower line) and 1065 Ma. These hypothetical alteration ages do not coincide with known events in the history of the area and are probably artifacts of complex alteration.

Fig. 9 Sm-Nd isochron plot for banded skarn 5013 A and massive skarn 0832. The most deviant points of each data set (A3 for 5013A and A2 for 0832) were omitted from the quoted isochrons. Inset shows all 0832 samples, i.e. four thin slabs and three mineral separates.

Fig. 10 $\varepsilon_{\text{Nd}}$ versus time plot showing relative position of U-REE ore at $1472 \pm 40$ Ma compared to unmineralized metasediments, skarns and Burstall Granite. The Nd isotopic evolution of the country rocks is extrapolated back to the intersection with model curves for chondritic (CHUR) and depleted mantle (DM) evolution. Numbers in parentheses are average $^{147}\text{Sm}/^{144}\text{Nd}$ ratios. The intersections with the DM curve provide the Nd model ages given in Table 2b. It is apparent that no rock types with DM model ages older than about 2350 Ma are present amongst the country rocks that could have supplied REE with appropriate $^{143}\text{Nd}/^{144}\text{Nd}$ to the ore. The evolution of a 1730 Ma old model U-REE ore source with $^{147}\text{Sm}/^{144}\text{Nd} = 0.037$ is shown (see text for discussion).

Fig. 11 Typical REE patterns for REE-U rich accessory phases in the Burstall granite. Data are reported in Table 3. Other accessory minerals such as zircon are not shown because they are enriched in HREE and therefore not immediately relevant to this study. The REE-Ca phase has not been identified; it may be bastnaesite.
Table 1a. REE, U and Th abundances of minerals from Mary Kathleen U-REE ore and mine skarn

<table>
<thead>
<tr>
<th></th>
<th>all-A</th>
<th>all-B</th>
<th>all-C</th>
<th>ap-A</th>
<th>ap-B</th>
<th>ap-C</th>
<th>sph-A</th>
<th>sph-B</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>62878</td>
<td>58664</td>
<td>57295</td>
<td>1340</td>
<td>2058</td>
<td>1270</td>
<td>465</td>
<td>335</td>
</tr>
<tr>
<td>Ce</td>
<td>111612</td>
<td>100808</td>
<td>99436</td>
<td>6909</td>
<td>8732</td>
<td>4184</td>
<td>3947</td>
<td>2171</td>
</tr>
<tr>
<td>Nd</td>
<td>15977</td>
<td>17718</td>
<td>16964</td>
<td>3644</td>
<td>4508</td>
<td>2650</td>
<td>2259</td>
<td>1428</td>
</tr>
<tr>
<td>Gd</td>
<td>&lt;141</td>
<td>&lt;222</td>
<td>&lt;216</td>
<td>150</td>
<td>&lt;134</td>
<td>&lt;131</td>
<td>&lt;127</td>
<td>&lt;101</td>
</tr>
<tr>
<td>Yb</td>
<td>559</td>
<td>760</td>
<td>517</td>
<td>637</td>
<td>286</td>
<td>&lt;215</td>
<td>&lt;235</td>
<td>425</td>
</tr>
<tr>
<td>Th</td>
<td>538</td>
<td>641</td>
<td>748</td>
<td>540</td>
<td>&lt;204</td>
<td>&lt;196</td>
<td>&lt;227</td>
<td>&lt;227</td>
</tr>
</tbody>
</table>

Abbreviations: all = allanite; ap = apatite; sph = sphene; ur = uraninite; gt = garnet; cpx = clinopyroxene. All concentrations in ppm except where stated otherwise.

TABLE 1b. REE, U and Th concentrations for whole rocks from Mary Kathleen U-REE ore, Burstall Granite, skarn and Corella Formation metasediments (in ppm).*from Nance and Taylor (1976)

<table>
<thead>
<tr>
<th>Alkali feldspar</th>
<th>fresh granite</th>
<th>altered granite</th>
<th>metasediments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MK68</strong></td>
<td><strong>MK69</strong></td>
<td><strong>MK70</strong></td>
<td><strong>237G</strong></td>
</tr>
<tr>
<td>----------------</td>
<td>-------------</td>
<td>-------------</td>
<td>-----------</td>
</tr>
<tr>
<td><strong>La</strong></td>
<td>54675</td>
<td>60845</td>
<td>46922</td>
</tr>
<tr>
<td><strong>Ce</strong></td>
<td>77113</td>
<td>87015</td>
<td>80692</td>
</tr>
<tr>
<td><strong>Pr</strong></td>
<td>7648</td>
<td>7503</td>
<td>5325</td>
</tr>
<tr>
<td><strong>Nd</strong></td>
<td>16252</td>
<td>15680</td>
<td>10584</td>
</tr>
<tr>
<td><strong>Sm</strong></td>
<td>1002</td>
<td>637</td>
<td>487</td>
</tr>
<tr>
<td><strong>Eu</strong></td>
<td>93</td>
<td>34</td>
<td>33</td>
</tr>
<tr>
<td><strong>Gd</strong></td>
<td>&lt;227</td>
<td>1.49%</td>
<td>1.69%</td>
</tr>
<tr>
<td><strong>Tb</strong></td>
<td>&lt;231</td>
<td>&lt;138</td>
<td>&lt;131</td>
</tr>
<tr>
<td><strong>Ho</strong></td>
<td>&lt;131</td>
<td>&lt;231</td>
<td>2.25</td>
</tr>
<tr>
<td><strong>Yb</strong></td>
<td>605</td>
<td>965</td>
<td>1202</td>
</tr>
<tr>
<td><strong>Lu</strong></td>
<td>&lt;131</td>
<td>&lt;231</td>
<td>335</td>
</tr>
<tr>
<td><strong>U</strong></td>
<td>5200</td>
<td>8340</td>
<td>8270</td>
</tr>
<tr>
<td><strong>Th</strong></td>
<td>2890</td>
<td>1760</td>
<td>1150</td>
</tr>
<tr>
<td><strong>Th/U</strong></td>
<td>0.55</td>
<td>0.21</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Abbreviations: *all = allanite; ap = apatite; sph = sphene; ur = uraninite; gt = garnet; cpx = clinopyroxene. All concentrations in ppm except where stated otherwise.

TABLE 1c. REE, U and Th abundances of minerals from Mary Kathleen U-REE ore and mine skarn

<table>
<thead>
<tr>
<th></th>
<th>all-A</th>
<th>all-B</th>
<th>all-C</th>
<th>ap-A</th>
<th>ap-B</th>
<th>ap-C</th>
<th>sph-A</th>
<th>sph-B</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>62878</td>
<td>58664</td>
<td>57295</td>
<td>1340</td>
<td>2058</td>
<td>1270</td>
<td>465</td>
<td>335</td>
</tr>
<tr>
<td>Ce</td>
<td>111612</td>
<td>100808</td>
<td>99436</td>
<td>6909</td>
<td>8732</td>
<td>4184</td>
<td>3947</td>
<td>2171</td>
</tr>
<tr>
<td>Nd</td>
<td>15977</td>
<td>17718</td>
<td>16964</td>
<td>3644</td>
<td>4508</td>
<td>2650</td>
<td>2259</td>
<td>1428</td>
</tr>
<tr>
<td>Gd</td>
<td>&lt;141</td>
<td>&lt;222</td>
<td>&lt;216</td>
<td>150</td>
<td>&lt;134</td>
<td>&lt;131</td>
<td>&lt;127</td>
<td>&lt;101</td>
</tr>
<tr>
<td>Yb</td>
<td>559</td>
<td>760</td>
<td>517</td>
<td>637</td>
<td>286</td>
<td>&lt;215</td>
<td>&lt;235</td>
<td>425</td>
</tr>
<tr>
<td>Th</td>
<td>538</td>
<td>641</td>
<td>748</td>
<td>540</td>
<td>&lt;204</td>
<td>&lt;196</td>
<td>&lt;227</td>
<td>&lt;227</td>
</tr>
</tbody>
</table>
TABLE 2a. Sm-Nd and Rb-Sr isotopic data for whole rocks and minerals from Mary Kathleen uranium-REE ore

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Sm</th>
<th>Nd</th>
<th>Rb</th>
<th>Sr</th>
<th>Sm/144Nd</th>
<th>Nd/144Nd</th>
<th>ε^143Nd/144Nd</th>
<th>ε^147Sm/144Nd</th>
<th>ε^87Rb/86Sr</th>
<th>ε^87Sr/86Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>whole rock</td>
<td>68</td>
<td>1002</td>
<td>21008</td>
<td>0.41</td>
<td>77.89</td>
<td>0.0289</td>
<td>0.509724±24</td>
<td>-4.3</td>
<td>0.0154</td>
<td>0.72654±7</td>
</tr>
<tr>
<td>whole rock</td>
<td>69</td>
<td>637</td>
<td>14300</td>
<td>1.75</td>
<td>54.20</td>
<td>0.0269</td>
<td>0.509722±16</td>
<td>-3.8</td>
<td>0.0934</td>
<td>0.72720±3</td>
</tr>
<tr>
<td>whole rock</td>
<td>70</td>
<td>487</td>
<td>11393</td>
<td>1.16</td>
<td>98.92</td>
<td>0.0259</td>
<td>0.509667±23</td>
<td>-4.6</td>
<td>0.0339</td>
<td>0.72481±4</td>
</tr>
</tbody>
</table>

Nd isotope ratios were normalized to 146Nd/144Nd = 0.636151, 143Nd/144Nd for standard rock BCR-1 = 0.511833 ± 10 (n=7). Sr isotope ratios were normalized to 86Sr/88Sr = 0.1194. NBS 987 is 0.71022 ± 2 (n=7). All concentrations are in ppm. Errors in isotope ratios are 2σ mean.

ε^143Nd(t) is the Nd initial isotopic ratio at time T relative to the Nd isotope ratio at time Tin a reference model, the chondritic uniform reservoir, CHUR (see DePaolo, 1981).

ε^143Nd(t) = ([143Nd/144Nd]_t / [143Nd/144Nd]_CHUR - 1) x 10^4, where

([143Nd/144Nd]_t)_CHUR = ([143Nd/144Nd]_t)_OCHUR x (147Sm/144Nd)_OCHUR x 10^(-At);

([143Nd/144Nd]_t)_OCHUR is the measured ratio in the sample corrected for its age t,
present day (143Nd/144Nd)_OCHUR = 0.511836, present day (147Sm/144Nd)_OCHUR = 0.1967, λ_Sm = 6.54 x 10^{-12} yr^-1.
TABLE 2b. Sm-Nd isotopic data for minerals and whole rocks from Mary Kathleen mine skarn, and for whole rocks from surrounding skarns, Burstall Granite and Corella Formation metasediments

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Sample No.</th>
<th>Sm</th>
<th>Nd</th>
<th>147Sm/144Nd</th>
<th>143Nd/144Nd</th>
<th>$e_{T1}$</th>
<th>$e_{T2}$</th>
<th>TDM $^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mine skarn minerals and whole rock</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>garnet</td>
<td>69-3</td>
<td>30.78</td>
<td>120</td>
<td>0.1558</td>
<td>0.511046±30</td>
<td>-6.4</td>
<td>-7.7</td>
<td></td>
</tr>
<tr>
<td>garnet</td>
<td>69-4</td>
<td>35.13</td>
<td>145</td>
<td>0.1469</td>
<td>0.511009±44</td>
<td>-5.2</td>
<td>-6.8</td>
<td></td>
</tr>
<tr>
<td>garnet-residue</td>
<td>69-5</td>
<td>92</td>
<td>1406</td>
<td>0.0396</td>
<td>0.509863±20</td>
<td>-4.8</td>
<td>-5.5</td>
<td></td>
</tr>
<tr>
<td>garnet-leach</td>
<td>69-5</td>
<td>55</td>
<td>970</td>
<td>0.0333</td>
<td>0.509753±28</td>
<td>-4.8</td>
<td>-5.5</td>
<td></td>
</tr>
<tr>
<td>diopside (cpx)</td>
<td>69-1</td>
<td>3.07</td>
<td>17.58</td>
<td>0.1056</td>
<td>0.510562±25</td>
<td>-4.8</td>
<td>-5.5</td>
<td></td>
</tr>
<tr>
<td>altered igneous rock</td>
<td>K 9447</td>
<td>27.77</td>
<td>350</td>
<td>0.0475</td>
<td>0.509947±28</td>
<td>-3.9</td>
<td>-5.5</td>
<td></td>
</tr>
<tr>
<td><strong>Corella Formation non-skarn metasediments</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>impure marble</td>
<td>716</td>
<td>2.31</td>
<td>11.01</td>
<td>0.1271</td>
<td>0.510846±30</td>
<td>-3.9</td>
<td>-6.2</td>
<td>2331</td>
</tr>
<tr>
<td>calc-sil. granofels</td>
<td>754</td>
<td>3.61</td>
<td>19.38</td>
<td>0.1127</td>
<td>0.510697±36</td>
<td>-3.6</td>
<td>-6.4</td>
<td>2234</td>
</tr>
<tr>
<td>calc-sil. granofels</td>
<td>755</td>
<td>4.12</td>
<td>22.56</td>
<td>0.1106</td>
<td>0.510624±19</td>
<td>-4.6</td>
<td>-7.4</td>
<td>2290</td>
</tr>
<tr>
<td>calc-sil. granofels</td>
<td>756</td>
<td>4.23</td>
<td>22.81</td>
<td>0.1122</td>
<td>0.510697±38</td>
<td>-3.5</td>
<td>-6.3</td>
<td>2224</td>
</tr>
<tr>
<td><strong>Burstall Granite and rhyolitic dikes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>granite</td>
<td>241 A</td>
<td>10.17</td>
<td>59.11</td>
<td>0.1040</td>
<td>0.510624±39</td>
<td>-3.1</td>
<td>-6.2</td>
<td>2166</td>
</tr>
<tr>
<td>granite</td>
<td>242 A</td>
<td>11.12</td>
<td>62.49</td>
<td>0.1077</td>
<td>0.510674±26</td>
<td>-2.9</td>
<td>-5.9</td>
<td>2169</td>
</tr>
<tr>
<td>altered granite</td>
<td>240 A</td>
<td>2.32</td>
<td>6.12</td>
<td>0.2211</td>
<td>0.511443±23</td>
<td>-13.2</td>
<td>-12.3</td>
<td></td>
</tr>
<tr>
<td>altered granite</td>
<td>240 E</td>
<td>0.84</td>
<td>2.63</td>
<td>0.1942</td>
<td>0.510906±35</td>
<td>-17.7</td>
<td>-17.7</td>
<td></td>
</tr>
<tr>
<td>rhyolite dike</td>
<td>237 G</td>
<td>8.87</td>
<td>44.48</td>
<td>0.1206</td>
<td>0.519781±21</td>
<td>-3.7</td>
<td>-6.2</td>
<td>2281</td>
</tr>
<tr>
<td><strong>Non-mineralized skarns</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>brecc. banded skarn</td>
<td>1262 D1</td>
<td>3.71</td>
<td>19.15</td>
<td>0.1173</td>
<td>0.510735±21</td>
<td>-3.9</td>
<td>-6.5</td>
<td></td>
</tr>
<tr>
<td>brecc. banded skarn</td>
<td>1262 D5</td>
<td>4.33</td>
<td>19.15</td>
<td>0.1173</td>
<td>0.510735±22</td>
<td>-4.8</td>
<td>-7.3</td>
<td></td>
</tr>
<tr>
<td>cobble conglomerate</td>
<td>0822 C1</td>
<td>5.35</td>
<td>19.68</td>
<td>0.1322</td>
<td>0.510887±22</td>
<td>-4.2</td>
<td>-6.4</td>
<td></td>
</tr>
<tr>
<td>cobble conglomerate</td>
<td>0822 C2</td>
<td>4.87</td>
<td>24.91</td>
<td>0.1182</td>
<td>0.510666±25</td>
<td>-5.4</td>
<td>-8.0</td>
<td></td>
</tr>
<tr>
<td>banded skarn$^3$</td>
<td>5013 A1</td>
<td>7.28</td>
<td>64.65</td>
<td>0.0681</td>
<td>0.510176±21</td>
<td>-4.6</td>
<td>-8.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5013 A2</td>
<td>7.26</td>
<td>36.03</td>
<td>0.1219</td>
<td>0.510826±38</td>
<td>-3.1</td>
<td>-5.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5013 A3</td>
<td>8.78</td>
<td>36.56</td>
<td>0.1453</td>
<td>0.510978±26</td>
<td>-5.4</td>
<td>-7.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5013 A4</td>
<td>5.69</td>
<td>22.52</td>
<td>0.1529</td>
<td>0.511147±24</td>
<td>-3.7</td>
<td>-5.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5013 A5</td>
<td>3.79</td>
<td>27.73</td>
<td>0.0827</td>
<td>0.510329±33</td>
<td>-4.1</td>
<td>-7.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5013 A6</td>
<td>3.62</td>
<td>29.84</td>
<td>0.0734</td>
<td>0.51023±17</td>
<td>-3.9</td>
<td>-8.0</td>
<td></td>
</tr>
<tr>
<td>massive skarn$^4$</td>
<td>0832 A1</td>
<td>5.31</td>
<td>36.17</td>
<td>0.0889</td>
<td>0.510429±11</td>
<td>-7.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0832 A2</td>
<td>8.12</td>
<td>23.59</td>
<td>0.2082</td>
<td>0.511697±25</td>
<td>-4.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0832 B1</td>
<td>3.86</td>
<td>17.71</td>
<td>0.1319</td>
<td>0.510846±19</td>
<td>-7.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0832 B2</td>
<td>8.94</td>
<td>25.68</td>
<td>0.2107</td>
<td>0.511681±15</td>
<td>-5.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K-feldspar</td>
<td>0832 Kf</td>
<td>3.02</td>
<td>18.73</td>
<td>0.0975</td>
<td>0.510474±22</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>clinopyroxene</td>
<td>0832 cpx</td>
<td>1.59</td>
<td>7.01</td>
<td>0.1377</td>
<td>0.510939±34</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>garnet</td>
<td>0832 gt</td>
<td>14.41</td>
<td>21.35</td>
<td>0.4082</td>
<td>0.513683±14</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 $e_{Nd}$ calculated at $T1 = 1730$ Ma and $T2 = 1472$ Ma, for calculation see Table 2a
2 TDM = Nd model age in Ma for depleted mantle parameters ($^{143}Nd/^{144}Nd = 0.51235, ^{147}Sm/^{144}Nd = 0.225$, see Liew and McCulloch, 1985)
3 6 adjacent thin slabs of this skarn were used for Sm-Nd dating
4 4 adjacent thin slabs of this skarn plus 3 mineral separates from the same hand specimen were used for Sm-Nd dating
### TABLE 3. REE, U and Th abundances in typical accessory minerals from Burstall Granite

<table>
<thead>
<tr>
<th>REE-Ca phase</th>
<th>allanite</th>
<th>thorite A</th>
<th>thorite B</th>
<th>sphene</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>144239</td>
<td>40317</td>
<td>2795</td>
<td>510</td>
</tr>
<tr>
<td>Ce</td>
<td>256064</td>
<td>105158</td>
<td>25692</td>
<td>6264</td>
</tr>
<tr>
<td>Nd</td>
<td>79212</td>
<td>33008</td>
<td>24681</td>
<td>12575</td>
</tr>
<tr>
<td>Sm</td>
<td>5974</td>
<td>2998</td>
<td>9896</td>
<td>8679</td>
</tr>
<tr>
<td>Gd</td>
<td>4557</td>
<td>2301</td>
<td>9283</td>
<td>9695</td>
</tr>
<tr>
<td>Er</td>
<td>&lt;257</td>
<td>&lt;224</td>
<td>1651</td>
<td>2765</td>
</tr>
<tr>
<td>Y</td>
<td>1513</td>
<td>970</td>
<td>20663</td>
<td>22004</td>
</tr>
<tr>
<td>U</td>
<td>&lt;510</td>
<td>&lt;888</td>
<td>&lt;2586</td>
<td>5984</td>
</tr>
<tr>
<td>Th</td>
<td>6755</td>
<td>10579</td>
<td>482661</td>
<td>438298</td>
</tr>
</tbody>
</table>
Fig. 1
Mary Kathleen ore and uraninites

allanite, sphene, apatite

relict skarn garnet and clinopyroxene

Fig. 2
Fig. 3

Fig. 4

Fig. 5
Fig. 5

Fig. 6

Fig. 7
Mary Kathleen country rocks: Sm-Nd

Fig. 7

Fig. 8

Fig. 9
Fig. 10

Fig. 11
APPENDIX 3

A. Nd-Sr isotope constraints on the age and origin of unconformity-type uranium deposits in the Alligator Rivers Uranium Field, Northern Territory, Australia

Roland Maas and Malcolm T. McCulloch

Research School of Earth Sciences, Australian National University, PO Box 4, Canberra, ACT 2601, Australia

B. REE measurements on standard and U ore samples from Nabarlek

The new data lend support to models of ore deposition which involve reaction of late (100-300°C) U-bearing carbonatite with the Koonalda Formation with remobilisation of the Lower Precambrian basement. Highly variable mantle sources of the Koonalda Formation are favoured as major U sources.

The origin of the mineralization at Ranger may have involved different processes. Ranger U-Pb data indicates a 1737 Ma for material at this deposit, significantly earlier than 1970 Ma for Koonalda. The Nd/Sr ratios for the Ranger deposits are distinctly high, particularly for the southern portion. The high Nd/Sr ratios are consistent with a protracted period of U mineralization of 1730 Ma, which is consistent with the geological setting and Nd-Sr model ages for the latest disturbed samples suggest an age between 1500-1550 Ma, identical to the upper age limit of primary mineralization at the Koonalda deposit II. The Nd-Sr data on U ores and altered rocks from the Nabarlek samples are older than published U-Pb data which range from 1000 Ma to 1437 Ma. The Nd data on samples from Rooparna are strongly consistent with the geological setting and Nd model ages for the most disturbed samples suggest an age between 1600-1800 Ma, identical to the age of primary mineralization at the Rooparna deposit II. The presence of high Nd/Sr ratios in the U ores and altered rocks from the diagenesis is consistent with the new model ages for Rooparna which range from 1437 Ma to 1500 Ma.
We report the results of a Sm-Nd and Rb-Sr isotopic study of the large and rich unconformity-type uranium - (gold - PGE) deposits of Northern Australia. Our findings indicate identical Sm-Nd ages for primary uranium mineralization at Nabarlek (1616±50 Ma) and Jabiluka II (1614±132 Ma), in excellent agreement with new and previously published Rb-Sr data on U ores and altered host rocks. In contrast, the Sm-Nd ages are older than published U-Pb ages which range from 900 Ma to 1437 Ma. Sm-Nd data on uraninites from Koongarra are strongly scattered but the geological setting and Nd model ages for the least disturbed samples suggest an age between 1600-1650 Ma, identical to the age of primary mineralization at Nabarlek and Jabiluka II. The narrow range of Sm-Nd ages for these three deposits (1600-1650 Ma) indicates that mineralization took place soon after deposition of sandstones and volcanics of the 1650 Ma Kombolgie Formation which unconformably overlies the mineralized basement.

Relatively high initial $\varepsilon_{Nd}$ and low $^{87}Sr/^{86}Sr$ ratios in the ores suggest ore fluids derived their metal content from two main sources, the local wall rocks comprising Lower Proterozoic metasediments and - at Nabarlek - amphibolites, and the volcano-sedimentary rocks of the Kombolgie Formation. At Nabarlek, the Kombolgie Formation isotopic signature is obscured by the intensive wallrock alteration involving isotopically similar amphibolites and dolerites, but mass balance calculations indicate major contributions of U and HREE from sources outside the alteration halo which surrounds the orebody. The most likely external metal sources are again the post-unconformity volcanics and sandstones. In contrast, isotopically highly evolved sources such as U-rich Late Archean basement gneisses and post-tectonic high-level granites are less probable metal sources on the basis of their much lower $\varepsilon_{Nd}$ and higher $^{87}Sr/^{86}Sr$ values, suggesting that the ore-forming hydrothermal activity did not penetrate the metamorphic basement except in the mineralized shear zones.

The new data lend support to models of ore deposition which involve reaction of hot (100-200°C) U-bearing oxidized formation/meteoric waters in the Kombolgie Formation with reducing metasediments of the Lower Proterozoic basement. Highly altered volcanics of the Kombolgie Formation are favoured as major U sources.

The origin of the mineralization at Ranger may have involved different processes. Recent U-Pb data indicate a 1737 Ma for mineralization at this deposit, significantly earlier than in the other deposits and, most importantly, earlier than deposition of the Kombolgie Formation. The Sm-Nd data for Ranger uraninites do not form an isochron but indicate a possible age range from 1600 to 1750 Ma. Data resolution is insufficient to allow reliable distinction between a pre- or post-Kombolgie age. However, Nd-Sr initial ratios for Ranger point to unreasonably high $\varepsilon_{Nd}$ - high $^{87}Sr/^{86}Sr$ sources for any age younger than 1650 Ma, the age of Kombolgie sedimentation and basin formation. In contrast, uraninite Nd-Sr initial ratios at 1737 Ma are easily explained as mixtures involving Nd and Sr leached from various Lower Proterozoic and Late Archean sources. The data are thus more compatible with a pre-Kombolgie origin for uranium mineralization at Ranger.
I. Introduction

Unconformity-type uranium deposits are vein-like deposits of often large size and high ore grades characterized by their proximity to a prominent unconformity separating contrasting rock types (Nash et al., 1981; Dahlkamp, 1978a). Deposits of this type are primarily known from two areas, the Athabasca Basin in Saskatchewan/Canada and the Pine Creek Geosyncline in the Northern Territory/Australia; in both cases the unconformity separates a metamorphosed and variably deformed Archean to Early Proterozoic basement from essentially undeformed Mid Proterozoic fluviatile sandstones. Unconformity-type uranium deposits represent the world’s largest resource of low-cost uranium, yet their origin is poorly understood. Several genetic models have been proposed to explain the origin of this enigmatic type of mineralization, ranging from models which emphasize supergene U enrichment processes (Knipping, 1974; Ferguson et al., 1980) to those which advocate hypogene metamorphic-hydrothermal processes (Dahlkamp, 1978b; Binns et al., 1980a). More recently, Hoeve and Sibbald (1978), Gustafson and Curtis (1983), Johnston and Wall (1984) and Wilde et al. (1986) have developed models which involve uranium deposition in breccia zones at and below the buried unconformity by large amounts of circulating formation and/or surface-derived water.

A critical factor in genetic models is the timing of ore deposition and its relationship to magmatic, sedimentary and tectonic processes that marked the evolution of the uranium districts. For the Canadian deposits, isotopic data suggest primary mineralization in the deposits along the eastern part of the Athabasca Basin occurred between 1350 and = 1250 Ma (Bray et al., 1987). This narrow age bracket places tight constraints on the relation of uranium mineralization to the evolution of the Athabasca Basin and lends support to models involving ore genesis from oxygenated, U-rich formation/ground waters penetrating reducing basement rocks along breccia zones (Hoeve and Sibbald, 1978).

For the North Australian deposits, published isotopic age determinations on U ores and associated wallrock alteration range from 1740 Ma to 900 Ma (Hills and Richards, 1976; Gulson and Mizon, 1980; Page et al., 1980; Riley et al., 1980; Ludwig et al., 1985). Conflicting ages on some deposits differ by up to 700 Ma. Further, comparison of results from U-Pb and Pb isotope studies on mineral separates and microsamples by Hills and Richards (1976) and Gulson and Mizon (1980) with more recent U-Pb work using whole rocks (Ludwig et al., 1985, 1987) indicates the potential for serious problems in the interpretation of the data and extraction of reliable age information. Clearly there is the need for additional geochronological data on carefully selected primary ore material to help establish a better time framework for mineralization in this important uranium district.

In this study, we present Sm-Nd and Rb-Sr isotopic analyses on ore material from Nabarlek, Jabiluka, Koongarra and Ranger, the four large unconformity-type uranium deposits known in the Alligator Rivers Uranium Field which contains ≈ 90% of the presently known U reserves in the Pine Creek Geosyncline (Needham and Roarty, 1980). Sm-Nd dating of unconformity-type uranium ores utilizes the large range in Sm/Nd ratios generated by the spectacular fractionation of the rare earth elements (REE) in U-mineralized metasediments and ores from various deposits in Australia and Canada (McLennan and
Taylor, 1979; Fryer and Taylor, 1984). Because of the low REE solubility in general and the chemical similarity of Sm and Nd as neighboring REE, Sm-Nd isotope systems are generally less sensitive to isotopic disturbance (e.g. by low-temperature alteration) than the Rb-Sr system and in particular the U-Pb systems of ore minerals. Previous attempts to apply Sm-Nd dating to uraninites (Fryer and Taylor, 1984; Maas et al., 1987) yielded ages in general agreement with results from other dating methods.

Rb-Sr dating was applied to chlorite-sericite schists from alteration halos around unconformity-type U mineralization in two of the North Australian deposits (Page et al., 1980; Riley et al., 1980). It was found that Sr model ages in highly $^{87}\text{Sr}$-enriched alteration phases gave the most useful information on the timing of metasomatic events in the alteration zones. We report Rb-Sr isotopic data both on unmineralized and ore samples. The combined Sm-Nd and Rb-Sr dating should yield independent information on the timing of mineralization and alteration.

Initial Nd and Sr isotopic ratios in the highest grade ore (i.e. the purest hydrothermal product) can be used to make inferences about the provenance of Nd and Sr and probably other cations in the ore fluids, such as U. Combined with petrographic, fluid inclusion, geochemical and stable isotope data, likely fluid sources and/or pathways can be identified with important implications for petrogenetic models of ore deposition. In particular, Nd and Sr isotopic data can potentially help to evaluate the relative roles of fluids derived from deep-seated versus basinal sources. Nd data may also prove useful in the discussion on the possible role remobilized older U mineralization may have played in the formation of unconformity-type U deposits (Dahlkamp, 1978b; Brookins, 1980; Williams-Jones and Sawiuk, 1985; Kirchner et al., 1980).

2. Geological Setting

The unconformity-type U deposits of Nabarlek, Jabiluka, Koongarra and Ranger 1 are the largest of numerous U occurrences of this type known in the Alligator Rivers Uranium Field (ARUF) which is located ca. 250 km east of Darwin, N.T. in the Pine Creek Geosyncline (Fig.1). Detailed accounts of the regional geology in ARUF are given in Needham and Stuart-Smith (1980), Hegge et al. (1980), Ewers et al. (1983) and Needham (1985).

Briefly, the oldest rocks in the ARUF region are granitoids and granitic gneisses concentrated in the Nanambu Complex, which have concordant U-Pb zircon and Rb-Sr whole rock ages of $\approx2470\text{ Ma}$ (Page et al., 1980). This Late Archean basement is overlain up to 14 km of Lower Proterozoic metamorphosed marine shallow water carbonates and pelites, evaporites, and minor volcanics. Carbonaceous schists and impure carbonates of the Lower Cahill Formation, which occurs near the base of the Early Proterozoic sequence, host most unconformity-type uranium in the area including the Jabiluka, Koongarra and Ranger deposits. The Nabarlek deposit is hosted by schists of the Myra Falls Metamorphics which are considered stratigraphic equivalents of the Cahill Formation. At a late stage of the Early Proterozoic evolution, extensive mafic sills were emplaced.
During the Top End Orogeny (1870-1800 Ma) the Late Archean and Lower Proterozoic rocks were metamorphosed to amphibolite facies with attendant multiphase deformation; I-type granites of the Nimbuwah Complex, emplaced 1866±8 Ma (Page et al., 1980), recrystallized in granulite facies. Rb-Sr ages in most rocks including the Lower Proterozoic schists, parts of the Late Archean basement and the 1866 Ma granites, were reset at about 1800 Ma.

Following deformation, numerous high-level granite bodies were emplaced which are often associated with minor base metal mineralization (Stuart-Smith et al., 1985). Rb-Sr ages for several of these granites range from 1790 to 1730 Ma but cluster between 1790-1780 Ma (Page et al., 1980; Riley, 1980). A stable hiatus of about 150 Ma before the beginning of Middle Proterozoic deposition is marked by a saprolitic weathering profile on the older rocks, forming a prominent unconformity plane. During this interval, thick sills of the Oenpelli Dolerite were emplaced 1-2 km below the surface at about 1690 Ma.

Mid Proterozoic fluviatile sandstones and conglomerates of the Kombolgie Formation unconformably overlie the metamorphic basement. A Rb-Sr whole rock - mineral isochron age of 1648±29 Ma for interbedded basaltic to rhyolitic rocks of the Nungbalgarri Volcanic Member (NVM) sets a minimum age for the onset of Kombolgie sedimentation and burial of the unconformity (Page et al., 1980). Around the U deposits, Early Proterozoic schists and Kombolgie Formation sandstones have been affected by pervasive chloritization which reset Rb-Sr ages in chloritic and sericitic schists at Jabiluka and Nabarlek at around 1600 Ma. An even younger metasomatic event (<920 Ma) is recorded in some ore zone schists at Nabarlek.

Minor phonolitic to doleritic dikes, some of which intrude the Kombolgie Formation have Rb-Sr and K-Ar ages between 1200-1400 Ma and may be related to more widespread doleritic dikes in eastern Arnhem Land (Page et al., 1980).

2.1 Nabarlek

The Nabarlek mine is described by Anthony (1975); more detailed accounts of the petrography and geochemistry are given in Ewers et al. (1983), Wilde et al. (1986) and Wilde and Wall (1987). Much of the summary given here is based on the recent work by A.R. Wilde.

The Nabarlek deposit contained ca. 10^4 t of U at the exceptionally high average grade of 1.98 % U3O8, a grade only matched by some of the Canadian unconformity-type deposits such as Key Lake (Dahlkamp, 1978b) and Cigar Lake (Fouques et al., 1985). Immediate host rocks to the mineralized breccia zone are complexely deformed and metasomatized amphibolites (possibly a metadolerite), and chlorite - muscovite - phengitic mica schists of the Lower Proterozoic Myra Falls Metamorphics. The most striking difference in the otherwise similar host rock lithologies of Nabarlek and the other ARUF deposits is the conspicuous absence of carbonates and the smaller amount of graphite at Nabarlek (Ewers et al., 1983). Below the orebody, the host metasediments are intruded by the 250 m thick Oenpelli Dolerite itself cut by the mineralized Nabarlek Shear, and the ~1780 Ma post-orogenic Nabarlek Granite. Both the dolerite and the granite are strongly altered at their
margins. Although not directly exposed above the orebody, basal units of the Kombolgie Sandstone showing hematite-chlorite-clay alteration and silicification are present nearby demonstrating the proximity of the unconformity. Late Archean basement is not known from the area.

Uraninite and minor brannerite are the major ore minerals in primary ore and are intimately associated with chlorite. As in all ARUF deposits, several morphological types of uraninite are present; however, this does not necessarily indicate multiple stages of mineralization (Ewers and Ferguson, 1980). The massive uraninite used in this study occurs in completely chloritized and uraninite-cemented fault breccia. Conspicuous white-red illite-hematite alteration of primary uraninite-chlorite ore and fine hematite veining represent what is called 'primary residual ore' by Wilde and Wall (1987), which corresponds to the 'sericitisation' described by Ewers et al. (1983). According to the former authors, uraninite is partially transformed to coffinite surrounded by peculiar illite-hematite halos devoid of radioactivity.

Wallrock alteration is a prominent feature at Nabarlek; Wilde and Wall (1987) distinguished several lithological types in two distinct alteration halos (Fig.2). The extensive outer halo extends up to 1 km from ore and is characterized by chloritization and sericitisation of metamorphic minerals, and quartz deposition in faults and basal sandstones. The inner halo is marked by the striking disappearance of quartz and its replacement by a fine-grained paragenesis of chlorite, phengitic mica and hematite ~ 50 m from ore. At the core of the inner halo, within the breccia zone, is a discontinuous zone of extreme alteration comprising almost pure phengitic mica. Uraninite deposition together with chlorite postdates this intense hydrothermal alteration. The chlorite associated with uraninite is chemically distinct from the pervasive alteration chlorite of the inner halo which coexists with phengitic mica. The change from pre-ore phengitic mica to syn-ore chlorite is therefore interpreted as evidence for a sharp change in fluid characteristics (Wilde and Wall, 1987). Ore was richest in these intensely altered zones at the centre of the breccia zone.

Hills and Richards (1976) report a U-Pb age of ~900 Ma for Nabarlek uraninites. Partial Pb loss from the samples occurred at ~200 Ma. On the basis of these and supporting galena Pb isotope systematics it was concluded that uranium was deposited at ~ 900 Ma. Rb-Sr studies on orezone rocks by Page et al. (1980) yielded some evidence for a metasomatic event which reset Sr isotope systems in four chlorite-'sericite' schists and one 'sericite' separate between 900 and 1260 Ma ago. However, most of their samples which are from the inner halo as defined by Wilde and Wall (1987), clustered around a Sr model age mean (±1sd) of 1610±40 Ma which they interpreted as the average age of metasomatic alteration in these schists. A similar age was obtained for 8 out of 9 whole rock samples of the Nabarlek Granite obtained from drillcore beneath the orebody which yield a Rb-Sr isochron of 1561±17 Ma with high initial ratio of 0.726; this age is distinctly younger than the biotite Rb-Sr age for this granite (1780 Ma) and is again interpreted as the age of metasomatic alteration. Finally, there are scattered K-Ar mineral ages on amphibole from Nabarlek amphibolites, clinopyroxenes from the Oenpelli Dolerite and biotite from outer halo schist ranging from 1580 to 1670 Ma. There is thus abundant isotopic evidence for a major
hydrothermal alteration event affecting the inner halo rocks at about 1600 Ma, clearly post-dating the intrusion of the Oenpelli Dolerite at 1688±13 Ma (Page et al., 1980). The significance of this and the 900 Ma event to ore deposition is uncertain.

2.2 Jabiluka

The Jabiluka uranium deposit is the largest among the unconformity-type deposits in ARUF. With its presently known reserves in excess of 2×10^5 tonnes of uranium oxide Jabiluka ranks among the five largest U deposits in the world (Bray et al., 1987). Although the other ARUF deposits are known to contain gold, Jabiluka II is unique in its economic gold concentration which amounts to ~7-8 tonnes. Geological descriptions are given in Hegge et al. (1980), Binns et al. (1980a,b), Ewers and Ferguson (1980) and Gustafson and Curtis (1983).

Among the three known orebodies at Jabiluka, Jabiluka II contains the bulk of the presently delineated uranium reserves (Fig.3). Host rocks to ore are ca. 240 m thick semi-pelitic and psammitic schists of the lower Cahill Formation which contain several layers of graphite schist. The schists are overlain to the south by thick dolomite and magnesite marbles. Underlying the schists are up to 290 m of amphibolite. Late Archean gneisses and biotite schists are known in drillhole and outcrop a few km to the south. Jabiluka II is completely covered by 20-220 m of Kombolgie sandstones. The ore is contained predominantly in southerly dipping breccia zones running more or less parallel to the lithological layering in the schists. The breccia zones are part of a 100 m wide reverse fault zone which evidently controlled both ore deposition and hydrothermal alteration patterns (Johnston and Wall, 1984; Wilde et al., 1987); extension of brecciation into the overlying sandstone suggests that at least part of the brecciation was post-Kombolgie (Gustafson and Curtis, 1983).

The breccia fragments in the basement are cemented by fine-grained Mg-rich chlorite and white mica which are the products of intense hydrothermal alteration within and around the breccia zones. Uraninite, the major ore mineral, occurs as 1) massive breccia cement, associated with chlorite cement and as rims to altered breccia fragments, 2) in thin veins which represent the highest grade ore and contain ~60% of the U, and 3) disseminated in pervasive alteration chlorite adjacent to veins and breccia. The overlying sandstone is devoid of mineralization apart from minor uraninite within massive chlorite just above the unconformity.

Wallrock alteration is present in both the metamorphic basement, where it is characterized by pre-ore pervasive and vein-type white mica which is variably replaced by syn-ore chlorite, and in the sandstone cover, where earlier diagenetic features such as clay alteration and silicification were overprinted by chlorite plus hematite as far as 312 m above the unconformity (Wilde et al., 1987; Gustafson and Curtis, 1983). The ubiquitous association of Mg-rich chlorite with U ore is common to all ARUF deposits (Ewers and Ferguson, 1980). Between the Jabiluka I and II orebodies, several layers of bedded magnesite marbles are interlayered with the schists. These layers become silicified near the orebody and, where preserved, are brecciated in the ore zone. Several workers have
speculated on their role as possible sources of Mg and as channelways for the alteration and ore fluids (Gustafson and Curtis, 1983; Eupene, 1980).

U-Pb isotope studies by Hills and Richards (1976) on uraninites from Jabiluka I yielded a 920 Ma upper intercept on the concordia diagram. The data points for the Jabiluka samples were colinear with those from Nabarlek. Gulson and Mizon (1980) analysed both microsamples (uraninites, sulfides, and uraniferous chlorites) and whole rocks from Jabiluka II. Their uraninites formed a scattered array on a concordia plot with an upper intercept of 1280±100 Ma. $^{207}\text{Pb}/^{206}\text{Pb} - ^{204}\text{Pb}/^{206}\text{Pb}$ systematics for barren sulphides from within meters of U mineralization yielded an apparent age of 1380±110 Ma, whereas a poorly correlated line defined by sulfides from an ore sample corresponds to an age of 1600±150 Ma. In the absence of clear criteria to reject either age, the authors did not suggest which age was more likely to represent the time of U deposition.

Ludwig et al. (1985) present U-Pb data on a large number of ore whole rocks from Jabiluka II. The data points for the least altered samples from the eastern part of the orebody yield an age of 1437±40 Ma which they interpreted as the age of U mineralization.

Average Rb-Sr model ages on retrogressed chlorite-white mica schists presented by Page et al. (1980) gave a mean of 1600±80 Ma, indistinguishable from the mean Sr model ages on similar rocks from Nabarlek. This age was interpreted as the average age of a major metasomatic event possibly related to ore formation. Riley et al. (1980) report a Rb-Sr isochron age of 1534±90 Ma for 'sericites' related to alteration but noted that better correlated subsets of the data fell on parallel 1400 Ma isochrons with variable initial Sr isotope ratios. Regardless of the apparent complexities, the Rb-Sr, U-Pb and Pb-Pb isotope data provide evidence for hydrothermal alteration event(s) associated with U mineralization between ~1600 and 1380 Ma.

### 2.3 Koongarra

The U mineralization at Koongarra is described by Foy and Pederson (1975), Hegge et al. (1980) and Ewers and Ferguson (1980). A total of 12300 tonnes $U_3O_8$ at a grade of 0.35% (Needham and Roarty, 1980) are contained in two orebodies. The ore is hosted by Cahill Formation quartz-chlorite schists and is concentrated in breccia zones which are parallel to the nearby Koongarra Reverse Fault. This fault juxtaposes schists and strongly altered Kombolgie Sandstone implying a post-Kombolgie age of faulting and mineralization. Uraninite occurs in veins, as botryoidal masses within a chlorite breccia cement, or as coatings on fractures. Wallrock alteration patterns are similar to those at Nabarlek; in the extensive outer halo, alteration is restricted to metamorphic minerals like biotite and feldspars, while the inner halo closer to ore is characterized by quartz depletion, chloritization and white mica alteration, in particular within the breccia zones (Wilde et al., 1986). Although bedded carbonates are known within the host rock sequence outside the orezone, none are found within this zone. Brecciated siliceous bands within the orezone are interpreted as their silicified equivalents (Foy and Pederson, 1975).

U-Pb isotope data on uraninites from Koongarra indicate crystallization of part of the U at 870 Ma (Hills and Richards, 1976). Two of five sample, however, plot below a discordia
line from 870 Ma to 0 Ma and have $^{207}\text{Pb}/^{206}\text{Pb}$ ages older than 900 Ma, which suggests the presence of radiogenic Pb derived from older U mineralization.

2.4 Ranger orebody I

The No.1 orebody at Ranger is one of 6 high radiation anomalies hosted by the Cahill Formation over a strike length of ≈ 6 km. It contains pre-production reserves of 53000 tonnes of uranium oxide at a grade of 0.33$\%$ $\text{U}_3\text{O}_8$ (Ranger Uranium Mines, 1985). Eupene et al. (1975) describe a host rock stratigraphy which is inverse to that found at Jabiluka, i.e. a host sequence made up of dolomitic and calc-silicate marbles in its lower part overlain by typical Cahill Formation psammitic and semi-pelitic schists which contain graphitic-pyritic layers and host the mineralization. The schists are overlain by a hanging-wall sequence comprising schists and amphibolites. The footwall sequence contains gneisses and schists which, on the basis of Sr isotopic modeling (Page et al., 1980) are interpreted to be of Lower Proterozoic age. The Kombolgie erosional margin is 3 km south of the orebody but mineralization must have been within tens of meters of the unconformity prior to erosion.

In the mineralized zone, the mine sequence rocks are brecciated and pervasively chloritized. Most of the ore in the mine sequence schists is either disseminated throughout the chlorite in small uraninite particles (5 µm) or occupies thin veinlets and hairline fractures where uraninite forms coatings. In general, uraninite grainsize is considerably smaller than in the other ARUF deposits (Ewers and Ferguson, 1980). Major gangue mineral is chlorite which can coexist with quartz in fractures. The apparent thinning of carbonate layers towards the orezone and their replacement by the 'mine chert' caused Eupene (1980) and Hegge et al. (1980) to consider a solution collapse origin for the breccia zones.

Age relations of uranium mineralization are uncertain apart from a clearly post-metamorphic (post-1800 Ma) age. Possible chloritized sandstones in drillcore at the No.3 orebody are interpreted to suggest a post-unconformity age of chloritization (Eupene et al., 1975). In contrast, Hills and Richards (1976) analyzed two ore whole rocks from Ranger 1 which define a discordia line intersecting the concordia at ≈ 1700 Ma while two uraninite separates indicate a similar age but with superimposed Pb loss at 900 Ma. An event at around 900 Ma is also indicated in their U-Pb data for Nabarlek, Koongarra and Jabiluka I. Similarly, Ludwig et al. (1985) found a well-defined whole rock discordia array with several near-concordant points for Ranger 3 which gave an age of 1737±20 Ma. They interpreted this age as the age of primary mineralization. This interpretation creates an interesting problem. If the 1737 Ma age is the true age of uranium deposition at Ranger, it is clearly older than the deposition of the Kombolgie Formation as indicated by the 1650 Ma Rb-Sr age for the extrusion of NVM volcanics. By implication, it would also be older than the unconformity and hence unrelated to it. In this context, Ranger mineralization would not be an unconformity-related deposit and the geological similarities with other ARUF deposits would be fortuitous. This would also cast doubt on the significance of the unconformity for uranium mineralization in ARUF in general.
3. Sampling and analytical procedures

Sm-Nd and Rb-Sr isotope data were obtained on high grade ores and uraninite separates for Nabarlek, and exclusively on uraninite separates in the case of the other deposits. This approach was chosen to minimize the risk of contaminating the hydrothermal material with host rock material which may not be isotopically equilibrated. In addition, a suite of variably mineralized schists and amphibolites from Nabarlek and two high grade ore whole rocks from Jabiluka was analyzed to investigate the isotopic response to mineralization in samples with increasing U content. One unmineralized sample from Nabarlek was leached and both residue and leach were measured in the hope to separate the mineralization-related REE component from the host rock component. Finally, Sm-Nd and, for many samples, Rb-Sr isotopes were determined on a total of 45 unmineralized host and country rocks from the vicinity of the deposits and the wider ARUF region in order to characterize potential Nd and Sr source reservoirs for the mineralizations. With the exception of three ore samples from the Nabarlek stock pile, all ore and most of the country rocks are from drill core. Locations of sampled drill holes at Nabarlek and Jabiluka are shown in Figs. 2 and 3. At Koongarra, two drillholes were sampled which intersect ore lenses No. 1 and 2, respectively. The ore samples from Ranger were collected from the pit.

Uraninite separates were prepared using a micropanner. The final separates generally contained < 5% sulfide and hematite impurities. One hematite and one white mica plus illite separate were prepared from two Nabarlek samples that showed extreme hematite alteration and white mica and/or illite, respectively, using the same method.

Samples containing significant silicates were spiked and dissolved at 200°C in PTFE pressure vessels using HF, HClO₄ and HCl, centrifuged and Rb, Sr and REE were separated using standard cation exchange chemistry. High grade U ores were dissolved in hot concentrated HNO₃ which usually left little residue (hematite, sulfides, minor silicates) and processed as above. Preliminary experiments had indicated that different dissolution procedures for high grade ores made little difference to the results and HNO₃ digestion was found to be fast and efficient. Sm and Nd were isolated from other REE using cation exchange with 0.2M methyl-lactic acid adjusted to pH = 4.6. Procedural blanks during the course of this study were < 3 ng Sr, < 0.5 ng Rb, 0.7 ng Nd and 0.1 ng Sm; except for some small low-Rb samples, blanks were negligible. Nd and Sr isotope ratios were measured in the MSZ mass spectrometer (Clement and Compston, 1972) or on a Finnigan MAT 261 multicollector mass spectrometer in static mode. Mass fractionation during analysis of Nd was corrected by normalizing to $^{146}$Nd/$^{142}$Nd = 0.636151 and $^{146}$Nd/$^{144}$Nd = 0.7219, respectively. Measured $^{87}$Sr/$^{86}$Sr ratios were normalized to $^{86}$Sr/$^{88}$Sr = 0.1194. Results for standard measurements are given in Table 1. U was determined by isotope dilution (8 ore samples) using standard methods, electron microprobe analysis on fused sample buttons and XRF on fused buttons and pressed pellets. The relative uncertainties for the microprobe and XRF U results is estimated at 10%. All isochron parameters have been calculated using a modified version of McIntyre et al. (1966) and are reported on the 95% confidence level.
4. Results

Correction for fission effects

The Nd isotopic data for all Nabarlek samples with U contents exceeding 1 wt%, and most of the uraninite data for the other three deposits have been corrected for the effects of U fission. This became necessary after it was recognized that Nd, Sm and Gd isotopic ratios in a suite of ores from Nabarlek were slightly different from those in normal, uranium-poor samples. The distribution and relative magnitudes of the anomalies in Nd indicate they are caused by addition of isotopically distinct Nd from spontaneous and neutron-induced fission of U (Maas and McCulloch, in prep.). The magnitude of the fission effects depends on the U/Nd ratio in the sample; for example, U fission in uraninite of 60 wt% U would produce 19-30 ng/g Nd over 1600 Ma. As the Nd contents in the studied samples are usually high (100-1900 ppm), fission Nd would constitute only small proportions of the total Nd (maximum 0.03%). The critical $^{143}\text{Nd}/^{144}\text{Nd}$ ratio is nevertheless significantly affected through a combination of low atomic abundance of $^{143}\text{Nd}$, high relative fission yields and propagation of small systematic errors via a wrong mass fractionation correction. However, the major cause of the observed $^{143}\text{Nd}/^{144}\text{Nd}$ variations in the U ores is the $\alpha$ decay of $^{147}\text{Sm}$.

To correct for the fission effects we have carefully measured all Nd isotope ratios in unspiked aliquots for 26 of our samples using $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ and the power law for mass fractionation correction. Measured apparent anomalies were present in all stable isotope ratios and for most samples did not exceed $1.5 \varepsilon$ units (1 in $10^{-4}$). A few of the samples showed maximum apparent anomalies in $^{142}\text{Nd}/^{144}\text{Nd}$ of $-3 \varepsilon$ units. The measured deviations from standard values compared well with mass fractionation-corrected synthetic data sets which were obtained from numerical modeling of Nd isotope ratios affected by U fission in a high grade ore over an assumed period of 1600 Ma (see below). The modeling produced correlated deviations in $\varepsilon_{142}$, $\varepsilon_{145}$ and $\Delta_{143}$ (the fissionogenic component in $^{143}\text{Nd}/^{144}\text{Nd}$ as opposed to $\varepsilon_{143}$ or $\varepsilon_{\text{Nd}}$ which represents the radiogenic component plus $\Delta_{143}$). Because $^{143}\text{Nd}/^{144}\text{Nd}_{\text{fission}} = 1.2$, measured $\varepsilon_{\text{Nd}}$ values were too high by 0.2-2.5 $\varepsilon$ units (corresponding to a maximum effect in the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of + 0.025%; i.e. $\Delta$). As the fissionogenic contribution $\Delta_{143}$ to measured $\varepsilon_{\text{Nd}}$ values cannot be separated from the radiogenic contribution, their relative contribution had to be estimated using the correlated anomalies obtained from the modeling. Measured $\varepsilon_{145}$ values were compared with calculated values and appropriate corrections were applied to measured $\varepsilon_{143}$ values. Some of the Nabarlek ores for which $\varepsilon_{145}$ were not available were corrected using a theoretical relationship between $\Delta_{143}$ and U/Nd (Maas, 1987). To account for possible errors introduced by the corrections, the $2\sigma_{\text{mean}}$ errors for all corrected samples were increased up to 150 % to 0.00005. Fission effects on the $^{147}\text{Sm}/^{144}\text{Nd}$ ratio are entirely covered by the 0.1-0.2 % error associated with this ratio and no corrections were applied. Changes in some Sm and Nd isotopes due to neutron irradiation are either negligible or occur in isotopes irrelevant to this study.

Fission-produced $^{88}\text{Sr}$ increases measured $^{88}\text{Sr}/^{86}\text{Sr}$ ratios and propagates a positive bias of <2 parts in $10^{-4}$ into mass fractionation-corrected $^{87}\text{Sr}/^{86}\text{Sr}$ ratios; these error levels are
negligible for the purpose of this study and no corrections were applied.

4.1 Host and country rocks

The age distribution of igneous and metamorphic events in ARUF has been outlined above; the new Sm-Nd and Rb-Sr data are given in Table 2. Nd model ages (relative to a depleted mantle model evolution, Liew and McCulloch, 1985) for the Late Archean gneisses and Cahill Formation metasediments range from 2672 to 2010 Ma, consistent with the U-Pb zircon ages of the gneisses and the presence of Archean zircons in metasediments of detrital origin (Page et al., 1980). Cahill Formation carbonates have near-chondritic or higher Sm/Nd ratios and future model ages. Lower Proterozoic amphibolites at Jabiluka I and Nabarlek are LREE-enriched and isotopically distinct from each other and surrounding schists; the measured samples do not provide meaningful isochron ages. Oenpelli Dolerite from drillcore at Nabarlek is also LREE-enriched and has initial $\varepsilon_{Nd}$ values around 0 (at 1688 Ma); new Rb-Sr whole rock data support the 1688 Ma age by Page et al. (1980). Least altered samples of the Nabarlek Granite with typical LREE-enriched REE patterns have Archean model ages only slightly younger than the Nanambu Complex gneisses, which is surprising in view of the granite's proximity to the Nimbuwah Complex with model ages = 300 Ma younger. Sm-Nd and Rb-Sr systems in the severely altered margins of both the granite and the Oenpelli Dolerite have been disturbed but the data do not yield reliable ages for the alteration. Kombolgie Formation sandstones have typical Lower Proterozoic Nd model ages, consistent with their derivation from Lower Proterozoic and late Archean source regions. Finally, 1650 Ma old basalts from the Nungbalgarri Volcanics are LREE-enriched, possess initial $\varepsilon_{Nd}$ values around -4 and have Nd model ages between 2250-2320 Ma.

Although we do not claim that our sampling is necessarily representative of the studied rock types, the overall consistency of the data with the known age framework and the distribution of initial $\varepsilon_{Nd}$ values among the different rock types suggests that we covered most of the Nd isotopic variation present in the ARUF region.

4.2 Nabarlek

Sm-Nd isotopic data for samples from the Nabarlek orezone (Table 3) are shown in Fig.4. The analyzed samples encompass the entire range from unmineralized but highly altered host rocks and alteration minerals to pure uraninite. The data points scatter considerably, in particular at $^{147}$Sm/$^{144}$Nd >0.25. Ten high grade primary ores (2-64 wt % U) and the three uraninite separates define a best fit line (MSWD=2.9) with an age of 1617±30 Ma. The more appropriate model 2 isochron has an age of 1616±50 Ma with initial $\varepsilon_{Nd}$ = -3.3±0.9. This calculation excludes sample 4/40 which is an obvious outlier; inclusion of this sample would change the model 2 age to 1593±60 Ma at somewhat higher MSWD (4.52). Inclusion of two of the altered host rocks (2/30, 2/55) plus a nitric acid leach of 2/55 yields a similar age (1584±15, MSWD=4.39), but the larger range in Sm/Nd ratios improve the precision of the model 2 age and initial ratio (1578±31 Ma, $\varepsilon_{Nd}$ = -2.4±0.4).

The scatter about the isochrons exceeds that attributable to experimental errors and is no doubt in part related to insufficiently compensated fission effects although the applied
corrections and the larger assigned errors did remove a portion of the scatter present in the uncorrected data (MSWD reduced from 21 to 7.7, further reduced to 4.52 after recalculation with $2\sigma_{\text{mean}}$ error of 0.00005). It should be noted that regression of the uncorrected data points yields an age of 1630±35 Ma with $\varepsilon_{\text{Nd}} = -2.3\pm0.3$, identical within errors to the results obtained from the corrected data.

The orezone samples which make up the $=1600$ Ma array show all stages of alteration from fresh, solid uraninite with smooth fracture surfaces and submetallic lustre to advanced stages of white-red illite-hematite alteration present in at least part of the specimens. Most have uranium >12 wt%, but two (193/19.1, #3, uraninite in chlorite matrix) have 2-4 wt% U. In contrast, the two altered host rocks 2/30 and 2/55 possess <20 ppm U. As we cannot distinguish whether these samples reached isotopic equilibrium with the ore fluid or whether their position on the isochron is coincidental, we prefer not to include these data points; the ores-only result of 1616±50 Ma is thus regarded as the best estimate for the age of high grade mineralization. This age is in excellent agreement with the 1610±40 Ma mean for Sr model ages in alteration zone schists, and it is identical within errors with the 1561±17 Ma alteration age for the Nabarlek Granite (Page et al., 1980).

The remainder of the orezone samples plots below the 1616 Ma isochron. The majority of these are dominated by uraniferous chloritic alteration with occasional appreciable amounts of U (94/45.5, 2/25); the reason why these two samples do not fall on the 1616 Ma isochron is unclear. Three of the orezone samples define a well-fitted correlation line (MSWD=0.74) whose slope corresponds to an age of 1125±400 Ma ($^{143}$Nd/$^{144}$Nd$_i = 0.5097\pm9$, $\varepsilon_{\text{Nd}} = -12.2\pm7.5$). The large uncertainties are mainly a result of the small number of data points. If the age is recalculated using the two extreme data points (96/65, 94/41.3) with their $2\sigma_{\text{mean}}$ errors, an age of 1125±90 Ma is obtained. Although this age is within the range of Sr model ages for some of the altered host rocks analysed in this study (see below) and those reported by Page et al. (1980), only one of the three samples, 94/41.3, shows obvious mineralogical changes that could be attributed to alteration. 94/41.3 consists almost entirely of white mica enclosing ovoid-shaped, strongly corroded clots of dark uranium minerals; fine hematite and probably also illite are dispersed in the white mica mass. Hematite and white mica/illite separates plot above the 1125 Ma isochron. Both Ewers et al. (1983) and Wilde and Wall (1987) describe such textures as a typical alteration feature in primary ore and suggest a 900 Ma age for this type of alteration. The low initial ratio of $\varepsilon_{\text{Nd}} = -12.2$ would suggest that the Nd was derived from or equilibrated with normal country rocks or low grade U ores rather than the main mineralization which had $\varepsilon(1125\text{Ma})$ values between 2-20. Because of their mineralogical diversity, the significance of the 1125 Ma Sm-Nd age for these samples to the proposed timing of illite-hematite alteration is ambiguous; it is possible that the 1125 Ma line represents a mixing line rather than an isochron.

The potential for age bias in Sm-Nd dating due to mixing is highlighted in recent studies (e.g.Chauvel et al., 1986) and should not be ignored in a complex setting such as a hydrothermal ore deposit. At Nabarlek, one possible mixing scenario would involve inclusion of non-equilibrated wallrock material in the uranium ore during sampling. Such a mechanism can be ruled out for the present case because the Sm-Nd correlation line is
defined by pure uraninites and very high grade ores (associated with little or no chlorite or other gangue material) over the entire range of the data population used to calculate the isochron age. Another possible mechanism would involve mixing of radiogenic Nd (for example derived from older uranium mineralization or other radiogenic sources) and unradiogenic Nd (derived from older crustal sources) at the time of mineralization. In other words, the ore would have been isotopically heterogeneous at the time of mineralization. To introduce serious bias in the ages deduced from a data array produced in that fashion, the degree of mixing and the Sm/Nd ratio would have to be correlated (a 'zero age isochron'). This possibility seems unlikely for two reasons: first, mixing of isotopically distinct fluids producing correlated $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ on an isochron plot would seem to require a great deal of coincidence in a hydrothermal setting like Nabarlek, and second, the Sm-Nd age is in excellent agreement with Rb-Sr isochron and model ages which, in this case, would be insensitive to mixing. Although some of the scatter on the Sm-Nd isochron may be caused by non-correlated initial isotopic heterogeneities, mixing is unlikely to have had a serious influence on the Sm-Nd age for primary ore at Nabarlek.

The Rb-Sr isotope analyses (Table 3) are plotted in Fig. 5. Most of the high grade primary ores do not display any isochron relationship. They have low $^{87}\text{Rb}/^{86}\text{Sr}$ ratios near zero and cluster between $^{87}\text{Sr}/^{86}\text{Sr} = 0.710-0.714$. Fig.5b shows the other samples including three layer silicate-rich high grade primary ores with high Rb/Sr ratios and all lower grade ores. Isochron analysis of three low grade ores (which do not fall on the 1616 Ma Sm-Nd isochron), three altered but unmineralized host rocks, and nine analyses on altered host schists reported by Page et al. (1980) yields a poorly fitted isochron (MSWD=21.9) with a model 2 age of 1619±30 Ma and an initial Sr isotope ratio of $^{87}\text{Sr}/^{86}\text{Sr}_i = 0.704±3$. Data scatter about the isochron far exceeds experimental error, probably due to incomplete Sr isotopic equilibration during hydrothermal alteration and/or subsequent open system behaviour. The relatively small errors on the age are due to the large dispersion in $^{87}\text{Rb}/^{86}\text{Sr}$ ratios.

To avoid possible age bias caused by inhomogenous $^{87}\text{Sr}/^{86}\text{Sr}_i$, Page et al. (1980) used Sr model ages of highly radiogenic samples to extract more realistic age information. Their average of 1610±40 Ma ($±1\text{sd}$) on 7 samples is indistinguishable from the average of 1592±26 Ma ($±1\text{sd}$, $^{87}\text{Sr}/^{86}\text{Sr}_i = 0.705$) based on 5 of the new analyses which are sufficiently enriched in $^{87}\text{Sr}$ to be insensitive to the choice in $^{87}\text{Sr}/^{86}\text{Sr}_i$. Thus the Sm-Nd age for primary ores and Rb-Sr isochron and model ages on ores and altered host rocks are in general agreement which provides strong evidence for essentially contemporaneous alteration and high grade uranium mineralization at Nabarlek at about 1610-1620 Ma.

Another four orezone samples define a reasonably well-fitted (MSWD=2.5) isochron with $^{87}\text{Sr}/^{86}\text{Sr}_i = 0.9215±4$ (Fig.5b). The samples on this isochron comprise altered ore 94/41.3 and a white mica - illite separate of the same sample plus another sample with apparent Sm-Nd age of 1125 Ma (96/65). The 880 Ma age is similar to the =900 Ma U-Pb age and the Rb-Sr age of the last recorded alteration at Nabarlek (Page et al., 1980). It is therefore considered the most precise estimate for the age of profound illite-hematite-coffinite alteration of primary ores obtained so far. This is supported by Sr model ages of 860 and
1090 Ma for two samples which represent advanced stages of illite-hematite alteration as defined by Wilde and Wall (1987a) (2/21, 94/44.6-hematite).

The other samples below the 1619±30 Ma model 2 isochron possess Sr model ages between 1086 and 1480 Ma (relative to $^{87}\text{Sr}/^{86}\text{Sr}_i = 0.705$). If it is assumed that these samples were all disturbed at ~900 Ma, the range in Sr model ages could be interpreted to reflect variable response to hydrothermal alteration and isotopic resetting at this time. Alternatively, if initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were heterogeneous and significantly higher than 0.705 (as is suggested by the high initial ratio of the 880 Ma isochron) many of the model ages could be too old and their true model ages would be closer to 900 Ma.

Initial Nd and Sr isotope ratios of the U ores can be used to infer potential sources of dissolved cations in the fluid. The systematic covariation of U and REE found in ARUF U ores (McLennan and Taylor, 1979) could be interpreted to indicate transport by the same ore-forming solution (Fryer and Taylor, 1984). On the other hand, uraninite is known to incorporate up to several weight percent REE, in particular high temperature uraninites (Fryer and Taylor, 1987). Even the relatively low-temperature uraninites (~200°C) of the ARUF U deposits contain up to 3000 ppm total REE and it could be argued that uraninites were merely very efficient scavengers of REE liberated during hydrothermal alteration at the site of ore deposition. In either case Nd isotope ratios would reflect the source material.

Fig.6 shows the initial Nd and Sr isotope data for nine of those ore samples which fall on the 1616 Ma isochron. This selection naturally limits the range in initial $\varepsilon_{\text{Nd}}$ values but is necessary to exclude material of non-hydrothermal origin which may not have equilibrated fully with the ore solution. Further, the age correction for $^{87}\text{Sr}/^{86}\text{Sr}$ was minimal for these samples. Only those high grade ores could be used which gave meaningful $^{87}\text{Sr}/^{86}\text{Sr}_i$ (i.e. ≥ 0.704, the lowest initial ratio known in the area).

The ore samples scatter around $\varepsilon_{\text{Nd}} = -3$ and possess a range in $^{87}\text{Sr}/^{86}\text{Sr}_i = 0.706-0.714$. They overlap with the fields for amphibolites and NVM but extend to higher $^{87}\text{Sr}/^{86}\text{Sr}_i$ ratios towards the schist field. In principle, the data are consistent with local derivation of fluid Nd and Sr from the host schists and amphibolites, but contributions from a NVM-type reservoir and the Oenpelli Dolerite cannot be ruled out. In contrast, the Nabarlek Granite which has been considered as a potential U source (Ewers et al., 1983), has considerably lower $\varepsilon_{\text{Nd}}$ and higher $^{87}\text{Sr}/^{86}\text{Sr}_i$ than the ore. This implies that the granite was either not important as a source of metals in the ore fluids or that the granite isotopic signatures were not preserved during ore deposition. Late Archean basement is not known at Nabarlek; the isotopic data suggest that it would be an even more unlikely metal source than the Nabarlek Granite.

It is apparent from Fig.6 that local host rocks and the Oenpelli Dolerite may have been important sources of Nd and Sr incorporated in the uraninites. Mass balance estimates can be used to test this hypothesis. The altered rocks of the inner halo (~350m x 100m x 100m ~ $10^7$ tonnes of rock) contain between 150-300 t Nd and 1500-200 t Sr depending on the proportions of amphibolite and average schist; the entire alteration zone with 2000m x 1000m x 300 m ~ $1.7 \times 10^9$ tonnes of rock carries up to $5 \times 10^4$ t Nd and up to $2.5 \times 10^5$ t Sr. The Oenpelli Dolerite is altered along its margin and adjacent to faults. If Nd was decreased from
17 to 6 ppm (see Table 1) in a volume of 1 m x 100 m x 500 m = 1.5 x 10^5 tonnes of altered dolerite, a total of 1.5 t Nd would be released. These reserves far exceed the small amounts of Nd (2 t) and Sr (0.6 t) contained in the ore; the rocks of the inner halo alone could buffer the Nd and Sr isotopic compositions in the ore fluids, even at extraction efficiencies as low as 1-2 %.

However, the mass balance does not hold as well for HREE and breaks down in the case of U. If Dy with background levels of ≈3 ppm is used to represent HREE, about 1/6 to 1/2 of the inner halo's total original Dy content would now reside in the ore. This sort of HREE depletion is clearly unrealistic considering the generally low mobility of the REE. Further, REE patterns on inner halo amphibolites and schists (A.R. Wilde, unpublished data) show signs of HREE addition rather than removal. Outer halo contributions to the HREE enrichment in the orezone are considered unimportant because the degree of alteration is much lower than in the inner halo. Finally, the entire alteration halo contains ≈16000 t of uranium compared to about 10000 tonnes in the orebody. U reserves in the orebody would have been even greater before erosion of its upper part. It appears that while not resolvable from Nd and Sr isotopic data alone, there has been massive influx of fluids carrying HREE and U which were derived from sources outside the alteration zones in the basement. If these fluids have come from concealed Archean basement as suggested for other ARUF deposits (e.g. Binns et al., 1980a), their Nd and Sr isotopic signature must have been overprinted before ore deposition. On the other hand, if the ore-fluids and at least part of the ore metals originated above the unconformity as suggested by Johnston and Wall (1984) and Wilde et al. (1986), its isotopic signatures would have been dominated by the rock types present there, i.e. the Kombolgie sandstones and NVM, both of which are isotopically similar to Naborlek host rocks. The isotopic data can be explained more conveniently in terms of this latter model as it requires only minimal changes in the fluid isotope ratios during mineralization to produce the observed isotopic variation.

4.3 Jabiluka

Ore samples for Sm-Nd and Rb-Sr isotopic analysis were collected from six drillcores (Fig. 3). One of the samples is from rare mineralized Kombolgie Sandstone which was described by Gustafson and Curtis (1983). Analytical results for two high grade ores and 10 uraninite separates are given in Table 4. Six of the ten uraninite fractions define an isochron (MSWD=3.9) with an age of 1614±67 Ma and initial 143Nd/144Nd = 0.50941±17; the mode 3 age for these samples is 1614±132 Ma with identical initial ratio corresponding to εNd = -6.6±3.1 (Fig. 7). The other four uraninite fractions plot below the 1614 Ma isochron and do not form a linear array. The two high grade ore total rocks are isotopically similar to the uraninite fractions separated from them but displaced to lower Sm/Nd ratio and, in the case of W141V2/88tr, lower 143Nd/144Nd. A line between W141V2/88 total rock and the uraninite separate from this sample has a slope similar to that of the 1614 Ma isochron. We can only speculate as to the reasons for the excess scatter about the 1614 Ma isochron and between the 1614 Ma samples and the rest of the uraninites. It may be caused by variable degrees of isotopic equilibration between the ore fluids and local wallrocks and/or fluids.
derived from them if it is assumed that the two were isotopically different. Alternatively, the samples may not all have the same age or they may have experienced variable degrees of recurrent remobilization which has clearly disturbed U-Pb systems in Jabiluka ores and sulfides (Hills and Richards, 1976; Ludwig et al., 1987).

Two samples of uraniferous, chloritized Kombolgie Sandstone collected within meters of the unconformity (X141V/65.8, S141S/95.5) have quite variable Sm/Nd ratios and lie close to the 1614 Ma isochron. If it is assumed that chloritization in these rocks was contemporaneous with chloritization in the uranium ores (Wilde et al., 1987), these samples could be used to improve the precision of the ore isochron. The pooled age for the six uraninites plus the two chloritized sandstones is 1645±22 Ma (MSWD=2.96) with $\varepsilon_{Nd} = -7.4±1.3$, within errors of the uraninites-only isochron age. However, as these data points may represent a mixture of pre-ore Nd and Nd introduced during chlorite metasomatism, we prefer the age obtained using uraninites only.

The 1614±132 Ma age is similar to the 1600±150 Ma Pb model age for sulfides extracted from mineralized sample 54955 (DDH S180V/231.7m, Gulson and Mizon, 1980). Their sample was collected close to one of the 1614 Ma samples of this study (S180V/232). Further, the Sm-Nd age is indistinguishable from the 1600±80 Ma (±1.s.d.) mean of Rb-Sr model ages on seven altered schists from Jabiluka I (Page et al., 1980). This agreement between results from three different isotope systems provides strong evidence for an important hydrothermal event which produced at least part of the uranium mineralization at around 1600 Ma.

However, the relatively large errors on the Sm-Nd age overlap marginally with the U-Pb whole rock age of 1437±40 Ma by Ludwig et al. (1985). Further, Riley et al. (1980) suggest that Rb-Sr model ages for hydrothermal alteration at Jabiluka could be as young as 1400 Ma if initial Sr isotopic ratios were heterogeneous. Gulson and Mizon (1980) obtained 1380 Ma Pb model ages for sulfides from unmineralized samples. If this age variability reflects real age differences for different parts of the mineralization, it would provide support for models which advocate semi-continuous rather than periodic uranium mineralization (e.g. Ypma and Fuzikawa, 1980; Johnston and Wall, 1984). On the other hand, both the Sm-Nd and the U-Pb age by Ludwig et al. have the potential for bias. Sample S180V/238 exerts considerable control over the Sm-Nd age; if this sample is excluded from the regression, the Sm-Nd age for the remaining samples could lie anywhere between about 1650 and 1350 Ma. The U-Pb data by Ludwig et al. (1987) show increasing scatter with increasing degrees of discordancy and indicate isotopic disturbance(s) between about 400 to 600 Ma ago. Their data treatment therefore weights the data points according to the degree of discordancy, assuming that the most concordant data points are least disturbed. Although their approach appears adequate, the resultant age may nevertheless be in error if the U-Pb systems have been disturbed not only between 400-600 Ma as suggested by their data array, but also earlier than 600 Ma ago. For example, if it is assumed that the 1280 - 1380 Ma age for uraninites and sulfides (Gulson and Mizon, 1980) and the ~900 Ma age for uraninites (Hills and Richards, 1976) reflect the times of remobilization and partial Pb loss in U ores initially formed at 1614 Ma, a scattered data array as found by Ludwig and coworkers would
be expected. The data points would plot in a polygon with edges at 1614 Ma, 1280-1380 Ma, 900 Ma and 400-600 Ma. In such a scenario, even the most concordant data points would give spurious U-Pb ages younger than the true age of mineralization.

In Fig.8 the Nd isotopic evolution lines for our samples are shown on a $\varepsilon_{\text{Nd}}(T)$ vs. time plot. It is obvious that for ages older than about 1550 Ma the evolution lines for the '1614 Ma' samples intersect those of Cahill Formation schists and other country rocks. In contrast, at 1437 Ma, apparent initial $\varepsilon_{\text{Nd}}$ for these uraninites are between -4 and +1, significantly higher than any potential source rock at this time. Thus, if it is assumed that the Nd was derived from normal country rocks such as those in Fig.8 and that the Sm/Nd ratios of these uraninite samples have not been significantly affected by open system behaviour, the samples must be older than 1550 Ma. It is therefore concluded that primary mineralization at Jabiluka II was at around 1600 Ma. We admit, however, that further (Sm-Nd) work is needed to substantiate the 1614 Ma age.

The remaining four uraninite analyses have intersections with source rock evolution lines range between 800-1500 Ma. These 'Nd model ages' suggest uraninite separate O186V/241 from mineralized Kombolgie sandstone and W141V2/88, a breccia ore collected < 20 m below the unconformity may have been formed up to 700 Ma later than the other samples. This would imply that virtually all the (unradiogenic) Nd present in these samples was derived from the country rocks and not remobilized from the older ore, similar to the 1125 Ma ore samples from Nabarlek but quite different from secondary ore at Collins Bay (Fryer and Taylor, 1984) which incorporated highly radiogenic Nd derived from the primary ore.

The Rb-Sr data for the Jabiluka uraninites do not show any isochron relationships; most have similar present-day $^{87}\text{Sr}/^{86}\text{Sr}$ around 0.720 at a range of Rb/Sr ratios (Fig.9) This may be coincidental or it may suggest young Rb-Sr redistribution. Recent disturbance is likely in the case of S180V/232.8 which was analyzed four times with poor reproducibility and has an unrealistically low initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio.

Fig.10 shows initial Nd and Sr isotope ratios for the six 1614 Ma uraninite samples compared to those country rocks at Jabiluka. In contrast to Nabarlek, Late Archean gneisses and Cahill Formation carbonates are present here while amphibolites, although known in the vicinity, were probably much less important as a source for Nd, Sr and U than at Nabarlek where they form a significant proportion of the immediate host rocks. Oenpelli Dolerite is not known in the Jabiluka area.

The variation in initial $\varepsilon_{\text{Nd}}$ values of the uraninites is limited because only those samples which define the 1614 Ma isochron are plotted. The data points lie between the fields of Kombolgie Sandstone and Cahill Formation schists suggesting the ore fluids acquired their Nd and Sr isotopic compositions through mixing of Nd and Sr from these two sources. Dissolved bedded carbonates could represent a third source which would have contributed mainly unradiogenic Sr (i.e. $^{87}\text{Sr}/^{86}\text{Sr} < 0.710$); hence the pseudo-binary mixing array in Fig. 10. It should be noted that Late Archean gneisses appear to be the most unlikely Nd-Sr source rocks present, a situation quite similar to that at Nabarlek.
4.4 Koongarra

The two ore lenses at Koongarra were sampled in drillcores 87 (No.1 lens) and 94 (No.2 lens). Sm-Nd and Rb-Sr isotope data for ten uraninite fractions from 9 samples are listed in Table 5. The Sm-Nd data are plotted in Fig.11 where the two ore lenses occupy distinct fields, lens No.2 samples having generally lower present-day $^{143}$Nd/$^{144}$Nd ratios than the No.1 lens samples at overlapping $^{147}$Sm/$^{144}$Nd. Five of the No.1 lens analyses plot around a correlation line which, if interpreted as an isochron, would have an age of $\approx 420$ Ma and $\varepsilon_{\text{Nd}}(420 \text{ Ma}) = 65$, while the data points on the steeper line would have an age of $\approx 210$ Ma with $\varepsilon_{\text{Nd}}(2130 \text{ Ma}) = -26$. This age is considered to have little relevance to initial ore deposition but may date the time of remobilization in parts of the No.1 lens which is supported by the high initial ratio. Lower intercept ages between 400-600 Ma have been found for the Ranger and Jabiluka ores (Ludwig et al., 1987) and for U-Pb systems in zircons from the Nimbuwah Complex (Page et al., 1980). They are interpreted to suggest a thermal event or regional groundwater activity related to basin formation elsewhere.

Fig.12 shows the analyses in a $\varepsilon_{\text{Nd}}(T)$ vs. time diagram. The sample evolution lines were not extended to ages older than 1650 Ma because the ore locating breccia zone is younger than the Kombolgie Formation (1650 Ma); an age of 1650 Ma is therefore regarded as a maximum age of uranium mineralization at Koongarra. An obvious conclusion from Fig. 12 is that the analyzed samples are certainly older than $\approx 900$ Ma, the age indicated by the U-Pb data of Hills and Richards (1976). At 900 Ma, all samples had apparent $\varepsilon_{\text{Nd}}(T)$ exceeding +25; this implies that the 900 Ma age probably represents a time of partial remobilization of an older uranium ore. This is consistent with U-Pb data for three of their samples which Hills and Richards (1976) interpret in terms of Pb inheritance from an older radiogenic Pb reservoir.

While this conclusion appears straightforward regardless of possible resetting effects, the extraction of a reliable and meaningful age for primary mineralization is problematic. The No.1 lens evolution lines do not intersect local country rocks at any time before 1650 Ma. The only exception is sample 87/91.7 which has $\varepsilon_{\text{Nd}}(1650) \approx -9$. However, because of indications for possible $\approx 420$ Ma Sm-Nd redistribution for this and four other analyses from No.1 lens, the $\varepsilon_{\text{Nd}}(1650)$ values for these samples are considered artifacts. Three of the No.2 lens samples intersect the evolution band for NVM, Kombolgie Sandstone and Cahill Fm. schists in the interval from 1580 to 1650 Ma. This would imply an age of $\approx 1600$ Ma for uranium mineralization at Koongarra, provided the samples have developed as closed systems with respect to Sm and Nd. However, the evidence to support this hypothesis is certainly weaker than in the case of Nabarlek and Jabiluka, where other dating methods give ages comparable to the Sm-Nd ages of uraninites.

The Rb-Sr isotopic data are shown in Fig.9. The data points for the No.1 lens samples scatter strongly between 0.7128 and 0.7197 with no correlation of present-day $^{87}$Sr/$^{86}$Sr and $^{87}$Rb/$^{86}$Sr ratios. This suggests Rb and Sr have been redistributed relatively recently but an age for this redistribution cannot be assigned. As Sr abundances are remarkably constant between 22 and 26 ppm while Rb concentrations vary by a factor of 20, it is likely that Rb was more mobile than Sr. The situation is further complicated by the fact that some of the
samples have a HCl-leachable Sr component which is more radiogenic than the HCl-insoluble residue. No.2 lens analyses are less scattered but again provide no age constraints.

Calculation of initial Nd and Sr ratios for the Koongarra uraninites is hampered by the evidence for young (Phanerozoic) disturbances of both Sm-Nd and Rb-Sr isotope systems at least in the No.1 lens samples, and by the lack of reliable age information. The No.2 lens samples are shown in Fig.10 where they are age-corrected for ages of 1600 and 1650 Ma. Obviously any age younger than $\approx$1600 Ma would shift the uraninite data points rapidly towards higher $\varepsilon_{\text{Nd}}(T)$ and would generate an unrealistic gap between ore and reasonable Nd and Sr sources. It should be noted that even the No.2 lens samples may have suffered minor isotopic disturbance; nevertheless the data seem to follow the same general mixing relationship as the Jabiluka samples. Cahill Formation schists plus the interbedded carbonates and the volcano-sedimentary rocks above the unconformity appear to be suitable sources of Nd and Sr while the Late Archean basement is again a much more unlikely source.

4.5 Ranger

Only six uraninite fractions from Ranger were analyzed because of the difficulty in obtaining suitable ore material for uraninite separation. The samples were collected from Upper Mine Series schists in the pit in December 1986. The Sm-Nd and Rb-Sr isotope data are given in Table 6. Fig.11 shows the Sm-Nd data in comparison with those for Koongarra uraninites. Three of the Ranger data points define a correlation line with an age of $\approx$1270 Ma and $\varepsilon_{\text{Nd}}(T) = +17.7$. As in the case of the 420 Ma line for the Koongarra samples, the high initial ratio of the 1270 Ma isochron would suggest partial remobilization and isotopic resetting of the ore at this time rather than initial mineralization. However, the correlation line could just as well represent a mixing line or result from mere coincidence.

On a $\varepsilon_{\text{Nd}}(T)$ vs. time plot (Fig.13), Nd isotopic evolution trajectories for three of the Ranger uraninites intersect local country rocks at ages younger than 1650 Ma while the other three samples have $\varepsilon_{\text{Nd}}(1650 \text{ Ma}) = 0$, i.e. higher than any country rock. In contrast, at 173 Ma, the U-Pb age for Ranger ores by Ludwig et al. (1985), all six uraninite Nd trajectories are within the range of local country rocks. If the samples have not been isotopically disturbed since the time of ore deposition, the overlap in $\varepsilon_{\text{Nd}}(T)$ would lend some support to the results of Ludwig and coworkers. However, this does by no means prove a pre-Kombolgie Sm-Nd age for Ranger. For example, extrapolation of Nd isotopic evolution paths to ages older than 1650 Ma would allow some of the Koongarra uraninites as well as primary Nabarlek and Jabiluka uraninites to be older than the unconformity, a conclusion which is clearly inconsistent with the geological evidence for a post-Kombolgie origin of these deposits. In this sense, the Sm-Nd data for Ranger do not provide a conclusive solution as to the age of primary mineralization.

The Rb-Sr data for the Ranger samples scatter between 0.726-0.738 and do not show any isochron relationships (Fig.9). Initial Nd and Sr isotopic ratios are shown in Fig.14 where they have been recalculated for two ages: a hypothetical 1614 Ma age and the 1737 Ma
U-Pb age of Ludwig et al. (1985). Five of the six data points form a linear array from low $\varepsilon_{\text{Nd}}$ - low $^{87}\text{Sr}/^{86}\text{Sr}$ to high $\varepsilon_{\text{Nd}}$ - high $^{87}\text{Sr}/^{86}\text{Sr}$; sample Ranger I has low $\varepsilon_{\text{Nd}}$ (T) but high $^{87}\text{Sr}/^{86}\text{Sr}$ (T). Due to the high Sm/Nd ratios in the samples, the arrays for 1614 Ma and 1737 Ma are offset mainly in the $\varepsilon_{\text{Nd}}$ direction as Rb/Sr ratios are generally low with little change in $^{87}\text{Sr}/^{86}\text{Sr}$ over 120 Ma. The 1737 Ma array can be explained conveniently in terms of mixing between a carbonate-type and a schist-type component (Fig.14b). For the Cahill Formation carbonates no initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios lower than = 0.709 have been found in this work, but Sr isotope data on bedded and vein carbonates from Jabiluka (RW Page, unpublished data) indicate initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in Cahill Formation carbonates could have been as low as = 0.707, close to the most unradiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ value in the uraninites. Sample Ranger I plots in the field for Late Archean gneisses which are known in the immediate vicinity of Ranger I. The direction of the Ranger linear array is in marked contrast to the Nd-Sr isotopic characteristics of the Nabarlek and Jabiluka samples which consistently suggest mixing involving important contributions from either amphibolites or NVM/Kombolgie Sandstone-type sources. This would be expected if the 1737 Ma age for Ranger is the true age rather than a post-Kombolgie age because Kombolgie Formation sandstones and NVM volcanics did not exist at that time and amphibolites are unimportant in the Ranger area. The position of the sample array would thus lend support to the 1737 Ma age for U deposition at Ranger.

In contrast, the '1614 Ma' array does not form a meaningful mixing array as one endmember is undefined (Fig.14a). The high $\varepsilon_{\text{Nd}}$ - high $^{87}\text{Sr}/^{86}\text{Sr}$ data points would require a source with $\varepsilon_{\text{Nd}}$ $\geq +4$ and $^{87}\text{Sr}/^{86}\text{Sr}$ $\geq 0.732$, a highly unusual combination not known in the area. It appears a pre-Kombolgie age for mineralization can explain the Sm-Nd data more conveniently; on this basis we accept the 1737 Ma U-Pb age by Ludwig et al. (1985).

5. Discussion

The most important findings of this study are: (1) Sm-Nd ages for primary mineralization at Nabarlek and Jabiluka II of 1616±50 Ma and 1614±132 Ma, respectively; (2) the age of primary mineralization at Koongarra is less well defined; Sm-Nd data and the geologic setting suggest an age between 1550 and 1650 Ma; (3) Sm-Nd isotope data for uraninites from Ranger do not provide clear age constraints. They are consistent with but do not prove published pre-Kombolgie U-Pb ages between 1700 and 1740; (4) Nd-Sr initial ratios for Nabarlek and Jabiluka primary uraninites indicate ore fluids reacted extensively with the host rocks but mass balance calculations and - at least at Jabiluka - the isotopic results suggest some of the Nd and Sr was derived from rocks above the unconformity, i.e. Mid-Proterozoic sandstones and volcanics of the Kombolgie Formation. At Koongarra, partial isotopic resetting has obscured initial Nd-Sr values but the least disturbed samples suggest similar mixing relationships. There is no indication in the isotope data of a contribution by the Late Archean gneissic basement underlying part of the ARUF area; (5) Nd-Sr initial ratios of Ranger uraninites calculated at the U-Pb age of 1737 Ma form a distinct linear array suggesting mixing of Nd and Sr derived the host Cahill Formation with possible
contributions from the gneissic basement. In contrast to the other three deposits, a post-Kombolgie Nd-Sr isotopic signature is absent at Ranger, suggesting its formation involved different fluid sources.

5.1 Age of mineralization: Nabarlek, Jabiluka and Koongarra

The \(1615\) Ma Sm-Nd ages for Nabarlek and Jabiluka are significantly older than previous estimates based on U-Pb ages of uranium minerals and galena (Hills and Richards, 1976). The same conclusion holds for Koongarra even though the Sm-Nd age is less well constrained. Previous isotopic evidence for mineralization ages older than about 900 Ma includes the Pb isotope results on Jabiluka sulfides (Gulson and Mizon, 1980), U-Pb data on Jabiluka ores (Ludwig et al., 1985) and uraninites (Gulson and Mizon, 1980), and \(^{207}\text{Pb}/^{206}\text{Pb}\) model ages for some Koongarra uraninites (Hills and Richards, 1976). The Sm-Nd ages indicate a remarkably uniform period of primary uranium mineralization in the entire ARUF region. This suggests the ore-forming processes were widespread, consistent with the abundance of unconformity-type uranium occurrences in ARUF (Needham and Roarty, 1980). A similarly confined range of initiation dates for uranium mineralization has been found for many of the unconformity-type uranium deposits in Saskatchewan (Bray et al., 1987).

Despite some statistical overlap, the 1600 - 1615 Ma age range found for the three deposits is consistent with a post-Kombolgie age (i.e. later than \(1648\pm29\) Ma, Page et al., 1980) as inferred from their geology, in particular the fact that ore-related alteration features extend into the overlying sandstone (Gustafson and Curtis, 1983; Wilde et al., 1987). On the other hand, magmatic activity associated with the intrusion of alkaline dikes and dolerites between 1370 and 1200 Ma (Page et al., 1980) appears to clearly post-date the mineralizing period. This relative age sequence suggests uranium mineralization occurred under a substantial cover of Mid Proterozoic sediments and volcanics at a rather advanced stage of basin formation, consistent with paleotemperature and paleopressure estimates in the range of 100-200°C and \(\approx500\) bars (Wilde et al., 1986; Ypma and Fuzikawa, 1980; Walshe, 1986). Similar mineralization conditions have been identified in the Saskatchewan deposits (Hoeve and Sibbald, 1978; Pagel et al., 1980). The deep burial during mineralization removes the need for magmatic or other deep-seated heat sources to drive the ore-forming hydrothermal system (Johnston and Wall, 1984) but by no means disproves possible contributions from such sources. For example, hypogene heat sources have been suggested for Jabiluka by Binns et al. (1980a) and Gustafson and Curtis (1983).

Several 100 Ma after initial mineralization, ores at Nabarlek, Jabiluka and Koongarra were partially remobilized and altered. U-Pb ages by Hills and Richards (1976) indicate an age of around 900 Ma for this event, but other U-Pb evidence suggests there may have been additional alteration events between 400 and 600 Ma (Ludwig et al., 1987). New Rb-Sr data for Nabarlek confirm the importance of the \(\approx900\) Ma alteration event. As has been speculated by Ewers et al. (1983) and Wilde and Wall (1987), illite-hematite-coffinite alteration of primary uraninite ore has a Rb-Sr isochron age of \(880\pm11\) Ma and several high grade, partially altered ores and altered host rocks have Sr model ages around 900 Ma,
consistent with Sr model ages determined by Page et al. (1980) and possibly also the 1150±90 Ma Sm-Nd age for some of these samples. However, the 1150 Ma 3-point isochron has large associated errors and we do not assign too much significance to this age.

Uraninite formation younger than 1614±132 Ma at Jabiluka is indicated by two of the Jabiluka uraninites with Sm-Nd 'model ages' that are several 100 Ma younger (Fig.8). This includes the uraninite from 0186V/241, a sample of rare mineralized Kombolgie Sandstone. As noted earlier, these young uraninites appear to have formed with common Nd rather than recycled radiogenic Nd from the main orebody, assuming the 'model ages' are the true ages. This would imply that alteration fluids could selectively leach U but not Nd from the ore. Alternatively, the 'model ages' may be artifacts of variable degrees of radiogenic ore-derived Nd with common Nd. If this was the case, the samples could be even younger than ~800 Ma. At Koongarra, uraninite formation at ~ 900 Ma is well established by the U-Pb data of Hills and Richards (1976). The Sm-Nd results do not indicate a 900 Ma age but instead suggest some Sm-Nd redistribution at 420 Ma. In contrast to Jabiluka, young uraninites at Koongarra incorporated highly radiogenic Nd, probably a function of their position within the high grade zone of the No.1 lens.

5.2 Uranium sources

The source of uranium in the ARUF deposits is much debated in the literature. Most authors agree that the generally high U background of the Lower Proterozoic and Late Archean rocks was an important prerequisite for U mineralization in the area (e.g. Needham, 1985). McAndrew and Finlay (1980) suggest disseminated uraninite in Nanambu Complex gneisses as a possible source of U. The U may be incorporated into the mineralized breccia zones either directly via ascending hydrothermal fluids (Binns et al., 1980a), or indirectly after an intermediate erosional step (Ferguson et al., 1980; Crick and Muir, 1980). Ewers et al. (1983) suggest the U-rich Nabarlek Granite as a possible source of U for Nabarlek. In contrast, Johnston and Wall (1984) and Wilde et al. (1986) propose the ore-bearing fluids and therefore at least part of the uranium originated in the rocks above the unconformity.

Initial Nd-Sr isotope data for uraninites from Nabarlek, Jabiluka and possibly also Koongarra would lend support to the latter hypothesis; both the Sr and the Nd found in the ores are isotopically sufficiently different from measured isotope signatures in both the Late Archean gneisses and the Nabarlek Granite to render these rock types the most unlikely possible source rocks. Of course, buffering of Nd and Sr isotopic ratios by local host rocks prior to ore deposition may have obscured deep-seated isotopic signatures; indeed, Sr and Nd mass balance considerations for Nabarlek suggest local buffering was important. On the other hand, the Jabiluka data (Fig.10) would suggest an important contribution from post-unconformity rocks. Further, leaching of the Nabarlek alteration halos could not account for the amounts of U and HREE present in the Nabarlek orebody. The only reasonable source of these components and the enormous quantities of water involved in mineralization (Wilde and Wall, 1987) would therefore be the Kombolgie Formation.

Contrary to some workers who discounted the sandstones as a possible source of U on the basis of their low U concentrations, the Kombolgie Formation may in fact represent a
favourable U source rock, in particular the interbedded Nungbalgarri Volcanics. Porous volcanic deposits rich in glass have long been recognized as important U sources for many groundwater-related U deposits (Rosholt et al., 1969; Walton et al., 1981; Zielinski, 1982) and the wide distribution and appreciable thickness of the NVM (up to 170 m, Page et al., 1980) would make it an ideal U source for circulating oxygenated ground and formation waters. Indeed, Hoeve et al. (1980) go even further and hypothesise unconformity-type U deposits in Canada may represent a special class of sandstone-type deposits.

An entirely different source of uranium is envisaged by Dahlkamp (1978b) who suggested that unconformity-type uranium at Key Lake in Canada may in fact be derived from remobilized older uranium mineralizations dating back to the 1800 Ma regional metamorphism. Similarly, Ferguson et al. (1980) postulate present uranium ores in ARUF are merely the remobilized equivalents of pre-Kombolgie colluvial concentrations. As such U protores would produce radiogenic Pb, U-Pb studies are ideally suited to address the possibility of protores recycling, however, recent U-Pb studies (Troclci et al., 1984; Ludwig et al., 1987) did not identify any traces of inherited radiogenic Pb. Another indicator of old U protores are Nd isotopic data. Because many uranium mineralizations have high Sm/Nd ratios (e.g. Fryer and Taylor, 1987), recycled Nd derived from such protores would be highly radiogenic and useful as a tracer of this inheritance. Mixing of country rock-derived Nd with highly radiogenic Nd is not supported by our data; high apparent initial $\varepsilon_{\text{Nd}}$ values (e.g. Figs.12 and 14a) can be explained by isotopic resetting or an inappropriate age correction and argue against admixture of protores-derived radiogenic Nd. The same conclusion was reached by Fryer and Taylor (1984) in their study of Sm-Nd systematics in the Collins Bay unconformity-type uranium deposit.

Although alternative interpretations of the Nd-Sr data presented here are possible, the combined Sm-Nd and Rb-Sr isotopic evidence and fluid inclusion and mineralogical data (Wilde and Wall, 1987) would strongly favour a model similar to the diagenetic-hydrothermal model of Hoeve and Sibbald (1978). Recent investigations in Canada reach essentially identical conclusions (Bray et al., 1987).

5.3 Ranger: age and origin

The origin of the Ranger mineralization, commonly considered a typical unconformity-type uranium deposit in terms of host rocks, ore controls, wallrock alteration and geological setting, becomes enigmatic in the light of the recently confirmed pre-Kombolgie U-Pb ages. The isotopic data obtained in this study cannot prove but are consistent with a pre-Kombolgie age for Ranger. The linear variation of initial Nd-Sr ratios of Ranger uraninites does not make much sense if a post-unconformity age for mineralization is assumed (Fig.14b). In contrast, if the initial ratios are calculated for an age of 1737 Ma the straight Nd-Sr isotopic array (Fig.14a) can be plausibly explained in terms of binary mixing of fluids having distinct schist-type and carbonate-type isotopic signatures, respectively. It appears more than fortuitous that the Nd-Sr isotopic data should indicate only pre-1650 Ma metal sources in the only deposit with pre-1650 Ma U-Pb ages but suggest important contributions from post-1650 Ma metal sources for those deposits with post-1650 Ma ages.
The lack of curvature in the data array would indicate very similar Sr/Nd ratios in the endmember fluids. A linear array of initial Nd-Sr isotope ratios was also found in hydrothermal minerals of a young tungsten deposit in Queensland by Higgins et al. (1987). We propose that original mixing arrays in the other ARUF deposits were probably linear as well but the original shapes of their Nd-Sr arrays were almost certainly obscured by Rb-Sr redistribution.

One Ranger analysis falls in the field defined by Nanambu Complex gneisses suggesting that in this case the basement was involved in the ore-forming hydrothermal system. This fact may be used as evidence to suggest that ore formation at Ranger was somewhat different compared to the other ARUF deposits, in particular in terms of fluid sources and/or fluid pathways.

6. Conclusions

Although we do not intend to present a detailed genetic model for ARUF uranium mineralization, a number of points relevant to ore genetic models can be derived from the data discussed in this study. The relatively narrow, post-Kombolgie Sm-Nd age range for mineralization in the three vein-type ARUF deposits Nabarlek, Jabiluka and Koongarra suggests burial of the unconformity was an important factor in the ore-forming process:

(1) it provided the heat necessary to drive the ore-forming hydrothermal alteration; Ypma and Fuzikawa (1980) suggest it may have also acted as a thermal blanket allowing radiogenic heat build up from the uraniferous basement,

(2) the sandstones are a more likely source of the vast quantities of water involved in ore deposition and alteration than the relatively impermeable basement rocks which were previously dehydrated during regional metamorphism,

(3) fluids capable of mobilizing and transporting U as uranyl complexes were oxidized (i.e. in equilibrium with hematite) and therefore must have contained a considerable meteoric component (or interacted with hematite in the sandstone) (Wilde et al., 1986),

(4) the sandstones and in particular the interbedded volcanics would represent a favourable source of U for leaching by circulating hot, oxidized waters,

(5) access of fluids to the reducing (carbonaceous) basement rocks via brecciated parts of reverse faults at the unconformity may have been in response to basin wide faulting which would explain the narrow range of Sm-Nd ages. Bray et al. (1987) have used similar arguments to explain U-Pb ages for the unconformity-type deposits associated with the Athabasca Basin in Saskatchewan.

Interestingly, recent thermoluminescence studies on quartz from an unconformity-type setting in South Australia which is similar to that in ARUF, indicate long-lived (≈1400 Ma) uranium enrichment (≈100 ppm) spatially confined to the unconformity, with rapidly decreasing irradiation effects away from the unconformity surface into underlying pyrite-rich metamorphic basement and overlying Mid-Proterozoic sandstones (Ypma and Hochman, 1987). Particularly noteworthy is the absence of anomalous U anywhere in the basement except in narrow shear zones which suggests a post-sandstone U source. The authors favour
an origin of U from the lithophile element-enriched Gawler Volcanics overlying the sandstones; U was leached out and transported to the unconformity contact where it spread and only entered the basement via shear zones. While no economic U mineralization is known in the study area, similar irradiation effects have been found along the base of the Kombolgie Sandstone and the Athabasca Sandstone, i.e. in highly mineralized areas. The results of Ypma and Hochman (1987) are entirely consistent with the findings presented here and would, if substantiated in the ARUF region, provide strong support for models such as those of Hoeve and Sibbald (1978) and Wilde et al. (1986).

The origin of uranium mineralization at Ranger I remains unclear in the light of the U-Pb and Sm-Nd isotopic evidence and more work is needed to clarify the relationships between Ranger and the other ARUF uranium deposits.

Acknowledgements: We thank A.R Wilde for his part in organizing field work in the Northern Territory and for providing some of the samples. Our work benefitted greatly from his expertise and constant encouragement. Our thanks go to Pancontinental Mining Ltd. and Queensland Mines Ltd. for their generous help during field work and permission to sample drill core material at Jabiluka and Nabarlek, respectively. Denison Pty Ltd. kindly permitted sampling of Koongarra drill core material; Andy Snelling assisted during sample selection at Koongarra. We are indebted to John Farthing of E.R.A. (Ranger) for permission to obtain samples from Ranger, and to Colin Kendall for his efforts to obtain excellent ore samples from the Ranger pit. We thank Les Kinsley and Suresh Bargava for technical assistance. RM was funded by an ANU postgraduate scholarship.
References


Wilde AR and Wall VJ (1987) Geology of the Nabarlek deposit, Northern Territory, Australia. Econ Geol 82 (in press)

Wilde AR et al (1987) Spatial and temporal distribution of alteration in unconformity-related uranium deposits, Northern Territory, Australia: implications for metal transport and depositional mechanisms (in prep.)


Figure Captions

Fig.1 Simplified geological map of the Alligator Rivers Uranium Field (ARUF). From Ewers et al. (1983).

Fig.2 Schematic map of the Nabarlek orebody showing spatial realtionshipships of faulting with mineralization and wallrock alteration. Squares: drillcores sampled for this study (modified after Wilde and Wall, 1987).

Fig.3 Schematic map of the Jabiluka U deposit showing location of sampled drillcores. The intersections of mineralized zones with the unconformity and/or the present surface are indicated.

Fig.4 Sm-Nd isochron plot for Nabarlek ores and altered rocks. The 1616 Ma isochron is calculated for 10 high grade ores (>4 wt% U) and 3 mineral separates (all termed h-g primary ore). Primary high grade sample 4/40 (*) is excluded. The other ore samples with generally lower U contents are termed "l-g ore" (lower grade ore) and "altered ore" where hematite-illite alteration is strong. "Altered rocks" are unmineralized host schists and amphibolites from the inner halo. The 1125 Ma line is calculated for 3 samples, see text for details.

Fig.5 Rb-Sr isochron plots for Nabarlek samples. A) Low-Rb high grade primary ore. These comprise all those high grade samples with little layer silicate matrix plus one chloritic ore (#3). 1620 Ma reference line shown for comparison. B) Data points are for 3 high grade primary ores with high Rb/Sr, illite-hematite altered ore plus white mica-illite and hematite separates, 9 lower grade ores, 4 altered host rocks (partly shown in large inset) and 9 analyses on altered schists from Page et al. (1980, filled circles). Other symbols as in Fig.4. Small inset shows area covered by A; 900 Ma reference line shown for comparison.

Fig.6 Initial Nd and Sr isotope ratios for Nabarlek primary ores (filled squares) compared with potential Nd-Sr source rocks. O.D.=Oenpelli Dolerite; amph=amphibolites from Nabarlek and Jabiluka; NVM=Nungbalgarri Volcanic Member; schists=schists in Myra Falls Metamorphics and Cahill Formation.

Fig.7 Sm-Nd isochron plot for uraninites, ores and chloritized Kombolgie Sandstone from Jabiluka. The 1614 Ma isochron is calculated for 6 uraninite fractions. Inclusion of the 2 chloritized sandstones increases the age by 20 Ma. The short tieline connects total rock W141V2/88 and the uraninite separate from the same sample. O 186 V/241 is uraninite from rare mineralized sandstone.

Fig.8 $\varepsilon_{Nd}$ versus time plot for Jabiluka uraninites. All Nd isotope evolution trajectories are relative to the Nd isotope evolution in a model chondritic uniform reservoir (CHUR) with present-day $\varepsilon_{Nd}$ =0, $^{143}Nd/^{144}Nd =0.51836,^{147}Sm/^{144}Nd = 0.1967, \lambda_{Sm} = 6.54 \times 10^{-12} \text{ y}^{-1}; \varepsilon_{Nd}(T)$ in CHUR is set at zero at all times. The U-Pb age of 1437 Ma (Ludwig et al., 1985) and the Sm-Nd age (1614 Ma) are indicated. The fields for country rocks are; lower stippled band, Archean basement; cross-hatched area, Lower Proterozoic schists; dotted band, Kombolgie Fm. sandstones; upper stippled band, NVM.

Fig.9 Rb-Sr isochron plot for uraninites from Jabiluka, Koongarra No.1 lens and No.2 lens, and Ranger. A 1600 Ma reference line is shown for comparison. The dashed tielines connect the 2 high grade total rocks from Jabiluka and their respective uraninite separates which have lower $^{87}Sr/^{86}Sr$ and Rb/Sr. The 4 data points surrounded by a dashed line are repeats of sample S180V2/232.8.

Fig.10 Initial Nd and Sr isotope ratios for 1614 Ma Jabiluka uraninites and Koongarra No.2 lens uraninites. The Koongarra data were recalculated at 1600 and 1650 Ma. The country rocks were calculated at 1614 Ma but their positions change only little from 1600-1650 Ma. Abbreviations as in Fig.6, carbonates = Cahill Formation carbonates from Jabiluka.
Fig. 11 Sm-Nd isochron plot for uraninites from Koongarra and Ranger.

Fig. 12 $\varepsilon_{\text{Nd}}$ versus time plot for Koongarra uraninites. CHUR parameters and country rock signatures as in Fig. 8. Numbers 1 and 2 on the uraninite trajectories refer to ore lens No.1 and 2, respectively.

Fig. 13 $\varepsilon_{\text{Nd}}$ versus time plot for Ranger uraninites. CHUR parameters and country rock signatures as in Fig. 8. The 1737 Ma U-Pb age is indicated.

Fig. 14 Initial Nd and Sr isotope ratios for Ranger uraninites compared with country rocks. A) at 1614 Ma, B) at 1737 Ma. Change in schist field due to changes in Sr isotope ratios. Fields for NVM and KF (Kombolgie Formation) omitted in B) because post-unconformity rocks did not exist at 1737 Ma. Abbreviations as in Figs. 6 and 10.
Table 1. Sr and Nd isotopic compositions of standards:  
A comparison between 2 mass spectrometers at the ANU

<table>
<thead>
<tr>
<th>Nd standards</th>
<th>$^{143}$Nd/$^{144}$Nd</th>
<th>n</th>
<th>$^{143}$Nd/$^{144}$Nd</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCR-1(^1)</td>
<td>0.511824 ± 5</td>
<td>6</td>
<td>0.511824 ± 12</td>
<td>10</td>
</tr>
<tr>
<td>BHVO-1</td>
<td>0.512169 ± 5</td>
<td>1</td>
<td>0.512166 ± 16</td>
<td>8</td>
</tr>
<tr>
<td>La Jolla</td>
<td>0.511045 ± 5</td>
<td>17</td>
<td>0.511036 ± 11</td>
<td>11</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sr standards</th>
<th>$^{87}$Sr/$^{86}$Sr</th>
<th>n</th>
<th>$^{87}$Sr/$^{86}$Sr</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>E&amp;A SrCO(^3)</td>
<td>0.707966 ± 15</td>
<td>6</td>
<td>0.708008 ± 11</td>
<td>15</td>
</tr>
<tr>
<td>NBS 987(^2)</td>
<td>0.710197 ± 4</td>
<td>67</td>
<td>0.710260 ± 14</td>
<td>33</td>
</tr>
</tbody>
</table>

The MSZ measurements were made over the period from 2/85 to 8/87; MAT measurements from 9/86 to 9/87. \(^1\)The MAT Nd results are renormalized using the $^{143}$Nd/$^{144}$Nd for BCR-1 (MSZ); the MAT values given here and in Tables 2 to 6 correspond to the original MAT results multiplied by 0.511824/0.512653. \(^2\)Note the ratio reported for the MAT mass spectrometer includes 11 analyses of 0.5 to 2.0 nanograms Sr with an average ratio equal to that given.
Table 2. Sm-Nd and Rb-Sr isotopic data for unmineralized host and country rocks to U deposits in the ARUF region

<table>
<thead>
<tr>
<th>sample</th>
<th>Sm</th>
<th>Nd</th>
<th>$^{147}$Sm/$^{144}$Nd</th>
<th>$^{143}$Nd/$^{144}$Nd</th>
<th>$\varepsilon_{Nd(0)}^2$</th>
<th>$T_{DM}^3$</th>
<th>Rb</th>
<th>$^{87}$Rb/$^{86}$Sr</th>
<th>$^{87}$Sr/$^{86}$Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Archean gneisses, Nanambu Complex</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4009A$^4$</td>
<td>10.11</td>
<td>73.78</td>
<td>0.0829</td>
<td>0.509845</td>
<td>-38.9</td>
<td>2672</td>
<td>149.4</td>
<td>250.5</td>
<td>1.732</td>
</tr>
<tr>
<td>4016$^4$</td>
<td>9.31</td>
<td>53.39</td>
<td>0.1055</td>
<td>0.510235</td>
<td>-31.3</td>
<td>2683</td>
<td>232.9</td>
<td>120.5</td>
<td>5.688</td>
</tr>
<tr>
<td>4048A$^4$</td>
<td>6.8</td>
<td>42.3</td>
<td>0.0977</td>
<td>0.51015</td>
<td>-32.9</td>
<td>2620</td>
<td>159.0</td>
<td>120.8</td>
<td>3.851</td>
</tr>
<tr>
<td>Lower Proterozoic gneisses, Nimbuwah Complex</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4081C</td>
<td>7.0</td>
<td>40.0</td>
<td>0.1055</td>
<td>0.51059</td>
<td>-24.4</td>
<td>2236</td>
<td>17.1</td>
<td>20.1</td>
<td>17.494</td>
</tr>
<tr>
<td>4069D$^4$</td>
<td>5.6</td>
<td>44.3</td>
<td>0.0771</td>
<td>0.51018</td>
<td>-32.4</td>
<td>2227</td>
<td>217</td>
<td>301</td>
<td>2.089</td>
</tr>
<tr>
<td>Lower Proterozoic schists, Cahill Formation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M096V/223.5</td>
<td>4.31</td>
<td>32.48</td>
<td>0.0804</td>
<td>0.510437</td>
<td>-27.3</td>
<td>2010</td>
<td>117</td>
<td>20.1</td>
<td>17.494</td>
</tr>
<tr>
<td>T141V/240.6$^6$</td>
<td>5.61</td>
<td>33.32</td>
<td>0.1017</td>
<td>0.510477</td>
<td>-26.6</td>
<td>2305</td>
<td>178</td>
<td>21.20</td>
<td>25.715</td>
</tr>
<tr>
<td>JA185/78.2$^6$</td>
<td>7.48</td>
<td>41.63</td>
<td>0.1087</td>
<td>0.510494</td>
<td>-26.2</td>
<td>2421</td>
<td>178</td>
<td>21.20</td>
<td>25.715</td>
</tr>
<tr>
<td>R4037$^4$</td>
<td>2.68</td>
<td>12.39</td>
<td>0.1308</td>
<td>0.510707</td>
<td>-22.1</td>
<td>2644</td>
<td>122</td>
<td>131.5</td>
<td>2.703</td>
</tr>
<tr>
<td>R4024$^6$</td>
<td>16.93</td>
<td>103.3</td>
<td>0.0960</td>
<td>0.510105</td>
<td>-33.8</td>
<td>2638</td>
<td>295.3</td>
<td>153</td>
<td>5.681</td>
</tr>
<tr>
<td>R4018$^6$</td>
<td>6.11</td>
<td>34.37</td>
<td>0.1075</td>
<td>0.510351</td>
<td>-29.0</td>
<td>2579</td>
<td>39.6</td>
<td>98.7</td>
<td>10.369</td>
</tr>
<tr>
<td>N116/85</td>
<td>5.35</td>
<td>30.81</td>
<td>0.1051</td>
<td>0.510485</td>
<td>-26.6</td>
<td>2360</td>
<td>178</td>
<td>21.20</td>
<td>25.715</td>
</tr>
<tr>
<td>N96/30</td>
<td>11.07</td>
<td>56.52</td>
<td>0.1184</td>
<td>0.510561</td>
<td>-24.9</td>
<td>2470</td>
<td>127</td>
<td>20.00</td>
<td>19.116</td>
</tr>
<tr>
<td>N83/38$^6$</td>
<td>25.34</td>
<td>131.0</td>
<td>0.1169</td>
<td>0.510631</td>
<td>-23.5</td>
<td>2412</td>
<td>190.4</td>
<td>14.71</td>
<td>41.63</td>
</tr>
<tr>
<td>K87/85$^6$</td>
<td>4.15</td>
<td>21.68</td>
<td>0.1157</td>
<td>0.510700</td>
<td>-22.2</td>
<td>2291</td>
<td>178</td>
<td>21.20</td>
<td>25.715</td>
</tr>
<tr>
<td>Lower Proterozoic carbonates, Cahill Formation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X081V/87.6</td>
<td>2.02</td>
<td>6.43</td>
<td>0.1900</td>
<td>0.511243</td>
<td>-11.6</td>
<td>0.09</td>
<td>22.90</td>
<td>0.011</td>
<td>0.71013</td>
</tr>
<tr>
<td>S111V/104.1</td>
<td>0.55</td>
<td>1.62</td>
<td>0.2048</td>
<td>0.511030</td>
<td>-15.8</td>
<td>0.05</td>
<td>24.25</td>
<td>0.006</td>
<td>0.70988</td>
</tr>
<tr>
<td>Y069V/76.3</td>
<td>1.02</td>
<td>2.29</td>
<td>0.2710</td>
<td>0.512318</td>
<td>9.4</td>
<td>0.19</td>
<td>4.04</td>
<td>0.1402</td>
<td>0.71236</td>
</tr>
<tr>
<td>Lower Proterozoic amphibolite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N259/30</td>
<td>4.22</td>
<td>17.85</td>
<td>0.1431</td>
<td>0.510971</td>
<td>-16.9</td>
<td>2448</td>
<td>43.62</td>
<td>125.3</td>
<td>1.0076</td>
</tr>
<tr>
<td>N259/72</td>
<td>3.93</td>
<td>16.84</td>
<td>0.1411</td>
<td>0.510935</td>
<td>-17.6</td>
<td>2458</td>
<td>30.10</td>
<td>178</td>
<td>0.4900</td>
</tr>
<tr>
<td>N2/70$^6$</td>
<td>1.72</td>
<td>7.00</td>
<td>0.1485</td>
<td>0.511069</td>
<td>-15.0</td>
<td>2539</td>
<td>51.48</td>
<td>26.45</td>
<td>5.8067</td>
</tr>
<tr>
<td>B1054/200.4</td>
<td>2.03</td>
<td>7.31</td>
<td>0.1677</td>
<td>0.511426</td>
<td>-8.0</td>
<td>2466</td>
<td>7.35</td>
<td>68.8</td>
<td>0.3086</td>
</tr>
<tr>
<td>B1054/203.5</td>
<td>2.22</td>
<td>7.58</td>
<td>0.1773</td>
<td>0.511573</td>
<td>-5.1</td>
<td>2471</td>
<td>33.73</td>
<td>109.2</td>
<td>0.8939</td>
</tr>
<tr>
<td>B1054/251.8</td>
<td>1.56</td>
<td>5.95</td>
<td>0.1598</td>
<td>0.511317</td>
<td>-10.2</td>
<td>2404</td>
<td>32.23</td>
<td>137.8</td>
<td>0.6762</td>
</tr>
<tr>
<td>B1054/465.3</td>
<td>2.67</td>
<td>11.68</td>
<td>0.1428</td>
<td>0.511197</td>
<td>-12.5</td>
<td>2130</td>
<td>13.10</td>
<td>6.21</td>
<td>6.1731</td>
</tr>
<tr>
<td>B1054/542.5</td>
<td>7.29</td>
<td>29.00</td>
<td>0.1522</td>
<td>0.511228</td>
<td>-11.9</td>
<td>2339</td>
<td>35.19</td>
<td>119.0</td>
<td>0.8579</td>
</tr>
<tr>
<td>Oenpelli Dolerite (margin m, granophyric g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N23/129.4g</td>
<td>11.47</td>
<td>48.48</td>
<td>0.1431</td>
<td>0.511246</td>
<td>-11.5</td>
<td>26.39</td>
<td>87.52</td>
<td>0.8711</td>
<td>0.72425</td>
</tr>
<tr>
<td>N23/196.2</td>
<td>2.68</td>
<td>10.97</td>
<td>0.1479</td>
<td>0.511283</td>
<td>-10.8</td>
<td>17.42</td>
<td>299.0</td>
<td>0.1682</td>
<td>0.70776</td>
</tr>
<tr>
<td>Sample</td>
<td>Sm</td>
<td>Nd</td>
<td>147Sm/144Nd</td>
<td>143Nd/144Nd</td>
<td>εNd(0)^2</td>
<td>TDM</td>
<td>Rb</td>
<td>Sr</td>
<td>87Sr/86Sr</td>
</tr>
<tr>
<td>-----------------</td>
<td>-----</td>
<td>-----</td>
<td>-------------</td>
<td>-------------</td>
<td>----------</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>----------</td>
</tr>
<tr>
<td>N23/302.4</td>
<td>3.61</td>
<td>14.94</td>
<td>0.1461</td>
<td>0.511267</td>
<td>-11.1</td>
<td>46.54</td>
<td>289</td>
<td>0.4653</td>
<td>0.71488</td>
</tr>
<tr>
<td>N83/53.4m</td>
<td>1.92</td>
<td>6.35</td>
<td>0.1828</td>
<td>0.511368</td>
<td>-9.2</td>
<td>1.10</td>
<td>3.73</td>
<td>0.8542</td>
<td>0.72541</td>
</tr>
<tr>
<td>N83/73.7g</td>
<td>10.04</td>
<td>43.61</td>
<td>0.1393</td>
<td>0.511175</td>
<td>-12.9</td>
<td>32.18</td>
<td>83.09</td>
<td>1.1193</td>
<td>0.73084</td>
</tr>
<tr>
<td>N83/185</td>
<td>2.75</td>
<td>11.06</td>
<td>0.1504</td>
<td>0.511291</td>
<td>-10.7</td>
<td>38.66</td>
<td>334</td>
<td>0.3338</td>
<td>0.71260</td>
</tr>
<tr>
<td>N83/298m</td>
<td>4.13</td>
<td>17.27</td>
<td>0.1447</td>
<td>0.511216</td>
<td>-12.1</td>
<td>32.57</td>
<td>285</td>
<td>0.3317</td>
<td>0.71380</td>
</tr>
</tbody>
</table>

Nabarlek Granite (strongly altered, a)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sm</th>
<th>Nd</th>
<th>147Sm/144Nd</th>
<th>143Nd/144Nd</th>
<th>εNd(0)^2</th>
<th>TDM</th>
<th>Rb</th>
<th>Sr</th>
<th>87Sr/86Sr</th>
<th>87Sr/86Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>N23/492</td>
<td>11.44</td>
<td>64.05</td>
<td>0.1081</td>
<td>0.510352</td>
<td>-29.0</td>
<td>2540</td>
<td>322</td>
<td>26.72</td>
<td>51.916</td>
<td>1.61365</td>
</tr>
<tr>
<td>N23/482</td>
<td>12.85</td>
<td>73.55</td>
<td>0.1056</td>
<td>0.510321</td>
<td>-29.4</td>
<td>2577</td>
<td>351</td>
<td>52.84</td>
<td>20.461</td>
<td>1.20846</td>
</tr>
<tr>
<td>N83/463a</td>
<td>5.53</td>
<td>11.16</td>
<td>0.2998</td>
<td>0.512571</td>
<td>14.4</td>
<td>294</td>
<td>9.32</td>
<td>93.79</td>
<td>2.20766</td>
<td></td>
</tr>
<tr>
<td>N83/484a</td>
<td>3.71</td>
<td>8.29</td>
<td>0.2709</td>
<td>0.511836</td>
<td>0.0</td>
<td>426</td>
<td>25.07</td>
<td>55.329</td>
<td>1.99949</td>
<td></td>
</tr>
</tbody>
</table>

Mid Proterozoic Kombolgie Formation sandstones (chloritized, ch)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sm</th>
<th>Nd</th>
<th>147Sm/144Nd</th>
<th>143Nd/144Nd</th>
<th>εNd(0)^2</th>
<th>TDM</th>
<th>Rb</th>
<th>Sr</th>
<th>87Sr/86Sr</th>
<th>87Sr/86Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z141V/59</td>
<td>2.71</td>
<td>19.04</td>
<td>0.0862</td>
<td>0.510408</td>
<td>-27.9</td>
<td>2125</td>
<td>17.19</td>
<td>14.76</td>
<td>3.3879</td>
<td>0.78768</td>
</tr>
<tr>
<td>Z141ND/71</td>
<td>2.66</td>
<td>20.12</td>
<td>0.0799</td>
<td>0.510260</td>
<td>-30.8</td>
<td>2187</td>
<td>28.25</td>
<td>20.64</td>
<td>3.9899</td>
<td>0.80413</td>
</tr>
<tr>
<td>Z141ND/71$^5$</td>
<td>10.63</td>
<td>90.61</td>
<td>0.0709</td>
<td>0.510257</td>
<td>-30.8</td>
<td>2063</td>
<td>126</td>
<td>98.10</td>
<td>4.5345</td>
<td>0.81365</td>
</tr>
<tr>
<td>X141V/65.8ch</td>
<td>17.41</td>
<td>38.47</td>
<td>0.2737</td>
<td>0.512290</td>
<td>8.9</td>
<td>0.64</td>
<td>15.87</td>
<td>0.1174</td>
<td>0.71322</td>
<td></td>
</tr>
<tr>
<td>S141S/95.5ch$^6$</td>
<td>10.75</td>
<td>78.73</td>
<td>0.0826</td>
<td>0.510215</td>
<td>-31.7</td>
<td>2275</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Mid Proterozoic Nungbalgerri Volcanics

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sm</th>
<th>Nd</th>
<th>147Sm/144Nd</th>
<th>143Nd/144Nd</th>
<th>εNd(0)^2</th>
<th>TDM</th>
<th>Rb</th>
<th>Sr</th>
<th>87Sr/86Sr</th>
<th>87Sr/86Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>4073$^4$</td>
<td>5.76</td>
<td>27.43</td>
<td>0.1270</td>
<td>0.510856</td>
<td>-19.2</td>
<td>2313</td>
<td>35.4</td>
<td>161</td>
<td>0.6364</td>
<td>0.72099</td>
</tr>
<tr>
<td>4075$^4$</td>
<td>5.66</td>
<td>26.51</td>
<td>0.1292</td>
<td>0.510892</td>
<td>-18.5</td>
<td>2310</td>
<td>106</td>
<td>249</td>
<td>1.2309</td>
<td>0.73522</td>
</tr>
<tr>
<td>4076$^4$</td>
<td>5.68</td>
<td>26.78</td>
<td>0.1282</td>
<td>0.510917</td>
<td>-18.0</td>
<td>2247</td>
<td>43.6</td>
<td>166.3</td>
<td>0.7574</td>
<td>0.72371</td>
</tr>
</tbody>
</table>

1. Uncertainties in $^{143}$Nd/$^{144}$Nd ≤ 0.000035 (2σmean); uncertainties in $^{87}$Sr/$^{86}$Sr ≤ 0.00010 (2σmean).
2. $\varepsilon_{Nd}(0)$ standard notation as defined in Table 3.
3. $T_{DM}$, depleted mantle model age. For definition and DM parameters see Liew and McCulloch (1985).
4. Rb-Sr data from Page et al. (1980).
5. Fine-grained matrix (< 2µm) of sandstone.
6. Measured on MAT 261 and recalculated, see Table 1.

Samples labelled N are from Nabarlek, R=Ranger, K=Koongarra, those with other letters as prefixes are from Jabiluka. Samples names starting with '4' are regional samples; sample locations in Page et al. (1980).
<table>
<thead>
<tr>
<th>sample</th>
<th>U(%)</th>
<th>Sm</th>
<th>Nd</th>
<th>$^{147}\text{Sm}/^{144}\text{Nd}$</th>
<th>$^{143}\text{Nd}/^{144}\text{Nd}$</th>
<th>$\varepsilon_{\text{Nd}}(O)^{3}$</th>
<th>Rb</th>
<th>Sr</th>
<th>$^{87}\text{Rb}/^{86}\text{Sr}$</th>
<th>$^{87}\text{Sr}/^{86}\text{Sr}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA2/21</td>
<td>12.65</td>
<td>76.7</td>
<td>137.5</td>
<td>0.3374</td>
<td>0.513223$^{2}$</td>
<td>27.1</td>
<td>144.6</td>
<td>15.96</td>
<td>27.029</td>
<td>1.04405</td>
</tr>
<tr>
<td>NA2/25</td>
<td>8.4</td>
<td>56.3</td>
<td>138</td>
<td>0.2462</td>
<td>0.512067$^{2}$</td>
<td>4.5</td>
<td>52.3</td>
<td>11.9</td>
<td>13.071</td>
<td>1.00678</td>
</tr>
<tr>
<td>NA2/30</td>
<td>1.35</td>
<td>4.70</td>
<td>0.1737</td>
<td>0.511434</td>
<td>-7.9</td>
<td>1.25</td>
<td>22.49</td>
<td>0.1638</td>
<td>0.92359</td>
<td></td>
</tr>
<tr>
<td>NA2/35</td>
<td>69 ppm</td>
<td>0.96</td>
<td>2.23</td>
<td>0.2598</td>
<td>0.511955</td>
<td>2.31</td>
<td>96.0</td>
<td>5.51</td>
<td>56.513</td>
<td>1.97321</td>
</tr>
<tr>
<td>NA2/50</td>
<td>18 ppm</td>
<td>1.98</td>
<td>7.78</td>
<td>0.1537</td>
<td>0.511180</td>
<td>-12.8</td>
<td>64.05</td>
<td>5.03</td>
<td>40.123</td>
<td>1.64384</td>
</tr>
<tr>
<td>NA2/55</td>
<td>17 ppm</td>
<td>3.33</td>
<td>10.75</td>
<td>0.1877</td>
<td>0.511644</td>
<td>-3.8</td>
<td>111.6</td>
<td>3.93</td>
<td>100.152</td>
<td>2.97570</td>
</tr>
<tr>
<td>- leach</td>
<td>4</td>
<td>7.1</td>
<td>33.5</td>
<td>0.1276</td>
<td>0.511001</td>
<td>-16.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NA4/31.5</td>
<td>26.9</td>
<td>56.3</td>
<td>75.8</td>
<td>0.4492</td>
<td>0.514293$^{2}$</td>
<td>48.0</td>
<td>4.24</td>
<td>37.86</td>
<td>0.3236</td>
<td>0.71581</td>
</tr>
<tr>
<td>NA4/40</td>
<td>57.42</td>
<td>137</td>
<td>172</td>
<td>0.4823</td>
<td>0.514544$^{2}$</td>
<td>52.9</td>
<td>0.84</td>
<td>34.31</td>
<td>0.0708</td>
<td>0.71386</td>
</tr>
<tr>
<td>NA #2</td>
<td>59.7</td>
<td>94</td>
<td>142</td>
<td>0.3998</td>
<td>0.513809$^{2}$</td>
<td>38.6</td>
<td>0.53</td>
<td>52.27</td>
<td>0.0293</td>
<td>0.71189</td>
</tr>
<tr>
<td>NA #3</td>
<td>4.07</td>
<td>15.25</td>
<td>20.49</td>
<td>0.4500</td>
<td>0.514431$^{2}$</td>
<td>50.7</td>
<td>1.28</td>
<td>8.29</td>
<td>0.4481</td>
<td>0.71776</td>
</tr>
<tr>
<td>NA #4</td>
<td>56.96</td>
<td>96</td>
<td>149</td>
<td>0.3888</td>
<td>0.513732$^{2}$</td>
<td>37.1</td>
<td>0.23</td>
<td>57.55</td>
<td>0.0114</td>
<td>0.71208</td>
</tr>
<tr>
<td>- ur</td>
<td>111</td>
<td>166</td>
<td>0.4028</td>
<td>0.513804$^{2}$</td>
<td>38.5</td>
<td>2.88</td>
<td>58.71</td>
<td>0.2496</td>
<td>0.71167</td>
<td></td>
</tr>
<tr>
<td>NA69/42</td>
<td>64.35</td>
<td>124</td>
<td>275</td>
<td>0.2740</td>
<td>0.512471$^{2}$</td>
<td>12.4</td>
<td>0.22</td>
<td>36.27</td>
<td>0.0175</td>
<td>0.71460</td>
</tr>
<tr>
<td>- ur</td>
<td>145</td>
<td>323</td>
<td>0.2707</td>
<td>0.512425$^{2}$</td>
<td>11.5</td>
<td>0.59</td>
<td>32.40</td>
<td>0.0525</td>
<td>0.71330</td>
<td></td>
</tr>
<tr>
<td>NA69/43.2</td>
<td>46.48</td>
<td>129</td>
<td>292</td>
<td>0.2671</td>
<td>0.512419$^{2}$</td>
<td>11.4</td>
<td>4.44</td>
<td>91.67</td>
<td>0.1399</td>
<td>0.71246</td>
</tr>
<tr>
<td>- ur</td>
<td>179</td>
<td>405</td>
<td>0.2661</td>
<td>0.512409$^{2}$</td>
<td>11.3</td>
<td>1.27</td>
<td>33.37</td>
<td>0.0624</td>
<td>0.71440</td>
<td></td>
</tr>
<tr>
<td>NA69/44</td>
<td>2.9</td>
<td>3.78</td>
<td>6.44</td>
<td>0.3557</td>
<td>0.512373$^{2}$</td>
<td>10.5</td>
<td>48.17</td>
<td>12.46</td>
<td>11.398</td>
<td>0.92086</td>
</tr>
<tr>
<td>NA94/41.3</td>
<td>14.5</td>
<td>3.27</td>
<td>4.69</td>
<td>0.4209</td>
<td>0.512875$^{2}$</td>
<td>20.3</td>
<td>269</td>
<td>33.51</td>
<td>24.346</td>
<td>1.22823</td>
</tr>
<tr>
<td>- wm</td>
<td>1.49</td>
<td>2.25</td>
<td>0.3989</td>
<td>0.513016</td>
<td>23.1</td>
<td>287</td>
<td>28.97</td>
<td>30.265</td>
<td>1.30464</td>
<td></td>
</tr>
<tr>
<td>NA94/44.6 - hem</td>
<td>2.39</td>
<td>4.78</td>
<td>0.3034</td>
<td>0.251505</td>
<td>13.1</td>
<td>113</td>
<td>31.29</td>
<td>10.563</td>
<td>0.87576</td>
<td></td>
</tr>
<tr>
<td>NA94/45.3</td>
<td>23.8</td>
<td>87.4</td>
<td>185.3</td>
<td>0.2854</td>
<td>0.512609$^{2}$</td>
<td>15.1</td>
<td>161</td>
<td>32.31</td>
<td>14.573</td>
<td>0.84749</td>
</tr>
<tr>
<td>NA94/45.5</td>
<td>6.4</td>
<td>22.32</td>
<td>41.24</td>
<td>0.3273</td>
<td>0.512619$^{2}$</td>
<td>15.3</td>
<td>191</td>
<td>29.29</td>
<td>19.380</td>
<td>1.01107</td>
</tr>
<tr>
<td>NA96/65</td>
<td>9.7</td>
<td>9.99</td>
<td>24.35</td>
<td>0.2482</td>
<td>0.511601$^{2}$</td>
<td>-4.6</td>
<td>230</td>
<td>41.90</td>
<td>16.469</td>
<td>1.12676</td>
</tr>
<tr>
<td>NA193/17.1</td>
<td>0.25</td>
<td>8.46</td>
<td>38.99</td>
<td>0.1312</td>
<td>0.510672</td>
<td>-22.7</td>
<td>152</td>
<td>29.21</td>
<td>15.532</td>
<td>1.05744</td>
</tr>
<tr>
<td>NA193/19</td>
<td>3.65</td>
<td>8.28</td>
<td>0.2667</td>
<td>0.512276</td>
<td>8.6</td>
<td>90</td>
<td>9.15</td>
<td>30.138</td>
<td>1.34363</td>
<td></td>
</tr>
<tr>
<td>NA193/19.1</td>
<td>2.1</td>
<td>15.81</td>
<td>34.45</td>
<td>0.2775</td>
<td>0.512583$^{2}$</td>
<td>14.6</td>
<td>48.65</td>
<td>8.27</td>
<td>17.450</td>
<td>0.99147</td>
</tr>
<tr>
<td>NA193/22</td>
<td>15.0</td>
<td>121</td>
<td>148</td>
<td>0.4932</td>
<td>0.514846$^{2}$</td>
<td>58.8</td>
<td>76.5</td>
<td>16.00</td>
<td>14.180</td>
<td>0.98629</td>
</tr>
<tr>
<td>NA256/26</td>
<td>0.46</td>
<td>5.54</td>
<td>22.03</td>
<td>0.1521</td>
<td>0.511108</td>
<td>-14.2</td>
<td>7.52</td>
<td>21.78</td>
<td>0.9993</td>
<td>0.73001</td>
</tr>
<tr>
<td>NA256/23-30</td>
<td>1.02</td>
<td>11.48</td>
<td>52.91</td>
<td>0.1313</td>
<td>0.510845</td>
<td>-19.4</td>
<td>51.28</td>
<td>58.47</td>
<td>2.5461</td>
<td>0.76228</td>
</tr>
</tbody>
</table>

1. uncertainties in $^{143}\text{Nd}/^{144}\text{Nd} \leq 0.000035$ (2σ$_{\text{mean}}$) except for samples labelled $^{2}$; uncertainties in $^{87}\text{Sr}/^{86}\text{Sr}$ = 0.00010
2. uncertainties in $^{143}\text{Nd}/^{144}\text{Nd}$ ratios corrected for fission Nd assumed to be 0.00005 (2σ$_{\text{mean}}$).
3. $\varepsilon_{\text{Nd}} = \left( \frac{^{143}\text{Nd}/^{144}\text{Nd}_{\text{meas}}}{^{143}\text{Nd}/^{144}\text{Nd}_{\text{CHUR}}} - 1 \right) \times 10^{4}$, with present day $^{143}\text{Nd}/^{144}\text{Nd}_{\text{CHUR}} = 0.511836$
4. sample leached with hot HNO$_{3}$ for ca. 2 hours; leach solution decanted, spiked and measured. Sample weight in leach solution determined by difference on dried residue.

ur = uraninite, wm = white mica, possibly with illite, hem = hematite
<table>
<thead>
<tr>
<th>Sample</th>
<th>Sm</th>
<th>Nd</th>
<th>$^{147}$Sm/$^{144}$Nd</th>
<th>$^{143}$Nd/$^{144}$Nd</th>
<th>$\epsilon_{Nd}(O)$</th>
<th>Rb</th>
<th>$^{87}$Rb/$^{86}$Sr</th>
<th>$^{87}$Sr/$^{86}$Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>S153V/238.8tr</td>
<td>145</td>
<td>228</td>
<td>0.3839</td>
<td>0.513586</td>
<td>34.2</td>
<td>4.03</td>
<td>31.84</td>
<td>0.3660</td>
</tr>
<tr>
<td>S153V/238.8</td>
<td>257</td>
<td>395</td>
<td>0.3940</td>
<td>0.513581</td>
<td>34.1</td>
<td>2.41</td>
<td>38.88</td>
<td>0.1790</td>
</tr>
<tr>
<td>&quot;</td>
<td>250</td>
<td>385</td>
<td>0.3931</td>
<td>0.513600</td>
<td>34.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W141V2/88tr</td>
<td>420</td>
<td>826</td>
<td>0.3078</td>
<td>0.511906</td>
<td>1.4</td>
<td>0.31</td>
<td>11.77</td>
<td>0.0761</td>
</tr>
<tr>
<td>W141V2/88</td>
<td>1069</td>
<td>1962</td>
<td>0.3297</td>
<td>0.512154</td>
<td>6.2</td>
<td>0.28</td>
<td>32.25</td>
<td>0.0247</td>
</tr>
<tr>
<td>T141V/237</td>
<td>518</td>
<td>923</td>
<td>0.3395</td>
<td>0.513037</td>
<td>23.5</td>
<td>0.62</td>
<td>61.32</td>
<td>0.0294</td>
</tr>
<tr>
<td>T141V/238</td>
<td>499</td>
<td>850</td>
<td>0.3551</td>
<td>0.513135</td>
<td>25.4</td>
<td>4.70</td>
<td>54.16</td>
<td>0.2511</td>
</tr>
<tr>
<td>T141V/238vein</td>
<td>505</td>
<td>867</td>
<td>0.3520</td>
<td>0.513093</td>
<td>24.6</td>
<td>0.80</td>
<td>56.44</td>
<td>0.0409</td>
</tr>
<tr>
<td>T141V/248.8</td>
<td>449</td>
<td>880</td>
<td>0.3086</td>
<td>0.512752</td>
<td>17.9</td>
<td>1.31</td>
<td>49.71</td>
<td>0.0762</td>
</tr>
<tr>
<td>S180V/232</td>
<td>668</td>
<td>787</td>
<td>0.5132</td>
<td>0.514882</td>
<td>59.5</td>
<td>5.76</td>
<td>35.51</td>
<td>0.4692</td>
</tr>
<tr>
<td>&quot;</td>
<td>667</td>
<td>787</td>
<td>0.5125</td>
<td>0.514853</td>
<td>59.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S180V/232.8</td>
<td>657</td>
<td>636</td>
<td>0.6252</td>
<td>0.515560</td>
<td>73.8</td>
<td>8.34</td>
<td>29.91</td>
<td>0.8060</td>
</tr>
<tr>
<td>&quot;</td>
<td>661</td>
<td>637</td>
<td>0.6278</td>
<td>0.515540</td>
<td>72.4</td>
<td>11.04</td>
<td>31.87</td>
<td>1.0017</td>
</tr>
<tr>
<td>&quot;</td>
<td>654</td>
<td>633</td>
<td>0.6254</td>
<td>0.515544</td>
<td>72.5</td>
<td>7.79</td>
<td>28.80</td>
<td>0.8004</td>
</tr>
<tr>
<td>&quot;</td>
<td>7</td>
<td>494</td>
<td>455</td>
<td>0.515531</td>
<td>74.0</td>
<td>6.85</td>
<td>27.29</td>
<td>0.8052</td>
</tr>
<tr>
<td>M141ND/328.2</td>
<td>612</td>
<td>1235</td>
<td>0.2996</td>
<td>0.512398</td>
<td>11.0</td>
<td>1.71</td>
<td>45.00</td>
<td>0.1098</td>
</tr>
<tr>
<td>O186V/2418</td>
<td>1034</td>
<td>1503</td>
<td>0.4164</td>
<td>0.512349</td>
<td>10.1</td>
<td>3.81</td>
<td>40.52</td>
<td>0.2719</td>
</tr>
</tbody>
</table>

1 samples dissolved in hot HNO3, one aliquot spiked with mixed Sm-Nd and Rb-Sr tracers
2 as in Table 3 except for samples labelled 3.
3 uncertainties in $^{143}$Nd/$^{144}$Nd ratios corrected for fission Nd are 0.000050 (2σ_{mean})
4 as in Table 3
5 sample fully spiked with mixed Sm-Nd and Rb-Sr tracers prior to HNO3 dissolution
6 sample finely crushed, boiled repeatedly with distilled water to remove fluid inclusions, the spiked and dissolved in HNO3
7 sample leached in warm, dilute HCl; one aliquot spiked, dissolved in HNO3
9 uraninite in Kombolgie Formation

tr = total rock sample, concentrations in ppm
Table 5 Sm-Nd and Rb-Sr isotopic data for uraninites from Koongarra

<table>
<thead>
<tr>
<th>sample</th>
<th>Sm</th>
<th>Nd</th>
<th>$^{147}$Sm/$^{144}$Nd</th>
<th>$^{143}$Nd/$^{144}$Nd</th>
<th>$\varepsilon_{Nd}(0)$</th>
<th>Rb</th>
<th>Sr</th>
<th>$^{87}$Rb/$^{86}$Sr</th>
<th>$^{87}$Sr/$^{86}$Sr$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.1 lens</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>87/90.5</td>
<td>264</td>
<td>266</td>
<td>0.5993</td>
<td>0.516270$^3$</td>
<td>86.6</td>
<td>7.41</td>
<td>21.99</td>
<td>0.9732</td>
<td>0.71276</td>
</tr>
<tr>
<td>87/90.77</td>
<td>288</td>
<td>307</td>
<td>0.5671</td>
<td>0.516118$^3$</td>
<td>83.7</td>
<td>2.72</td>
<td>23.45</td>
<td>0.3361</td>
<td>0.71329</td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.31</td>
<td>22.69</td>
<td>0.4220</td>
<td>0.71293</td>
</tr>
<tr>
<td>87/90.8vein</td>
<td>288</td>
<td>301</td>
<td>0.5786</td>
<td>0.516154$^3$</td>
<td>84.4</td>
<td>4.15</td>
<td>22.36</td>
<td>0.5366</td>
<td>0.71323</td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.03</td>
<td>23.62</td>
<td>0.4926</td>
<td>0.71261</td>
</tr>
<tr>
<td>87/90.8vein-2</td>
<td>276</td>
<td>296</td>
<td>0.5633</td>
<td>0.516139$^3$</td>
<td>84.1</td>
<td>4.45</td>
<td>22.99</td>
<td>0.5589</td>
<td>0.71398</td>
</tr>
<tr>
<td>&quot;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.54</td>
<td>23.48</td>
<td>0.4350</td>
<td>0.71252</td>
</tr>
<tr>
<td>87/91.7</td>
<td>337</td>
<td>304</td>
<td>0.6693</td>
<td>0.516446$^3$</td>
<td>90.1</td>
<td>0.38</td>
<td>26.17</td>
<td>0.0421</td>
<td>0.71406</td>
</tr>
<tr>
<td>87/94.2</td>
<td>251</td>
<td>216</td>
<td>0.7025</td>
<td>0.517586</td>
<td>112.4</td>
<td>0.44</td>
<td>23.66</td>
<td>0.0538</td>
<td>0.71969</td>
</tr>
<tr>
<td>No.2 lens</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>94/146.6</td>
<td>232</td>
<td>249</td>
<td>0.5626</td>
<td>0.515796</td>
<td>77.4</td>
<td>5.21</td>
<td>63.89</td>
<td>0.2354</td>
<td>0.71616</td>
</tr>
<tr>
<td>94/147.4</td>
<td>358</td>
<td>418</td>
<td>0.5186</td>
<td>0.515015$^3$</td>
<td>62.1</td>
<td>1.83</td>
<td>41.65</td>
<td>0.1270</td>
<td>0.71558</td>
</tr>
<tr>
<td>94/147.8</td>
<td>366</td>
<td>379</td>
<td>0.5837</td>
<td>0.515721</td>
<td>75.9</td>
<td>1.23</td>
<td>48.91</td>
<td>0.0727</td>
<td>0.71546</td>
</tr>
<tr>
<td>94/147.9</td>
<td>224</td>
<td>243</td>
<td>0.5585</td>
<td>0.515568</td>
<td>72.9</td>
<td>1.46</td>
<td>36.36</td>
<td>0.1163</td>
<td>0.71741</td>
</tr>
</tbody>
</table>

1 samples dissolved in HNO$_3$, one aliquot spiked with mixed Sm-Nd and Rb-Sr tracers
2 as in Table 3
3 corrected for fissionogenic Nd, uncertainty in $^{143}$Nd/$^{144}$Nd set to 0.000050 (2σ$_{mean}$)
4 samples leached in warm diluted HCl, then spiked and dissolved in HNO$_3$
Table 6 Sm-Nd and Rb-Sr isotopic data for uraninites from Ranger

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sm</th>
<th>Nd</th>
<th>$^{147}\text{Sm}/^{144}\text{Nd}$</th>
<th>$^{143}\text{Nd}/^{144}\text{Nd}$</th>
<th>$\varepsilon_{\text{Nd}}(0)$</th>
<th>Rb</th>
<th>Sr</th>
<th>$^{87}\text{Rb}/^{86}\text{Sr}$</th>
<th>$^{87}\text{Sr}/^{86}\text{Sr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ranger F</td>
<td>257</td>
<td>219</td>
<td>0.7115</td>
<td>0.516953$^3$</td>
<td>100.0</td>
<td>7.38</td>
<td>26.23</td>
<td>0.8140</td>
<td>0.72603</td>
</tr>
<tr>
<td>Ranger G</td>
<td>163</td>
<td>161</td>
<td>0.6128</td>
<td>0.516134$^3$</td>
<td>84.0</td>
<td>3.91</td>
<td>23.49</td>
<td>0.4816</td>
<td>0.72999</td>
</tr>
<tr>
<td>Ranger H</td>
<td>281</td>
<td>305</td>
<td>0.5575</td>
<td>0.515806$^3$</td>
<td>77.6</td>
<td>0.72</td>
<td>18.74</td>
<td>0.1120</td>
<td>0.73399</td>
</tr>
<tr>
<td>Ranger I</td>
<td>138</td>
<td>155</td>
<td>0.5391</td>
<td>0.515514$^3$</td>
<td>71.9</td>
<td>2.11</td>
<td>22.22</td>
<td>0.2748</td>
<td>0.73087</td>
</tr>
<tr>
<td>Ranger J</td>
<td>1409</td>
<td>1307</td>
<td>0.6522</td>
<td>0.516311$^3$</td>
<td>87.4</td>
<td>0.41</td>
<td>24.34</td>
<td>0.0493</td>
<td>0.72791</td>
</tr>
<tr>
<td>Ranger K</td>
<td>297</td>
<td>267</td>
<td>0.6731</td>
<td>0.517004$^3$</td>
<td>101.0</td>
<td>4.33</td>
<td>21.39</td>
<td>0.5859</td>
<td>0.73838</td>
</tr>
</tbody>
</table>

1. samples dissolved in hot HNO$_3$, aliquot spiked with mixed Sm-Nd and Rb-Sr tracers
2. as in Table 3
3. corrected for fissionogenic Nd, uncertainty set at 0.000050 ($2\sigma_{\text{mean}}$)
4. sample spiked before dissolution
5. sample finely crushed, boiled repeatedly in distilled water to remove fluid inclusions, spiked, then dissolved in HNO$_3$
Fig. 2

Nabarlek Shear

Outcrop of U orebody before mining

Drillholes sampled

Fault

100 m

Inner halo alteration
(pre-ore chlorite, hematite, phengitic mica)

Outer halo alteration

No ore-related alteration
Fig. 3

Fig. 4
Fig. 5

A

B

1619±30 Ma 0.704±3

880±11 Ma 0.9215±4

= 900 Ma

see A

0.710 0.712 0.714 0.716 0.718

0.000 0.100 0.200 0.300 0.400 0.500

87Sr/86Sr

87Rb/86Sr
Nabarlek ores at 1616 Ma

Fig. 6
Jabiluka

1614±132 Ma

\( \varepsilon_{Nd} = -6.6 \pm 3.1 \)

Fig. 7

\[ \frac{^{147}Sm}{^{144}Nd} \]

Fig. 8
**Fig. 11**

Koongarra and Ranger uraninites

- 420 Ma
  - $\varepsilon_{\text{Nd}} = 64.6$
- 1270 Ma
  - $\varepsilon_{\text{Nd}} = 17.7$

**Fig. 12**

**Fig. 13**
Fig. 13
Fig. 14
APPENDIX 3B

REE measurements on standard and U ore samples from Nabarlek

Abundances of La, Ce, Sm, Eu, Dy and Yb were measured in 11 U ore samples using Inductively Coupled Plasma Spectrometry (ICP) (see Fig. App3B-1). To check analytical accuracy, 3 samples of known REE concentrations were measured in the same batch. These were: standard reference sample BHVO-1 and two in-house standards, the basanite 2128 and the Burstall Granite rhyolite dike 237G. Ca. 200 mg of sample powder were dissolved in open beakers using HF-HClO4-HCl for silicate-rich samples, and HNO3 for samples consisting predominantly of uraninite. Apart from some undissolved sulfide and hematite in the HNO3 experiments, complete dissolution was achieved. The sample solutions were dried down, redissolved in 10 ml 1N HCl and centrifuged. Except for the mentioned undissolved minerals no residue was visible. To remove the major elements including U, the HCl solution was loaded onto a cation exchange column with 1 cm internal diameter packed with ca. 5 g of AG W50 X-8, giving a settled height of ca. 5 cm in water. After elution of the major and most trace elements in 2 N HCl, the REE were recovered as a group using 4N HCl. This procedure is a variation of commonly used methods for ICP REE analysis (e.g Crock et al, 1984); it concentrates the REE and increases the detection limit by removing most of the background noise caused by major elements.

The measurements were done on a high resolution ICP equipped with dual 1.26 m monochromators with 2400 lines/mm gratings (Shelley and Taylor, 1981). Wavelengths used were: La 3988 Å, Ce 4137 Å, Sm 3468 Å, Eu 4205 Å, Dy 3582 Å second order, Yb 3694 Å. The results for standards and samples are given in Table App 3B-1, the standard results are compared with reference values in Fig. App3B-1. Agreement between ICP data and the reference values is generally good. Fig. Ap3B-2 compares ICP Sm data with isotope dilution Sm results (see appendix 3a). Isotope dilution results are equal to or higher than the ICP results but there is no systematic offset. This suggests that the differences may be largely due to sample heterogeneity and probably some minor yield problems in the sample preparation for ICP analyses.
<table>
<thead>
<tr>
<th>Sample</th>
<th>La</th>
<th>Ce</th>
<th>Sm</th>
<th>Eu</th>
<th>Dy</th>
<th>Yb</th>
</tr>
</thead>
<tbody>
<tr>
<td>BHVO ST</td>
<td>17</td>
<td>39</td>
<td>6.1</td>
<td>2.0</td>
<td>5</td>
<td>1.9</td>
</tr>
<tr>
<td>BHVO M</td>
<td>16.4</td>
<td>37.4</td>
<td>4.8</td>
<td>1.7</td>
<td>5</td>
<td>1.0</td>
</tr>
<tr>
<td>2128 ST</td>
<td>48.7</td>
<td>101</td>
<td>9.7</td>
<td>3</td>
<td>6.4</td>
<td>1.7</td>
</tr>
<tr>
<td>2128 M</td>
<td>48.4</td>
<td>98</td>
<td>8.8</td>
<td>2.9</td>
<td>6</td>
<td>1.4</td>
</tr>
<tr>
<td>237G ST</td>
<td>51</td>
<td>93.6</td>
<td>8.4</td>
<td>0.25</td>
<td>9.5</td>
<td>4.2</td>
</tr>
<tr>
<td>237G M</td>
<td>58</td>
<td>100</td>
<td>8.7</td>
<td>0.25</td>
<td>10</td>
<td>4</td>
</tr>
<tr>
<td>NA 4/40</td>
<td>26.6</td>
<td>197</td>
<td>110</td>
<td>35</td>
<td>744</td>
<td>237</td>
</tr>
<tr>
<td>NA 4/31.5</td>
<td>16</td>
<td>121</td>
<td>54</td>
<td>17</td>
<td>334</td>
<td>121</td>
</tr>
<tr>
<td>NA 69/42</td>
<td>43</td>
<td>529</td>
<td>117</td>
<td>46</td>
<td>637</td>
<td>174</td>
</tr>
<tr>
<td>NA 69/43.2</td>
<td>50</td>
<td>584</td>
<td>123</td>
<td>50</td>
<td>628</td>
<td>176</td>
</tr>
<tr>
<td>NA #2</td>
<td>39</td>
<td>191</td>
<td>77</td>
<td>32</td>
<td>481</td>
<td>158</td>
</tr>
<tr>
<td>NA 193/22</td>
<td>11.6</td>
<td>126</td>
<td>117</td>
<td>44</td>
<td>219</td>
<td>66</td>
</tr>
<tr>
<td>NA 193/19.1</td>
<td>1.9</td>
<td>19.6</td>
<td>9</td>
<td>2.7</td>
<td>11</td>
<td>3.4</td>
</tr>
<tr>
<td>NA 2/21</td>
<td>10.4</td>
<td>115</td>
<td>75</td>
<td>22</td>
<td>141</td>
<td>42</td>
</tr>
<tr>
<td>NA 94/45.3</td>
<td>41</td>
<td>213</td>
<td>87</td>
<td>23</td>
<td>294</td>
<td>82</td>
</tr>
<tr>
<td>NA 69/44</td>
<td>1.2</td>
<td>5.1</td>
<td>2.5</td>
<td>0.7</td>
<td>5</td>
<td>4.2</td>
</tr>
<tr>
<td>NA256A</td>
<td>106</td>
<td>204</td>
<td>11.5</td>
<td>2.6</td>
<td>19.4</td>
<td>8.6</td>
</tr>
</tbody>
</table>

1 Govindaraju (1984); 2 Mt Porndon basanite, Frey et al (1978), Dy estimated; 3 Burstall Granite rhyolite dike 237G, see Table 1b appendix 2, Dy estimated.

Fig.App3B-1 Chondrite-normalized REE abundances in 3 standard samples measured by ICP. The ICP analyses (labelled 'M') compare well with data obtained by other methods (labelled 'ST').
Fig. App3B-2 Sm concentrations in Nabarlek U ores determined by ICP compared with isotope dilution data on the same samples. The deviation from the 1:1 line may be due to sample heterogeneity.
Part 2

Gd, Sm and Nd isotopic anomalies in uranium ores and uraninites from the Nabarlek, Jabiluka, Koongarra and Ranger uranium deposits
1 Introduction

The discovery of natural nuclear reactor zones in the Lower Proterozoic U deposit at Oklo, Gaboun (IAEA, 1975) has encouraged the search for similar phenomena in other Precambrian U deposits. In contrast to younger deposits, any high grade U deposit of about 1500 Ma age or more should have been sufficiently enriched in the fuel isotope $^{235}$U (>2% of natural U) to sustain a nuclear chain reaction at about that time, given that other conditions were favourable. These include the availability of adequate masses of high grade ore (critical mass), light element neutron moderators such as water, graphite etc., and low abundances of strong neutron absorbers such as the rare earth elements (REE), B and others.

Evidence for fossil nuclear reactor activity at Oklo includes drastic isotopic changes in the REE (Loubet and Allegre, 1977), trace alkali and earth-alkali elements (Brookins et al., 1975), noble gases (Drozd et al., 1974) and many other elements due to sustained thermal neutron-induced fission of $^{235}$U plus a small contribution from fast-neutron fission of $^{238}$U. Accordingly, large depletions in $^{235}$U compared to natural U are a prominent feature of the Oklo reactor zones (IAEA, 1975).

Early isotopic studies of the noble gases xenon, krypton and argon contained in old U minerals (Wetherill, 1953; Fleming and Thode, 1953) showed that their isotopic compositions were dominated by fission products from the spontaneous fission of $^{238}$U, but that small and variable amounts of isotopically distinct fission gas from neutron induced fission of $^{235}$U were present. This has been substantiated more recently for the large Rabbit Lake deposit in Saskatchewan (Drozd et al. 1974). However, evidence for Oklo-type fossil nuclear reactor zones has not been found in any of the old U deposits studied so far.

Because of its unusually high U grade with an average of about 2% $U_3O_8$ (Ewers et al., 1983) and drill core intersections of several tens of cm of solid uraninite, the Nabarlek deposit in the Alligator Rivers Uranium Field (ARUF) was considered a promising candidate for possible fossil nuclear reactor activity. Although U-Pb isotope studies suggested an age of only 900 Ma (Hills and Richards, 1976), considerably younger than the enclosing rocks of at least 1800 Ma, it was suspected that primary mineralization was in fact much older, possibly as old as 1600 Ma (Ewers et al., 1983). This was based on average Rb-Sr model ages of hydrothermally altered schists from the alteration zone surrounding the ore (Page et al., 1980). Recent Sm-Nd and Rb-Sr isotope data on Nabarlek (Maas and McCulloch, in prep.) confirm the antiquity of mineralization at Nabarlek and indeed in the other large unconformity-type uranium deposits in the area, the Jabiluka, Koongarra and Ranger deposits. This old age greatly improves the chances of detecting effects of possible fission processes in the ore.

In a study on possible extinct natural reactor activity in EARUF deposits, Riley and Korsch (1980) have measured one of the most diagnostic features, the U isotopic abundances in the ore. Within their analytical precision (0.1 %), the majority of their samples from Nabarlek, Jabiluka and Koongarra had normal $^{235}$U/$^{238}$U ratios. Only one sample appeared slightly depleted, two others slightly enriched in $^{235}$U relative to U standard SRM 950b. One analysis of Nd from Nabarlek high grade ore showed close to normal isotopic
abundances with possible minor effects from $^{143}\text{Nd}$ (n,$\gamma$) $^{144}\text{Nd}$ reactions resulting in lowered $^{145,146}\text{Nd}/^{144}\text{Nd}$ ratios. Thus, there is no evidence for Oklo type nuclear reactor zones at Nabarlek; if parts of the Nabarlek orebody did in fact become critical, it was either overlooked during sampling or the isotopic evidence for it was erased by post-reactor processes.

In the course of a Sm-Nd geochronological investigation of uranium ores from the Alligator Rivers Uranium Field, we have measured isotopic compositions of Sm, Nd and Gd in selected Nabarlek ore samples, both to examine more closely the nature and extent of possible nuclear reactions such as those suggested by Riley and Korsch (1980), and to assess possible effects on the radiogenic ratio $^{143}\text{Nd}/^{144}\text{Nd}$. The data allow to place limits on neutron fluences in individual samples and on the partition of fission yield contributions from $^{238}\text{U}$ spontaneous fission and thermal neutron fission of $^{235}\text{U}$. In addition, Nd and, for some samples, Sm isotopic ratios were measured in 18 uraninite samples from Jabiluka II, Koongarra and Ranger to investigate possible fission effects and to allow correction of measured $^{143}\text{Nd}/^{144}\text{Nd}$ ratios in uraninites from these deposits.

2 Analytical techniques

2.1 Chemical procedures

Following initial dissolution of the sample powders (30-70 mg) in hot concentrated nitric acid (only little residue was present consisting of hematite, sulfides and silicates) the sample solutions for the Nabarlek samples were allowed to cool, diluted with distilled water and aliquots were taken for determination of $^{143}\text{Nd}/^{144}\text{Nd}$ and Nd, Sm and U concentrations (appendix 3a). The remainder was transferred to HCl-operated cation exchange columns to isolate the REE. U was not determined for the uraninites from Jabiluka, Koongarra and Ranger. The dried REE cut was redissolved in 2 drops of 0.1 N HCl and loaded onto a 31 x 0.3 cm cation exchange column packed with previously purified AG W50 X-4, -400 mesh resin which had been preconditioned with ca. 1.5 column volumes of 0.2N methyl-lactic acid adjusted to a pH of 4.6. Fresh resin was used for each sample. A HREE cut containing Gd and relatively clean Sm and Nd cuts were then taken using the same acid. During preconditioning and sample run, a constant overpressure was applied to give a flow rate of ca. 3 ml/hr. The HREE cut containing the Gd was treated further on the same column using fresh resin and a fairly clean Gd cut was obtained using 0.2 N methyl-lactic acid with pH=4.0. Yields for all three elements were between 70 and 85%. Most of the cation exchange procedures are routinely used in this laboratory; the Gd cleaning step was adopted from Eugster et al. (1970). Some of the Nd cuts showed unacceptable levels of Sm contamination. These samples were further cleaned on columns packed with HDEHP-coated teflon powder (modified from Richard et al., 1976) which resulted in Sm and Ce-free Nd samples. Only sub-boiling distilled acids were used throughout the sample preparation with procedural blanks for Nd and Sm of 100 and 20 pg, respectively. Gd blanks were not measured but are assumed to be of the same order and therefore negligible.
2.2 Mass spectrometry

Sample amounts corresponding to about 1-2 µg were loaded at sub-red heat onto a carefully outgassed Re filament of a Re double filament assembly using 1 N HCl for Sm and Nd, and 1 N HNO₃ for Gd. Nd samples treated on HDEHP columns were loaded in HNO₃ mixed with a drop of phosphoric acid. All three elements were run as the metal even though Nd and Gd are known to ionize better as oxides (e.g. Eugster et al., 1970). However, ion currents (0.6 V on 10⁻¹² Ω resistor for ¹⁵⁸Gd) and lifetime (ca. 1 hr) of the Gd⁺ ion beams were usually sufficient to obtain good analyses. Sm and Nd ion currents were typically 2-6 x 10⁻¹² amps and could be sustained for several hours.

The samples were run using a Finnigan MAT 261 thermal ionization mass spectrometer equipped with 7 Faraday cups, 6 of which are adjustable. Data were collected in static mode; the 7 cup assembly enabled all 7 isotopes of Sm and Nd to be measured simultaneously, thus greatly reducing analysis time. For Gd, mass 152 was not measured as one cup was required for monitoring Dy interference. Each run consisted of five sets of twelve 8 second scans each, giving a total of 60 individual ratios, each corrected for mass fractionation. Total analysis time was about 16 minutes after which 2σM uncertainties were usually ≤30 ppm. Raw data were corrected for mass fractionation using ¹⁴⁷Sm/¹⁵²Sm = 0.56083 (McCulloch and Wasserburg, 1978), ¹⁵⁶Gd/¹⁶⁰Gd = 0.9361 (Eugster et al., 1970) and ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219 (Wasserburg et al., 1981). These values were chosen to be consistent with work in other laboratories. Raw ¹⁴⁷Sm/¹⁵²Sm and ¹⁵⁶Gd/¹⁶⁰Gd ratios measured during typical sample runs were usually higher than the respective values used for normalization; ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219 is within the commonly measured range.

Between runs, amplifier drift was checked and correction factors were applied to the measured ratios. As environmental conditions in the mass spectrometer room are held within narrow tolerances, amplifier drift was very slow and changes in amplifier drift correction factors were typically less than the in-run precision of any ratio. Longer runs without amplifier gain checks did not show systematic changes that could be attributed to possible amplifier drift.

2.3 Interfering isotopes

As the possible isotope anomalies were expected to be subtle, interferences were closely monitored.

(1) Nd analyses: The most severe potential interferences come from Sm and Ce on masses 144, 148, 150 and 142, respectively. As all 7 Faraday cups were used for Nd peaks, Ce and Sm could not be monitored continuously but the relevant mass spectra were scanned before and after the run. Ce was monitored on ¹⁴⁰Ce and the ¹⁴²Ce contribution was < 0.0015 % to ¹⁴²Nd in all cases. Sm was present in most Nd runs at the start but evaporated off rapidly. In some cases this could be accelerated by decreasing the temperature of the ionization filament while increasing the evaporation filament temperature for a minute. However, subsequent scans using the electron multiplier often revealed that some Sm was left even after this treatment. Thus, although data acquisition was commenced only at Sm ion beams amounting to <10⁻⁵ of ¹⁴⁴Nd (which would contribute a maximum +0.62 and +0.42x
10^{-4} to the 148\textsuperscript{Nd}/144\textsuperscript{Nd} and 150\textsuperscript{Nd}/144\textsuperscript{Nd} ratios, respectively), larger Sm levels during the run are possible. Potential BaO interference on Nd (134\textsuperscript{Ba}O on 150\textsuperscript{Nd}) cannot be directly checked in the presence of traces of Sm and Eu, but as 138\textsuperscript{Ba} was always <5\times10^{-6} of the 142\textsuperscript{Nd} signal, we assume BaO interferences to be negligible at our running conditions.

(2) Sm analyses: Potential important interferences are from Nd on masses 144,148 and 150 and from BaO on mass 154. As the chemical separation is quite effective, Nd is not usually a problem; in the few cases during this study where Nd was detected it was <5\times10^{-5} of the 144\textsuperscript{Sm} signal. BaO is difficult to detect in the presence of Eu; however, as 138\textsuperscript{Ba} is 10 times larger than any other BaO peak only this BaO interference needs to be considered. 138\textsuperscript{Ba} was present in about half of the sample runs in amounts of <10 mV corresponding to <5\times10^{-3} of the 154\textsuperscript{Sm} signals. No obvious correlation exists between measured 154\textsuperscript{Sm}/152\textsuperscript{Sm} ratios and Ba\textsuperscript{+}; the deviations of this ratio in the ore samples are all within <10^{-4} of the accepted normal value and appear to be normally distributed around this value. Further interferences are possible from LaO, CeO and Gd, however neither La nor Ce were ever detected nor are they likely to be present, because they elute after Nd on the methyl-lactic acid column. Very small Gd peaks in the mass range 155 to 160 were sometimes present but the low isotopic abundances of 152\textsuperscript{Gd} and 154\textsuperscript{Gd} preclude any significant interference on Sm for the analyses reported here.

(3) Gd analyses: The main potential interference comes from Dy which is not completely removed by the separation, on masses 156,158 and 160. As 160\textsuperscript{Dy} is 23 and 38 times larger than 158\textsuperscript{Dy} and 156\textsuperscript{Dy}, respectively, only 160\textsuperscript{Dy} was corrected for by monitoring mass 161. Sm, which could interfere on masses 152 and 154 was never observed. NdO interferences on masses 158 and 160 could not be checked directly as 143\textsuperscript{NdO} and 150\textsuperscript{NdO} are obscured by Tb and Er, respectively. However, Nd\textsuperscript{+} was never present in amounts >4\times10^{-4} and the NdO/Nd ratio under the running conditions is extremely small. LaO was observed during the early stages in reagent Gd runs (excess in mass 155) but was readily removed by cleaning the reagent on the methyl-lactic acid columns. CeO (probably from the column blank) could cause higher 156\textsuperscript{Gd}/160\textsuperscript{Gd} and 158\textsuperscript{Gd}/160\textsuperscript{Gd} and the resulting wrong mass fractionation correction would tend to lower all ratios but cancel the effect in 158\textsuperscript{Gd}/160\textsuperscript{Gd}. Because of complete spectral overlap, CeO cannot be directly observed but as 140\textsuperscript{Ce} was never present in amounts >10^{-5} of the signal at mass 156, the effect is considered negligible.

PrO interference on mass 157 is also considered negligible, both because of its low natural abundance and the small amounts of both Nd and Ce seen in the spectrum. Finally, BaO and BaF can both interfere with Gd. BaO interference on mass 154 may have been present but would be completely covered by the rather large measurement uncertainties (2\sigma_m = 0.4\% compared to ca. 0.02\% on the other ratios) due to the small ion currents obtained for this mass. BaF interferes with masses 154-157 with the effect on mass 157 ca. 10 times larger than that on the other masses and cannot be directly corrected for; however Ba\textsuperscript{+} was rarely observed and rapidly burnt off to levels of <3\times10^{-4} of the 157 signal.
3 Results

3.1 Normal compositions

The isotopic compositions of normal Sm, Gd and Nd from reagents and U-poor rocks are given in Tables 1 to 3. The data are summarized in Fig.1. Agreement between different normal samples is quite good even though the high precision of the multicollector analyses sometimes precludes statistical overlaps even between consecutive runs of the same filament load. The measured ratios (±2σ_mean) vary to within one ε-unit (i.e. ±10^-4 of any one ratio) around the calculated averages with the exception of the 144Sm/152Sm and 154Gd/160Gd data which vary by ±2 and ±10 parts in 10^-4 respectively. To check the efficiency of our chemical separation in particular with regard to Ba (a source of potential interferences, see previous section) we have used normal rocks samples with a wide range in Ba contents (120 to 1200 ppm); no significant differences are apparent in diagnostic Sm and Gd isotope ratios.

The measured Nd normals show some scatter around the values chosen for ANU NORMAL. In particular, 148Nd/144Nd and 150Nd/144Nd ratios in most normal runs possess positive deviations (normal sample - ANU NORMAL) up to 1.6 and 2.15 parts in 10^-4, respectively. These ratios are very sensitive to Sm interference during the measurement which may be a reason for the positive bias in some normal runs. Another possible reason for the offset is possible long-term drift in the multicollector mass spectrometer. The MERCK Nd reagent (Table 3) was run many times during the setup period of the instrument in August-September 1986 and a grand average of the results on this standard is used as ANU NORMAL for the purpose of this study. The other normals and many of the samples were run 6 months later. However, the consistently positive bias in 148-150Nd/144Nd ratios of some normals compared to both positive and negative scatter in the 142-145Nd/144Nd ratios is more consistent with Sm interference.

Comparison of our results with terrestrial averages obtained by the CALTECH group shows good agreement within ±1 part in 10^-4 (Tables 1-3); the only exceptions are again the small ratios 144Sm/152Sm and 154Gd/160Gd which are lower by 1.8 and 3.4 parts in 10^-4 respectively.

3.2 U ores

Isotopic data on U ores and uraninites are listed in Tables 1 to 3. To a first approximation all measured samples have isotopic compositions close to normal confirming the findings by Riley and Korsch (1980) that there is no conclusive evidence for Oklo type nuclear reactor activity at Nabarlek nor in any of the other deposits. The most deviant ore sample from Nabarlek shows differences on the order of 0.1 % for the most affected ratio while the Oklo sample studied by Loubet and Allegre (1977) shows deviations of up to 98 % (e.g. 149Sm/147Sm). On this basis we conclude that we can find no evidence for Oklo type critical zones.

However, small but significant anomalies are present in some of the ratios. The largest deviations occur in Sm with systematic depletions in 149Sm/152Sm and enrichments in 150Sm/152Sm, while Gd shows enrichment in 158Gd/160Gd and depletions in 157Gd and 155Gd
abundances. The variations in these ratios are correlated and plot on or close to neutron capture lines (Fig. 2). These lines represent the theoretical loci of isotopic variations in Sm and Gd that have undergone (n/γ) reactions involving variable doses of thermal neutrons. In this case, the neutrons are obviously derived from U fission. Among the Sm isotopes, only 149Sm has a high thermal neutron capture cross section (149σ_{220m/sec} = 41500 barns, Lederer et al., 1967) while those of the other isotopes are lower by a factor of 200 and more. For neutron capture at the neutron fluences involved (see below), only 149Sm and the stable neutron capture product 150Sm are thus expected to have abnormal isotopic abundances. Samples of normal isotopic composition exposed to varying neutron fluences are therefore expected to plot along a line with slope = -1. Deviations from the theoretical line can be caused by other nuclear effects superimposed on the neutron capture and/or artifacts in the measurement due to interferences. For example, addition of fissionogenic 147Sm to neutron-irradiated Sm would raise the 147Sm/152Sm ratio used for mass fractionation corrections, resulting in small decreases in mass fractionation corrected 149Sm/152Sm and 150Sm/152Sm ratios. This mechanism would move the data points from the neutron capture line (slope -1) to a line with somewhat smaller slope, a possible explanation for the small but significant deviations of many of the data points from the neutron capture line (see Fig.2a).

Thermal neutron capture of Gd predominantly affects two isotopes with large thermal neutron capture cross sections, 155Gd (61000 barns) and 157Gd (255000 barns), while the other Gd isotopes possess small cross sections. The data in Table 2 were corrected for mass fractionation by normalizing to 156Gd/160Gd which was assumed constant. In samples that show neutron capture effects, this ratio would be higher than normal because of the 155Gd (n/γ) 156Gd reaction. This introduces a wrong mass fractionation correction of 1/4155σΨ(155Gd/156Gd)_{n} per mass unit, where 155σ is the cross section for thermal neutron capture by 155Gd, Ψ is the thermal neutron fluence and (155Gd/156Gd)_{n} the isotopic ratio in normal samples (Eugster et al., 1970). Normalization to a constant 154Gd/160Gd would avoid this problem but the relative precision of this ratio is more than 10 times lower than for the 156Gd/160Gd.

One consequence of the wrong mass discrimination correction in irradiated samples is that the calculated neutron capture line in the plot of 157Gd/160Gd vs. 158Gd/160Gd is not of slope -1. Using equation 8 in Eugster et al. (1970) we calculate a slope of -0.764. For the 157Gd/160Gd vs. 155Gd/160Gd plot, the slope of the neutron capture line is calculated to ≈ 0.37. These neutron capture lines are shown in Figs.2b and 2c. Despite some deviations, the fit of the data points to the theoretical neutron capture lines is generally satisfactory and suggests that thermal neutron capture was the main cause for the observed anomalous abundances in 149Sm, 150Sm, 155Gd, 157Gd and 158Gd.

Neutron capture effects in Sm and Gd virtually identical to those in the Nabarlek ore have been reported from the Norton County achondrite (Eugster et al., 1970) and are a well known feature of some lunar surface rocks and soils (Russ et al., 1971, 1972; Lugmair and Marti, 1971; Russ, 1973). In these cases the neutron flux is initiated and sustained by incident cosmic rays which produce neutrons as they interact with the surface material. Typical thermal neutron fluences in lunar surface material range between 1 to 18 x 10^{15}
n/cm². Corresponding instantaneous thermal neutron fluxes can be calculated if exposure ages are known and vary between about 0.4 and 2.4 n/cm² sec (Lugmair and Marti, 1971).

The isotopic ratios most sensitive to neutron capture, ¹⁵⁰Sm/¹⁴⁹Sm and ¹⁵⁸Gd/¹⁵⁷Gd, can be used to calculate thermal neutron fluences (time-integrated neutron flux), Ψ, in the uranium ores and uraninites using equation 9 from Eugster et al. (1970):

\[
\Psi = \frac{¹⁵⁸Gd/¹⁵⁷Gd_m}{¹⁵⁸Gd/¹⁵⁷Gd_n} \cdot \frac{¹⁵⁸Gd/¹⁵⁷Gd_n}{¹⁵⁷Gd/¹⁵⁷Gd_n} \cdot \frac{¹⁵⁸Gd/¹⁵⁷Gd_n}{¹⁵⁵Gd/¹⁵⁶Gd_n} \cdot \frac{¹⁵⁷Gd/¹⁵⁷Gd_n}{¹⁵⁵Gd/¹⁵⁶Gd_n} 
\]

where the subscripts m and n refer to the measured and the normal ratio, respectively. This equation accounts to a close approximation for the error introduced by the wrong fractionation correction. A somewhat simpler relationship is used to calculate thermal neutron fluence from the Sm data:

\[
\Psi = \frac{¹⁵⁰Sm/¹⁵²Sm_m}{¹⁵⁰Sm/¹⁵²Sm_n} \cdot \frac{¹⁵⁰Sm/¹⁵²Sm_n}{¹⁵⁰Sm/¹⁵²Sm_n} \cdot \frac{¹⁵⁰Sm/¹⁵²Sm_n}{¹⁵⁰Sm/¹⁵²Sm_n} \cdot \frac{¹⁵⁰Sm/¹⁵²Sm_n}{¹⁵⁰Sm/¹⁵²Sm_n} 
\]

Neutron capture cross sections for thermal neutron energies (i.e. 0.025 eV or 2200 m/sec) were used in the calculations; the results are listed in Table 4. The fluences derived from the Gd data range from 0.8 - 5.68 x 10¹⁵ n/cm² while those calculated from the Sm data are 3-4 times higher at 7.04-21.52 x 10¹⁵ n/cm². These differences are not unexpected in view of the non 1/v behaviour of Sm and Gd neutron capture cross sections in the thermal region (large low energy resonances); the cross sections are therefore strongly dependant on bulk rock composition and temperature. An indication of the neutron energy spectrum below 0.2 eV is given by the relative magnitudes of neutron capture-related anomalies in Sm and Gd, i.e. the ratio of the number of neutrons captured per atom of a particular isotope. ¹⁴⁹Sm has a large neutron capture resonance near 0.1 eV while ¹⁵⁷Gd has one at lower energies (near 0.03 eV), hence the relative magnitudes of the neutron capture anomalies in Sm and Gd provide a means to evaluate the 'hardness' of the energy spectrum in that energy region. The relative magnitudes of the neutron capture anomalies are conveniently expressed in form of the \( \varepsilon_{Sm}/\varepsilon_{Gd} \) ratio, \( \varepsilon \) being equal to the product of fluence and the cross section weighted over the neutron energy spectrum. Thus \( \varepsilon_{Sm}/\varepsilon_{Gd} \) is equal to the ratio of the average cross sections, \( (<\sigma>) \), for ¹⁵⁷Gd and ¹⁴⁹Sm where the average is carried out over the total energy spectrum (Russ et al., 1971; Russ, 1973):

\[
\varepsilon_{Sm} = \frac{¹⁵⁰Sm/¹⁴⁹Sm_m}{¹⁵⁰Sm/¹⁴⁹Sm_m} \cdot \frac{¹⁵⁰Sm/¹⁴⁹Sm_n}{¹⁵⁰Sm/¹⁴⁹Sm_n} \cdot \frac{¹⁵⁰Sm/¹⁴⁹Sm_n}{¹⁵⁰Sm/¹⁴⁹Sm_n} \cdot \frac{¹⁵⁰Sm/¹⁴⁹Sm_n}{¹⁵⁰Sm/¹⁴⁹Sm_n} 
\]

An analogous definition is made for \( \varepsilon_{Gd} \). The arbitrarily normalized ¹⁵⁸Gd/¹⁵⁷Gd ratios are corrected for the wrong normalization procedure by multiplication with a correction factor

\[
D = 1 - (0.25 \cdot ¹⁵⁵\sigma \cdot \Psi \cdot ¹⁵⁵Gd/¹⁵⁶Gd_n) 
\]
This correction procedure introduces a small error because $^{155}\sigma$ and $\Psi$ values for the samples are not known precisely; we have used $^{155}\sigma_{2200 \text{ m/sec}} = 61000$ barns and the preliminary fluences tabulated in Table 4. However, recalculation with updated cross section and fluence values (see below) effected only minor changes.

Calculated $\varepsilon_{\text{Sm}} / \varepsilon_{\text{Gd}}$ range between 0.47 and 0.66 (see Table 4); in comparison $(^{149}\langle\sigma\rangle/^{157}\langle\sigma\rangle)_{2200 \text{ m/sec}}$ is 0.17. The samples having the lowest $\varepsilon_{\text{Sm}} / \varepsilon_{\text{Gd}}$ are those with the lowest U content but otherwise there is no correlation. The higher $\varepsilon_{\text{Sm}} / \varepsilon_{\text{Gd}}$ in the very concentrated ores are explicable by their greater proportions of neutron absorbers such as U and REE. The maxima of their neutron energy spectra are shifted to higher energies and are closer to the $^{149}$Sm resonance than the maxima in the lower grade ores which have a greater proportion of moderators and hence a 'softer' energy spectrum.

The high $\varepsilon_{\text{Sm}} / \varepsilon_{\text{Gd}}$ values clearly demonstrate that the ores were irradiated at neutron energies with maxima greater than 0.025 eV and that the $\sigma_{2200 \text{ m/sec}}$ values used to calculate the thermal neutron fluences are inappropriate. Thermal neutron fluences were therefore recalculated using neutron capture cross sections at neutron energies between the respective resonance energies of $^{157}$Gd and $^{149}$Sm (i.e. in the energy interval 0.03 to 0.1 eV). It was assumed that Sm and Gd in a sample were subjected to the same thermal neutron doses, i.e. fluences, and capture cross sections were therefore selected from the neutron cross section curves of Garber and Kinsey (1976) which yielded converging fluences according to (1) and (2). This recalculation yields converging fluences of $\approx 11 \times 10^{15} \text{ n/cm}^2$ ($\sigma$ values in the energy range 0.06-0.065 eV) for the highly concentrated ores and lower fluences of ca. 4.7 and $10 \times 10^{15} \text{ n/cm}^2$ for the less concentrated ores NA2/21 and NA#3, respectively ($\sigma$ values taken at energies slightly below 0.06 eV). These results are qualitatively consistent with the proportions of moderators available and the expected neutron energy distribution in the samples.

Another method to calculate effective capture cross sections as a function of sample chemistry is given by Lingenfelter et al. (1972) and Curtis and Wasserburg (1975). However, their procedures cannot easily be applied to the U ores, mainly because of the much larger abundances of non 1/ν absorbers such as REE and U.

Apparent thermal neutron fluences for uraninites from Jabiluka and Koongarra have been calculated from the Sm isotopic data and range from 2.96-17.66$\times 10^{15}$ n/cm² (Table 5), similar to the range observed in Nabarlek samples. As Gd data are not available, we can not evaluate the term $\varepsilon_{\text{Sm}} / \varepsilon_{\text{Gd}}$ but the calculated fluences are likely to represent maximum values (as for the Nabarlek samples) because the high abundances in U and REE (e.g. 257-256 ppm Sm) in the uraninites would shift the thermal neutron energy spectrum to energies higher than 0.025 eV with corresponding changes in $\sigma$ values. If Nd isotopic anomalies, which reflect the relative amount of accumulated fissionogenic Nd in the samples, are used as an indication of fission activity (see below), the generally smaller Nd anomalies in the Jabiluka and Ranger uraninites compared to the Nabarlek samples would suggest that true thermal neutron fluences in the uraninites were well below $11 \times 10^{15}$ n/cm² for the most irradiated samples.
Neutron generation and economics

Noble gas studies indicate that both spontaneous and induced fission contribute to the fission gases in uranium deposits (e.g. Drozd et al., 1974). A comparison of neutron production rates and observed thermal neutron fluences in the Nabarlek ore samples should indicate whether spontaneous fission alone could account for the observed anomalies or whether significant burnup of \(^{235}\text{U}\) is required.

In U ores, neutrons are primarily produced by the spontaneous fission of \(^{238}\text{U}\) which releases \(2\) neutrons per fission (cf. Hyde, 1964), and by \((\alpha,\text{n})\) reactions involving the large number of \(\alpha\) particles released during the radioactive decay of U (e.g. \(8\) \(\alpha\) particles per decayed atom of \(^{238}\text{U}\)). Further contributions come from slow neutron fission of \(^{235}\text{U}\) which releases ca. \(2.5\) neutrons per fission (cf. Friedlander et al., 1981) and induced fission of \(^{238}\text{U}\) by fast neutrons. We can estimate the number of neutrons (i.e. the neutron density per gram or per cm\(^3\)) produced by these sources using Bateman's equations (Rubinson, 1949). The neutron generation in 1 gram of sample over 1600 Ma (the approximate age of the studied uranium deposits, Maas and McCulloch, in prep) from the first reaction is found as:

\[
\text{neutrons/g} = 2 \times \lambda_{sf} / \lambda_{238} 137.88 / 138.88 N_{now} (e^{\Lambda T} - 1)
\]

where \(\lambda_{sf}\) is the spontaneous fission constant = \(7.03 \times 10^{-17}\) a\(^{-1}\) (Roberts et al., 1968), \(\lambda_{238}\) is the decay constant = \(0.155125 \times 10^{-9}\) a\(^{-1}\), \(N_{now}\) is the number of U atoms present in the sample, \(\Lambda\) is the combined decay constant \((\lambda_{238} + \lambda_{sf}) = \lambda_{238}\). For example, spontaneous fission of \(^{238}\text{U}\) in NA#2 (59.7 wt% U, i.e. \(N_{now} = 1.5098 \times 10^{21}\) atoms per gram) generates \(3.8 \times 10^{14}\) neutrons/g.

The \((\alpha,\text{n})\) contribution is more difficult to evaluate as it is dependent on \(\alpha\)-particle energy and sample chemistry. Feige et al. (1968) have calculated the neutron yield by \((\alpha,\text{n})\) of common rocks containing 1 ppm of U; extrapolation of these data to ca. 60% U gives a fictitious neutron production rate of \(10^6\) n/g year, which represents an upper limit to the true production rate. Wetherill (1953) reported a value of \(0.32 \times 10^5\) n/g year for a high-REE euxenite with 6% U which is probably more applicable to REE-rich U minerals. Extrapolated to the U content of NA#2 (i.e. \(0.32 \times 10^5 \times 59.7/6 = 3.2 \times 10^5\) n/g year) a minimum of \(5 \times 10^{14}\) neutrons/g could be expected from \((\alpha/\text{n})\) reactions in this sample.

The contribution from thermal neutron induced \(^{235}\text{U}\) fission is found as:

\[
\text{neutrons/g} = 2.5 \times \Phi \sigma_{nf} / \lambda_{235} \times \frac{1}{138.88} N_{now} (e^{\Lambda T} - 1)
\]

where \(\Phi\) is the annual thermal neutron flux, \(\sigma_{nf}\) is the thermal neutron fission cross section of 580 barns, \(\lambda_{235}\) is the decay constant = \(0.98485 \times 10^{-9}\) a\(^{-1}\), and \(\Lambda\) is the combined disintegration constant \((\Phi \sigma_{nf} + \lambda_{235}) = \lambda_{235}\). If revised thermal neutron fluences are used in the calculation, we obtain an average annual neutron flux \(\Phi = 6.9 \times 10^6\) n/cm\(^2\) yr for sample #2 (for simplicity the flux is assumed to be constant over 1600 Ma) which would induce \(1.7 \times 10^{14}\) fissions of \(^{235}\text{U}\) per gram and produce \(4.25 \times 10^{14}\) neutrons/gram, corresponding to a net neutron production of \(2.55 \times 10^{14}\) n/g or \(= 30\%\) of the neutron production by
spontaneous fission and \((\alpha/n)\) reactions. The three sources together would produce \(= 11.3 \times 10^{14}\) neutrons per gram of \#2 over 1600 Ma. The neutron production for the Nabarlek samples is summarized in Table 6. Neutron fission would affect only small proportions on the order of \(2.5 \times 10^{-5}\) of the total number of the \(^{235}\text{U}\) atoms present in the ores; such small degrees of burnup would be impossible to measure at the attainable analytical precisions.

The contribution from fission of \(^{238}\text{U}\) induced by fast neutrons relative to slow neutron fission of \(^{235}\text{U}\) (the fast-fission factor) is difficult to estimate because the fast neutron flux is unknown. If this flux was similar in magnitude to the slow neutron flux, fast fission of \(^{238}\text{U}\) (\(\sigma_f = 0.29\) barns at energies greater than the fission threshold of \(= 1.1\) MeV, Glasstone and Edlund, 1952) would produce a neutron density equivalent to \(1-3\%\) of the neutron production from \(^{235}\text{U}\) slow neutron fission and would thus be unimportant for the overall neutron budget.

The number of thermal neutrons required to generate the isotopic anomalies can be calculated using the relationship

\[
R = \Sigma \Psi
\]

where \(R\) is the total number of thermal neutron captures per \(\text{cm}^3\) over 1600 Ma (equal to the number of thermal neutrons involved), \(\Psi\) is the thermal neutron fluence and \(\Sigma\) is the macroscopic thermal neutron capture cross section, defined as

\[
\Sigma = N_i \sigma_i
\]

where \(N_i\) is the number of atoms of isotope \(i\) and \(\sigma_i\) its capture cross section. Macroscopic cross sections were calculated using \(\sigma_{2200\text{ m/sec}}\) values for the major absorbers present in the ores: \(^{149}\text{Sm}, \, ^{155}\text{Gd}, \, ^{157}\text{Gd}, \, ^{151}\text{Eu}, \, ^{235}\text{U}\) and \(^{238}\text{U}\). Measured U abundances were corrected for decay since mineralization 1600 Ma ago. The resultant values (Table 6) are therefore maximum values because \(\alpha\) decay rapidly depleted the number of absorbing \(^{235}\text{U}\) atoms over 1600 Ma. Further, calculated macroscopic cross sections for the main absorbers, \(^{157}\text{Gd}\) and \(^{235}\text{U}\), depend strongly on the \(\sigma\) values used which decrease rapidly at the neutron energies relevant to the ore samples, i.e. energies \(>0.025\) eV.

The calculated \(R\) values (Table 6) range from \(0.012\) to \(4.27 \times 10^{15}\) n/cm\(^3\); they represent only a fraction of the total neutron density as some of neutrons generated in the samples would be lost from the rocks. Mean free neutron path lengths before thermalization and absorption are inversely related to \(\Sigma\) and range from 2-3 cm for the very concentrated ores to \(=66\) cm for 256A, the lowest grade ore. These data suggest that fast neutrons produced in high grade ores would be absorbed rather rapidly. Thermalization of these neutrons would occur mainly by collisions with oxygen and hydrogen atoms, (cf. Kuroda, 1982) and partly by inelastic collisions with U atoms (Glasstone and Edlund, 1952). In contrast, fast neutron produced in lower grade ores have a greater chance to escape and may in fact provide part of the thermal neutrons in adjacent high grade domains.

Comparison of \(R\) values and the expected neutron production in the Nabarlek samples
shows that neutron production is greater than thermal neutron consumption in all cases except for ores 69/43.2 and #3 where consumption equals and exceeds neutron generation, respectively. It should be noted, however, that the R values are maximum values and could be up to 50% too high for reasons given above. Thus, if a resonance escape probability p on the order of 0.4 is assumed (Kuroda, 1982), neutron generation and consumption appear reasonably balanced in most samples, implying that no significant burnup of $^{235}$U would be required to generate the thermal neutron fluence observed in the Nabarlek ores and most likely also the uraninites from the other deposits.

### 3.4 U-REE mobility

The isotopic data and the concentrations of U, Sm and Gd (Table 6) can be used to evaluate possible open system behaviour in the samples. In Fig.3 anomalous $^{150}$Sm/$^{149}$Sm and $^{158}$Gd/$^{157}$Gd ratios are plotted against U/Sm and U/Gd, respectively. The position of the samples on the two diagrams is very similar: samples 2/21, 4/40, 69/42, #2 and #4 are located on or close to correlation lines ('CS') which could be interpreted as isotopic evolution paths in closed U/Sm and U/Gd systems. Samples 69/43.2 and #3 lie off this trend and have substantially lower U/Sm and U/Gd at isotopic ratios comparable to those in the 'closed system' group, i.e. their isotope anomalies are unsupported. This is consistent with the results of the neutron production - neutron consumption balance discussed in 3.3 which indicates lower production/consumption ratios in samples #3 and 69/43.2 compared to the other samples. Unsupported isotopic anomalies such as those observed could be caused simply by young U loss and/or Sm-Gd addition. On the other hand, differences in REE patterns, i.e. variable proportions of Sm and Gd, do not seem to of importance in determining the distribution of the isotopic anomalies. Gd/Sm ratios in the ores do not show detailed correlations with either isotope ratios or U/Sm and U/Gd (Fig.3a).

Addition of Sm and other REE to the samples is possible but appears less feasible than U loss because it would probably disturb the Sm-Nd isotopic systematics in the samples which is not observed. The studied Nabarlek ores lie on or close to a 1616±50 Ma isochron (with the exception of 4/40), an age which has been interpreted as the age of primary mineralization (Maas and McCulloch, in prep.). REE addition to #3 and 69/43.2 without disruption of the Sm-Nd isochron would require that the contaminant originates from other cogenetic ores. Contamination of this type would have the effect of moving the samples along the isochron and probably add some isotopically anomalous Sm and Gd.

U loss in relatively recent times could at least partly account for the observed low U/Sm and U/Gd ratios. We can place limits on the magnitude of possible U loss by comparing the maximum possible U content of uraninite with sample U contents. Uraninite, UO$_2$ in its ideal form, can accommodate a maximum of ca. 88 wt% U but is usually less concentrated due to impurities such as Ca, REE and others. As it ages it accumulates radiogenic Pb with concomittant U decrease amounting to $\approx$25% in 1620 Ma. Initially pure uraninite formed 1620 Ma ago would have 63% U now. By this reasoning, NA69/43.2 would appear to have lost ca. 40% of its U; however, if this amount is added back to the sample, it would still not lie on the correlation lines shown in Fig.3. NA#3 would have lost most of its U and by
adding back an appropriate amount (e.g. by doubling the present U content) could be moved onto the ‘closed system’ lines. On the other hand, young U loss from the ores is not supported by U-Pb studies on the Alligator Rivers uranium deposits which indicate pronounced loss of Pb rather than U between ~200-600 Ma ago (Hills and Richards, 1976; Ludwig et al., 1987). We conclude that both mechanisms could have contributed to the unsupported Sm and Gd anomalies in samples #3 and 69/43.2 but the available evidence does not allow to exclude either alternative.

3.5 Further anomalies in Gd and Sm

In the following discussion, the isotopic data will be expressed in e units (i.e. parts in 10^-4 of the measured ratio). The ε notation as used here is somewhat different from the ε_{Sm} and ε_{Gd} values defined in (3):

\[
\epsilon(\text{Gd}) = 10^4 \left[ \frac{\text{iGd}/\text{iGd}_{\text{meas}}}{\text{iGd}/\text{iGd}_{\text{normal}}} - 1 \right]
\]

where \text{iGd}/\text{iGd}_{\text{meas}} is the measured isotope ratio of isotope i in the sample. Analogous definitions are made for Sm and Nd isotopes. The results are presented in Table 7.

Apart from the isotopic anomalies in 155-158 Gd/160 Gd (see section 3.2), 154 Gd/160 Gd ratios in the Nabarlek samples possess marked deviations from the accepted normal composition which span a range corresponding to ε = -19 to +6. These anomalies are certainly in part related to the error introduced by the wrong mass fractionation correction in irradiated samples which should generate values lower than normal (Russ, 1973). However, poor analytical quality due to the small 154 Gd ion currents for the 154 Gd isotope are probably the main cause for the observed negative and positive deviations in this ratio.

The correlated anomalies in 149 Sm and 150 Sm and their relationships with U/Sm (Figs. 2a and 3a) have been discussed earlier. Further anomalies are present in 144 Sm/152 Sm, 148 Sm/152 Sm and, to a lesser degree, 154 Sm/152 Sm (Table 7). These can be explained quite satisfactorily by addition of fissionogenic 147 Sm to the ore samples which would increase measured 147 Sm/152 Sm ratios. The effect would be slightly enhanced by 152 Sm (n/p) 153 Sm reactions and would generate negative bias in 144-150 Sm/152 Sm ratios and positive bias in 154 Sm/152 Sm ratios which are normalized to 147 Sm/152 Sm. For example, the 147 Sm yield from spontaneous fission alone would be sufficient to cause a systematic shift of -0.213 ε units per atomic mass in sample #2. This mechanism can explain the consistently negative ε_{144} and ε_{148} values as well as their broad correlations with U/Sm (Fig.4b). In addition, covariations of ε_{148} with ε_{149} (Fig.4a) and ε_{150} are to be expected. In contrast, both positive and negative ε values are found for 154 Sm/152 Sm which is not entirely compatible with the proposed mechanism. However, the range of 154 Sm/152 Sm obtained in normal runs (-0.51 to +0.73) is identical to the range observed in the samples (-0.50 to +0.81); the anomalies in this ratio can therefore not be considered significant.

3.6 Nd isotope ratios

In the studied ores, stable Nd isotope ratios are sensitive indicators of U fission because
the Nd mass region is close to the top of the high mass peak of fission fragment yields from both spontaneous and thermal neutron U fission (von Gunten, 1969) and because Nd isotopic abundances are not significantly affected by thermal neutron capture at the neutron fluences found in this study. The Nd isotopic data are reported in Tables 3 and 7.

Similar to Sm and Gd, the Nd isotopic ratios in the U ores and uraninites are subject to a wrong mass fractionation. The $^{146}\text{Nd}/^{144}\text{Nd}$ ratio used for normalization is affected by the reaction $^{143}\text{Nd} (n/\gamma) ^{144}\text{Nd} (\sigma_c = 330 \text{ barns})$ and by the addition of fission Nd with $^{146}\text{Nd}/^{144}\text{Nd}_f = 0.542$, which introduce a small negative bias. Consequently, mass fractionation corrected $^{142}\text{Nd}/^{144}\text{Nd}$ ratios will be too low while corrected $^{145-150}\text{Nd}/^{144}\text{Nd}$ ratios will be too high in such samples, depending on the thermal neutron fluence and the number of U fissions. This wrong mass fractionation correction is superimposed on the fission-related anomalies expected in these ratios.

Measured apparent anomalies in Nabarlek Nd are small and variable, the largest amounting to $\approx 3 \epsilon$-units for $^{142}\text{Nd}/^{144}\text{Nd}$ and $^{145}\text{Nd}/^{144}\text{Nd}$. Uraninites from the other three U deposits have less anomalous Nd. The deviations in $^{142}\text{Nd}/^{144}\text{Nd}$ and $^{145}\text{Nd}/^{144}\text{Nd}$ are well correlated with each other and U/Nd ratios (Fig.5). They do not correlate with any of the other Nd isotope ratios but show weak correlations with $\epsilon_{150}\text{Sm}$ (Fig.7) and $\epsilon_{149}$. The apparent anomalies in $^{148}\text{Nd}/^{144}\text{Nd}$ and $^{150}\text{Nd}/^{144}\text{Nd}$ show a broad correlation. Surprisingly, the trend shown in Fig.6a does not start at the origin, i.e. $\epsilon = 0/0$, but traverses $\epsilon_{150}\text{Nd} = 0$ at $\epsilon_{148}\text{Nd} = 0.6 \pm 0.3$. Both ratios display some covariation with U/Nd but the trends are disrupted by outliers; interestingly, the largest $\epsilon_{150}\text{Nd}$ values are associated with the highest U/Nd (Fig.6b).

Together with data on U and Nd concentrations and the number of spontaneous fissions in $^{238}\text{U}$, the Nd isotope data on the Nabarlek samples can be used to estimate the proportion of $^{235}\text{U}$ atoms involved in slow neutron fission. The results should be comparable to the proportion of $^{235}\text{U}$ slow neutron fission inferred from the Sm and Gd isotopic data which indicate variable slow fission/spontaneous fission ratios ranging from 0.37-0.89. The lowest grade ore, 256A, has a ratio of 0.06.

In the calculations, the number of atoms of each Nd isotope (except $^{142}\text{Nd}$ which has extremely low yield) produced by spontaneous fission and slow neutron fission were estimated according to (5) and (6) using published fission yield data (Table 8). Nd fission yields for $^{238}\text{U}$ spontaneous fission are not well known and may be associated with relatively large errors. However, their absolute magnitudes and distribution are comparable to the better known $^{235}\text{U}$ fission yields, implying that they are reasonably accurate. The fractions of fissionogenic Nd atoms were added to isotopically normal Nd already present in the samples at the start of the fission process, the isotope ratios recalculated and corrected for apparent mass fractionation, and the resulting deviations from the start composition expressed as $\epsilon$ units.

As expected, the calculated anomalies vary approximately linearly with U/Nd ratio (Table 9); three model solutions are illustrated in Figs.5 and 6a. Due to slight variations in yield ratios between Nd isotopes, the model trends for purely spontaneous fission and spontaneous fission plus variable proportions of slow neutron fission have somewhat
different slopes. In general, model trends A and B in Fig. 5a coincide well with the $\varepsilon_{142} - \varepsilon_{145}$ data array and yield reasonable fits to the $\varepsilon_{142,145}$ - U/Nd arrays in Fig. 5b, especially to the lower U/Nd data points. However, it is evident from Table 9 that neither pure $^{238}$U spontaneous fission nor spontaneous fission plus slow neutron fission (number of slow neutron fissions derived from (6)) can account for the measured anomalies in 6 of the 8 samples. As the number of spontaneous fissions is fixed by the U content, an increase in the number of $^{235}$U fissions by a factor of 3 is required to generate the anomalies in these samples (line C). Combined with the $^{238}$U yield, this increased $^{235}$U yield also provides a better fit to the data in Fig. 5b. The modeling therefore suggests that $^{235}$U consumption was up to three times larger than inferred from the Sm and Gd isotopic data. Although this would imply that the values for macroscopic cross section $\Sigma$, rate of neutron capture $R$ and neutron production $NP$ are too low by comparable factors, the principal conclusion concerning balance between neutron production and consumption remain valid. However, the Nd data suggest that $^{235}$U fission was a more important source of neutrons (and fission products) than spontaneous fission of $^{238}$U, at least with respect to the the highest grade Nabarlek samples.

In contrast to the satisfactory fit of the model trends to the data in Fig. 5, the model anomaly trends in Fig. 6a do not adequately describe the measured isotopic compositions. Calculated anomalies in $^{150}$Nd/$^{144}$Nd range between $\varepsilon = -0.5$ to +0.1 while the measured ratios range from $\varepsilon = -1.99$ to +1.78. Further, the large measured $\varepsilon_{150}$Nd values at low U/Nd (Fig. 6b) are inconsistent with the modeling. As noted earlier, $^{148-150}$Nd/$^{144}$Nd analyses are highly sensitive to Sm interference; this is indicated by the arrow in Fig. 6a which indicates the expected shift of the data points produced by Sm interference. A combination of fission-related anomalies (lines A-C) and shifts due to Sm interference could explain the apparent anomalies in 50-60% of the data and the data distribution in Fig. 6b. However, we have no ready explanation for the comparatively large negative $\varepsilon_{150}$Nd values in the remainder of the samples. It is unlikely that these negative $\varepsilon_{150}$Nd were caused by an unidentified interference on mass 144 as this would also affect the $\varepsilon_{142}$ and $\varepsilon_{145}$ values and produce more scatter in Fig. 5a. An inadequate mass fractionation correction or serious errors in the fission yields of $^{150}$Nd and/or $^{146}$Nd are possible alternative causes of the apparent $^{150}$Nd deficiency.

4 Conclusions

The principal conclusion of this study is that we can find no evidence for Oklo-type nuclear reactor activity in the unconformity-type U deposits of the ARUF region. This confirms the conclusions of Riley and Korsch who found no significant $^{235}$U depletions in U ores from these deposits. These findings are in accord with noble gas studies by Drozd et al. (1974) on the Rabbit Lake U deposit which is geologically similar to the ARUF deposits. In contrast to the more mobile fission gases studied by Drozd et al. (1974), the REE investigated in this study can be assumed to provide a reliable record of the fission history throughout the entire evolution of the U ores (at least in the case of Nabarlek and Jabiluka where the studied samples indicate Sm-Nd ages of $\approx 1600$ Ma). Nevertheless, the conclusions drawn from either approach are more or less identical.
The thermal neutron fluences found for Nabarlek appear to converge at maximum values of \(1 \times 10^{15} \text{n/cm}^2\), higher than the \(3 \times 10^{13} \text{n/cm}^2\) neutron fluences reported from Rabbit Lake where the fission gas record may only sample a fraction (10-50 Ma, Drozd et al., 1974) of the total fission period. Sm isotopic data for Jabiluka and Koongarra indicate maximum values for the thermal neutron fluence of 7 and \(18 \times 10^{15} \text{n/cm}^2\), respectively, but true thermal neutron fluences are likely to be lower by about 50%. These neutron fluences are lower by \(10^4\) than neutron fluences reported for the Oklo natural reactor (Drozd et al., 1974; Loubet and Allègre, 1977; IAEA, 1975).

Both spontaneous fission of \(^{238}\text{U}\) and thermal neutron induced fission of \(^{235}\text{U}\) contributed to the neutron production in the U ores. For two Nabarlek samples with the lowest U contents, spontaneous fission could account for both the observed thermal neutron fluence and the Nd isotopic anomalies. This may also be the case for many of the Jabiluka, Koongarra and Ranger uraninites but cannot be substantiated in the absence of data on U concentrations. For the higher grade Nabarlek ores and possibly some of the uraninites from the other deposits, a substantial contribution from \(^{235}\text{U}\) fission to the neutron budget and the Nd fission products is required. Calculations suggest that \(^{235}\text{U}\) fission may be more important as a source of neutrons and fission products than the fission of \(^{238}\text{U}\). Up to 70% of the anomalies in \(^{145}\text{Nd}\) appear to be due to the \(^{235}\text{U}\) fission component. Some of the fission products may be derived from fast neutron fission of \(^{238}\text{U}\) and from slow neutron fission of \(^{239}\text{Pu}\) which is formed through radiative neutron capture by \(^{238}\text{U}\) followed by a series of rapid \(\beta\) decays. However, the contributions from these sources are very small compared to those already mentioned.

Due to the variable and significant contributions from \(^{235}\text{U}\) fission to the neutron budget in the Nabarlek samples, \(^{150}\text{Sm}/^{149}\text{Sm}\) - U/Sm and \(^{158}\text{Gd}/^{157}\text{Gd}\) - U/Gd systematics (neutron capture chronometers) can not be used to derive the age of the U-REE system. In comparison with Oklo, the ARUF deposits have much higher REE contents and hence a lower proportion of thermal neutrons available for thermal fission of \(^{235}\text{U}\) (the thermal utilization factor), which is considered the main factor that prevented the Nabarlek uranium pile from becoming critical.
References


Figure captions

Fig.1 Summary of Sm, Gd and Nd isotopic ratios measured in normal samples and reagents. The quoted ratios represent the averages (±2σ_{mean}) of the normal runs; for Nd, the values obtained for MERCK reagent are used as ANU NORMAL.

Fig.2 Isotopic anomalies caused by neutron capture on $^{149}$Sm, $^{157}$Gd and $^{155}$Gd compared to normal compositions. A. $^{149}$Sm/$^{152}$Sm versus $^{150}$Sm/$^{152}$Sm. 2σ_{mean} errors are smaller than size of symbols. The sample data points fall on or near the neutron capture line with slope -1. B. $^{158}$Gd/$^{160}$Gd versus $^{157}$Gd/$^{160}$Gd. 2σ_{mean} error bars shown. The neutron capture line has a slope=1 due to a wrong normalization procedure based on the $^{156}$Gd/$^{160}$Gd ratio which is enhanced by neutron capture. C. $^{155}$Gd/$^{160}$Gd versus $^{157}$Gd/$^{160}$Gd. $^{155}$Gd/$^{160}$Gd should be plotted against $^{156}$Gd/$^{160}$Gd but this ratio is used for mass fractionation correction.

Fig.3 Neutron capture anomalies versus U/Sm,Gd ratios. In a closed system dominated by spontaneous fission and small amounts of thermal neutron fission, the neutron capture anomalies would be expected to plot along correlation lines as illustrated by the lines marked "CS" (= closed system) which are visual fits through most of the data points. A. $^{150}$Sm/$^{149}$Sm versus U/Sm. The numbers in parentheses next to the sample numbers are Gd/Sm ratios. Errors on isotope ratios are smaller than size of symbols, errors on U/Sm are rel. 10%. B. $^{158}$Gd/$^{157}$Gd versus U/Gd. Errors as in A.

Fig.4 Isotopic anomalies in $^{148}$Sm expressed in ε units (difference from normal in parts of 10^{-4}). A. ε_{148} versus ε_{149}. Note broad positive correlation. B. ε_{148} versus U/Sm. Despite one outlier there is a broad negative correlation. Errors as in Fig.3.

Fig.5 Covariation of Nd isotopic ratios with each other and U/Nd. A. ε_{142} versus ε_{145} for ores from Nabarlek and uraninites from Jabiluka, Koongarra and Ranger. The strong covariation indicates a common origin for these anomalies. Lines A and B illustrate the growth trends of fission-related isotopic anomalies expected from $^{238}$U spontaneous fission and spontaneous fission plus a certain amount of $^{235}$U thermal neutron fission (calculated from equation 5, see text), respectively. These lines cover only about half the observed range of ε values but can account for the measured anomalies in most samples. Line C represents the anomaly trend expected if the number of $^{235}$U fissions is increased by a factor of 3. B. Variation of ε_{142} and ε_{145} with U/Nd. Lines A, B and C calculated as before. Lines B and C cover the entire range of anomalies. Errors as in Fig.3.

Fig.6 Isotopic anomalies in $^{150}$Nd and $^{148}$Nd. A. ε_{150} versus ε_{148} for all samples. The data array can not be explained solely in terms of fission effects (lines A-C). The trend towards large positive ε_{150} and ε_{148} values could be caused by Sm interference during analysis superimposed on the fission effects. No satisfactory explanation can be given for the large negative ε_{150} values. B. ε_{150} versus U/Nd for the Nabarlek ores. The large positive anomalies at low U/Nd ratios are considered artifacts of Sm interference.

Fig.7 Weak positive correlation between ε_{145}(Nd) and ε_{150}(Sm). Similar correlations exist for ε_{142}(Nd) and ε_{149}(Sm).
Table 1
Isotopic compositions of Sm from normal terrestrial material, U ores from Nabarlek and uraninites from Jabiluka and Koongarra

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{144}$Sm/$^{152}$Sm</th>
<th>$^{148}$Sm/$^{152}$Sm</th>
<th>$^{149}$Sm/$^{152}$Sm</th>
<th>$^{150}$Sm/$^{152}$Sm</th>
<th>$^{154}$Sm/$^{152}$Sm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Normal samples</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BHVO-1-1</td>
<td>0.114950±7</td>
<td>0.420441±4</td>
<td>0.516840±4</td>
<td>0.276001±3</td>
<td>0.850770±7</td>
</tr>
<tr>
<td>BHVO-1-1</td>
<td>0.114964±7</td>
<td>0.420455±4</td>
<td>0.516851±4</td>
<td>0.276005±3</td>
<td>0.850788±8</td>
</tr>
<tr>
<td>T.D. 84/70-1</td>
<td>0.114935±5</td>
<td>0.420447±4</td>
<td>0.516835±4</td>
<td>0.276008±4</td>
<td>0.850813±10</td>
</tr>
<tr>
<td>T.D. 84/70-2</td>
<td>0.114973±7</td>
<td>0.420446±3</td>
<td>0.516832±3</td>
<td>0.276004±2</td>
<td>0.850873±6</td>
</tr>
<tr>
<td>Kimberlite DN23</td>
<td>0.114959±4</td>
<td>0.420447±3</td>
<td>0.516837±4</td>
<td>0.276005±4</td>
<td>0.850819±8</td>
</tr>
<tr>
<td>ANU NORMAL</td>
<td>0.114956±13</td>
<td>0.420447±2</td>
<td>0.516839±9</td>
<td>0.276005±2</td>
<td>0.850813±35</td>
</tr>
<tr>
<td>CALTECH</td>
<td>0.11499±1</td>
<td>0.42045±2</td>
<td>0.51686±2</td>
<td>0.27600±2</td>
<td>0.85079±3</td>
</tr>
<tr>
<td><strong>Nabarlek U ores</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NA2/21</td>
<td>0.114941±4</td>
<td>0.420432±4</td>
<td>0.516687±4</td>
<td>0.276157±3</td>
<td>0.850795±8</td>
</tr>
<tr>
<td>NA#2</td>
<td>0.114910±11</td>
<td>0.420357±7</td>
<td>0.516382±10</td>
<td>0.276444±5</td>
<td>0.850882±16</td>
</tr>
<tr>
<td>NA#3</td>
<td>0.114938±9</td>
<td>0.420403±5</td>
<td>0.516467±4</td>
<td>0.276356±4</td>
<td>0.850785±10</td>
</tr>
<tr>
<td>NA#4</td>
<td>0.114921±2</td>
<td>0.420371±4</td>
<td>0.516362±5</td>
<td>0.276459±3</td>
<td>0.850837±8</td>
</tr>
<tr>
<td>NA4/40</td>
<td>0.114941±13</td>
<td>0.420404±6</td>
<td>0.516543±8</td>
<td>0.276309±6</td>
<td>0.850825±14</td>
</tr>
<tr>
<td>NA4/31.5</td>
<td>0.114968±6</td>
<td>0.420434±7</td>
<td>0.516502±7</td>
<td>0.276349±5</td>
<td>0.850850±12</td>
</tr>
<tr>
<td>NA69/42</td>
<td>0.114934±2</td>
<td>0.420388±4</td>
<td>0.516376±4</td>
<td>0.276436±3</td>
<td>0.850821±5</td>
</tr>
<tr>
<td>NA69/43.2</td>
<td>0.114949±13</td>
<td>0.420404±6</td>
<td>0.516363±8</td>
<td>0.276460±5</td>
<td>0.850818±12</td>
</tr>
<tr>
<td><strong>Jabiluka uraninites</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S153V/238.8</td>
<td>0.114926±5</td>
<td>0.420420±3</td>
<td>0.516665±4</td>
<td>0.276151±3</td>
<td>0.850879±7</td>
</tr>
<tr>
<td>S180V/232.8</td>
<td>0.114934±10</td>
<td>0.420435±6</td>
<td>0.516766±6</td>
<td>0.276075±5</td>
<td>0.850827±9</td>
</tr>
<tr>
<td><strong>Koongarra uraninites</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K87/90.8 vein 2</td>
<td>0.114933±7</td>
<td>0.420428±6</td>
<td>0.516503±6</td>
<td>0.276325±3</td>
<td>0.850771±12</td>
</tr>
<tr>
<td>K87/90.77</td>
<td>0.114945±8</td>
<td>0.420420±5</td>
<td>0.516504±5</td>
<td>0.276335±4</td>
<td>0.850759±12</td>
</tr>
<tr>
<td>K94/147.4</td>
<td>0.114950±6</td>
<td>0.420343±5</td>
<td>0.516776±6</td>
<td>0.276069±3</td>
<td>0.850810±11</td>
</tr>
<tr>
<td>K87/91.7</td>
<td>0.114925±10</td>
<td>0.420422±6</td>
<td>0.516706±6</td>
<td>0.276136±4</td>
<td>0.850793±10</td>
</tr>
<tr>
<td>K87/90.5</td>
<td>0.114955±12</td>
<td>0.420418±6</td>
<td>0.516440±6</td>
<td>0.276373±5</td>
<td>0.850791±12</td>
</tr>
<tr>
<td>K87/90.8 vein</td>
<td>0.114938±7</td>
<td>0.420426±4</td>
<td>0.516499±3</td>
<td>0.276324±3</td>
<td>0.850796±7</td>
</tr>
</tbody>
</table>

Quoted errors are $2\sigma_{\text{mean}}$. Sm isotope ratios are normalized to $^{147}\text{Sm}/^{152}\text{Sm} = 0.56083$. 1 BHVO-1 is a NBS standard basalt, 2 kimberlite from Walloway, South Australia, 3 T.D. 84/70 is Tasmanian Dolerite, 4 normal composition adopted in this paper, 5 data from McCulloch and Wasserburg (1978), updated from Russ et al. (1971).
### Isotopic compositions of Gd from normal terrestrial material and Nabarlek U ores

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{158}$Gd/$^{160}$Gd</th>
<th>$^{157}$Gd/$^{160}$Gd</th>
<th>$^{155}$Gd/$^{160}$Gd</th>
<th>$^{154}$Gd/$^{160}$Gd</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPEX-1</td>
<td>1.135897±21</td>
<td>0.715874±21</td>
<td>0.676926±25</td>
<td>0.099806±31</td>
</tr>
<tr>
<td>SPEX-2</td>
<td>1.135917±12</td>
<td>0.715871±12</td>
<td>0.676921±13</td>
<td>0.099745±39</td>
</tr>
<tr>
<td>Kimberlite DN23-1</td>
<td>1.135900±21</td>
<td>0.715875±23</td>
<td>0.676889±22</td>
<td>0.099718±35</td>
</tr>
<tr>
<td>Kimberlite DN23-2</td>
<td>1.135857±21</td>
<td>0.715874±18</td>
<td>0.676904±23</td>
<td>0.099786±54</td>
</tr>
<tr>
<td>AGV-1-1</td>
<td>1.135905±28</td>
<td>0.715879±21</td>
<td>0.676893±23</td>
<td>0.099620±48</td>
</tr>
<tr>
<td>AGV-1-2</td>
<td>1.135872±22</td>
<td>0.715835±20$^4$</td>
<td>0.676884±23</td>
<td>0.099665±38</td>
</tr>
<tr>
<td>T.D. 84/70</td>
<td>1.135855±28</td>
<td>0.715879±21</td>
<td>0.676943±23</td>
<td>0.099602±42</td>
</tr>
<tr>
<td>ANU NORMAL$^2$</td>
<td>1.13586±20</td>
<td>0.715875±15</td>
<td>0.676909±16</td>
<td>0.099706±60</td>
</tr>
<tr>
<td>CALTECH$^3$</td>
<td>1.13582±5</td>
<td>0.71588±4</td>
<td>0.67687±5</td>
<td>0.09974±3</td>
</tr>
</tbody>
</table>

**Nabarlek U ores**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{158}$Gd/$^{160}$Gd</th>
<th>$^{157}$Gd/$^{160}$Gd</th>
<th>$^{155}$Gd/$^{160}$Gd</th>
<th>$^{154}$Gd/$^{160}$Gd</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA2/21</td>
<td>1.136237±29</td>
<td>0.715409±25</td>
<td>0.676735±25</td>
<td>0.099765±53</td>
</tr>
<tr>
<td>NA #2</td>
<td>1.136722±15</td>
<td>0.714777±12</td>
<td>0.676461±16</td>
<td>0.099693±27</td>
</tr>
<tr>
<td>NA #3</td>
<td>1.136779±30</td>
<td>0.714699±23</td>
<td>0.676505±32</td>
<td>0.099675±63</td>
</tr>
<tr>
<td>NA #4</td>
<td>1.136771±21</td>
<td>0.714765±17</td>
<td>0.676481±23</td>
<td>0.099755±33</td>
</tr>
<tr>
<td>NA4/40</td>
<td>1.136501±22</td>
<td>0.715084±17</td>
<td>0.676577±22</td>
<td>0.099683±27</td>
</tr>
<tr>
<td>NA69/42</td>
<td>1.136642±22</td>
<td>0.714807±14</td>
<td>0.676577±17</td>
<td>0.099517±38</td>
</tr>
<tr>
<td>NA69/43.2</td>
<td>1.136743±25</td>
<td>0.714737±20</td>
<td>0.676495±24</td>
<td>0.099626±45</td>
</tr>
<tr>
<td>NA256</td>
<td>1.136099±23</td>
<td>0.715759±24</td>
<td>0.676784±23</td>
<td>0.099713±42</td>
</tr>
</tbody>
</table>

Data are corrected for mass fractionation by normalizing to $^{156}$Gd/$^{160}$Gd = 0.9361. Quoted errors are $2 \sigma_{\text{mean}}$. $^1$AGV-1 is NBS standard andesite. $^2$ Normal composition adopted in this study. $^3$ From Russ et al. (1972). $^4$ Outlier excluded from ANU NORMAL.
Isotopic compositions of Nd from normal terrestrial material, U ores from Nabarlek and uraninites from Jabiluka, Koongarra and Ranger

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{142}$Nd/$^{144}$Nd</th>
<th>$^{145}$Nd/$^{144}$Nd</th>
<th>$^{147}$Nd/$^{144}$Nd</th>
<th>$^{150}$Nd/$^{144}$Nd</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Normal samples</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MERCK reagent¹</td>
<td>1.141895±20</td>
<td>0.348387±10</td>
<td>0.241556±8</td>
<td>0.236439±8</td>
</tr>
<tr>
<td>LaJolla-1</td>
<td>1.141884±39</td>
<td>0.348384±9</td>
<td>0.241560±10</td>
<td>0.236437±10</td>
</tr>
<tr>
<td>LaJolla-2</td>
<td>1.141958±11</td>
<td>0.348387±3</td>
<td>---</td>
<td>0.236439±4</td>
</tr>
<tr>
<td>LaJolla-3</td>
<td>1.141906±24</td>
<td>0.348369±7</td>
<td>---</td>
<td>0.236477±4</td>
</tr>
<tr>
<td>LaJolla-4</td>
<td>1.141882±9</td>
<td>0.348381±2</td>
<td>---</td>
<td>0.236463±4</td>
</tr>
<tr>
<td>LaJolla mean</td>
<td>1.141909±20</td>
<td>0.348384±8</td>
<td>---</td>
<td>0.236452±17</td>
</tr>
<tr>
<td>Tasman. Dolerite 84/70</td>
<td>1.141860±34</td>
<td>0.348392±6</td>
<td>0.241608±8</td>
<td>0.23652±11</td>
</tr>
<tr>
<td>SPEX reagent</td>
<td>1.141900±30</td>
<td>0.348381±7</td>
<td>0.241575±10</td>
<td>0.236470±20</td>
</tr>
<tr>
<td>Kimberlite DN23-1</td>
<td>1.141946±29</td>
<td>0.348383±8</td>
<td>0.241569±12</td>
<td>0.236447±15</td>
</tr>
<tr>
<td>Kimberlite/B</td>
<td>1.141910±29</td>
<td>0.348389±10</td>
<td>0.241573±11</td>
<td>0.236460±9</td>
</tr>
<tr>
<td>ANU NORMAL²</td>
<td>1.141895±20</td>
<td>0.348387±10</td>
<td>0.241556±8</td>
<td>0.236439±8</td>
</tr>
<tr>
<td>CALTECH³</td>
<td>1.141827</td>
<td>0.348417</td>
<td>0.241578</td>
<td>0.236418</td>
</tr>
<tr>
<td><strong>Nabarlek U ores</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NA2/21</td>
<td>1.141862±10</td>
<td>0.348387±2</td>
<td>0.241570±3</td>
<td>0.236475±4</td>
</tr>
<tr>
<td>NA #2</td>
<td>1.141591±33</td>
<td>0.348504±6</td>
<td>0.241588±8</td>
<td>0.236440±11</td>
</tr>
<tr>
<td>NA #3</td>
<td>1.141804±13</td>
<td>0.348431±3</td>
<td>0.241566±4</td>
<td>0.236450±4</td>
</tr>
<tr>
<td>NA #4</td>
<td>1.141604±26</td>
<td>0.348490±6</td>
<td>0.241604±9</td>
<td>0.236476±10</td>
</tr>
<tr>
<td>NA4/40</td>
<td>1.141738±14</td>
<td>0.348455±3</td>
<td>0.241572±4</td>
<td>0.236441±5</td>
</tr>
<tr>
<td>NA69/42</td>
<td>1.141762±17</td>
<td>0.348440±4</td>
<td>0.241565±5</td>
<td>0.236441±7</td>
</tr>
<tr>
<td>NA69/43.2</td>
<td>1.141794±13</td>
<td>0.348434±3</td>
<td>0.241580±4</td>
<td>0.236455±4</td>
</tr>
<tr>
<td>NA256</td>
<td>1.141890±9</td>
<td>0.348382±2</td>
<td>0.241579±2</td>
<td>0.236481±3</td>
</tr>
<tr>
<td><strong>Jabiluka uraninites</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S180V/232</td>
<td>1.141837±32</td>
<td>0.348409±7</td>
<td>0.241600±8</td>
<td>0.236471±11</td>
</tr>
<tr>
<td>T141V/248.8</td>
<td>1.141884±19</td>
<td>0.348399±5</td>
<td>0.241582±5</td>
<td>0.236461±6</td>
</tr>
<tr>
<td>T141V/237</td>
<td>1.141877±25</td>
<td>0.348400±24</td>
<td>0.241581±5</td>
<td>0.236450±8</td>
</tr>
<tr>
<td>S153V/238.8</td>
<td>1.141804±21</td>
<td>0.348420±5</td>
<td>0.241579±6</td>
<td>0.236450±6</td>
</tr>
<tr>
<td>S180V/232.8</td>
<td>1.141863±28</td>
<td>0.348401±5</td>
<td>0.241565±6</td>
<td>0.236440±9</td>
</tr>
<tr>
<td>T141V/238</td>
<td>1.141884±18</td>
<td>0.348396±4</td>
<td>0.241563±4</td>
<td>0.236440±5</td>
</tr>
<tr>
<td>T141V/238 vein</td>
<td>1.141922±21</td>
<td>0.348396±24</td>
<td>0.241553±6</td>
<td>0.236414±6</td>
</tr>
<tr>
<td><strong>Koongarra uraninites</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K87/90.5</td>
<td>1.141725±38</td>
<td>0.348460±5</td>
<td>0.241563±7</td>
<td>0.236392±9</td>
</tr>
<tr>
<td>K87/90.8 vein</td>
<td>1.141792±17</td>
<td>0.348432±3</td>
<td>0.241568±4</td>
<td>0.236426±5</td>
</tr>
<tr>
<td>K87/91.7</td>
<td>1.141798±17</td>
<td>0.348435±3</td>
<td>0.241576±5</td>
<td>0.236448±5</td>
</tr>
<tr>
<td>K87/90.8 vein2</td>
<td>1.141799±17</td>
<td>0.348437±5</td>
<td>0.241560±5</td>
<td>0.236420±7</td>
</tr>
<tr>
<td>K94/147.4</td>
<td>1.141900±24</td>
<td>0.348406±5</td>
<td>0.241555±6</td>
<td>0.236408±6</td>
</tr>
<tr>
<td>K87/90.77</td>
<td>1.141746±46</td>
<td>0.348442±7</td>
<td>0.241581±6</td>
<td>0.236447±10</td>
</tr>
</tbody>
</table>
Table 3 continued

**Ranger uraninites**

<table>
<thead>
<tr>
<th></th>
<th>146Nd/144Nd</th>
<th>148Nd/144Nd</th>
<th>150Nd/144Nd</th>
<th>152Nd/144Nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ranger F</td>
<td>1.14189±18</td>
<td>0.348432±4</td>
<td>0.241569±4</td>
<td>0.236422±5</td>
</tr>
<tr>
<td>Ranger J</td>
<td>1.14189±20</td>
<td>0.348395±3</td>
<td>0.241572±4</td>
<td>0.236454±6</td>
</tr>
<tr>
<td>Ranger H</td>
<td>1.141826±21</td>
<td>0.348412±5</td>
<td>0.241527±5</td>
<td>0.236428±8</td>
</tr>
<tr>
<td>Ranger K</td>
<td>1.141833±23</td>
<td>0.348424±4</td>
<td>0.241572±7</td>
<td>0.236432±8</td>
</tr>
<tr>
<td>Ranger G</td>
<td>1.141826±23</td>
<td>0.348436±5</td>
<td>0.241551±5</td>
<td>0.236417±8</td>
</tr>
<tr>
<td>Ranger I</td>
<td>1.141686±33</td>
<td>0.348439±8</td>
<td>0.241570±11</td>
<td>0.236398±11</td>
</tr>
</tbody>
</table>

Data are corrected for mass discrimination by normalizing to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$. Quoted errors are $2 \sigma_{\text{mean}}$.\(^1\) Average of 10 runs.\(^2\) This composition is adopted as our terrestrial normal for the purpose of this study.\(^3\) Wasserburg et al. (1981).
### Table 4

**Summary of neutron capture effects in Nabarlek U ores**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{158}\text{Gd}/^{157}\text{Gd}$</th>
<th>$\varphi^3$</th>
<th>$\varepsilon_{\text{Gd}}^4$</th>
<th>$^{150}\text{Sm}/^{149}\text{Sm}$</th>
<th>$\varphi^5$</th>
<th>$\varepsilon_{\text{Sm}}^6$</th>
<th>$\varepsilon_{\text{Sm}}^6/\varepsilon_{\text{Gd}}^7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2/21</td>
<td>1.588197±70</td>
<td>2.24</td>
<td>5.75</td>
<td>0.534476±7</td>
<td>7.04(4.7)</td>
<td>2.94</td>
<td>0.51</td>
</tr>
<tr>
<td>#2</td>
<td>1.590228±34</td>
<td>5.31</td>
<td>13.58</td>
<td>0.535348±14</td>
<td>20.74(11)</td>
<td>8.62</td>
<td>0.63</td>
</tr>
<tr>
<td>#3</td>
<td>1.590475±30</td>
<td>5.68</td>
<td>14.53</td>
<td>0.535089±10</td>
<td>16.67(10)</td>
<td>6.93</td>
<td>0.47</td>
</tr>
<tr>
<td>#4</td>
<td>1.590321±20</td>
<td>5.45</td>
<td>13.94</td>
<td>0.535398±8</td>
<td>21.52(11)</td>
<td>8.94</td>
<td>0.64</td>
</tr>
<tr>
<td>4/40</td>
<td>1.589261±22</td>
<td>3.85</td>
<td>9.85</td>
<td>0.534920±14</td>
<td>14.01(11)</td>
<td>5.83</td>
<td>0.59</td>
</tr>
<tr>
<td>4/31.5</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>0.535040±12</td>
<td>15.89(11)</td>
<td>6.61</td>
<td>---</td>
</tr>
<tr>
<td>69/42</td>
<td>1.590054±22</td>
<td>5.05</td>
<td>12.91</td>
<td>0.535339±7</td>
<td>20.59(11)</td>
<td>8.56</td>
<td>0.66</td>
</tr>
<tr>
<td>69/43.2</td>
<td>1.590343±30</td>
<td>5.49</td>
<td>14.03</td>
<td>0.535399±13</td>
<td>21.54(11)</td>
<td>8.95</td>
<td>0.64</td>
</tr>
<tr>
<td>256A</td>
<td>1.587252±23</td>
<td>0.80</td>
<td>2.09</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Normal</td>
<td>1.586710±15</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>0.534025±6</td>
</tr>
</tbody>
</table>

1 corrected for the error introduced by normalizing to $^{156}\text{Gd}/^{160}\text{Gd}=0.9361$.

2 2 sigma mean errors calculated by quadratic addition of in-run errors quoted in Tables 1 and 2, number of ratios per analysis = 60.

3 calculated according to equation 1, $^{157}\sigma_c = 255000$ b, $^{155}\sigma_c = 61000$ b, $^{155}\text{Gd}/^{156}\text{Gd} = 0.723116$.

4 see text

5 fluence calculated according to equation 2, $^{149}\sigma_c = 41500$ b.

6 numbers in brackets are revised thermal neutron fluences ($\times 10^{15}$ n/cm²), for details see text.

7 calculated according to equation 3
<table>
<thead>
<tr>
<th>sample</th>
<th>$^{150}\text{Sm}/^{149}\text{Sm}$</th>
<th>$\psi^2$</th>
<th>$\text{Sm}^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$10^{15}\text{n/cm}^2$</td>
<td>ppm</td>
</tr>
<tr>
<td><strong>Jabiluka</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S153V/238.8</td>
<td>0.534488±7</td>
<td>7.27</td>
<td>257</td>
</tr>
<tr>
<td>S180V/232.8</td>
<td>0.534236±11</td>
<td>3.31</td>
<td>657</td>
</tr>
<tr>
<td><strong>Koongarra</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K87/90.5</td>
<td>0.535150±11</td>
<td>17.66</td>
<td>264</td>
</tr>
<tr>
<td>K87/90.8vein</td>
<td>0.534994±6</td>
<td>15.21</td>
<td>288</td>
</tr>
<tr>
<td>K87/91.7</td>
<td>0.534416±10</td>
<td>6.14</td>
<td>337</td>
</tr>
<tr>
<td>K87/90.8vein2</td>
<td>0.534992±9</td>
<td>15.18</td>
<td>276</td>
</tr>
<tr>
<td>K94/147.4</td>
<td>0.534214±9</td>
<td>2.96</td>
<td>358</td>
</tr>
<tr>
<td>K87/09.77</td>
<td>0.535010±9</td>
<td>15.46</td>
<td>288</td>
</tr>
<tr>
<td>Normal</td>
<td>0.534025±6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 2 sigma mean errors calculated by quadratic addition of in-run errors quoted in Table 1, number of ratios per analysis = 60.

2 calculated according to equation 2, $^{149}\sigma_c = 41500$ b.

3 from Maas and McCulloch (in prep.)
Table 6

U and REE concentrations, macroscopic cross sections, neutron consumption and neutron production estimates for Nabarlek U ores

<table>
<thead>
<tr>
<th>sample</th>
<th>U now</th>
<th>Sm</th>
<th>Nd</th>
<th>Gd</th>
<th>Eu</th>
<th>( \Sigma^1 )</th>
<th>R^2</th>
<th>NP^3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>cm^2/g</td>
<td>( 10^{15} ) n/cm^3</td>
<td>( 10^{15} ) n/cm^3</td>
</tr>
<tr>
<td>2/21</td>
<td>12.65</td>
<td>76.7</td>
<td>137.5</td>
<td>86</td>
<td>22</td>
<td>0.0258</td>
<td>0.52</td>
<td>0.95</td>
</tr>
<tr>
<td>#2</td>
<td>59.7</td>
<td>94</td>
<td>142</td>
<td>194</td>
<td>39</td>
<td>0.0747</td>
<td>3.78</td>
<td>5.14</td>
</tr>
<tr>
<td>#3</td>
<td>4.07</td>
<td>15.25</td>
<td>20.5</td>
<td>25</td>
<td>4.6</td>
<td>0.0075</td>
<td>0.37</td>
<td>0.34</td>
</tr>
<tr>
<td>#4</td>
<td>59.96</td>
<td>96</td>
<td>149</td>
<td>198</td>
<td>40</td>
<td>0.0739</td>
<td>3.70</td>
<td>4.9</td>
</tr>
<tr>
<td>4/40</td>
<td>57.42</td>
<td>137</td>
<td>172</td>
<td>248</td>
<td>46</td>
<td>0.0845</td>
<td>4.27</td>
<td>4.95</td>
</tr>
<tr>
<td>4/31.5</td>
<td>26.9</td>
<td>56.3</td>
<td>75.8</td>
<td>92</td>
<td>17</td>
<td>0.0347</td>
<td>1.75</td>
<td>2.31</td>
</tr>
<tr>
<td>69/42</td>
<td>64.35</td>
<td>124</td>
<td>275</td>
<td>225</td>
<td>46</td>
<td>0.0840</td>
<td>4.25</td>
<td>5.5</td>
</tr>
<tr>
<td>69/43.2</td>
<td>46.48</td>
<td>129</td>
<td>292</td>
<td>250</td>
<td>50</td>
<td>0.0785</td>
<td>3.97</td>
<td>4.0</td>
</tr>
<tr>
<td>256A</td>
<td>1.02</td>
<td>11.5</td>
<td>52.9</td>
<td>13.0</td>
<td>2.6</td>
<td>0.0033</td>
<td>0.012</td>
<td>0.08</td>
</tr>
</tbody>
</table>

U analyses are by isotope dilution and microprobe on fused discs, errors set uniformly at ±10%; Sm and Nd are by isotope dilution, Eu by ICP, Gd was interpolated from REE patterns.

1 calculated according to equation 8

2 calculated according to equation 7 using revised fluences (Table 4) and \( \Sigma \) values multiplied by a density \( \rho = 4.5 \) g/cm^3. Fluence used for 256A=0.8x10^{15} n/cm^2, for 4/31.5 fluence is 11x10^{15} n/cm^2.

3 NP = neutron production from \(^{238}\)U spontaneous fission (equation 5), (\( \alpha/n \)) reactions assumed to produce \( 1.32x\text{NP}_{sf} \) neutrons, and slow neutron fission of \(^{235}\)U (equation 6), all adjusted to an arbitrary sample density \( \rho = 4.5 \) g/cm^3. This uniform density was chosen because the sample densities in the studied ores are highly variable depending on the relative proportions of uraninite and chlorite matrix. Densities measured on kept fragments of the samples may not be representative of the density in the analysed part of the sample. For our purposes, the absolute density is not important; systematic errors introduced by a wrong \( \rho \) value occur in both R and NP and cancel.
Table 7
Summary of isotopic anomalies in Nd, Sm and Gd in parts of $10^{-4}$ ($\pm 2\sigma_{\text{mean}}$)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nd</th>
<th>Sm</th>
<th>Gd</th>
<th>Nd</th>
<th>Sm</th>
<th>Gd</th>
<th>Nd</th>
<th>Sm</th>
<th>Gd</th>
<th>Nd</th>
<th>Sm</th>
<th>Gd</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\varepsilon_{142}$</td>
<td>$\varepsilon_{145}$</td>
<td>$\varepsilon_{148}$</td>
<td>$\varepsilon_{150}$</td>
<td>$\varepsilon_{144}$</td>
<td>$\varepsilon_{149}$</td>
<td>$\varepsilon_{150}$</td>
<td>$\varepsilon_{154}$</td>
<td>$\varepsilon_{154}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nabarlek</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2/21</td>
<td>-0.29</td>
<td>0.00</td>
<td>0.58</td>
<td>1.52</td>
<td>-1.31</td>
<td>-0.36</td>
<td>-2.94</td>
<td>5.51</td>
<td>-0.21</td>
<td>5.92</td>
<td>±0.10</td>
<td>±0.05</td>
</tr>
<tr>
<td>#2</td>
<td>-2.67</td>
<td>3.36</td>
<td>1.33</td>
<td>0.04</td>
<td>-4.00</td>
<td>-2.14</td>
<td>-8.84</td>
<td>15.91</td>
<td>0.81</td>
<td>-1.30</td>
<td>±0.29</td>
<td>±0.17</td>
</tr>
<tr>
<td>#3</td>
<td>-0.80</td>
<td>1.26</td>
<td>0.41</td>
<td>0.47</td>
<td>-1.57</td>
<td>-1.05</td>
<td>-7.20</td>
<td>12.72</td>
<td>-0.33</td>
<td>-3.11</td>
<td>±0.11</td>
<td>±0.08</td>
</tr>
<tr>
<td>#4</td>
<td>-2.55</td>
<td>2.96</td>
<td>1.99</td>
<td>1.57</td>
<td>-3.05</td>
<td>-1.81</td>
<td>-9.23</td>
<td>16.45</td>
<td>0.28</td>
<td>4.91</td>
<td>±0.23</td>
<td>±0.17</td>
</tr>
<tr>
<td>4/40</td>
<td>-1.38</td>
<td>1.95</td>
<td>0.66</td>
<td>0.09</td>
<td>-1.31</td>
<td>-1.02</td>
<td>-5.72</td>
<td>11.01</td>
<td>0.14</td>
<td>-2.31</td>
<td>±0.12</td>
<td>±0.08</td>
</tr>
<tr>
<td>4/31.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.04</td>
<td>-0.31</td>
<td>-6.52</td>
<td>12.46</td>
<td>0.43</td>
<td></td>
<td>±0.52</td>
<td>±0.17</td>
</tr>
<tr>
<td>69/42</td>
<td>-1.17</td>
<td>1.52</td>
<td>0.37</td>
<td>0.09</td>
<td>-1.91</td>
<td>-1.40</td>
<td>-8.96</td>
<td>15.62</td>
<td>0.09</td>
<td>-18.96</td>
<td>±0.15</td>
<td>±0.11</td>
</tr>
<tr>
<td>69/43.2</td>
<td>-0.89</td>
<td>1.35</td>
<td>0.99</td>
<td>0.68</td>
<td>-0.61</td>
<td>-1.02</td>
<td>-9.21</td>
<td>16.49</td>
<td>0.06</td>
<td>-8.02</td>
<td>±0.11</td>
<td>±0.08</td>
</tr>
<tr>
<td>256</td>
<td>-0.05</td>
<td>-0.14</td>
<td>0.95</td>
<td>1.78</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>±0.08</td>
<td>±0.05</td>
</tr>
</tbody>
</table>

Jabiluka

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nd</th>
<th>Sm</th>
<th>Gd</th>
<th>Nd</th>
<th>Sm</th>
<th>Gd</th>
</tr>
</thead>
<tbody>
<tr>
<td>S180V/232</td>
<td>-0.51</td>
<td>0.63</td>
<td>1.82</td>
<td>1.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>±0.28</td>
<td>±0.20</td>
<td>±0.33</td>
<td>±0.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S153V/238.8</td>
<td>-0.80</td>
<td>0.95</td>
<td>0.95</td>
<td>0.47</td>
<td>-2.61</td>
<td>-0.64</td>
</tr>
<tr>
<td></td>
<td>±0.18</td>
<td>±0.14</td>
<td>±0.25</td>
<td>±0.25</td>
<td>±0.43</td>
<td>±0.07</td>
</tr>
<tr>
<td>T141V/248.8</td>
<td>-0.10</td>
<td>0.34</td>
<td>1.08</td>
<td>0.93</td>
<td>±0.17</td>
<td>±0.11</td>
</tr>
<tr>
<td></td>
<td>±0.17</td>
<td>±0.11</td>
<td>±0.21</td>
<td>±0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T141V/237</td>
<td>-0.16</td>
<td>0.37</td>
<td>1.04</td>
<td>0.47</td>
<td>±0.22</td>
<td>±0.11</td>
</tr>
<tr>
<td></td>
<td>±0.22</td>
<td>±0.11</td>
<td>±0.21</td>
<td>±0.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S180V/232.8</td>
<td>-0.28</td>
<td>0.40</td>
<td>0.37</td>
<td>0.04</td>
<td>-1.91</td>
<td>-0.29</td>
</tr>
<tr>
<td></td>
<td>±0.24</td>
<td>±0.14</td>
<td>±0.25</td>
<td>±0.38</td>
<td>±0.87</td>
<td>±0.14</td>
</tr>
<tr>
<td>T141V/238</td>
<td>-0.10</td>
<td>0.26</td>
<td>0.29</td>
<td>0.04</td>
<td>±0.16</td>
<td>±0.11</td>
</tr>
<tr>
<td></td>
<td>±0.16</td>
<td>±0.11</td>
<td>±0.17</td>
<td>±0.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T141V/238v</td>
<td>0.23</td>
<td>0.26</td>
<td>-0.12</td>
<td>-1.06</td>
<td>±0.18</td>
<td>±0.11</td>
</tr>
<tr>
<td></td>
<td>±0.18</td>
<td>±0.11</td>
<td>±0.25</td>
<td>±0.25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 7 continued

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\varepsilon_{142}$</th>
<th>$\varepsilon_{145}$</th>
<th>$\varepsilon_{148}$</th>
<th>$\varepsilon_{150}$</th>
<th>$\varepsilon_{144}$</th>
<th>$\varepsilon_{148}$</th>
<th>$\varepsilon_{149}$</th>
<th>$\varepsilon_{150}$</th>
<th>$\varepsilon_{154}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Koongarra</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>87/90.5</td>
<td>-1.49</td>
<td>2.09</td>
<td>0.29</td>
<td>-1.99</td>
<td>-0.09</td>
<td>-0.69</td>
<td>-7.72</td>
<td>13.33</td>
<td>-0.26</td>
</tr>
<tr>
<td></td>
<td>±0.33</td>
<td>±0.14</td>
<td>±0.29</td>
<td>±0.38</td>
<td>±0.61</td>
<td>±0.14</td>
<td>±0.12</td>
<td>±0.11</td>
<td>±0.14</td>
</tr>
<tr>
<td>87/90.8v</td>
<td>-0.90</td>
<td>1.29</td>
<td>0.50</td>
<td>-0.55</td>
<td>-1.57</td>
<td>-0.50</td>
<td>-6.58</td>
<td>11.56</td>
<td>-0.20</td>
</tr>
<tr>
<td></td>
<td>±0.15</td>
<td>±0.08</td>
<td>±0.17</td>
<td>±0.21</td>
<td>±0.70</td>
<td>±0.12</td>
<td>±0.10</td>
<td>±0.14</td>
<td>±0.14</td>
</tr>
<tr>
<td>87/91.7</td>
<td>-0.85</td>
<td>1.38</td>
<td>0.83</td>
<td>0.38</td>
<td>-2.70</td>
<td>-0.59</td>
<td>-2.57</td>
<td>4.75</td>
<td>-0.24</td>
</tr>
<tr>
<td></td>
<td>±0.15</td>
<td>±0.08</td>
<td>±0.21</td>
<td>±0.21</td>
<td>±0.52</td>
<td>±0.12</td>
<td>±0.12</td>
<td>±0.11</td>
<td>±0.13</td>
</tr>
<tr>
<td>87/90.8v2</td>
<td>-0.84</td>
<td>1.43</td>
<td>0.17</td>
<td>-0.80</td>
<td>-2.00</td>
<td>-0.45</td>
<td>-6.50</td>
<td>11.59</td>
<td>-0.50</td>
</tr>
<tr>
<td></td>
<td>±0.15</td>
<td>±0.14</td>
<td>±0.21</td>
<td>±0.30</td>
<td>±0.87</td>
<td>±0.14</td>
<td>±0.12</td>
<td>±0.14</td>
<td>±0.12</td>
</tr>
<tr>
<td>94/147.4</td>
<td>0.04</td>
<td>0.54</td>
<td>-0.04</td>
<td>-1.31</td>
<td>-0.52</td>
<td>-0.31</td>
<td>-1.22</td>
<td>2.32</td>
<td>-0.04</td>
</tr>
<tr>
<td></td>
<td>±0.21</td>
<td>±0.14</td>
<td>±0.25</td>
<td>±0.25</td>
<td>±1.04</td>
<td>±0.14</td>
<td>±0.12</td>
<td>±0.18</td>
<td>±0.14</td>
</tr>
<tr>
<td>87/90.77</td>
<td>-1.31</td>
<td>1.58</td>
<td>1.04</td>
<td>0.34</td>
<td>-0.96</td>
<td>-0.64</td>
<td>-6.48</td>
<td>11.96</td>
<td>-0.64</td>
</tr>
<tr>
<td></td>
<td>±0.40</td>
<td>±0.20</td>
<td>±0.25</td>
<td>±0.42</td>
<td>±0.61</td>
<td>±0.10</td>
<td>±0.06</td>
<td>±0.11</td>
<td>±0.08</td>
</tr>
<tr>
<td>Ranger</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>-0.93</td>
<td>1.29</td>
<td>0.54</td>
<td>-0.72</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>±0.16</td>
<td>±0.11</td>
<td>±0.17</td>
<td>±0.21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>J</td>
<td>-0.06</td>
<td>0.23</td>
<td>0.66</td>
<td>0.64</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>±0.17</td>
<td>±0.08</td>
<td>±0.17</td>
<td>±0.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>-0.61</td>
<td>0.72</td>
<td>0.66</td>
<td>-0.46</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>±0.18</td>
<td>±0.14</td>
<td>±0.21</td>
<td>±0.20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>-0.55</td>
<td>1.06</td>
<td>0.66</td>
<td>-0.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>±0.20</td>
<td>±0.11</td>
<td>±0.29</td>
<td>±0.20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>-0.61</td>
<td>1.41</td>
<td>-0.21</td>
<td>-0.93</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>±0.20</td>
<td>±0.14</td>
<td>±0.21</td>
<td>±0.20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>-1.83</td>
<td>1.49</td>
<td>0.58</td>
<td>-1.73</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>±0.29</td>
<td>±0.22</td>
<td>±0.46</td>
<td>±0.47</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table 8. Fission yields

<table>
<thead>
<tr>
<th>mass</th>
<th>$^{238}$U spont. fission$^1$</th>
<th>$^{235}$U thermal fission$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>142</td>
<td>---</td>
<td>$10^{-8}$</td>
</tr>
<tr>
<td>143</td>
<td>6.08</td>
<td>5.95</td>
</tr>
<tr>
<td>144</td>
<td>5.08</td>
<td>5.48</td>
</tr>
<tr>
<td>145</td>
<td>(4.4)</td>
<td>3.92</td>
</tr>
<tr>
<td>146</td>
<td>(3.85)</td>
<td>2.97</td>
</tr>
<tr>
<td>147</td>
<td>3.21</td>
<td>2.24</td>
</tr>
<tr>
<td>148</td>
<td>(2.5)</td>
<td>1.67</td>
</tr>
<tr>
<td>149</td>
<td>1.5</td>
<td>1.07</td>
</tr>
<tr>
<td>150</td>
<td>(0.67)</td>
<td>0.65</td>
</tr>
<tr>
<td>152</td>
<td>---</td>
<td>0.27</td>
</tr>
<tr>
<td>154</td>
<td>---</td>
<td>0.07</td>
</tr>
</tbody>
</table>

$^1$ data compiled by von Gunten (1968), $^2$ data taken from Murakami et al. (1982), numbers in parentheses are interpolated.

### Table 9. Comparison of measured and calculated Nd isotope anomalies produced by fission

<table>
<thead>
<tr>
<th>sample</th>
<th>U/Nd</th>
<th>$\xi_{142}$</th>
<th>$\xi_{145}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2/21</td>
<td>920</td>
<td>-0.29±0.1</td>
<td>-0.14</td>
</tr>
<tr>
<td>#2</td>
<td>4200</td>
<td>-2.67±0.1</td>
<td>-0.65</td>
</tr>
<tr>
<td>#3</td>
<td>1985</td>
<td>-0.80±0.11</td>
<td>-0.31</td>
</tr>
<tr>
<td>#4</td>
<td>4025</td>
<td>-2.55±0.23</td>
<td>-0.62</td>
</tr>
<tr>
<td>4/40</td>
<td>3340</td>
<td>-1.38±0.12</td>
<td>-0.52</td>
</tr>
<tr>
<td>69/42</td>
<td>2340</td>
<td>-1.17±0.15</td>
<td>-0.37</td>
</tr>
<tr>
<td>69/43.2</td>
<td>1590</td>
<td>-0.89±0.11</td>
<td>-0.25</td>
</tr>
<tr>
<td>256A</td>
<td>195</td>
<td>-0.05±0.08</td>
<td>-0.03</td>
</tr>
</tbody>
</table>

$m$ is the measured ratio in the sample with its 2sigma mean error; $A$ is expected anomaly from $^{238}$U spontaneous fission; $B$ is expected anomaly from $^{238}$U spont. fission plus thermal neutron fission of $^{235}$U (the number of thermal fissions depends on the U content and the neutron fluence in the sample, equation 5); $C$ is the expected anomaly from spontaneous fission plus 3x thermal fission of $^{235}$U. The 3fold increase in the number of fissioning $^{235}$U atoms is arbitrary.
\begin{align*}
\frac{^{144}\text{Sm}}{^{152}\text{Sm}} &= 0.114956 \pm 13 \\
\frac{^{148}\text{Sm}}{^{152}\text{Sm}} &= 0.420447 \pm 2 \\
\frac{^{149}\text{Sm}}{^{152}\text{Sm}} &= 0.516839 \pm 9 \\
\frac{^{150}\text{Sm}}{^{152}\text{Sm}} &= 0.276005 \pm 2 \\
\frac{^{154}\text{Sm}}{^{152}\text{Sm}} &= 0.850813 \pm 35 \\
\frac{^{154}\text{Gd}}{^{160}\text{Gd}} &= 0.099706 \pm 60
\end{align*}

Fig. 1a
<table>
<thead>
<tr>
<th></th>
<th>( ^{155}\text{Gd}/^{160}\text{Gd} = 0.676909\pm16 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6770</td>
<td><img src="image1" alt="Graph" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>( ^{157}\text{Gd}/^{160}\text{Gd} = 0.715875\pm15 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.71584</td>
<td><img src="image2" alt="Graph" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>( ^{158}\text{Gd}/^{160}\text{Gd} = 1.135886\pm20 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.13590</td>
<td><img src="image3" alt="Graph" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>( ^{142}\text{Nd}/^{144}\text{Nd} = 1.141895\pm20 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.14195</td>
<td><img src="image4" alt="Graph" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>( ^{145}\text{Nd}/^{144}\text{Nd} = 0.348387\pm10 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.34839</td>
<td><img src="image5" alt="Graph" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>( ^{150}\text{Nd}/^{144}\text{Nd} = 0.236439\pm8 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.23650</td>
<td><img src="image6" alt="Graph" /></td>
</tr>
</tbody>
</table>
Fig. 2

- **Fig. 2A**: Neutron capture line slope = -1
  - Plot of $^{149}\text{Sm}/^{152}\text{Sm}$ vs $^{150}\text{Sm}$
  - Points for Nabarlek, Jabiluka, Koongurra, and Normals

- **Fig. 2B**: Neutron capture line slope = -0.764
  - Plot of $^{150}\text{Gd}/^{160}\text{Gd}$ vs $^{157}\text{Gd}/^{160}\text{Gd}$
  - Points for normal Gd

- **Fig. 2C**: Neutron capture line slope = 0.3797
  - Plot of $^{150}\text{Gd}/^{160}\text{Gd}$ vs $^{157}\text{Gd}/^{160}\text{Gd}$
  - Points for normal Gd
Fig. 3
Fig. 4
Fig. 5
Fig. 6
Fig. 7
APPENDIX 4

Correction for U fission effects in Nd isotopic data
The Nd isotopic data in Table 7 (part 2) clearly demonstrate that stable Nd isotope ratios in most if not all measured samples have been changed to some extent. The largest anomalies are found in the ratios $^{142}$Nd/$^{144}$Nd and $^{145}$Nd/$^{144}$Nd; they are strongly correlated with each other (Fig.App4-1) and U/Nd ratios (see part 2).

$^{148}$Nd/$^{144}$Nd and $^{150}$Nd/$^{144}$Nd ratios are also anomalous in many samples but correlate poorly with each other, $^{142}$Nd/$^{144}$Nd, $^{145}$Nd/$^{144}$Nd and U/Nd ratios (for details see part 2 of this thesis). Isotopic anomalies in Nd and other REE are to be expected in high grade U ores (>1 wt% U), in particular those of Precambrian age. They are caused by fission of U which affects Nd isotope ratios in two ways: thermal neutron capture on some Nd isotopes, e.g. $^{143}$Nd (n/$\gamma$)$^{144}$Nd (capture cross section = 330 barns), and addition of isotopically distinct fissionogenic Nd to Nd of normal isotopic composition (with fission yields between 0.7-6 % for Nd isotopes).

Spectacular results of these processes have been reported from the 1800 Ma Oklo uranium deposit which contains zones that became critical for a period(s) of $= 5 \times 10^5$ Ma shortly after ore deposition (Loubet and Allègre, 1977). In one sample with 66.2 % U, $^i$Nd/$^{142}$Nd ratios have been increased by 51-80 % relative to normal isotopic ratios ($i$ being the $i$th isotope of Nd). Calculated thermal neutron fluences in this deposit are on the order of $5 \times 10^{20}$ n/cm$^2$. In contrast, the fission effects in the Nabarlek samples are much smaller (on the order of 0.01-0.03 %) and the thermal neutron fluence derived from Sm and Gd isotope data is $11 \times 10^{15}$ n/cm$^2$. If it is assumed that the REE in Nabarlek primary U ores were immobile, the small isotopic anomalies in Nd (and in Sm, Gd and U) would indicate that the fission products and the neutrons were dominantly derived from spontaneous fission of $^{238}$U over the lifetime of the ore rather than from a $^{235}$U chain reaction during a relatively short period of criticality. However, the isotopic evidence for Nabarlek and for many other U deposits (cf. Kuroda, 1982) suggests that thermal neutron
fission of $^{235}$U supplied at least part of the fission products accumulated in the ore.

At the relatively small neutron fluences involved, fissionogenic Nd addition becomes the major cause of changes in the Nd isotopic ratios. Using equations 4 and 5 (see part 2) and measured U-Nd abundances (in the Nabarlek samples), it is possible to estimate the number $N_{f}^i$ of fission product atoms of Nd isotope $i$ relative to the number of $N_i$ already present at the start of the fission process. This treatment assumes that U/Nd ratios were not influenced by mobility of either element. Calculations on the effect of purely spontaneous fission for Nabarlek high grade ores (U/Nd=1500-4000) indicate $N_{f}^i/N_i$ ratios on the order of $10^{-5}$ to $10^{-4}$ which would introduce model anomalies of $\leq 1\ \varepsilon\ unit$ in the isotope ratios (model A). If the contribution to $N_{f}^i$ from $^{235}$U thermal neutron fission is taken into account (from equation 5 using revised fluence values, Table 4, see part 2), the model $\varepsilon$ values are approximately doubled (model B). To account for the largest anomalies (in Nabarlek samples #2 and #4), $N_{f}^i$ from $^{235}$U thermal neutron fission has been increased 3 times and the ratios recalculated (model C). The calculations include corrections for mass fractionation (power law) assuming constant $^{146}$Nd/$^{144}$Nd = 0.7219. This introduces some error because both $^{146}$Nd and $^{144}$Nd are produced in fission and $^{144}$Nd grows by neutron capture on $^{143}$Nd. However, at the fluences and fission rates involved, the effects on the $^{146}$Nd/$^{144}$Nd ratio are very small, amounting to a maximum $\varepsilon_{146} = -0.29$.

Fig.App4-2 Results of model calculations for $\varepsilon_{142}$, $\varepsilon_{145}$ and $\Delta 143$ in 8 Nabarlek ores. Labels A, B and C refer to models A, B and C; their positions mark the maximum deviations possible for the Nabarlek U/Nd ratios. Note that $\Delta 143$ values are positive and strongly correlated with the other deviations.

Figs.App 4-2 to 4-4 show the results of the modeling for $\varepsilon_{142}$ and $\varepsilon_{145}$ as a function of $\Delta 143$ and U/Nd. $\Delta 143$ is the fission-related component in $^{143}$Nd/$^{144}$Nd (in parts of $10^{-4}$) and is introduced to avoid confusion with the standard $\varepsilon_{Nd}$ notation. The correlations are in good agreement with measured data (Fig.App4-3), indicating that the model calculations closely approximate the processes responsible for the Nd anomalies. They also show that $\Delta 143$
values are linearly related to both $\varepsilon_{142}$ and $\varepsilon_{145}$ (Fig.App4-2), thus providing a basis on which measured $^{143}\text{Nd}/^{144}\text{Nd}$ values in the samples can be corrected for $\Delta 143$. Because of the larger relative effects and smaller potential for interference problems, $\varepsilon_{145}$ values are more suitable as a monitor of $\Delta 143$ than $\varepsilon_{142}$ values.

![Fig.App 4-3 Plot of model anomalies $\varepsilon_{145}$ versus U/Nd. Model correlations A, B and C (crosses, open diamonds and closed squares, respectively) are indicated. Results for Nabarlek ores are shown.](image)

In the 26 ore and uraninite samples for which all Nd isotope ratios are available, $\varepsilon_{143}$ values measured during the same run have been reduced by 0.5-3 $\varepsilon$ units ($\Delta 143$) according to measured $\varepsilon_{145}$, assuming a constant $\Delta 143/\varepsilon_{145}$ ratio of $=0.89$. The corrected $\varepsilon_{143}$ values were converted into $^{143}\text{Nd}/^{144}\text{Nd}$ ratios and are given in Tables 3-6 of appendix 3a. To account for possible errors introduced by this procedure, $2\sigma_{\text{mean}}$ in-run errors for the corrected ratios are set at 0.00050 which is 1.5-5 times higher than normal in-run errors. For Nabarlek, 7 high grade primary ores were corrected in this way; nine other high grade samples from this deposit (indicated in appendix 3a, Table 3) were corrected using a somewhat different and potentially less accurate method. As only U/Nd data were available for these samples, they were corrected using the model relationship between $\Delta 143$ and U/Nd (Fig.App4-4). A disadvantage of this approach is that it is generally not known which of the fission models A to C might be appropriate for a particular sample. For example, if a sample had a greater $^{235}\text{U}$ burnup than assumed in model B, corrections estimated according to B could be too small by 1 $\varepsilon$ unit. The fission models for these samples were therefore chosen according to their U content and general similarities to the first group of samples for which $\varepsilon_{145}$ values were known. The three uraninite separates were corrected using the $\Delta 143$ values derived for their respective whole rocks because U-Nd ratios are likely to be very similar.

Measured anomalies for the samples from Jabiluka, Koongarra and Ranger are small with $\varepsilon_{145} \leq 1.5$ (only two results were between 1.5 and 2.1) and appropriate $\Delta 143$ corrections have been applied. For Jabiluka, only those samples on the $=1600$ Ma isochron (plus S180V/232.8) were analysed in detail and corrected for fission effects, the others are uncorrected. Similarly, only No.1 lens samples plus one sample from No.2 lens are corrected amongst the Koongarra samples. However, it is unlikely that possible anomalies
in the uncorrected samples exceed those in the corrected samples, implying that possible bias in the uncorrected samples would be small (Δ143 ≤ 1.5 parts in 10^-4) and would not critically influence the interpretations presented in Chapter 3 and appendix 3a.

Fig.App4-4 Plot of model Δ143 values versus U/Nd. Models A, B and C are indicated.