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PROCESSES OF CHEMICAL WEATHERING OF SELECTED CAINOZOIC EASTERN AUSTRALIAN BASALTS

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THIS THESIS IS PRESENTED
IN FULFILMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY (SCIENCE) IN
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DECLARATION OF ORIGINALITY

I, Cara Leah Moore, hereby declare that to the best of my knowledge the following thesis is original research carried out by me, unless otherwise stated.

[Signature]

Cara Leah Moore
~I dedicate this thesis to my grandparents~
~Sarah and Eric (Scotty) Watts~
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ABSTRACT

The processes of chemical weathering of basalt have been observed across a range of time and climate space, and studies from isolated areas in eastern Australia integrated into a single extensive work, with a view to understanding the variations in processes and products of basalt weathering. In particular geochemical and mineralogical variations are characterised, and an attempt to relate these to physicochemical variations in environment has been made.

For the first time the graphical isocon technique has been used to interpret the geochemical data of weathered basalts, and was found to be an appropriate technique to use in evaluating element enrichment and depletion, and mass change as an indication of degree of weathering. However, this technique must be used in close association with careful petrographic work and where possible X-ray diffraction. The graphical isocon technique is superior to other weathering indices because there is an internal check on the degree to which immobile elements have remained immobile during weathering.

The observed order of dissolution of the principal basalt phases is: basaltic glass, olivine, plagioclase, pyroxene and opaque oxides, but pyroxene weathers more rapidly than plagioclase feldspar, and is wholly weathered before plagioclase feldspar. In general, basalts weather through the stages: trioctahedral/dioctahedral smectites; dioctahedral smectites ± minor kaolinite; dioctahedral smectite, randomly interstratified kaolin-smectites, halloysite and minor kaolinite; halloysite and kaolinite; halloysite, kaolinite and gibbsite.

The trioctahedral smectites are mostly saponite and Fe-saponite, while the dioctahedral phases are dominantly nontronite and beidellite with some montmorillonite. The smectite phase in the randomly interstratified kaolin-smectite clays is nontronite and/or Fe-beidellite. Randomly interstratified kaolin-smectite clays, intermediate in the break down of smectite to kaolinite, are widespread in the products of basalt weathering in eastern Australia, but are difficult to distinguish using cation saturation, X-ray diffraction and cation exchange capacity alone. Halloysite is more widespread in the products of basalt weathering than previously documented and appears to be the kaolin group clay preferentially formed during the break down of smectite clays, although kaolinite is also produced.

A comprehensive compilation of major and trace element mobility for the Eastern Australian basalts, evaluated using the isocon technique, is presented. Many elements behave as previously documented for weathering of well drained basalt. For example: the rapid removal of alkali and alkaline earth cations from the weathering profiles;
progressive weathering of silica from the profiles; the oxidation of iron during weathering resulting in the fixation of iron, largely as goethite and hematite; similar oxidation of manganese to form coatings on weathered surfaces; the variable but limited mobility of zinc and vanadium reflecting the partitioning of these elements into resistant primary minerals, the relatively high mobility of copper once copper-sulphides were oxidised to sulphate; the limited mobility of the actinides; and, the residual concentration of chromium and nickel in weathering profiles.

For major cations and closely related trace elements, the general order in which elements are lost is: \( \text{Na} > \text{Sr} > \text{Ca} > \text{K} > \text{Rb} > \text{Mg} > \text{Al} > \text{Si} \), and this may be quantified using the slope of the elemental loss curve. If these data are normalised to silica, sodium is lost approximately three times faster than silica; rubidium, potassium, calcium and strontium are lost approximately 2.3 to 2.6 times more rapidly than silica; and, aluminium may be lost at a rate less than or similar to silica.

Some incipiently to moderately weathered basalts show significant enrichment in the rare earth elements, cerium and lanthanum, as well as yttrium, barium and lead. This may be attributed to the formation of secondary phosphate, carbonate and sulphate minerals, in particular secondary phosphates of the plumbogummite group. Other elements that show unusual behaviour are those that are generally considered immobile during weathering (niobium, zirconium, yttrium, aluminium, titanium, iron), but are apparently mobile under certain weathering conditions. Niobium and zirconium appear to be mobile in alkaline fluids. Titanium may be concentrated in smectite rich alkaline weathering profiles, and more depleted in kaolin rich acid profiles. Aluminium mobility varies with extremes of pH, and iron is known to be mobile under weathering conditions.

Once clay mineralogy and element mobility for a number of profiles is compiled, evaluations can be made in light of paleoclimate and contemporary climate and it is possible to relate the development of weathering profiles through time to the evolution of climate environment in Eastern Australia.

A study of aqueous geochemistry of fluids issuing from actively weathering basalt in the Monaro Volcanic Province has enabled explanation of the unusual juxtaposition of smectite and gibbsite in a cool climate weathering regime; has shown that zeolites may form in weathering in equilibrium with the percolating fluids; and, has allowed some evaluations with respect to tectonic stability of the Monaro Volcanic Province throughout the Tertiary. A calculated lowering rate, due to chemical dissolution, for the Monaro basalt is in the order of 0.7 mm/1000 years.
TABLE OF CONTENTS

ABSTRACT

ACKNOWLEDGEMENTS

CHAPTER 1: INTRODUCTION

1.1 RATIONALE
1.2 AIMS
1.3 METHODS AND TECHNIQUES
1.3.1 Regolith Sampling
1.3.2 Clay Chemistry and Cation Exchange Capacity (CEC)
1.3.3 X-ray Diffraction (XRD) Mineralogical Analysis
1.3.4 Water Sampling and Analysis
1.3.5 BIOCLIM Contemporary Climate Information
1.3.6 Petrography and Scanning Electron Microscopy
1.3.7 Whole Rock Geochemistry
1.3.8 Interpretation of Geochemical Data

CHAPTER 2: CONCEPTS OF BASALT WEATHERING

2.1 EASTERN AUSTRALIAN CAINOZOIC BASALTS
2.2 PRINCIPAL REACTIONS OF CHEMICAL WEATHERING
2.3 THE CHEMICAL WEATHERING OF BASALT LAVA FLOWS
2.3.1 Early Weathering Profile Classification Systems
2.3.2 Variability in the Field Expression of Weathered Basalts
2.3.3 Spheroidal Weathering
2.3.4 Microscale Weathering
2.3.5 The Weathering Sequence of Basalt Components
2.3.6 The Formation of Deep Weathering Profiles
2.4 ENVIRONMENTAL INFLUENCES ON BASALT WEATHERING
2.4.1 Water and Temperature
2.4.2 Oxidation, pH and Drainage (Topography)
2.4.3 Parent Material Composition
2.4.4 Vegetation

CHAPTER 3: BASALT MINERAL DISSOLUTION AND ELEMENT MOBILITY

3.1 DISSOLUTION OF THE PRINCIPAL BASALT FORMING MINERALS AND GLASS
3.1.1 Glass
3.1.2 Feldspar
3.1.3 Olivine
3.1.4 Pyroxene
3.1.5 Opaque Oxides
3.1.6 Iron Oxidation and Weathering of Ferromagnesian Minerals
Table of Contents

3.1.7 Chemistry of Accessory Minerals ...................................... 40
Zircon .............................................................................. 40
Apatite ............................................................................ 40
Titanite ........................................................................... 41
Rutile .................................................................................. 41
Feldspathoids .................................................................... 41
Zeolites ............................................................................. 41
Calcite ................................................................................ 42

3.2 ELEMENT MOBILITY DURING THE DISSOLUTION OF BASALT MINERALS .................................. 42
3.2.1 Potassium, Sodium, Calcium and Magnesium .................. 42
3.2.2 Silica ........................................................................ 44
3.2.3 Manganese, Lead, Copper and Zinc ............................. 45
3.2.4 Strontium, Barium, Rubidium, Nickel and Chromium ....... 46
3.2.5 Titanium, Zircon, Niobium and Aluminium .................... 48
3.2.6 Yttrium, Lanthanum, Cerium, Thorium and Uranium ....... 50
3.2.7 Iron, Vanadium, Sulphur and Phosphorus ...................... 50

3.3 PRINCIPAL SECONDARY BASALT WEATHERING PRODUCTS 52
3.3.1 Hematite and Goethite .................................................. 52
3.3.2 Anatase ....................................................................... 53
3.3.3 Gibbsite ....................................................................... 53
3.3.4 Kaolinite and Halloysite ................................................. 54
3.3.5 Interstratified Kaolin-Smectite Clays .............................. 55
3.3.6 Smectite Clays .............................................................. 56
3.3.7 Vermiculite .................................................................. 57

CHAPTER 4: CAINOZOIC CLIMATE EVOLUTION ......................... 58
4.1 INTRODUCTION ................................................................ 58
4.2 CAINOZOIC CLIMATE EVOLUTION .................................. 59
4.2.1 Paleocene (65 to 58 Ma) .............................................. 59
4.2.2 Eocene (58 to 36 Ma) .................................................. 60
Early Eocene ....................................................................... 60
Middle Eocene ..................................................................... 61
Late Eocene .......................................................................... 62
4.2.3 Oligocene (36 to 24 Ma) .............................................. 62
4.2.4 Miocene (24 to 6 Ma) .................................................. 64
Early Miocene ....................................................................... 64
Middle Miocene .................................................................... 65
Late Miocene ......................................................................... 66
4.2.5 Pliocene (6 to 2 Ma) ..................................................... 66
4.2.6 Quaternary (2 Ma to present) ....................................... 67
4.3 CONTEMPORARY CLIMATE ........................................... 68
4.3.1 Radiation ...................................................................... 68
4.3.2 Temperature ............................................................... 68
4.3.3 Precipitation ............................................................... 70
4.3.4 Seasonality ................................................................... 71
4.4 PALEOCLIMATE, CONTEMPORARY CLIMATE AND CAINOZOIC BASALT WEATHERING .......... 72

CHAPTER 5: BASALT WEATHERING PROFILES FROM TASMANIA ............................................. 73
5.1 LOCATION ........................................................................ 73
5.2 CONTEMPORARY CLIMATE .......................................... 74
5.3 PALEOCLIMATE AND VEGETATION ................................. 75
5.4 GEOLOGY - NORTH WEST TASMANIA .............................. 76
5.5 HELLYER RIVER BRIDGE, NORTH WEST TASMANIA VOLCANIC PROVINCE ............... 77
Table of Contents

5.5.1 Nature of the Exposure ............................................. 77
5.5.2 Geochemistry .......................................................... 78
5.5.3 Clay Mineralogy ....................................................... 81
5.5.4 Petrography ............................................................. 83
5.5.5 Profile Summary ...................................................... 85

5.6 GEOLOGY - CENTRAL TASMANIA VOLCANIC PROVINCE .......... 86

5.7 MONPEELY-ATA CANAL, CENTRAL TASMANIA VOLCANIC
PROVINCE 87
5.7.1 Nature of the Exposure ............................................... 87
5.7.2 Geochemistry .......................................................... 89
5.7.3 Clay Mineralogy ....................................................... 91
5.7.4 Petrography ............................................................. 95
5.7.5 Profile Summary ...................................................... 97

5.8 GEOLOGY - NORTH EAST TASMANIA VOLCANIC PROVINCE .... 98

5.9 BRANXHOLME, NORTH EAST TASMANIA VOLCANIC
PROVINCE 99
5.9.1 Nature of the Exposure ............................................... 99
5.9.2 Geochemistry .......................................................... 101
5.9.3 Clay Mineralogy ....................................................... 104
5.9.4 Petrography ............................................................. 108
5.9.5 Profile Summary ...................................................... 110

CHAPTER 6: BASALT WEATHERING PROFILES FROM
SOUTHERN NEW SOUTH WALES ........................................... 112

6.1 LOCATION ................................................................. 112
6.2 CONTEMPORARY CLIMATE ............................................ 113
6.3 PALEOCLIMATE AND VEGETATION .................................. 114
6.4 GEOLOGY - MONARO VOLCANIC PROVINCE ....................... 114

6.5 BIG WILLOW, MONARO VOLCANIC PROVINCE ................. 115
6.5.1 Nature of the Exposure ............................................... 115
6.5.2 Geochemistry .......................................................... 116
6.5.3 Clay Mineralogy ....................................................... 119
6.5.4 Petrography ............................................................. 122
6.5.5 Profile Summary ...................................................... 125

6.6 SHERWOOD, MONARO VOLCANIC PROVINCE ..................... 126
6.6.1 Nature of the Exposure ............................................... 126
6.6.2 Geochemistry .......................................................... 127
6.6.3 Clay Mineralogy ....................................................... 129
6.6.4 Petrography ............................................................. 132
6.6.5 Profile Summary ...................................................... 133

CHAPTER 7: BASALT WEATHERING PROFILES FROM
NORTHERN NEW SOUTH WALES .......................................... 135

7.1 LOCATION ................................................................. 135
7.2 CONTEMPORARY CLIMATE ............................................ 136
7.3 PALEOCLIMATE AND VEGETATION .................................. 136
7.4 GEOLOGY - WARRUMBUNGLES VOLCANIC PROVINCE .......... 137

7.5 NEWELL/OXLEY HIGHWAY, WARRUMBUNGLES
VOLCANIC PROVINCE ..................................................... 138
7.5.1 Nature of the Exposure ............................................... 138
7.5.2 Geochemistry .......................................................... 140
7.5.3 Clay Mineralogy ....................................................... 144
7.5.4 Petrography ............................................................. 148
7.5.5 Profile Summary ...................................................... 152

7.6 CHALK MOUNTAIN, WARRUMBUNGLES VOLCANIC
PROVINCE ................................................................. 153
7.6.1 Nature of the Exposure ............................................... 153
7.6.2 Geochemistry .......................................................... 154
CHAPTER 8: BASALT WEATHERING PROFILES FROM SOUTHERN QUEENSLAND/NORTHERN NEW SOUTH WALES

8.1 LOCATION
8.2 CONTEMPORARY CLIMATE
8.3 PALEOCLIMATE AND VEGETATION
8.4 GEOLOGY - TWEED VOLCANIC PROVINCE
8.5 EAST LISMORE, TWEED VOLCANIC PROVINCE
  8.5.1 Nature of the Exposure
  8.5.2 Geochemistry
  8.5.3 Clay Mineralogy
  8.5.4 Petrography
  8.5.5 Profile Summary
8.6 BEECHMONT, TWEED VOLCANIC PROVINCE
  8.6.1 Nature of the Exposure
  8.6.2 Geochemistry
  8.6.3 Clay Mineralogy
  8.6.4 Petrography
  8.6.5 Profile Summary

CHAPTER 9: BASALT WEATHERING PROFILES FROM CENTRAL QUEENSLAND

9.1 LOCATION
9.2 CONTEMPORARY CLIMATE
9.3 PALEOCLIMATE AND VEGETATION
9.4 GEOLOGY - SPRINGSURE VOLCANIC PROVINCE
9.5 WESTERN SPRINGSURE, SPRINGSURE VOLCANIC PROVINCE
  9.5.1 Nature of the Exposure
  9.5.2 Geochemistry
  9.5.3 Clay Mineralogy
  9.5.4 Petrography
  9.5.5 Profile Summary
9.6 GEOLOGY - PEAK RANGE VOLCANIC PROVINCE
9.7 STOCK ROUTE, PEAK RANGE VOLCANIC PROVINCE
  9.7.1 Nature of the Exposure
  9.7.2 Geochemistry
  9.7.3 Clay Mineralogy
  9.7.4 Petrography
  9.7.5 Profile Summary

CHAPTER 10: BASALT WEATHERING PROFILES FROM NORTHERN QUEENSLAND

10.1 LOCATION
10.2 CONTEMPORARY CLIMATE
10.3 PALEOCLIMATE AND VEGETATION
10.4 GEOLOGY - ATHERTON VOLCANIC PROVINCE
10.5 ARCHERS CREEK ATHERTON VOLCANIC PROVINCE
# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.5.1</td>
<td>Nature of the Exposure</td>
</tr>
<tr>
<td>10.5.2</td>
<td>Geochemistry</td>
</tr>
<tr>
<td>10.5.3</td>
<td>Clay Mineralogy</td>
</tr>
<tr>
<td>10.5.4</td>
<td>Petrography</td>
</tr>
<tr>
<td>10.5.5</td>
<td>Profile Summary</td>
</tr>
<tr>
<td>10.6</td>
<td>MILLAA MILLAA, ATHERTON VOLCANIC PROVINCE</td>
</tr>
<tr>
<td>10.6.1</td>
<td>Nature of the Exposure</td>
</tr>
<tr>
<td>10.6.2</td>
<td>Clay Mineralogy</td>
</tr>
<tr>
<td>10.6.3</td>
<td>Profile Summary</td>
</tr>
<tr>
<td>10.7</td>
<td>PALMERSTON HIGHWAY, INNISFAIL, ATHERTON VOLCANIC PROVINCE</td>
</tr>
<tr>
<td>10.7.1</td>
<td>Nature of the Exposure</td>
</tr>
<tr>
<td>10.7.2</td>
<td>Clay Mineralogy</td>
</tr>
<tr>
<td>10.7.3</td>
<td>Petrography</td>
</tr>
<tr>
<td>10.7.4</td>
<td>Profile Summary</td>
</tr>
<tr>
<td>10.8</td>
<td>GEOLOGY - MCBRIDE VOLCANIC PROVINCE</td>
</tr>
<tr>
<td>10.9</td>
<td>KENNEDY HIGHWAY, MCBRIDE VOLCANIC PROVINCE</td>
</tr>
<tr>
<td>10.9.1</td>
<td>Nature of the Exposure</td>
</tr>
<tr>
<td>10.9.2</td>
<td>Clay Mineralogy</td>
</tr>
<tr>
<td>10.9.3</td>
<td>Petrography</td>
</tr>
<tr>
<td>10.9.4</td>
<td>Profile Summary</td>
</tr>
<tr>
<td>10.10</td>
<td>GEOLOGY - NULLA VOLCANIC PROVINCE</td>
</tr>
<tr>
<td>10.11</td>
<td>FLETCHER VALE ROAD, NULLA VOLCANIC PROVINCE</td>
</tr>
<tr>
<td>10.11.1</td>
<td>Nature of the Exposure</td>
</tr>
<tr>
<td>10.11.2</td>
<td>Clay Mineralogy</td>
</tr>
<tr>
<td>10.11.3</td>
<td>Petrography</td>
</tr>
<tr>
<td>10.11.4</td>
<td>Profile Summary</td>
</tr>
</tbody>
</table>

**CHAPTER 11: PHYSICOCHEMICAL ANALYSIS OF BASALT GROUNDWATER MONARO VOLCANIC PROVINCE**

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.1</td>
<td>INTRODUCTION</td>
</tr>
<tr>
<td>11.2</td>
<td>HYDROLAB MEASUREMENTS</td>
</tr>
<tr>
<td>11.2.1</td>
<td>Water Temperature</td>
</tr>
<tr>
<td>11.2.2</td>
<td>Water pH</td>
</tr>
<tr>
<td>11.2.3</td>
<td>Dissolved Oxygen Concentration</td>
</tr>
<tr>
<td>11.2.4</td>
<td>Electrical Conductivity (EC)</td>
</tr>
<tr>
<td>11.3</td>
<td>TURBIDITY, COLOUR, ODOUR</td>
</tr>
<tr>
<td>11.4</td>
<td>ANION ANALYSES</td>
</tr>
<tr>
<td>11.4.1</td>
<td>Bicarbonate (HCO3-)</td>
</tr>
<tr>
<td>11.4.2</td>
<td>Chloride (Cl-)</td>
</tr>
<tr>
<td>11.4.3</td>
<td>Nitrates and Nitrites (NO3-, NO2-)</td>
</tr>
<tr>
<td>11.4.4</td>
<td>Sulphate (SO42-)</td>
</tr>
<tr>
<td>11.5</td>
<td>CATION ANALYSES</td>
</tr>
<tr>
<td>11.5.1</td>
<td>Calcium (Ca)</td>
</tr>
<tr>
<td>11.5.2</td>
<td>Magnesium (Mg)</td>
</tr>
<tr>
<td>11.5.3</td>
<td>Sodium (Na)</td>
</tr>
<tr>
<td>11.5.4</td>
<td>Potassium (K)</td>
</tr>
<tr>
<td>11.5.5</td>
<td>Iron (Fe) and Manganese (Mn)</td>
</tr>
<tr>
<td>11.6</td>
<td>DUROV-ZAPOROZEC INTERPRETATION</td>
</tr>
<tr>
<td>11.7</td>
<td>MINERAL STABILITY AND BASALT AQUIFER WATERS</td>
</tr>
<tr>
<td>11.7.1</td>
<td>Activity-Activity Ratios of Major Cations</td>
</tr>
<tr>
<td>11.7.2</td>
<td>Gibbsite and Smectite in the Secondary Mineral Suite</td>
</tr>
<tr>
<td>11.8</td>
<td>GROUNDWATER AND THE WEATHERING OF BASALT</td>
</tr>
</tbody>
</table>
# Table of Contents

## CHAPTER 12: DISCUSSION

### PART A: AN OVERVIEW OF MINERALOGICAL CHANGES DURING BASALT WEATHERING IN EASTERN AUSTRALIA

12(A).1 DISSOLUTION OF PRIMARY BASALT MINERALS .......................................................... 295  
12(A).2 MASS LOSS DURING WEATHERING ........................................................................... 297  
12(A).3 FORMATION OF THE SECONDARY MINERAL ASSEMBLAGES ........................................ 298  
  12(A).3.1 Secondary Mineral Assemblage Dynamics for Weathered Basalts in Eastern Australia .................................................................................. 298  
  12(A).3.2 Secondary Mineralogy - A Summary .................................................................. 304  
12(A).4 OTHER FACTORS AFFECTING FORMATION OF SECONDARY MINERALS ........ 308  
  12(A).4.1 Drainage, Eh, Topography, pH .......................................................................... 308  
  12(A).4.2 Textural Variations in Flow Basalts ................................................................. 309

### PART B: AN OVERVIEW OF ELEMENT MOBILITY DURING BASALT WEATHERING IN EASTERN AUSTRALIA

12(B).1 ELEMENTAL VARIATION DURING WEATHERING .................................................. 310  
  12(B).1.1 Alkali and Alkaline Earth Elements .................................................................. 311  
  12(B).1.2 Transition Elements and Semi-Metals ......................................................... 314  
  12(B).1.3 Actinides ......................................................................................................... 318  
12(B).2 RARE EARTH ELEMENTS, BARIUM AND LEAD .................................................. 319  
  12(B).2.1 The Implications of Enrichment of Rare Earth Elements (REE), Barium (Ba) and Lead (Pb) During Basalt Weathering ........................................ 323  
12(B).3 ELEMENTS GENERALLY CONSIDERED IMMOBILE DURING WEATHERING ........ 324  
  12(B).3.1 When are Relatively Immobile Elements Mobile? ........................................ 330  
12(B).4 CALCULATING THE RATE OF ELEMENTAL LOSS/GAIN ........................................ 332

### PART C: AQUEOUS GEOCHEMISTRY OF BASALT WEATHERING IN THE MONARO AND IMPLICATIONS FOR THE WEATHERING OF BASALT IN EASTERN AUSTRALIA

12(C).1 GROUNDWATER AND THE WEATHERING OF BASALT IN THE MONARO VOLCANIC PROVINCE ................................................................. 335  
  12(C).1.1 Chemistry of the Weathering Fluids .................................................................. 335  
  12(C).1.2 The Juxtaposition of Gibbsite and Smectite in the Big Willow Basalt Weathering Profile ................................................................. 336  
  12(C).1.3 Zeolite Formation During Basalt Weathering ............................................... 337  
12(C).2 IMPLICATIONS FOR THE AQUEOUS GEOCHEMISTRY OF BASALT WEATHERING ELSEWHERE IN AUSTRALIA .................................................. 337  
12(C).3 CALCULATED RATES OF CONTEMPORARY CHEMICAL WEATHERING OF MONARO VOLCANIC PROVINCE BASALT ............................................. 338  
12(C).4 IMPLICATIONS FOR THE TECTONIC STABILITY OF THE EASTERN HIGHLANDS...... 339

### PART D: PALEOCLIMATE, CONTEMPORARY CLIMATE AND BASALT WEATHERING IN EASTERN AUSTRALIA

12(D).1 RELATIONSHIPS BETWEEN BASALT WEATHERING AND CLIMATE IN EASTERN AUSTRALIA ................................................................. 341
Table of Contents

CONCLUSIONS .............................................................................................................. 347

The Isocon Technique ................................................................................................. 347
Mineral Changes During Basalt Weathering ............................................................... 347
Element Mobility During Basalt Weathering .............................................................. 348
Secondary Mineral Evolution ....................................................................................... 349
Paleo-weathering Versus Contemporary Weathering ................................................ 351
Aqueous Geochemistry and Basalt Weathering ......................................................... 351

APPENDIX 1: BASALT WEATHERING PROFILES ......................................................... A-1
APPENDIX 2: LEAST WEATHERED EQUIVALENTS ..................................................... A-27
APPENDIX 3: GEOCHEMICAL DATA ......................................................................... A-29
APPENDIX 4: CLAY SEPARATE CHEMISTRY AND CEC .......................................... A-43
APPENDIX 5: BASALT GROUNDWATER SAMPLING AND ANALYTICAL METHODS ....... A-57
APPENDIX 6: MEASURED SOIL pH VALUES ............................................................. A-62
APPENDIX 7: ANU CATALOGUE NUMBERS ............................................................... A-63
REFERENCES ............................................................................................................. R-1
### LIST OF PLATES

<table>
<thead>
<tr>
<th>Plate 5.1</th>
<th>Outcrop photo - Hellyer River Bridge profile</th>
<th>78</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plate 5.2</td>
<td>Photomicrograph - TAS 17/2</td>
<td>84</td>
</tr>
<tr>
<td>Plate 5.3</td>
<td>Photomicrograph - TAS17/1</td>
<td>84</td>
</tr>
<tr>
<td>Plate 5.4</td>
<td>Outcrop photo - Monpeelyata Canal profile</td>
<td>88</td>
</tr>
<tr>
<td>Plate 5.5</td>
<td>Scanning electron micrograph - Monpeelyata Canal</td>
<td>94</td>
</tr>
<tr>
<td>Plate 5.6</td>
<td>Scanning electron micrograph - Monpeelyata Canal</td>
<td>94</td>
</tr>
<tr>
<td>Plate 5.7</td>
<td>Scanning electron micrograph - Monpeelyata Canal</td>
<td>94</td>
</tr>
<tr>
<td>Plate 5.8</td>
<td>Scanning electron micrograph - Monpeelyata Canal</td>
<td>94</td>
</tr>
<tr>
<td>Plate 5.9</td>
<td>Photomicrograph - TAS 27/5</td>
<td>96</td>
</tr>
<tr>
<td>Plate 5.10</td>
<td>Photomicrograph - TAS27/4</td>
<td>96</td>
</tr>
<tr>
<td>Plate 5.11</td>
<td>Photomicrograph - TAS27/3</td>
<td>96</td>
</tr>
<tr>
<td>Plate 5.12</td>
<td>Photomicrograph - TAS27/1</td>
<td>96</td>
</tr>
<tr>
<td>Plate 5.13</td>
<td>Outcrop photo - Branxholme profile</td>
<td>100</td>
</tr>
<tr>
<td>Plate 5.14</td>
<td>Outcrop photo - Branxholme profile</td>
<td>101</td>
</tr>
<tr>
<td>Plate 5.15</td>
<td>Scanning electron micrograph - Branxholme profile</td>
<td>108</td>
</tr>
<tr>
<td>Plate 5.16</td>
<td>Scanning electron micrograph - Branxholme profile</td>
<td>108</td>
</tr>
<tr>
<td>Plate 5.17</td>
<td>Scanning electron micrograph - Branxholme profile</td>
<td>108</td>
</tr>
<tr>
<td>Plate 5.18</td>
<td>Scanning electron micrograph - Branxholme profile</td>
<td>108</td>
</tr>
<tr>
<td>Plate 5.19</td>
<td>Photomicrograph - TAS9/4</td>
<td>109</td>
</tr>
<tr>
<td>Plate 5.20</td>
<td>Photomicrograph - TAS9/4</td>
<td>109</td>
</tr>
<tr>
<td>Plate 5.21</td>
<td>Photomicrograph - TAS9/4</td>
<td>109</td>
</tr>
<tr>
<td>Plate 5.22</td>
<td>Photomicrograph - TAS9/3</td>
<td>109</td>
</tr>
<tr>
<td>Plate 6.1</td>
<td>Outcrop photo - Big Willow profile</td>
<td>115</td>
</tr>
<tr>
<td>Plate 6.2</td>
<td>Photomicrograph - BW3</td>
<td>123</td>
</tr>
<tr>
<td>Plate 6.3</td>
<td>Photomicrograph - BW4</td>
<td>123</td>
</tr>
<tr>
<td>Plate 6.4</td>
<td>Photomicrograph - BW4</td>
<td>123</td>
</tr>
<tr>
<td>Plate 6.5</td>
<td>Photomicrograph - BW4</td>
<td>123</td>
</tr>
<tr>
<td>Plate 6.6</td>
<td>Photomicrograph - BW2</td>
<td>124</td>
</tr>
<tr>
<td>Plate 6.7</td>
<td>Photomicrograph - BW2</td>
<td>124</td>
</tr>
<tr>
<td>Plate 6.8</td>
<td>Photomicrograph - BW2</td>
<td>124</td>
</tr>
<tr>
<td>Plate 6.9</td>
<td>Photomicrograph - BW-1</td>
<td>124</td>
</tr>
<tr>
<td>Plate 6.10</td>
<td>Outcrop photo - Sherwood profile</td>
<td>127</td>
</tr>
<tr>
<td>Plate 6.11</td>
<td>Photomicrograph - SW6</td>
<td>132</td>
</tr>
<tr>
<td>Plate 6.12</td>
<td>Photomicrograph - SW1</td>
<td>132</td>
</tr>
<tr>
<td>Plate 6.13</td>
<td>Photomicrograph - SW1</td>
<td>132</td>
</tr>
<tr>
<td>Plate 7.1</td>
<td>Outcrop photo - Newell/Oxley Highway profile</td>
<td>139</td>
</tr>
<tr>
<td>Plate 7.2</td>
<td>Photomicrograph - WFT4/1</td>
<td>149</td>
</tr>
<tr>
<td>Plate 7.3</td>
<td>Photomicrograph - WFT4/1</td>
<td>149</td>
</tr>
<tr>
<td>Plate</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>-------</td>
<td>--------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>7.4</td>
<td>Photomicrograph - WFT4/3</td>
<td>149</td>
</tr>
<tr>
<td>7.5</td>
<td>Photomicrograph - WFT4/3</td>
<td>149</td>
</tr>
<tr>
<td>7.6</td>
<td>Photomicrograph - WFT4/5</td>
<td>150</td>
</tr>
<tr>
<td>7.7</td>
<td>Photomicrograph - WFT4/4</td>
<td>150</td>
</tr>
<tr>
<td>7.8</td>
<td>Photomicrograph - WFT4/6</td>
<td>150</td>
</tr>
<tr>
<td>7.9</td>
<td>Photomicrograph - WFT4/7</td>
<td>150</td>
</tr>
<tr>
<td>7.10</td>
<td>Outcrop photo - Chalk Mountain profile</td>
<td>153</td>
</tr>
<tr>
<td>7.11</td>
<td>Photomicrograph - WFT2/7</td>
<td>161</td>
</tr>
<tr>
<td>7.12</td>
<td>Photomicrograph - WFT2/7</td>
<td>161</td>
</tr>
<tr>
<td>7.13</td>
<td>Photomicrograph - WFT2/8</td>
<td>161</td>
</tr>
<tr>
<td>7.14</td>
<td>Photomicrograph - WFT2/8</td>
<td>161</td>
</tr>
<tr>
<td>7.15</td>
<td>Photomicrograph - WFT2/6</td>
<td>162</td>
</tr>
<tr>
<td>7.16</td>
<td>Photomicrograph - WFT2/6</td>
<td>162</td>
</tr>
<tr>
<td>7.17</td>
<td>Photomicrograph - WFT2 1/1</td>
<td>162</td>
</tr>
<tr>
<td>7.18</td>
<td>Photomicrograph - WFT2 1/1</td>
<td>162</td>
</tr>
<tr>
<td>7.19</td>
<td>Outcrop photo - Dorrigo Plateau profile</td>
<td>165</td>
</tr>
<tr>
<td>7.20</td>
<td>Scanning electron micrograph - Dorrigo Plateau profile</td>
<td>169</td>
</tr>
<tr>
<td>7.21</td>
<td>Scanning electron micrograph - Dorrigo Plateau profile</td>
<td>169</td>
</tr>
<tr>
<td>7.22</td>
<td>Scanning electron micrograph - Dorrigo Plateau profile</td>
<td>169</td>
</tr>
<tr>
<td>7.23</td>
<td>Scanning electron micrograph - Dorrigo Plateau profile</td>
<td>169</td>
</tr>
<tr>
<td>8.1</td>
<td>Outcrop photo - East Lismore profile</td>
<td>175</td>
</tr>
<tr>
<td>8.2</td>
<td>Photomicrograph - TFT6/3</td>
<td>182</td>
</tr>
<tr>
<td>8.3</td>
<td>Photomicrograph - TFT6/4</td>
<td>182</td>
</tr>
<tr>
<td>8.4</td>
<td>Photomicrograph - TFT6/9</td>
<td>182</td>
</tr>
<tr>
<td>8.5</td>
<td>Photomicrograph - TFT6/9</td>
<td>182</td>
</tr>
<tr>
<td>8.6</td>
<td>Outcrop photo - Beechmont profile</td>
<td>184</td>
</tr>
<tr>
<td>8.7</td>
<td>Photomicrograph - TFT12/4</td>
<td>190</td>
</tr>
<tr>
<td>8.8</td>
<td>Photomicrograph - TFT12/4</td>
<td>190</td>
</tr>
<tr>
<td>9.1</td>
<td>Outcrop photo - West Springsure profile</td>
<td>195</td>
</tr>
<tr>
<td>9.2</td>
<td>Photomicrograph - EFT22/4</td>
<td>202</td>
</tr>
<tr>
<td>9.3</td>
<td>Photomicrograph - EFT22/3</td>
<td>202</td>
</tr>
<tr>
<td>9.4</td>
<td>Photomicrograph - EFT22/5</td>
<td>202</td>
</tr>
<tr>
<td>9.5</td>
<td>Photomicrograph - EFT22/5</td>
<td>202</td>
</tr>
<tr>
<td>9.6a</td>
<td>Outcrop photo - Stock Route profile</td>
<td>205</td>
</tr>
<tr>
<td>9.6</td>
<td>Photomicrograph - EFT9/9</td>
<td>210</td>
</tr>
<tr>
<td>9.7</td>
<td>Photomicrograph - EFT9/9</td>
<td>210</td>
</tr>
<tr>
<td>9.8</td>
<td>Photomicrograph - EFT9/10</td>
<td>210</td>
</tr>
<tr>
<td>9.9</td>
<td>Photomicrograph - EFT9/10</td>
<td>210</td>
</tr>
<tr>
<td>9.10</td>
<td>Photomicrograph - EFT9/10</td>
<td>211</td>
</tr>
<tr>
<td>9.11</td>
<td>Photomicrograph - EFT9/10</td>
<td>211</td>
</tr>
<tr>
<td>Plate</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>-------</td>
<td>-------------</td>
<td>------</td>
</tr>
<tr>
<td>9.12</td>
<td>Photomicrograph - EFT9/4</td>
<td>211</td>
</tr>
<tr>
<td>9.13</td>
<td>Photomicrograph - EFT9/5</td>
<td>211</td>
</tr>
<tr>
<td>10.1</td>
<td>Outcrop photo - Archers Creek profile</td>
<td>221</td>
</tr>
<tr>
<td>10.2</td>
<td>Photomicrograph - LMAC25</td>
<td>234</td>
</tr>
<tr>
<td>10.3</td>
<td>Photomicrograph - LMAC23</td>
<td>234</td>
</tr>
<tr>
<td>10.4</td>
<td>Photomicrograph - LMAC22</td>
<td>234</td>
</tr>
<tr>
<td>10.5</td>
<td>Photomicrograph - LMAC10</td>
<td>234</td>
</tr>
<tr>
<td>10.6</td>
<td>Photomicrograph - LMAC10</td>
<td>235</td>
</tr>
<tr>
<td>10.7</td>
<td>Photomicrograph - LMAC9</td>
<td>235</td>
</tr>
<tr>
<td>10.8</td>
<td>Photomicrograph - LMAC6</td>
<td>235</td>
</tr>
<tr>
<td>10.9</td>
<td>Photomicrograph - LMAC7</td>
<td>235</td>
</tr>
<tr>
<td>10.10</td>
<td>Outcrop photo - Millaa Millaa profile</td>
<td>239</td>
</tr>
<tr>
<td>10.11</td>
<td>Outcrop photo - Palmerston Highway profile</td>
<td>242</td>
</tr>
<tr>
<td>10.12</td>
<td>Scanning electron micrograph - Palmerston Highway</td>
<td>244</td>
</tr>
<tr>
<td>10.13</td>
<td>Outcrop photo - Kennedy Highway profile</td>
<td>246</td>
</tr>
<tr>
<td>10.14</td>
<td>Photomicrograph - QFT7/2</td>
<td>249</td>
</tr>
<tr>
<td>10.15</td>
<td>Photomicrograph - QFT7/4</td>
<td>249</td>
</tr>
<tr>
<td>10.16</td>
<td>Photomicrograph - QFT7/5</td>
<td>249</td>
</tr>
<tr>
<td>10.17</td>
<td>Photomicrograph - QFT7/6</td>
<td>249</td>
</tr>
<tr>
<td>10.18</td>
<td>Outcrop photo - Fletcher Vale Road profile</td>
<td>252</td>
</tr>
<tr>
<td>10.19</td>
<td>Photomicrograph - QFT1/6</td>
<td>255</td>
</tr>
<tr>
<td>10.20</td>
<td>Photomicrograph - QFT1/6</td>
<td>255</td>
</tr>
<tr>
<td>10.21</td>
<td>Photomicrograph - QFT1/7</td>
<td>256</td>
</tr>
<tr>
<td>10.22</td>
<td>Photomicrograph - QFT1/8</td>
<td>256</td>
</tr>
<tr>
<td>10.23</td>
<td>Photomicrograph - QFT1/2</td>
<td>256</td>
</tr>
<tr>
<td>10.24</td>
<td>Photomicrograph - QFT1/4</td>
<td>256</td>
</tr>
<tr>
<td>10.25</td>
<td>Scanning electron micrograph - Fletcher Vale Road</td>
<td>258</td>
</tr>
<tr>
<td>10.26</td>
<td>Scanning electron micrograph - Fletcher Vale Road</td>
<td>258</td>
</tr>
<tr>
<td>10.27</td>
<td>Scanning electron micrograph - Fletcher Vale Road</td>
<td>258</td>
</tr>
<tr>
<td>10.28</td>
<td>Scanning electron micrograph - Fletcher Vale Road</td>
<td>258</td>
</tr>
<tr>
<td>10.29</td>
<td>Scanning electron micrograph - Fletcher Vale Road</td>
<td>258</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 1.1  Isocon diagram, fresh rock versus fresh rock 6
Figure 1.2  Isocon diagram, fresh rock versus weathered rock 6
Figure 1.3a Isocon diagram, mass loss for the sample 9
Figure 1.3b Isocon diagram, mass gain for the sample 9
Figure 1.4a Isocon diagram, enriched and depleted elements 10
Figure 1.4b Histogram, enriched and depleted elements 11
Figure 2.1 Eastern Australian Cainozoic Basalts showing the volcanic provinces discussed in this study. 15
Figure 2.2 The weathering profile classification of (A) Meunier (1980) and (B) Ildefonse (1980) 17
Figure 4.1 Successive positions of Australia relative to Antartica as Australia moved northward during the Cainozoic (Kennett 1982) 58
Figure 4.2 Reconstruction of the Southern Ocean 65 Ma ago, about the time of the Cretaceous Tertiary boundary (Kennett 1982) 59
Figure 4.3 Reconstruction of Southern Ocean and suggested surface water circulation 53 Ma ago (Kennett 1982) 61
Figure 4.4 Reconstruction of the Southern Ocean and suggested surface water circulation 36 Ma ago (Kennett 1982) 62
Figure 4.5 Reconstruction of the Southern Ocean and suggested bottom water circulation 21 Ma ago (Kennett 1982) 64
Figure 4.6 Change in radiation (MJ/m²/yr) with latitude (°S) for the sample sites in this study 68
Figure 4.7 Change in temperature (°C) with latitude (°S) for the sample sites in this study greater than 150km from the coast 69
Figure 4.8 Change in temperature (°C) with latitude (°S) for the sample sites in this study less than 150km from the coast 69
Figure 4.9 Change in mean temperature (°C) for the wettest and driest quarters with latitude (°S) gives an indication of whether the region has summer of winter dominant rainfall 70
Figure 4.10 Change in annual precipitation (mm) with distance from the coast (km) for the sample sites studied 70
Figure 4.11 Change in seasonality of radiation, temperature and precipitation with latitude (°S) for the sample sites studied. 71
Figure 5.1 Sample localities in north west, north east and central Tasmania 73
Figure 5.2 Sample points in the Hellyer River Bridge profile, north west Tasmania 78
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3</td>
<td>Isocon diagrams and corresponding histograms for TAS17/3 and TAS17/5</td>
<td>79</td>
</tr>
<tr>
<td>5.4</td>
<td>Isocon diagrams and corresponding histograms for TAS17/1 and TAS17/2</td>
<td>80</td>
</tr>
<tr>
<td>5.5</td>
<td>Stacked X-ray diffraction (XRD) traces for samples TAS17/1, TAS17/2, TAS17/3 and TAS17/4</td>
<td>82</td>
</tr>
<tr>
<td>5.6</td>
<td>Sample points in the Monpeelyata profile, central Tasmania</td>
<td>88</td>
</tr>
<tr>
<td>5.7</td>
<td>Isocon diagrams and corresponding histograms for TAS27/4 and TAS27/5</td>
<td>89</td>
</tr>
<tr>
<td>5.8</td>
<td>Isocon diagrams and corresponding histograms for TAS27/1, TAS27/2 and TAS27/3</td>
<td>90</td>
</tr>
<tr>
<td>5.9</td>
<td>Stacked X-ray diffraction (XRD) traces for samples TAS27/1, TAS27/2, TAS27/3, TAS27/4 and TAS27/5</td>
<td>92</td>
</tr>
<tr>
<td>5.10</td>
<td>Sample points in the Branxholme profile, north east Tasmania</td>
<td>100</td>
</tr>
<tr>
<td>5.11</td>
<td>Isocon diagrams and corresponding histograms for TAS9/4 and TAS9/4b</td>
<td>102</td>
</tr>
<tr>
<td>5.12</td>
<td>Isocon diagrams and corresponding histograms for TAS9/2 and TAS9/3</td>
<td>103</td>
</tr>
<tr>
<td>5.13</td>
<td>Stacked X-ray diffraction (XRD) traces for samples TAS9/2, TAS9/3, TAS9/4 and TAS9/4b</td>
<td>106</td>
</tr>
<tr>
<td>6.1</td>
<td>Monaro Volcanic Province showing sample localities</td>
<td>112</td>
</tr>
<tr>
<td>6.2</td>
<td>Sample points in the Big Willow profile, Monaro volcanic province</td>
<td>115</td>
</tr>
<tr>
<td>6.3</td>
<td>Isocon diagrams and corresponding histograms for BW2, BW3 and BW4</td>
<td>117</td>
</tr>
<tr>
<td>6.4</td>
<td>Isocon diagrams and corresponding histograms for BW-2 and BW-1</td>
<td>118</td>
</tr>
<tr>
<td>6.5</td>
<td>Stacked X-ray diffraction (XRD) traces for samples BW4, BW2, BW-1 and BW-2</td>
<td>119</td>
</tr>
<tr>
<td>6.6</td>
<td>Sample points in the Sherwood profile, Monaro volcanic province</td>
<td>126</td>
</tr>
<tr>
<td>6.7</td>
<td>Isocon diagrams and corresponding histograms for SW1, SW5 and SW6</td>
<td>128</td>
</tr>
<tr>
<td>6.8</td>
<td>Stacked X-ray diffraction (XRD) traces for samples SW1, SW5 and SW6</td>
<td>130</td>
</tr>
<tr>
<td>7.1</td>
<td>Warrumbungle and Ebor Volcanic Provinces showing sample localities</td>
<td>135</td>
</tr>
<tr>
<td>7.2</td>
<td>Sample points in the Newell/Oxley Highway profile, Warrumbungle Volcanic Province</td>
<td>139</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>7.3</td>
<td>Isocon diagrams and corresponding histograms for WFT4/1 and WFT4/2</td>
<td>141</td>
</tr>
<tr>
<td>7.4</td>
<td>Isocon diagrams and corresponding histograms for WFT4/4, WFT4/5, WFT4/6, WFT4/7 and WFT4/9</td>
<td>142</td>
</tr>
<tr>
<td>7.5</td>
<td>Stacked X-ray diffraction (XRD) traces for samples WFT4/1, WFT4/3, WFT4/4, WFT4/6, WFT4/7 and WFT4/9</td>
<td>144</td>
</tr>
<tr>
<td>7.6</td>
<td>Sample points in the Chalk Mountain profile, Warrumbungle Volcanic Province</td>
<td>153</td>
</tr>
<tr>
<td>7.7</td>
<td>Isocon diagrams and corresponding histograms for WFT2/6 and WFT2/7</td>
<td>155</td>
</tr>
<tr>
<td>7.8</td>
<td>Isocon diagrams and corresponding histograms for WFT2/1/1</td>
<td>156</td>
</tr>
<tr>
<td>7.9</td>
<td>Stacked X-ray diffraction (XRD) traces for samples WFT2/4, WFT2/5, WFT2/7 and WFT2/6</td>
<td>157</td>
</tr>
<tr>
<td>7.10</td>
<td>Sample points in the Dorrigo Plateau profile, Ebor volcanic province</td>
<td>165</td>
</tr>
<tr>
<td>7.11</td>
<td>Isocon diagrams and corresponding histograms for WFT10/2, WFT10/8, WFT10/7 and WFT10/6</td>
<td>167</td>
</tr>
<tr>
<td>7.12</td>
<td>Stacked X-ray diffraction (XRD) traces for samples WFT10/2, WFT10/8 and WFT10/7</td>
<td>168</td>
</tr>
<tr>
<td>8.1</td>
<td>Sample localities in the Tweed Volcanic Province</td>
<td>171</td>
</tr>
<tr>
<td>8.2</td>
<td>Sample points in the East Lismore profile, Tweed Volcanic Province</td>
<td>175</td>
</tr>
<tr>
<td>8.3</td>
<td>Isocon diagrams and corresponding histograms for TFT6/3, TFT6/4, TFT6/5, TFT6/6 and TFT6/9</td>
<td>177</td>
</tr>
<tr>
<td>8.4</td>
<td>Stacked X-ray diffraction (XRD) traces for samples TFT6/4, TFT6/3, TFT6/6, TFT6/5, TFT6/9 and TFT6/10</td>
<td>179</td>
</tr>
<tr>
<td>8.5</td>
<td>Sample points in the Beechmont profile, Tweed volcanic province</td>
<td>184</td>
</tr>
<tr>
<td>8.6</td>
<td>Isocon diagrams and corresponding histograms for TFT12/1, TFT12/2, TFT12/3, TFT12/4 and TFT12/6</td>
<td>186</td>
</tr>
<tr>
<td>8.7</td>
<td>Stacked X-ray diffraction (XRD) traces for samples TFT12/1, TFT12/2, TFT12/3, TFT12/6 and TFT12/4</td>
<td>188</td>
</tr>
<tr>
<td>9.1</td>
<td>Sample localities in the Springsure and Peak Range volcanic provinces</td>
<td>191</td>
</tr>
<tr>
<td>9.2</td>
<td>Sample points in the West Springsure profile, Springsure Volcanic Province</td>
<td>194</td>
</tr>
<tr>
<td>9.3</td>
<td>Isocon diagrams and corresponding histograms for EFT22/2, EFT22/3, EFT22/3a, EFT22/4, EFT22/5, and EFT22/6</td>
<td>197</td>
</tr>
<tr>
<td>9.4</td>
<td>Stacked X-ray diffraction (XRD) traces for samples EFT22/2, EFT22/3a, EFT22/4, EFT22/5 and EFT22/6</td>
<td>199</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>Figure 9.5</td>
<td>Sample points in the Stock Route profile, Peak Range volcanic province</td>
<td>204</td>
</tr>
<tr>
<td>Figure 9.6</td>
<td>Isocon diagrams and corresponding histograms for EFT9/9 and EFT9/10</td>
<td>206</td>
</tr>
<tr>
<td>Figure 9.7</td>
<td>Isocon diagrams and corresponding histograms for EFT9/4 and EFT9/5</td>
<td>207</td>
</tr>
<tr>
<td>Figure 9.8</td>
<td>Stacked X-ray diffraction (XRD) traces for samples EFT9/10, EFT9/9, EFT9/5, EFT9/4</td>
<td>208</td>
</tr>
<tr>
<td>Figure 10.1</td>
<td>Sample localities in the Atherton, McBride and Nulla volcanic provinces, North Queensland</td>
<td>214</td>
</tr>
<tr>
<td>Figure 10.2</td>
<td>Sample points in the Archers Creek profile, Atherton volcanic province</td>
<td>220</td>
</tr>
<tr>
<td>Figure 10.3</td>
<td>Isocon diagrams and corresponding histograms for LMAC23, LMAC24 and LMAC25</td>
<td>223</td>
</tr>
<tr>
<td>Figure 10.4</td>
<td>Isocon diagrams and corresponding histograms for LMAC7, LMAC5, LMAC6, LMAC9, LMAC10, LMAC8, LMAC12 and LMAC22</td>
<td>224</td>
</tr>
<tr>
<td>Figure 10.5</td>
<td>Stacked X-ray diffraction (XRD) traces for samples LMAC23, LMAC24 and LMAC25</td>
<td>228</td>
</tr>
<tr>
<td>Figure 10.6</td>
<td>Stacked X-ray diffraction (XRD) traces for samples LMAC4, LMAC5, LMAC6, LMAC9, LMAC10, LMAC8 and LMAC12</td>
<td>230</td>
</tr>
<tr>
<td>Figure 10.7</td>
<td>Sample points in the Millaa Millaa profile, Atherton volcanic province</td>
<td>239</td>
</tr>
<tr>
<td>Figure 10.8</td>
<td>Stacked X-ray diffraction (XRD) traces for samples QFT11/1, QFT11/2, QFT11/3, QFT11/4, QFT11/5, QFT11/6 and QFT11/7</td>
<td>240</td>
</tr>
<tr>
<td>Figure 10.9</td>
<td>Sample points in the Palmerston Highway profile, Atherton Volcanic Province</td>
<td>241</td>
</tr>
<tr>
<td>Figure 10.10</td>
<td>Stacked X-ray diffraction (XRD) traces for samples QFT8/-1, QFT8/0, QFT8/1, QFT8/2, QFT8/3, QFT8/4, QFT8/5, QFT8/6 and QFT8/7</td>
<td>243</td>
</tr>
<tr>
<td>Figure 10.11</td>
<td>Sample points in the Kennedy Highway profile, McBride Volcanic Province</td>
<td>246</td>
</tr>
<tr>
<td>Figure 10.12</td>
<td>Stacked X-ray diffraction (XRD) traces for samples QFT7/1, QFT7/2, QFT7/3, QFT7/4, QFT7/5, QFT7/6 and QFT7/7</td>
<td>247</td>
</tr>
<tr>
<td>Figure 10.13</td>
<td>Sample points in the Fletcher Vale Road profile, Nulla volcanic province</td>
<td>251</td>
</tr>
<tr>
<td>Figure 10.14</td>
<td>Stacked X-ray diffraction (XRD) traces for samples QFT1/1, QFT1/2, QFT1/3, QFT1/4, QFT1/5, QFT1/10, QFT1/6, QFT1/9, QFT1/8, QFT1/7, QFT1/12 and QFT1/11</td>
<td>253</td>
</tr>
<tr>
<td>Figure 11.1</td>
<td>Water sample localities in the Monaro Volcanic Province - Big Willow and Sherwood</td>
<td>260</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>----------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>11.4</td>
<td>(1991/1992) Monthly dissolved oxygen concentrations (mg/L)</td>
<td>266</td>
</tr>
<tr>
<td>11.6</td>
<td>(1991/1992) Monthly bicarbonate concentration (mg/L)</td>
<td>271</td>
</tr>
<tr>
<td>11.7</td>
<td>(1991/1992) Monthly chloride concentration (mg/L)</td>
<td>273</td>
</tr>
<tr>
<td>11.8</td>
<td>(1991/1992) Monthly nitrate/nitrite concentration (mg/L)</td>
<td>275</td>
</tr>
<tr>
<td>11.9</td>
<td>(1991/1992) Monthly sulphate concentration (mg/L)</td>
<td>277</td>
</tr>
<tr>
<td>11.10</td>
<td>(1991/1992) Monthly calcium concentration (mg/L)</td>
<td>279</td>
</tr>
<tr>
<td>11.11</td>
<td>(1991/1992) Monthly magnesium concentration (mg/L)</td>
<td>281</td>
</tr>
<tr>
<td>11.12</td>
<td>(1991/1992) Monthly sodium concentration (mg/L)</td>
<td>283</td>
</tr>
<tr>
<td>11.14</td>
<td>Durov-Zaporozec diagram for 12 month water analyses - BW1</td>
<td>286</td>
</tr>
<tr>
<td>11.15</td>
<td>Durov-Zaporozec diagram for 12 month water analyses - BW2</td>
<td>287</td>
</tr>
<tr>
<td>11.16</td>
<td>Durov-Zaporozec diagram for 12 month water analyses - SW1</td>
<td>288</td>
</tr>
<tr>
<td>11.17</td>
<td>Durov-Zaporozec diagram for 12 month water analyses - SW2</td>
<td>289</td>
</tr>
<tr>
<td>11.18a</td>
<td>Activity diagram, for Big Willow and Sherwood aquifer waters, for the system CaO-Na2O-Al2O3-SiO2-H2O</td>
<td>291</td>
</tr>
<tr>
<td>11.18b</td>
<td>Activity diagram, for Big Willow and Sherwood aquifer waters, for the system CaO-MgO-Al2O3-SiO2-H2O</td>
<td>291</td>
</tr>
<tr>
<td>11.19a</td>
<td>Stability diagram, for Big Willow and Sherwood aquifer waters, for the system CaO-Al2O3-SiO2-H2O</td>
<td>293</td>
</tr>
<tr>
<td>11.19b</td>
<td>Stability diagram, for Big Willow and Sherwood aquifer waters, for the system MgO-Al2O3-SiO2-H2O</td>
<td>293</td>
</tr>
<tr>
<td>11.19c</td>
<td>Stability diagram, for Big Willow and Sherwood aquifer waters, for the system Na2O-Al2O3-SiO2-H2O</td>
<td>293</td>
</tr>
<tr>
<td>12.1</td>
<td>Cation exchange capacity (CEC) versus Si:Al ratio for the Eastern Australia basalt samples</td>
<td>298</td>
</tr>
<tr>
<td>12.2</td>
<td>Cation exchange capacity (CEC) versus Slope of Isocon (m) for the Eastern Australia basalt samples</td>
<td>299</td>
</tr>
<tr>
<td>12.3</td>
<td>Cation exchange capacity (CEC) versus Mass Change ΔM(%) for the Eastern Australia basalt samples</td>
<td>300</td>
</tr>
<tr>
<td>12.4</td>
<td>Cation exchange capacity (CEC) versus Soil pH for the Eastern Australia basalt samples</td>
<td>301</td>
</tr>
</tbody>
</table>
List of Figures

Figure 12.5  Cation exchange capacity (CEC) versus Contemporary Annual Rainfall (mm) for the Eastern Australia basalt samples 301

Figure 12.6  Cation exchange capacity (CEC) versus Estimated Clay Content for the Eastern Australia basalt samples 302

Figure 12.7  Mass Change (%) - Ca and Sr versus Slope of Isocon (m) 311

Figure 12.8  Mass Change (%) - Rb and K versus Slope of Isocon (m) 312

Figure 12.9  Mass Change (%) - Mg versus Slope of Isocon (m) 313

Figure 12.10 Mass Change (%) - Na versus Slope of Isocon (m) 314

Figure 12.11 Mass Change (%) - Si versus Slope of Isocon (m) 314

Figure 12.12 Mass Change (%) - Cu versus Slope of Isocon (m) 315

Figure 12.13 Mass Change (%) - Zn and V versus Slope of Isocon (m) 316

Figure 12.14 Mass Change (%) - Cr and Ni versus Slope of Isocon (m) 317

Figure 12.15 Mass Change (%) - Mn versus Slope of Isocon (m) 318

Figure 12.16 Mass Change (%) - Th and U versus Slope of Isocon (m) 319

Figure 12.17 Mass Change (%) - Ce versus Slope of Isocon (m) 320

Figure 12.18 Mass Change (%) - Pb and La versus Slope of Isocon (m) 320

Figure 12.19 Mass Change (%) - P versus Slope of Isocon (m) 321

Figure 12.20 Mass Change (%) - S and Ba versus Slope of Isocon (m) 322

Figure 12.21 Mass Change (%) - Nb and Zr versus Slope of Isocon (m) 325

Figure 12.22 Mass Change (%) - Y versus Slope of Isocon (m) 325

Figure 12.23 Mass Change (%) - Al versus Slope of Isocon (m) 327

Figure 12.24 Mass Change (%) - Ti versus Slope of Isocon (m) 328

Figure 12.25 Soil pH versus Net Mass Change (%) in Ti 328

Figure 12.26 Mass Change (%) - Fe versus Slope of Isocon (m) 328

Figure 12.27 Rate of cation loss with respect to silica 334

Figure A.1  Local Map for Hellyer River profile, north west Tasmania A-2

Figure A.2  Local Map for Monpeelyata profile, Central Tasmania A-4

Figure A.3  Local Map for Branxholme profile, north east Tasmania A-5

Figure A.4  Local Map for Big Willow profile, Monaro Volcanic Province A-7

Figure A.5  Local Map for Sherwood profile, Monaro Volcanic Province A-8
| Figure A.6 | Local Map for Newell/Oxley Highway profile, Warrumbungles Volcanic Province | A-9 |
| Figure A.7 | Local Map for Chalk Mountain profile, Warrumbungles Volcanic Province | A-11 |
| Figure A.8 | Local Map for Dorrigo Plateau profile, Ebor Volcanic Centre | A-12 |
| Figure A.9 | Local Map for East Lismore profile, Tweed Volcanic Province | A-14 |
| Figure A.10 | Local Map for Beechmont profile, Tweed Volcanic Province | A-15 |
| Figure A.11 | Local Map for Springsure profile, Springsure Volcanic Province | A-16 |
| Figure A.12 | Local Map for Peak Range profile, Peak Range Volcanic Province | A-18 |
| Figure A.13 | Local Map for Archers Creek profile, Atherton Volcanic Province | A-19 |
| Figure A.14 | Local Map for Millaa Millaa profile, Atherton Volcanic Province | A-21 |
| Figure A.15 | Local Map for Palmerston Highway profile, Atherton Volcanic Province | A-22 |
| Figure A.16 | Local Map for Kennedy Highway profile, McBride Volcanic Province | A-23 |
| Figure A.17 | Local Map for Fletcher Vale Road profile, Nulla Volcanic Province | A-24 |
List of Tables

Table 1.1  Element positions allocated for isocon diagrams in this study  8
Table 3.1  Cation location within the common smectite clay minerals  57
Table 5.1  Contemporary climate information for the Tasmanian sample localities (BIOCLIM)  74
Table 6.1  Contemporary climate information for the Monaro sample localities (BIOCLIM)  113
Table 7.1  Contemporary climate information for the Warrumbungle and Ebor sample localities (BIOCLIM)  136
Table 8.1  Contemporary climate information for the Tweed sample localities (BIOCLIM)  172
Table 9.1  Contemporary climate information for the West Springsure and Stock Route sample localities (BIOCLIM)  192
Table 10.1 Contemporary climate information for the Atherton sample localities (BIOCLIM)  215
Table 10.2  Contemporary climate information for the McBride and Nulla sample localities (BIOCLIM)  216
Table 12.1 Summary of the average values of: Net Mass Change (loss/gain) \( \Delta M(\%) \); Si:Al ratio; dominant clay type; and, Cation Exchange Capacity (CEC) for each clay content bracket, for the Eastern Australian basalt samples  303
Table 12.2 Ranges in Slope of the Elemental Mass Loss Curves for the Elements Affected by basalt weathering  334
Table A.2.1 Chemical analyses for unweathered basalts as used for isocon interpretation of geochemical data  A-27
Table A.3.1 Geochemical Analyses (XRF) for the samples in this study  A-30
Table A.4.1 Clay Separate Chemistry and Cation Exchange Capacity (CEC)  A-44
Table A.5.1 Detection limits for the analytical techniques employed for cation and anion analysis, Atomic Absorption Spectrophotometry (A.A.S.) and Flow Injection Analysis (F.I.A.) respectively  A-59
Table A.6.1 Measured Soil pH Values  A-62
Chapter 1

INTRODUCTION

Basalt is a glassy volcanic rock that is particularly susceptible to weathering. Intraplate volcanic provinces, many dominated by basaltic volcanics, are distributed along the eastern margin of the Australian continental landmass. The eastern Australian basalts straddle a large range of latitude, and the migration of Australia northward through the Cainozoic, has led to regolith development under evolving climatic conditions. This provides a unique opportunity to make a comparative study of basalt weathering under different contemporary climate and paleoclimate regimes.

1.1 RATIONALE

This project was designed as a regional study of the mineralogical and geochemical differences in weathering that might result from climatic variables. To this end, basaltic sites were selected of similar basalt composition and fabric and similar topographic position (crestal), but of different modern climatic environment, basalt weathering processes and age of basaltic eruption, and consequently differing paleoclimates. The study was designed as an analysis of clay mineral genesis and geochemical variation throughout the basalt weathering profile with weathering climate, both present and past.

This study clarifies the processes of chemical weathering of basalt across a range of time and climate space, and integrates studies from carefully selected areas into a single extensive work, with a view to understanding the variations in processes and products of basalt weathering. In particular geochemical and mineralogical variations are characterised and an attempt to relate these to physicochemical variations in environment has been made.

Regolith profiles were sampled at selected sites from Tasmania to Queensland. Samples were analysed geochemically and petrographically, whole rock and clay fraction mineralogy was defined and basalt aquifer water chemistry was monitored.
1.2 AIMS

The aims of this study were to:

- carry out a program of sampling of regolith profiles on eastern Australian Cainozoic flow basalts that would enable an case study style interpretation of basalt weathering profile processes, from a range of contemporary climate environments;

- establish a technique for evaluation of geochemical and mineralogical analyses in association with field and optical observations, and/or other analytical methods that will enable the characterisation of basalt regolith profiles at the key localities selected;

- clarify whether the observed order of dissolution of primary basalt forming minerals as suggested by Eggleton et al. (1987) holds for basalt weathering profiles from a range of contemporary and paleo- climate environments;

- compile, by means of a series of case studies, observed element pathways during basalt weathering, and establish whether this differs for profiles from differing contemporary climate environments within the eastern Australian Cainozoic basalts;

- describe the changes in secondary mineralogy with progressive weathering for profiles from a variety of contemporary climate environments, and to investigate whether a general sequence of clay mineral evolution can be defined for flow basalt weathering and if any unusual secondary products are formed during the weathering of basalt; and,

- assess the extent to which weathering profiles developed on the eastern Australian Cainozoic basalts approach equilibrium with contemporary climate environments or if they are dominantly paleo-weathering profiles overprinted by the effects of contemporary climate.

1.3 METHODS AND TECHNIQUES

1.3.1 Regolith Sampling

As part of the Eastern Australian Basalt Regolith (EABR) sampling program 144 regolith profiles were sampled on flow basalts and described in a preliminary fashion. Of these, seventeen sites were ultimately chosen for this study. Criteria for the selection of key regolith profiles required that:

- the profiles be as complete as possible, with a sequence from indurated weathered basalt to soil material;
the profiles be located in upper slope or crestal positions in order that profiles were taken from like topographic sites with like drainage regimes;

- the profiles be selected from a range of contemporary climate environments; and,

- the profiles be selected from a range of latitudes in order to cover a range of paleoclimates.

Where possible, sites from areas where paleoclimate had been established for the period from emplacement to the present were preferred. In order to allow long term analysis of basaltic ground-water, two localities in the Monaro were selected because they were closely associated with basalt aquifers.

The selection of upper slope to crestal sites for the profiles was a strategic decision made in order to ensure that the profiles represented in situ rather than transported regolith. Furthermore profiles from upper slope to crestal sites are more likely to be free draining than those in lower slope positions where waters may pond and profiles may have a strong water table influence on their chemistry. Exceptions to this catena drainage model are profiles from plains where variation in topography is negligible. Hence, in the main, this is a study of relatively free draining regolith profiles and the processes that take place in the profiles studied here may not be directly comparable with profiles that are located in lower slope positions. A better understanding of the processes that take place in free draining crestal profiles, and the fluids that issue from these profiles, will contribute to the understanding of processes affecting lower slope profiles.

Although the classification systems for regolith roughly correspond to horizons, the jointing in basalts allows considerable lateral and vertical variation in the degree of weathering. Hence, samples for this study were taken at relatively regular intervals up profile, but more emphasis was placed on sampling from corestones outward through onionskins to the saprolite and soil. In addition special attention was paid to sampling crack, vesicle and vein fill materials. In general the focus was not on sampling a regular stratigraphy in homogenised soil zones, but to document the variation and transition in chemical processes that takes place during neoformation of secondary weathering mineral suites (dominated by clays) in a vertically and laterally variable regolith profile. Detailed profile descriptions are presented in Appendix 1.

While as many variables as possible have been taken into consideration with respect to comparing like profiles with like, it is impossible to make evaluations within and between volcanic provinces based solely on evidence from one or two profiles. Rather each key profile represents an independent case study which can be interpreted in the context of the present understanding of regional geology, contemporary and paleo-climate regime, and basalt weathering processes. In explaining the observations made in these case studies,
hypotheses can be put forward to explain processes observed elsewhere within a volcanic province and variations between profiles of a similar nature in other volcanic provinces. Each key profile was selected from ten to twenty profiles initially examined from each province, because it best satisfied the selection criteria.

1.3.2 Clay Chemistry and Cation Exchange Capacity (CEC)

Cation exchange capacities and associated clay chemistry analysis of samples was carried out at the CSIRO Soils Division, Adelaide (Appendix 4). Analyses were run on a Philips PW 1480 X-ray Fluorescence (XRF) Spectrometer for barium saturated clay separate (<2 µm) samples prepared according to the Millipore Filter transfer method (detailed in Moore & Reynolds 1989). All CEC values are expressed as meq/100 g.

1.3.3 X-ray Diffraction (XRD) Mineralogical Analysis

Bulk samples were analysed from 2 to 66 °2θ, on a Siemens D501 X-ray Diffractometer, with Sietronics 122 XRD Automation, run at 20 mA and 40 kV using Cu-Kα radiation, in the X-ray Diffraction Laboratory, Geology Department, Australian National University. Samples that contained peaks at 12.5 Å or higher were glycolated to test for the presence of smectite clays. Clay fractions were separated in settling columns according to Stokes Law, saturated with Mg2+ ions and run under the same conditions as the bulk samples. In samples where the presence of halloysite was suspected, the formamide test was carried out (Churchman 1972, 1984, 1990). Where necessary samples were heat treated in a Carbolite furnace.

1.3.4 Water Sampling and Analysis

A twelve month water sampling program was carried out from November 1991, at two Monaro Volcanic Province localities (Figure 1.1). It was necessary to monitor the springs for a year in order to evaluate the effects of seasonal temperature, rainfall and vegetation changes. In addition to the sampling of water for analysis in the laboratory, measurements of water temperature, water pH, dissolved oxygen concentration and electrical conductivity were carried out using the HYDROLAB multiprobe; independent water temperature was measured using a mercury bulb thermometer; independent pH was measured using a portable pH meter; and bicarbonate concentrations were derived in the field using a field titration technique. Cation and anion concentrations (HCO₃⁻, Cl⁻, NO₃⁻ & NO₂⁻, SO₄²⁻, Ca²⁺, Mg²⁺, Na⁺, K⁺) were derived in the laboratory, using Atomic Absorption Spectrophotometry (AAS) and Flow Injection Analysis (FIA) respectively (Appendix 5).
1.3.5 BIOCLIM Contemporary Climate Information

Each locality was geocoded (input according to latitude, longitude and altitude) allowing estimation of climatic conditions using a bioclimatic prediction system (BIOCLIM) (Nix 1984) at the Centre for Resource and Environmental Studies (CRES), Australian National University. This system uses mathematically sophisticated surface-fitting procedures (Wahba & Wendleberger 1980) which have been adapted to permit estimation of contemporary climate parameters at any point in Australia (Hutchinson et al. 1984).

1.3.6 Petrography and Scanning Electron Microscopy

Optical microscopy was carried out on standard 30 µm thin sections. Some materials were sufficiently unconsolidated that impregnation of samples was required. Scanning electron microscope (SEM) observation of selected carbon coated samples was carried out on a Cambridge S360 Scanning Electron Microscope and chemistry of the phases present confirmed using Energy Dispersive X-ray Analysis on a Tracor Northern TN5500 Analyser.

1.3.7 Whole Rock Geochemistry

Geochemical analysis of all samples was carried out at the Geology Department, Australian National University (Appendix 3). Major analyses (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P, S) were run on a Siemens SRS 300 X-ray fluorescence (XRF) spectrometer from samples prepared by the lithium borate fusion technique (Norrish & Hutton 1969). Accuracy was estimated in reference to in-house standards and precision, better than ±1%, was controlled by running duplicate analyses. Trace elements (V, Cr, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Pb, Th, U) were determined by XRF analysis of pressed powder pellets (Norrish & Chappell, 1977) on a Philips PW 1400 XRF spectrometer. Precision varies up to ±3%. U was found to occur in concentrations close to the detection limit of the technique.

1.3.8 Interpretation of Geochemical Data

Graphical Isocon Method - First Principles

Gresens (1967) compared the chemistry and specific gravity data for a group of metasomatised rocks with equivalent data for their unaltered protolith, and was able to develop mass balance equations to describe the composition-volume relationships he observed. Subsequently Gresens' equations were modified by Grant (1986), who
endeavoured to simplify interpretation of compositional changes during alteration, by presenting the data graphically.

**Figure 1.1**
For a plot of fresh rock versus fresh rock both the mobile and immobile elements lie on a 1:1 line which is also the isocon-line.

**Figure 1.2.**
For a plot of fresh rock versus weathered rock, mobile elements lie above or below the isocon line. The isocon line plots through the immobile elements and is displaced from the 1:1 line of fresh rock.
These graphical representations of the compositional data are termed "isocon diagrams" and they enable element mobility pathways in altered rocks, to be traced. Elemental mass changes due to alteration, can be calculated relative to a unit mass of unaltered rock. Such mass balance calculations (Gresens, 1967) derived from graphical interpretations (Grant, 1986), provide a means of qualitative and quantitative evaluation of changes in rock chemistry during alteration.

If the chemical data for an unweathered rock are plotted on both axes of a graph, the resulting line will be a 1:1 line (Figure 1.1). As the rock weathers the element concentrations change and a new plot can be drawn where the chemical data for the weathered rock can be plotted versus the original fresh rock data (Figure 1.2). If an element remains immobile during weathering, the removal of other elements will cause it to be residually enriched. Hence, the ratio of the concentration of immobile element in the weathered rock to the concentration of immobile element in the fresh rock is no longer 1:1, and the data points for the immobile element will now plot above the 1:1 line (Figure 1.2).

Herein lies the key to the isocon technique: all immobile elements present in a rock during weathering will become residually concentrated in the same ratio. Therefore, when scaled chemical data for weathered rocks are plotted versus similarly scaled data for unweathered protolith, relatively immobile elements plot on a straight line through the origin. The elements which lie on this line have equal (weathered rock/fresh rock) chemical concentration ratios. This line is called the isocon line.

Scaling of Geochemical Data for Clear Representation on the Isocon Diagram

One problem with plotting geochemical concentration data for major and trace elements graphically is that many data points overlap. The graphical isocon method (Grant 1986) has been modified by Huston (1993), who recommends a scaling technique which allows clearer presentation of the graphical data.

The location of any data point on the isocon is defined by the ratio:

$$\frac{C_W}{C_O}$$

where $C_W$ is the concentration of an element in the weathered sample and $C_O$ is the concentration of the same element in fresh basalt (least weathered equivalent). If this relationship is multiplied by any number ($n$), the ratio remains the same.

$$\frac{C_W}{C_O} \text{ is equivalent to } (\frac{C_W}{C_O})_n$$
Graphically, the line that plots through the origin and the point represented by the ratio: $C^W/C^O$ is the same line that plots through the origin and the point represented by: $(C^W/C^O) \cdot n$. Data points can therefore be scaled in such a way that they are more clearly represented on the graphical isocon plot.

In this study elements have been allocated a position from 1 to 28 on the $x$-axis of the isocon plot (Table 1.1). The ratio for each element is multiplied by a factor $n$ that allows the scaled element concentration value on the $x$-axis to be the same as the order number it has been assigned.

The elements can be presented in any order, however, elements that are likely to show large variations with weathering cannot be assigned large factors ($n$ values), otherwise the diagrams will become too large to work with easily. In addition, for isocon construction, it is useful to distribute the elements that are most likely to be immobile, at a regular interval across the diagram.

### Table 1.1:

Element positions allocated for isocon diagrams in this study

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<tr>
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#### Application of the Isocon Technique

**Net mass loss/gain for a sample**

The steepness of the isocon line gives an indication of the degree of mass loss/gain of the rock as a result of weathering. If the slope of the isocon is steep, that is, above the 1:1 fresh rock analysis line, then there has been a mass loss (Figure 3a). This is because most of the other elements have been removed from the rock and the immobile elements are residually enriched. If the isocon lies below the 1:1 line of fresh basalt then there has been a mass gain (Figure 3b). In this case many other elements have been enriched with respect to the immobile elements because of secondary precipitation of phases within the weathering rock.
Figure 1.3a

The isocon line plots above the 1:1 line, therefore there has been a mass loss for the sample.

Figure 1.3b

The isocon line plots below the 1:1 line, therefore there has been a mass gain for the sample.
The slope of the isocon \((m)\) can be determined using the relationship:

\[
m = \frac{C_{iW}}{C_{iO}}
\]

where \(C_{iW}\) is the concentration of immobile element in the weathered sample \(C_{iO}\) is the concentration of immobile element in the least weathered equivalent.

Net mass changes \((\Delta M)\) for samples can be estimated from the isocon using the equation:

\[
\Delta M (\%) = 100 \left( \frac{1}{m} - 1 \right)
\]

**Elemental mass changes**

Data points falling in the fields above and beneath the isocon represent elemental mass gains and losses respectively (Figure 1.4a). That is, any element that is enriched with respect to the immobile elements lies above the isocon and any element that is depleted with respect to the immobile elements lies below the isocon line.

Elemental mass changes \((\Delta M_e)\) are calculated according to the equation:

\[
\Delta M_e (\%) = 100 \left( \frac{C_e W}{m \cdot C_e O} - 1 \right)
\]

**Figure 1.4a**

Mobile elements that lie above the isocon line are enriched in the sample. Mobile elements that lie below the isocon line are depleted from the sample.
where $C_{eW}$ is the concentration of an element in the weathered sample, $C_{eO}$ is the concentration of that element in the least weathered equivalent, and $m$ is the calculated slope of the isocon. Once elemental mass changes are calculated they can be plotted on a histogram which enables "at a glance" assessment of gains or losses for any elements analysed (Figure 1.4b).

**RELATIVE ELEMENTAL MASS CHANGE (%)**

![Histogram](image)

**Figure 1.4b**

Mobile elements that have a relative mass gain have positive values on the histogram. Mobile elements that have a relative mass loss have negative values on the histogram. Immobile elements show zero relative mass change.

**Interpretation of Isocon Plots**

1. If the slope of the isocon is steep, that is, above the 1:1 fresh rock analysis line, then there has been a mass loss for that sample. If the isocon lies below the 1:1 line of fresh basalt then there has been a mass gain for that sample (Figure 1.3a, Figure 1.3b).

2. If there has been a net mass gain the $\Delta M$ (%) value will be positive for that sample. If there has been a mass loss the $\Delta M$ (%) value will be negative for that sample.

3. When the isocon diagrams for a single profile are stacked one on top of the other the change in slope of the isocon gives an "at a glance" indication of the pattern of weathering. For example: if the slope of the isocon lines are progressively steeper from one isocon plot to the next, up-profile, then the profile is becoming increasingly more weathered. Each fresh rock/weathered rock pair can be compared with others from the
profile and stepwise changes in degree of weathering within the sequence can be examined.

4. Data points falling in the field above the isocon line represent elemental mass gains $+\Delta M_e$ (%). Data points falling in the field beneath the isocon line represent elemental mass losses $-\Delta M_e$ (%) (Figure 1.4a).

5. Elemental mass changes can be plotted on a histogram where losses plot in the negative direction and gains plot in the positive direction, enabling an "at a glance" assessment of gains or losses for any elements analysed (Figure 1.4b).

6. When the histograms showing the relative elemental mass change, for a single profile, are stacked one on top of the other, detailed changes in element concentration within the profile can be observed. Each fresh rock/weathered rock pair can be compared with others from the profile and stepwise changes in chemistry within the sequence can be examined.

A convention has been used for this study to describe the degree to which an element has been depleted or enriched, based on the relative mass change histograms for the elements analysed: on or near the isocon ($\pm 0-5\%$ relative mass change), slight depletion/enrichment ($5-30\%$ relative mass change), moderate depletion/enrichment ($30-60\%$ relative mass change), major depletion/enrichment ($60-90\%$ relative mass change), extreme depletion/enrichment ($>90\%$ relative mass change).

Geochemical data and the isocon interpretation has been presented locality by locality in Chapter 5 through Chapter 10. In order to avoid repetition of the descriptions of element pathways in the weathering basalts, discussion of the characteristic behaviour of each element is summarised in Chapter 12.

U is present in such low concentrations, at times in the same order as the detection limit of the analytical technique (XRF), that its mobility is not covered in geochemical discussions in this study.

Selection of Immobile Elements

The isocon is defined by elements that are considered relatively immobile during weathering. In a study of changes in chemistry during basalt weathering, Eggleton et al. (1987) state that Ti, V, Cr, Fe, Ni, Zr and Nb are essentially immobile within corestones as weathering proceeds. Al and Ti and some trace elements such as Y, Zr and Nb (Grant 1986, Glazner & Bartley 1991, Tobisch et al. 1991, Marquer & Burkhard 1992,
Prochaska et al. 1992, Streit 1994), are commonly assumed to have low mobility during alteration. In addition, many weathering indices rely on the assumption that Al (Harnois 1988, Nesbitt & Young 1982, Reiche 1943, Vogel 1975, Vogt 1927, Roaldset 1943, Ruxton 1968), Nb (Price et al. 1991) and Zr, B, Y and Ti (Chittleborough 1991) remain relatively immobile during weathering. Specific empirical studies confirm the relative immobility of groups of elements such as Al and Zr (Selverstone et al. 1991, Marquer & Burkhard 1992), or Ti, Zr, Y, P (O’Hara 1988, Marker and Burkhard 1992) during alteration. However, other studies also indicate the mobility of Al (Ohara 1988, Brimhall 1988, Chittleborough 1991), Ti (Selverstone et al. 1991, Van Baalen 1993) and Zr (Brimhall 1992, Huston 1993).

For this study isocons are constrained by a combination of two or more of Al, Ti, Zr, Y and Nb as these have been observed to be the elements most resistant to weathering for the basalt regolith samples analysed. Approximately half of the samples were analysed for the presence of FeO and Fe₂O₃. In all cases it was found that FeO (Fe²⁺) was strongly depleted in weathered basalts and Fe₂O₃ (Fe³⁺) was strongly enriched. This was the expected redox behaviour for iron, the oxidation of Fe²⁺ to Fe³⁺ during weathering in an aerated profile. Although this chemical reaction usually takes place rapidly enough that most of the iron is preserved in the weathering profile, the known mobility of iron was sufficient to discount its reliable use as an immobile element for application of the isocon technique in this study. Hence, even for localities where total iron is expressed as Fe₂O₃, iron has not been considered an immobile element for application of the isocon technique. In most cases total iron plots on or near the isocon defined by other immobile elements and for these examples redox reactions have been efficient enough to preserve most of the iron within the profile.

Selection of the Least Weathered Equivalents

Where fresh basalt was not exposed in the profile, fresh rock geochemistry was taken from the literature or from unpublished data of local workers. Where more than one analysis was available the data were averaged as per Huston (1993). The fresh rock geochemistry used for isocon construction in this study is presented in Appendix 2.

Graphical Isocon Method Versus Other Weathering Indices

With the exception of the Parker (1970) index and Herbillon’s (1989) Total Reserve in Bases (TRB) index, which both rely on calculating the balance of the major cations (Ca, Mg, Na and K) remaining in a weathered rock, most commonly used weathering indices assume Al to be immobile during weathering (Vogt 1927, Reiche 1943, Roaldset 1943, Ruxton 1968, Vogel 1975, Nesbitt & Young 1982, Harnois 1988), and make an
evaluation of major cation depletion relative to Al. Chittleborough (1991) discusses the potential mobility of Al as a result of eluviation in a weathering profiles and presents and alternative index which compares the cations Ca, Mg and Na with a single element, Zr, Y, B or Ti, believed to be immobile in the 20-90 µm fraction of the soil being studied. Similarly, in their study of the mobility of REE, Y and Ba in leaching experiments on basalts, Price et al. (1991) apply the CIA index (Nesbitt & Young 1982) and compare mobile elements with Nb, which is considered immobile.

In almost all cases, these weathering indices rely on the comparison of mobile elements versus a single relatively immobile element. However, often it is difficult to assess how immobile the index element really has been during the chemical and physical processes of weathering, as in the example above where Al concentration was affected by eluviation in Chittleborough's (1991) profiles. One solution to this problem is to make the comparison relative to more than one immobile element. This provides an internal check as all index elements must occur in the same ratio (weathered rock/unweathered rock) as each other to be truly considered immobile.

For this reason the isocon method (Gresens 1967, Grant 1986, Huston 1993) appears the most reliable comparative method for evaluation of degree of weathering, because at least two, and usually four or five immobile elements are used to define the isocon. If any elements do not have the same ratio of concentrations as the immobile index elements then they have been mobilised during weathering, and they will no longer plot on the isocon.

In some profiles almost all of the elements have been mobilised. In this case it is still possible to apply the isocon technique, using the least mobile elements for isocon construction, in order to gain a broad indication of the mass balance and elemental mass changes that have taken place. While this analysis is not as accurate as for those profiles where immobile elements are readily recognised, together with careful field observations it provides a framework within which evaluation of the processes taking place in the profile can be evaluated.
CHAPTER 2

CONCEPTS OF BASALT WEATHERING

2.1 EASTERN AUSTRALIAN CAINozoIC BASALTS

In this study profiles on flow basalts were considered from six regions, Tasmania, Southern New South Wales, Northern New South Wales, Southern Queensland/Northern New South Wales, Central Queensland, and Northern Queensland. The key profiles selected for detailed study come from twelve volcanic provinces: North East, North West and Central Tasmania, Monaro, Warrumbungles, Ebor, Tweed, Springsure, Peak Range, Atherton, McBride and Nulla (Figure 2.1).

Figure 2.1

The Eastern Australian Cainozoic Basalts showing the volcanic provinces discussed in this study.
A comprehensive summary of previous work on the intraplate volcanic geology of eastern Australia, has been compiled by Johnson et al. (1989). They provide a description of the distribution, tectonic setting, geomorphology, geochemistry and time-space relationships of volcanics from sixty provinces in eastern Australia.

2.2 PRINCIPAL REACTIONS OF CHEMICAL WEATHERING

Three principal reaction types are involved in the chemical weathering of basalt. These are hydration, hydrolysis (dissolution) and redox reactions.

Hydration occurs when water is taken into the structure of a mineral or into an interlayer site, or is adsorbed onto the surface of the mineral.

Hydrolysis takes place when the dissolution of a chemical compound is brought about by a reaction with water. Usually new compounds are formed by addition of atoms from \( \text{H}_2\text{O} \) molecules to one fragment of the decomposed compound and by addition of the other atoms of \( \text{H}_2\text{O} \) to the other fragment or fragments of the decomposed compound. Hence cations in the original compound are replaced by \( \text{H}^+ \) ions from the water, and are thereby released into solution. Congruent and incongruent dissolution reactions occur. If the compound dissolves readily the ratio of components in solid will be equal to that in solution and the reaction is congruent. But if some species from the weathering mineral pass into the solution as solutes and the other less soluble species form residuals coating the original solid, inhibiting dissolution, the dissolution reaction is incongruent (Muxart & Birot 1977).

Redox reactions take place as a result of oxidation or reduction of elements from one valency state to another. "Oxidation is the process by which electrons are removed from one or more atoms of a substance. Reduction is the process by which electrons are added to one or more atoms of a substance. A reducing agent (reductant or an electron donor) is a compound that reacts by releasing electrons and itself is oxidised in the process. An oxidising agent (oxidant or electron acceptor) is a compound that reacts by accepting an electron and thus itself is reduced. Because electrons cannot exist free in nature, there are always pairs of these reactions which balance each other" (Yatsu 1988).

2.3 THE CHEMICAL WEATHERING OF BASALT LAVA FLOWS

The chemical weathering of basalt begins when weathering agents, water and its solutes, introduced by precipitation (dew, rain water) or present as ground water, start to react with the minerals of the rock. Because basaltic rocks have a predominance of minerals with a low relative stability, they are extremely susceptible to chemical weathering.
Weathering of basalts appears to occur in two main stages (Velde 1985), an initial alteration of the parent basalt to smectites, kaolin group minerals and iron oxyhydroxides sometimes through short range order or X-ray amorphous intermediate phases, which may then be followed by partial or total alteration of these secondary minerals to produce the bulk of the overlying soil. In the past, reference has been made to these two steps as "weathering" and "soil forming" (Singer 1970) or "geochemical weathering" and "pedogenic transformation" (Millot 1982) respectively, but in many weathered profiles the mineral assemblage reflects a combination of, or a continuum between, the products of both stages. An important artefact of the formation of an intermediate clay mineral assemblage is that ultimately similar soil types may form from quite different primary parent materials.

2.3.1 Early Weathering Profile Classification Systems

Meunier (1980) and his co-workers developed a weathering classification scheme which is still widely used (Figure 2.2). They classify weathering into three geochemical zones:

1. The zone of incipient alteration where the rock is coherent in hand specimen. Here fracture zones and grain boundaries are the most active sites of new mineral formation.

2. The friable rock zone (saprock) is where individual high temperature mineral grains are distinguishable but where they tend to dissociate easily under moderate mechanical pressure. In these samples internal destabilisation of the initial phase is quite evident. The new minerals form a polyphase assemblage.
3. The saprolite zone is where the clay mineral assemblages are mixed with one another through mechanical collapse of the initial rock microstructure.

A very similar classification scheme (Figure 2.2) arose from the description of a weathered profile on meta-gabbro by Ildefonse (1980). Above the incipiently weathered parent rock lay the isalterite zone, the equivalent of Meunier's saprock zone. Above the isalterite zone lay the alloterite zone, the equivalent of Meunier's saprolite zone, and then a soil.

Although terminology differs with author, the ideal weathering profile starts with fresh rock or bed rock, followed by weathered coherent rock or incipiently weathered rock. Upon the incipiently weathered rock lies that part of the saprolite where the initial texture of the parent rock is preserved. This horizon corresponds with the saprock zone of Meunier (1980), and the isalterite zone of Ildefonse (1980). The upper part of the saprolite is characterised by an increase in density because pores within and between the altering minerals are closed due to collapse of the saprolite microstructure. In the upper saprolite, which may also be referred to as the saprolite zone or alloterite zone, the initial texture of the parent material is no longer preserved. Clay minerals recrystallise and the upper saprolite, along with the soil profile proper, can be treated as a series of horizons, in the manner of soil scientists, since a larger degree of homogeneity has been achieved.

2.3.2 Variability in the Field Expression of Weathered Basalts

Classification systems are important to the fundamental understanding of the nature and organisation of the mineral assemblages at different levels in ideal weathering profiles, which then allows extrapolation to explain variation in profiles elsewhere. The intermediate stages of weathering, between parent rock and soil, are represented by the formation of a saprolite zone or a weathering crust (Singer 1970). In a given climatic or geomorphic setting, changes in the relative thickness of the saprolite zone can be observed.

When basic rocks alter, the lower saprolite or saprock zone is poorly developed even in temperate climates. This is because of the high solubility of the elements composing the minerals in the primary rock (Velde 1985). If the weathering profile is frequently below the water table a monophase assemblage may develop in the saprolite (Proust & Velde 1978). In an ideal profile with good drainage, alteration is generally greatest at the surface and decreases in intensity downward toward the unaltered parent rock. This corresponds with the depth of saturation of the percolating waters. Relatively pure rain water on its passage down-profile becomes increasingly saturated with respect to the soluble
constituents of the soil and rock and as a result, the rate of mineral dissolution decreases (Loughnan 1969).

In field exposures, weathered basalts are rarely homogeneously altered. Most rocks are fractured allowing water to percolate through cracks and weather the minerals in these zones first. As a result, the areas around joints and fractures are generally more weathered than the parent basalt and these are often sites of secondary oxide concentration. The initial products in cracks are largely monophasic indicating that the fluids are controlling the reactions (Velde 1985). Eluviation down cracks leads to the translocation of minerals down profile, and is the mechanism by which clay-rich surface coatings or cutans on material adjacent to cracks, forms. However, through-flow in open cracks is relatively rapid and water has little time to become sufficiently saturated with elements weathered from silicates in the parent rock to re-precipitate them in the immediate vicinity. For this reason the principal process occurring in cracks is dissolution. Those minerals that are present have formed largely as a result of dissolution at sites higher in the profile and subsequent precipitation, or direct translocation (eluviation). Dissolution also leads to crack widening which facilitates further fluid percolation.

A characteristic of flow basalts is columnar jointing perpendicular to the cooling front of the flow. Field observations on flood basalts have prompted a model for columnar jointing in lava flows that suggests a lower colonnade of thick, well formed columns, an upper colonnade of thinner columns, and between the two an entablature of columns in a more chaotic array (Swanson & Wright 1981). This intense jointing allows weathering agents to enter flow basalts relatively easily and gives rise to the formation of stacks of corestones with rinds or "onion skins" in weathered profiles, where once there were columns bounded by cooling fractures.

2.3.3 Spheroidal Weathering

Spheroidal weathering occurs when dissolution proceeds in the fractures bounding an angular block of parent material. Because the corners of the block can be weathered on more than one front, weathering proceeds at the corners more rapidly than at the sides. Over time the weathering front becomes spheroidal and progressively migrates inward altering the less weathered parent material forming the core of the block. The thickness of weathering rinds can be used to make evaluations of the rate of rock weathering (Colman & Pierce 1981, Whitehouse et al. 1986) and in some cases, where both parent rock ages and weathering variables are known, weathering measurements can be used to assign ages to deposits (Colman & Dethier 1986).
Eggleton et al. (1987) observed that weathering intensity increased relatively smoothly from the centre of a corestone outward, except where it was interrupted by locally increased weathering adjacent to fractures. This observation holds true for that part of the corestone which has already been partially weathered, but the interface between the weathering front and the indurated basalt of the corestone may be sharp. If we consider the processes that are taking place at mineral surfaces, the elemental components released by weathering must be removed to enable the exposure of fresh surfaces to the weathering solution. Because these processes occur on a molecular scale, the transition zone from relatively fresh rock to weathering rind, except where microcracks cut, can be extremely narrow. This sharp transition from weathered to relatively unweathered (or incipiently weathered) basalt is a visual manifestation of basalt weathering. Chemically, residual boulders and corestones with "onionskins" provide a small scale analogue of the weathering profile as a whole. They show alteration from parent basalt through a secondary clay-mineral and Fe-oxyhydroxide assemblage where the original rock fabric is preserved, to a friable soil-clay mineral assemblage (Talkington et al. 1976, Carr et al. 1980, Eggleton et al. 1987).

2.3.4 Microscale Weathering

On the microscopic scale structural features again control the location and rates of chemical weathering. At sites of lattice dislocations, crystal defects, microfractures or twin boundaries where there is an excess of free energy, weathering proceeds most rapidly (Tchoubar 1965, Wilson 1975, Berner and Holdren 1977). Often grain boundaries show the first signs of alteration, then microfractures and defects in the mineral grains become sites of chemical activity. As a result the weathering rock is divided into a number of microsystems related to each other by the chemical activity of ions in the weathering solutions (Velde 1985). Once weathering has been initiated at these sites, and dissolution of elements from the mineral grains commences, the rate of weathering will depend upon the efficiency of diffusion within and between the microsystems (Eggleton 1986). There is short and long range chemical mobility associated with these microsystems, that is, intra- and inter-microsystem diffusion, and therefore chemical potential influences are important.

2.3.5 The Weathering Sequence of Basalt Components

The resistance of rocks to chemical weathering depends on the susceptibility of the component minerals (Goldich 1938, Franke & Teschner-Steinhardt 1994). Basalt mineralogy is relatively simple and generally comprises phenocrysts of olivine and less commonly plagioclase, augite and titanomagnetite and sometimes orthopyroxene in a groundmass dominated by plagioclase, augite, olivine, titanomagnetite, apatite and
volcanic glass. Some basalts have ilmenite, magnetite, nepheline, phlogopite, richterite, sanidine and leucite as minor phases. As a prelude to understanding the chemical weathering of basalts to secondary alteration products, it is important to understand the chemical and mineralogical changes associated with early weathering reactions.

Volcanic glass (or mesostasis) is the component most susceptible to weathering. Through a process of hydration and devitrification, volcanic glass alters to palagonite. Palagonite is a material with variable composition having the X-ray diffraction characteristics of a poorly crystalline layer silicate. Palagonites often have smectites as their only crystalline component, and many are X-ray amorphous (Eggleton & Keller 1982).

The ferromagnesian minerals olivine and pyroxene (in decreasing order of susceptibility), are the most readily weathered minerals in basalts followed by plagioclase and then alkali-feldspar (Craig & Loughnan 1964, Loughnan 1969, Singer 1970, Siever & Woodford 1979, Colman 1982). In some studies plagioclase feldspars are placed before pyroxenes in the order of susceptibility to weathering. In the basalt corestone study of Eggleton et al. (1987) plagioclase grains commence weathering before pyroxenes, but pyroxenes weather more rapidly once dissolution is initiated and are usually completely altered before the plagioclase.

2.3.6 The Formation of Deep Weathering Profiles

In intensely weathered profiles the uppermost horizon consists of a reddish soil which may contain a little organic matter. The horizon beneath is composed of cavernous, vesicular or pisolitic iron oxide with kaolinite or bauxite minerals or both. According to Sherman and Kanehiro (1954), much of the concretionary iron oxide in the deeply weathered soils of the Hawaiian Islands has magnetic properties and is probably maghemite rather than hematite. A sharply defined boundary separates this horizon from the underlying mottled zone which is kaolinite-rich and may extend to a depth of 6 m or more. This zone is believed to represent the upper and lower limits of the fluctuating water table. The permanently saturated pallid zone below the mottled zone consists of partly decomposed parent rock which has lost much of its original iron content through solution and upward migration toward the oxidised parts of the profile (Loughnan, 1969).

The bauxite formed on basalt, Country Antrim, Northern Ireland, apparently developed during a prolonged interflow period by two distinct processes, a preliminary stage in which Mg, Ca, K and Na were removed and the rock was converted to an assemblage of kaolin minerals, principally halloysite, and a later stage of desilication whereby the kaolin minerals were replaced by a residue enriched in gibbsite. In the zone of greatest
weathering, iron oxide became segregated from aluminium and an upper crust of highly ferruginous deeply weathered profiles, containing a high proportion of titanium, formed above the bauxite horizon (Eyles 1952).

Although deeply weathered soils are common in the tropics, particularly in well drained areas with consistent rainfall, it should be emphasised that not all tropical soils are lateritic. The essential requirements for their formation appear to be a high rainfall, intense leaching, good drainage, and a strongly oxidising environment. Under these conditions organic matter accumulation is inhibited while the leaching solutions tend to flush out all potentially mobile constituents leaving concentrations of Al-, Ti-, and Fe-oxide. Si may persist to the extent necessary to combine with the available Al in the formation of kaolinite but frequently it is deficient and the excess Al is present as gibbsite or, more rarely, boehmite. Where present, gibbsite generally attains maximum development in the more highly weathered surface horizons.

Experimental leaching of mafic rocks at varying pH and temperatures showed that although the rate of dissolution increased with increasing temperature, the same pattern of variation in dissolution rate with pH for 0°C and for 35°C was observed (Pickering 1962). Chemical weathering should therefore be more rapid in tropical climates, but the effects should be the same in cooler climates.

Carr et al. (1980) have developed a model for the formation of bauxites on basalt in Northland, New Zealand.

\[
\text{PARENT} \rightarrow \text{SAPROLITE} \rightarrow \text{BAUXITE} \\
\text{BASALT} \quad \text{HALLOYSITE} \quad \text{GIBBSITE} \\
\quad \text{AMORPHOUS TO SUBCRYSTALLINE} \quad \text{IRON} \\
\quad \text{IRON OXIDES AND HYDROXIDES} \quad \text{OXYHYDROXIDES} \\
\quad \text{RELICT MAGNETITE AND ILMENITE} \\
\]

Gibbsite bearing aluminous deeply weathered profiles occur above basalts of Plio-Pleistocene age (5.3-0.1 Ma) in the Kerikeri area. They are formed by processes initiated in late Pleistocene:

1. Initial alteration leached the parent basalt of alkalis and about half of its silica to produce a saprolite composed of halloysite, amorphous sub-crystalline iron oxides and oxyhydroxides, and relict magnetite and ilmenite.
2. Continued leaching removed further silica from halloysite forming gibbsite while dehydration of upper layers aided crystallisation of iron oxyhydroxides.
3. There was re-silicification at one locality.
In this study area, no higher land surfaces exist; drainage in each weathering horizon is fast with transport in solution being downward and parallel to slope; deeply weathered profiles are not developed on more recent lavas; mechanical erosion is restricted and chemical erosion is dominant. However, the climate under which deep weathering was initiated and promoted is somewhat cooler than the tropical temperatures suggested in the literature for development of deep weathering profiles.

Many authors regard a warm moist climate, with a high mean annual temperature and steady precipitation (i.e. a tropical climate), as one of the most important factors in bauxite formation (Valeton 1972, Norton 1973, Bardossy 1974, McFarlane 1983, Ollier 1984, Nahon 1986, Frakes et al. 1987, Chamley 1989, Tardy et al. 1990a, Bardossy and Aleva 1990). However, authors of a number of recent publications concur with the concept of cool climate bauxite development (Eggleton et al. 1987, Bird & Chivas 1988, Bird et al. 1990b, Taylor et al. 1990).

2.4 ENVIRONMENTAL INFLUENCES ON BASALT WEATHERING

The interplay of environmental factors can accelerate or retard leaching, control the redox potential within a profile and hence directly influence the rate of chemical weathering and the nature of the products.

2.4.1 Water and Temperature

Water

Chemical weathering is greatly influenced by climate. Rain is the principal source for recharge of groundwater. Water is essential for dissolution of the soluble constituents of the rock and mobilisation of these species around and out of the profile. Reaction rate is governed by the availability of water, and is influenced by temperature. Experimental investigations have confirmed that water is an important agent of chemical weathering, acting through the processes of dissolution and hydrolysis (Pedro 1961, Pickering, 1962, Parham 1969, White & Sarcia 1978).

Temperature

Temperature plays a dual role in chemical weathering. On one hand, increasing temperatures promote weathering by greatly accelerating the chemical reactions. On the other hand, increasing temperatures create greater evaporation and hence tend to retard chemical weathering by reducing the quantity of water percolating through the weathering
Chapter 2: Concepts of Basalt Weathering

zone. The effective temperature of an area is also modified by the surface relief. For every 50 metres in elevation the temperature decreases by approximately $1^\circ$C while aspect and steep slopes may considerably reduce the amount of sunlight reaching certain areas (Loughnan 1969).

Arid Regions

In arid regions where evaporation exceeds rainfall, water may penetrate the rocks but, during the ensuing long dry spell, it is returned to the surface and ultimately becomes lost through evaporation. As a result, soluble constituents of the rocks are not removed and the reactions slow down accordingly. Oxidising conditions ensure retention of iron in the ferric state and this imparts red, brown and yellow hues to the surfaces of the rocks. Loughnan (1969) states that the characteristic secondary minerals in arid settings are montmorillonite, illite and chlorite or, more probably, mixed layers of these minerals, and suggests that kaolinite is rare unless present in the parent rock, in which case it persists unaltered in composition. However, Dregne (1976) in his discussion of soil development in the Australian arid zones, comments that illite and kaolinite are the dominant clay minerals and that soil reaction is commonly acidic. In the colder deserts, oxidation is retarded and a little organic matter may accumulate with the partly decomposed parent materials and secondary products, producing grey rather than reddish colours. It appears that the profiles of Dregne (1976) are either preserved regolith profiles where there has been sufficient weathering in the past for kaolin group clay dominant secondary mineral suites to form under oxidising conditions, or, as is suggested by the grey colouration, the system is at least periodically anaerobic and those fluids that pass through the system are acid, resulting in weathering parent rock to a kaolin bearing suite.

Humid Regions

In contrast the rocks of the humid areas are generally intensely weathered as a result of the continual downward movement of the percolating waters. Most of the soluble products of the hydrolysing reactions taking place at mineral surfaces are carried down to the water table and are lost through the subsurface drainage. Because of high ground water recharge in wet areas, the water table is often at shallow depth and much of the altered zone may be permanently saturated and hence in a reduced state.

Eggleton et al. (1987) in his study of basalt corestone weathering in eastern Australia, made the point that although the climate varies from one sample locality to another, the samples studied were from near-surface positions and no obvious relation between climate and relative rate of loss of the elements was noted. This suggested that the mechanism of corestone weathering was not affected by climate, although the overall rate
of weathering may have differed. Claridge and Campbell (1984) reached the same conclusion in their study of dolerite weathering in Antarctica. The concept that weathering processes, leading to the ultimate development of lateritic profiles, occur in the same fashion in cool climate profiles with good fluid throughflow as in profiles located in humid tropical environments, is a relatively new idea, but has gained increasing support in recent years (Bird & Chivas 1988, Bird et al. 1990b, Taylor et al. 1990).

2.4.2 Oxidation, pH and Drainage (Topography)

Weathering is a process involving the interaction of many different factors and the resulting products are complex. The progress of chemical weathering in a given body is influenced by three principal factors: oxidation of the cations mobilised due to dissolution of primary minerals, pH of the weathering solutions, and drainage allowing flow through the profile (Cawsey & Mellon 1983).

**Oxidation**

Oxidising conditions convert Fe$^{2+}$ to Fe$^{3+}$ affecting Fe$^{2+}$ within silicate minerals and aiding disruption of the crystal lattice. In addition, Fe$^{2+}$ which has been removed from the minerals and is in solution, is converted to the more stable form Fe$^{3+}$. The insoluble Fe$^{3+}$ hydroxides, which are the principal product of the oxidation, remain in the zone of weathering. This leads to a residual concentration of iron in the weathering profile, and the familiar red and orange colouration of many weathered profiles. Under reducing conditions, the opposite effect occurs, enabling iron to be mobilised as soluble Fe$^{2+}$ and removed from the profile, hence the anoxic portion of the profile is more likely to be grey coloured. Other examples of elements that behave in this fashion are manganese, which oxidises from Mn$^{2+}$ to Mn$^{4+}$ and forms black surface coatings and black dendritic deposits on joint planes within weathering profiles, and cerium which partitions similarly to Mn in geochemical systems and may convert from Ce$^{3+}$ to Ce$^{4+}$ under oxidising conditions.

It is difficult to physically measure the Eh of a weathering system. Instead, whether a profile, or microenvironment within a profile, is or has been reducing or oxidising is evaluated based on the secondary products that are produced. Colouration is one indicator of oxic versus anoxic environments, the reds and yellows of iron oxides and oxyhydroxides like hematite and goethite reflecting the oxidising environment and gleyed grey coloured clays representing more anaerobic/anoxic conditions. Zones of saturation within regolith profiles are often anoxic. Where alternating redox conditions occur, the secondary mineral suite progressively changes in order to re-equilibrate with the prevailing conditions. This may lead to spatially irregular redox microenvironments and
hence variable colouration patterns, leading to the evolution of mottled zones in some weathering profiles.

**pH**

Low pH promotes hydrolysis of silicate minerals by providing additional H\(^+\) ions which enter the crystal lattice, displacing metal cations, and disrupting the silicate framework. The solubilities of several components common in the weathering system, are dependent on pH (Pickering 1962), but within the normal range of pH of natural waters (pH 4 to 9), these solubilities are relatively constant. Only when the pH is greater than 9 does the solubility of silica increase appreciably, and aluminium and iron hydroxides are soluble at pH less than 4 (Cawsey & Mellon 1983).

**Drainage**

Drainage conditions are particularly important in determining if alteration products are retained or removed from a profile during weathering. It is not so much the total rainfall which governs the rate of weathering but rather the proportion of rain water which percolates through the weathering zone, and ultimately leaves the profile by sub-surface drainage. The proportion may vary widely from area to area depending on many factors. For example, it is most likely to be at a maximum where the rainfall is evenly distributed and occurs as gentle persistent showers, and at a minimum where the rainfall is seasonal and restricted to short violent downpours.

In a study of weathering on Hawaiian olivine basalts, Bates (1962) observed that at sites which were seasonally wet and dry, the resulting weathering mineral assemblage differed from that at localities which had water passing through them continually. Where a definite dry period exists, the end products of the alteration are considerably enriched in ferric oxide and titanium, whereas in the absence of a dry period, aluminium is the dominant constituent of the surface horizon.

Thus, the quantity of water passing through the zone of weathering influences the nature of the secondary minerals which form. Where there is a large amount of water entering the zone of weathering, and drainage is good, even poorly soluble products of hydrolysis may be removed, ultimately leaving an insoluble residue, largely Fe\(^{3+}\) and Al hydroxides. Where drainage is impeded, or where there is insufficient water to remove all the products of weathering, clays will be the stable secondary minerals (Loughnan 1969).
Topography

Topography has a marked affect on the rate of chemical weathering and on the nature of the weathered products. It exerts this influence by controlling the rate of surface runoff of rain water and hence the rate of fluid infiltration, the rate of subsurface drainage and therefore the rate of removal of the soluble constituents, and the rate of erosion of the weathered products and thereby the rate of exposure of fresh mineral surfaces (Loughnan 1969). On very steep slopes most of the rain water is lost through surface runoff and little penetrates the parent rock. At the same time erosion by running water, landslides and other agents is particularly active. Consequently, in such environments, mechanical disintegration of rocks proceeds at a much greater rate than chemical breakdown and only superficial accumulations of secondary products result.

Flat, low-lying areas experience little surface runoff, and infiltration of rain water is at a maximum. However, in this type of environment, subsurface drainage tends to be slow and soluble products released by the hydrolysing reactions persist in the waters. Where the parent rocks are relatively rich in the alkalis or alkaline earths, or where the drainage waters from nearby hills are charged with such ions, the environment may become distinctly alkaline. Generally, in low lying areas the water table is at shallow depth and may, in places, rise above ground level forming swamps and promoting the accumulation of organic matter. A strongly reducing environment results.

Such observations of the physical configuration of weathering environments with associated change in redox regimes in different topographic positions reflects the catena model where crestal to upper slope free draining profiles are more likely to be oxidising while lower slope to valley floor profiles may be more saturated and hence more reducing. There is some gradation between these end members. Perched groundwaters also provide some variation to this basic model.

In a study of weathering on basalts in northern New Zealand, Carr et al. (1980) note that deeply weathered deposits form where thin basalt flows cover an irregular topography and yield a series of relatively flat surfaces which have excellent drainage. However, even in rolling country local variations in topography create distinctly different environments which may find expression in contrasting weathering products (Loughnan 1969).

Experimental work has shown that in oxidising environments, some weathering processes may be retarded by Fe hydroxide coatings on mineral surfaces, e.g. goethite rich clay rims on olivine, but in reducing environments these reactions proceed rapidly as there is no iron hydroxide coating to inhibit diffusion (Seiver & Woodford 1979).
The Zone of Saturation (Water Table)

If the alteration profile is frequently below the water table the complete saturation of the system by the fluids due to a collapse of the old rock fabric and replacement of primary phases by clay minerals forms a single chemical system (Proust & Velde 1978). Under these conditions the clay minerals previously formed react to produce a new monophase assemblage. The fluids impose a certain mineralogy on the system but the most important reaction is that of homogenisation of the different minerals present which puts all parts into the same chemical system. This material can then be described as a horizon where the mineralogy can be classified by layers as they approach the surface (Velde 1985).

Singer and Navrot (1977) observe that when basalt weathers under sub-aquatic conditions, such as are created by high water tables (permanent or perched), leaching is minimal and the only clay mineral formed is a low iron smectite. As long as the conditions of waterlogging are maintained, the predominance of smectite will persist and further clay mineral evolution is arrested. This is the case with hydromorphic soils formed in depressions on the basalt surface, even under relatively high rainfall conditions. If drainage improves, or fluid throughflow in the saturated zone increases, cations may be more readily transported from the system and may ultimately lead to the formation of more weathered profiles. Organic acids are sometimes associated with zones of saturation and anoxic conditions, for example in swamps. The percolation of acid fluids enhances the hydrolysis of primary phases and leads to the formation of clay mineral suites with a lower capacity to exchange cations.

2.4.3 Parent Material Composition

Physical Composition of Parent Rock

Variations in the rock texture, structure and composition can exert a considerable influence on the rate of weathering. Texture influences permeability and therefore the degree of infiltration of rain water into the rock. Laterally continuous clay layers may inhibit penetration of water when saturated. If layers of water saturated clays are concentrated near surface, this may reduce the amount of fluid percolating through a profile and enhance surface runoff. Where there are subsurface water saturated clay concentrations, permeability contrasts may cause ponding of fluids, and sometimes lateral transport of fluids above the impermeable layer.

Fractures and zones of weakness such as joints, faults, cleavage and bedding planes offer easy access to water and greatly accelerate the weathering process in their vicinity, in addition to providing channels for the subsurface drainage. The rate of rain water
infiltration progressively increases with the degree of alteration of the parent rock. Dissolution along cracks allows enhanced percolation in weathered materials. In addition, the more open microstructure and corresponding increase in porosity and permeability of most weathered materials enhances fluid percolation. Exceptions are weathered materials where the microstructure has collapsed forming dense, less permeable material, and laterally continuous layers of water saturated clays through which water can no longer permeate.

Schafer & McGarity (1980) looked at soil development on basalts near Armidale in northern New South Wales. They observe that a dark brown and black soil sequence forms on weathered flow basalts, and that reddish chocolate soils form on a mixed parent material of flow basalt and basalt pyroclastics. This occurs as a result of the differing permeability because of the differing physical composition or fabric of the parent materials.

Many weathering experiments have been concerned with simulating chemical effects of weathering (Pedro 1961, Pickering 1962, Parham 1969, White & Sarcia 1978) rather than physical weathering processes. Physical disintegration caused by weathering, however, can be of considerable importance in affecting the weathering of rock. For example, the effects of wetting and drying of rocks containing expanding minerals (Cáwsey & Mellon 1983).

**Chemical Composition of Parent Rock**

The reaction rates for the chemical reactions that occur during the dissolution of the minerals forming a basalt are governed by the chemistry of this rock. The greater the reaction rate, the more rapid the conversion of parent rock into secondary clay minerals and metal ion bearing hydroxides. As a consequence of increased reaction rate, the weathered rock zone would be thinner and saprolite-soil zone would be thicker.

Where the clay mineral products are multiphase, the weathering minerals have saturated the solutions with respect to certain elements and thus the elemental ratios in the reacting phases are found, approximately, in the new clay mineral assemblage. These elements can migrate from their site of origin displacing the bulk composition of the rock.

Environmental factors such as, drainage, total rainfall, temperature and organo-biologic activity, will determine the chemical potential of elements in solution which will influence the mineralogy of the silicate-oxide portion of the system.
2.4.4 Vegetation

In arid regions, vegetation is scant but plant debris is quickly destroyed by the oxidising atmosphere brought about by the high temperatures and the considerable depth to the water table. Consequently, such areas are characterised by an abundance of unaltered or slightly altered parent minerals, the presence of salts such as gypsum and carbonates, alkaline pH values (7.5 to 9.5), and a general paucity of organic matter.

In humid regions, profuse vegetation may lead to extensive accumulations of organic matter on and within the profile. Depending on the rate of supply and degree of oxidation, and with accompanying removal of the cations, low pH values (3.5 to 5.5) may result. Under these conditions chemical weathering tends to proceed rapidly through the loss of soluble constituents and the residue becomes progressively enriched in minerals containing a high proportion of aluminium (kaolinite, halloysite, gibbsite and boehmite) and titanium (anatase and rutile). Ferric oxide minerals (hematite and goethite) may become dominant constituents if the rate of destruction of the organic matter enables oxidation of Fe$^{2+}$ to Fe$^{3+}$. Translocation of aluminium and iron may also take place as a result of the formation of organometallic complexes.

There is always some difficulty in making evaluations about the effects of vegetation because it is uncertain to what degree vegetation is influenced by soil type, and to what extent the soil has been modified by the vegetation. However, there is no doubt that the activity of plants and animals greatly facilitates the physical disaggregation of weathered material thereby increasing its porosity and allowing deeper percolation of weathering solutions. In addition, many plants exude weak acids in order to extract nutrients from the soil, and acids are produced during the rotting of vegetation. These acids may increase the rate of chemical dissolution of the minerals they come into contact with.
CHAPTER 3

BASALT MINERAL DISSOLUTION AND ELEMENT MOBILITY

3.1 DISSOLUTION OF THE PRINCIPAL BASALT FORMING MINERALS AND GLASS

The geochemical changes incurred during the fresh rock to weathered rock (saprock) transition are related to the relative stabilities of the host minerals for the respective ions and to the mobility of these ions once they are released into solution. Interpretation of the changes induced by the fresh rock to clay transition are more complicated. While they are also indicative of host mineral stability and mobility of the respective element they are, in addition, related to the capacity of the released elements to be included or attached in some form or other in the neoformed minerals (Navrot & Singer 1976).

3.1.1 Glass

Devitrification of glass occurs early in weathering as glass is particularly susceptible to dissolution. Glass reactions consist of an initial rapid surface ion exchange followed by a slower (parabolic) solid state diffusion (White & Claussen 1980). At low pH (abundant H⁺ ions) surface exchange between aqueous hydrogen ions and surface cations produces aqueous compositions which reflect the mole fractions of the species in the glass (congruent dissolution). At neutral pH (fewer H⁺ ions) hydrogen ions selectively exchange for surface ions. Eggleton and Keller (1982) discuss the breakdown of glass to form palagonite, a smectitic mineral that shows compositions variable between amorphous phases (Wada 1982) and dioctahedral Mg-bearing smectite. Ti and Fe remain relatively stable during the dissolution of glass, but loss of other constituents follows the order Na~Ca~K>Al>Si>Mg (Eggleton & Keller 1982).

3.1.2 Feldspar

Feldspars are framework silicates in which the tetrahedra are linked through all four oxygen atoms in a three-dimensional configuration. Al substitution for Si within the tetrahedra creates a negative charge on the framework which is balanced by the addition of Na⁺, K⁺ or Ca²⁺ ions. Dissolution of feldspars proceeds via loss of these mono- or divalent cations, but the tetrahedral framework must rupture in order to release the cations. Alkali feldspars and sodic plagioclase have an Al to Si ratio of 1:3, and calcic plagioclase 1:1. Despite the similarities in structure of the feldspars, there is a
considerable difference in their weathering stability (Goldich 1938). Alkali feldspars are considerably more resistant to weathering than plagioclase feldspars. However, once the metallic ions are lost, the framework structure breaks down (Loughnan 1969, Anand et al. 1985).

The intensity of weathering influences whether or not feldspars will persist into the basaltic soil. The mineral stability scales (Goldich 1938, Pettijohn 1941, Reiche 1945, Craig & Loughnan 1964, Loughnan 1969, Singer 1970, Pettijohn 1973, Siever & Woodford 1979, Colman 1982, Eggleton et al. 1987), while varying in the relative positions given to other minerals, all accord plagioclase a low stability. In addition, the stability of plagioclase decreases with increasing Ca content. In the Galilee, young and immature soils contain plagioclase but in mature soils, plagioclase is nearly absent (Singer 1967).

The mechanisms by which feldspars weather are not well understood but possibly involve an early short range order or X-ray amorphous phase from which clay minerals crystallise (Wilson 1975). Rodgers and Holland (1979) found that microcracks in oligoclase (sodic plagioclase) contain a central zone of kaolinite surrounded by a zone of smectite, and concluded that the development of clay involved the diffusion of proton rich species, out of the cracks which must be an early step in feldspar weathering. Several authors have suggested that chemical weathering of feldspars takes place by diffusion of ions through a residual coating of hydrous aluminium silicate (Correns & von Engelhardt 1938, Correns 1961, Wollast 1967, Parham 1969, Helgeson 1971, Busenberg & Clemency 1976). Early work by Correns and von Engelhardt (1938) suggested that this layer maintained a constant thickness and influenced the rate of alteration. Helgeson (1971) later postulated that reaction products such as gibbsite, kaolinite and mica formed zoned layers on the mineral surface.

The non-stoichiometric dissolution of feldspars has been attributed to the presence of a depleted surface layer (Sjoberg 1989, Schmeda 1989, Shotyk & Nesbitt 1990, Hellman et al. 1989, Eggleston & Hellman 1989). Banfield and Eggleton (1990) describe the formation of a "protocrystalline" surface layer on weathering feldspar which was depleted in Ca, Na, K, and Si and significantly enriched in Fe. On plagioclase the protocrystalline material may be replaced by Ca-Fe-K smectite, another protocrystalline material and spherical halloysite. Abundant tubular halloysite on the corroded surface apparently formed by reprecipitation of components released by plagioclase dissolution. A cation depleted layer at the surface of feldspars through which diffusion must take place is also recognised by Goosens et al. (1989). They noted that the penetration of molecular water was a key step of the dissolution process of feldspar minerals. Althaus and Tirtadinata (1989) proposed that the first step of feldspar weathering was the
formation of a thin layer of hydroxonium feldspar \((\text{H}_3\text{O})\text{AlSi}_3\text{O}_8\) because of the ion exchange of \(\text{H}_3\text{O}^+\) for \(\text{K}^+\) and \(\text{Na}^+\). Hence, they suggest that a hydration front advances into the weathering material ahead of the leaching front.

However, weathering of feldspars apparently can occur without development of a cation depleted surface layer (Holdren & Bemer, 1979). Scanning electron microscopy (SEM) images show that weathered feldspars from soils and those from laboratory simulations have similar morphologies. The parabolic dissolution behaviour of feldspars observed in previous laboratory studies (Correns 1961, Parham 1969, Helgeson 1971) may result from experimental procedure. Holdren and Speyer (1986) showed experimentally that the release rates of Al and Si were markedly different at different pH values, and reaction rates were not proportional to the exposed surface area. Electron microscope studies (Tchoubar 1965, Wilson 1975, Bemer & Holdren 1977) confirm that dissolution during the weathering of silicates occurs mainly at the sites of excess energy on the crystal surface such as dislocations microfractures and other crystal defects, and not by uniform attack over the entire mineral surface. Distinctive etch pits develop on the feldspar surface, and with continued weathering they produce a very porous honeycomb microstructure with irregularly scattered clay mineral flakes (Dearman & Baynes 1979, Moore 1989).

Craig and Loughnan (1964) observed that montmorillonite and chlorite forms due to the weathering of feldspars in basalts from New South Wales. Loughnan (1969) suggests that magnesium and ferrous ions released from the breakdown of adjacent minerals in the parent rock may be incorporated into a structure of polymerised sheets of silica formed during feldspar weathering, and montmorillonite clays or chlorite or both result. In the lower parts of weathering profiles examined by Craig and Loughnan (1964) the clay minerals were composed of elements derived from parent minerals, such as Al-montmorillonite from plagioclase. As weathering proceeds the more unstable minerals of this stage are destroyed and some of the ions thereby released are incorporated into other montmorillonite forming from primary minerals still present in the profile. The montmorillonite formed in many profiles is unstable in the conditions of near surface horizons and three possible degradation products result: poorly crystalline montmorillonite, halloysite, and kaolinite. Intense weathering may cause desilicification of kaolinite and the formation of bauxite minerals (gibbsite, boehmite) higher in the profile.

A similar pattern of weathering within a profile was observed by Eswaran (1979) who found that in an alkaline environment plagioclase alters to montmorillonite with small amounts of amorphous aluminosilicates present. In acid environments plagioclase feldspar weathers to metahalloysite and some amorphous aluminosilicates. In a freely
draining environment the weathering of plagioclase leads to kaolinite formation, and locally to gibbsite. De Jou et al. (1982) observed that at the top of a weathering anorthosite profile, where the drainage was good, the clay separate was dominated by kaolinite. Near the base of the profile where drainage was poor, feldspars altered to smectite and vermiculite in addition to kaolinite. The rate of silicate weathering may also be affected by the presence of organic substances (Schenk et al. 1989).

Parham (1969) experimentally leached microcline (alkali-feldspar) and plagioclase in conditions simulating a hot, high rainfall climate and a site with good drainage. Electron microscope examination of the weathered surfaces identified bumps of amorphous material at various sites on cleavage surfaces and at grain edges. These grew into tapered projections and flame shaped sheets which rolled to form tubes of halloysite on the microcline. Sheets formed on the plagioclase feldspars developed into a platey material, probably boehmite. Hence the observed weathering sequence for the feldspars tested is: feldspar to allophane to halloysite and boehmite.

Wilson (1975) observes that in a confined environment mica may form during the weathering of feldspar, but in more open systems the K+ ions are removed and halloysite, vermiculite or montmorillonite form. In intensely weathered profiles feldspars may be converted to gibbsite either directly or through an intermediate halloysite stage. Kitigawa and Katitani (1977) studied the alteration of plagioclase in granite and propose a sequence of feldspar weathering from plagioclase through allophane, halloysite and metahalloysite to kaolinite. However, they found it is also possible for plagioclase to alter directly to halloysite or kaolinite.

**Chemistry**

Plagioclase feldspars form a solid solution series from Na-rich albite to Ca-rich anorthite. All plagioclase feldspars contain some K, and may also contain Ti, Fe3+, Fe2+, Mn, Mg, Ba and Sr. Fe2+ substitutes for Ca2+ while Fe3+ substitutes for Al3+. Sodic plagioclase feldspars are more resistant to weathering. Plagioclase is the most abundant mineral in many basic lavas in both the phenocryst and groundmass assemblages. Plagioclase may be zoned in basalts, often with a bytownite core and a more Na-rich rim (Deer et al. 1992). Minor or trace elements in feldspars are Sr, Rb, Cs, Cu, Pb, REE and possibly Fe2+, Mg and hydronium (H3O+) (Huang 1989).

3.1.3 **Olivine**

Olivine occurs in basaltic rocks as a groundmass constituent or as phenocrysts. The composition and structure of olivine and pyroxenes and other ferromagnesian minerals
make them highly susceptible to chemical weathering in most environments. Olivine is an orthosilicate composed of silica tetrahedra bonded together by ferrous and magnesium ions in octahedral co-ordination. The divalent cations may be mobilised from the outer surface of the mineral and along its inner fractures during weathering as they are largely unprotected by silica tetrahedra at these sites (Delvigne et al. 1979). Individual silica tetrahedral units are released exposing the fresh surface of the olivine to attack.

Brown and Stephen (1959) describe rims of iddingsite on olivines from poorly drained profiles. "Iddingsite" is described as an oriented intergrowth of iron oxide and trioctahedral layer silicates (Eggleton 1984, Smith et al. 1987). Subsequently Banfield et al. (1990) describe hematite-rich smectite rims on weathering olivines, and suggest that a metastable hexagonal phase in iddingsite rims, described by Eggleton (1984) but not identified, may be proto-hematite. Hence iddingsite is a reddish brown substance which consists of a combination of smectite, (chlorite), goethite and/or hematite. It is formed as a result of the diffusion of H+ ions into the olivine structure where they temporarily attach to $\text{O}^\text{-}$ ions releasing Mg and Fe and Si ions from their sites, permitting replacement by Fe$^{3+}$, Al and Ca (Siever & Woodford 1979, Eggleton 1984, Deer et al. 1992).

The presence of an X-ray amorphous intermediate product in the weathering of olivine to smectite clays was acknowledged by Grandstaff (1986) who suggested that in oxic conditions olivines weather rapidly and congruently to X-ray amorphous material. This material then slowly recrystallises to layer silicates (Eggleton 1986). Hisingerite, a partially X-ray amorphous product of the weathering of olivine, was thought to be an intermediate phase between nontronite and saponite (Kohyama & Sudo 1975). Clark et al. (1978) did not support a layer-structure for hisingerite, considered it part of the solid solution series between neotocite and hisingerite, and concluded that it was gel-like or very poorly crystalline. Brigatti (1982) described a more crystalline phase, and found it was similar to trioctahedral Fe saponite clay rather than dioctahedral nontronite clay. This was refuted by Eggleton et al. (1983) who confirmed an amorphous or gel structure for minerals of the neotocite-hisingerite series. Hisingerite has been described from basalts in Victoria (Shayan 1984, Shayan et al. 1988) and southern New South Wales (Le Gleuher 1990), Australia.

Sherman et al. (1962) found nontronite (dioctahedral Fe-smectite) the initial product of the weathering of olivine at Lualualei, Hawaii. Craig (1963) has shown that olivine may alter directly to Mg-rich montmorillonite. Loughnan (1969) suggests that released silica tetrahedra polymerise, fix some of the magnesium, and yield serpentine as the first alteration product. Wilson (1975) found that ferromagnesian minerals weather relatively
easily, and alter mainly to Mg-rich mixed layer trioctahedral expandable minerals as well as chlorites.

Delvigne et al. (1979) suggest that the intermediate weathering product of olivine is a mixture of iron oxide and hydrated magnesium silicate which produces smectites if silica and magnesium are partly retained in the profile. Nontronite and Fe$^{3+}$-bearing beidellites are frequently found as alteration products of olivine, especially in areas of poor drainage. If magnesium is removed a mixture of iron oxide or hydroxide with free silica forms. In areas of better drainage, magnesium and silica are totally released, nontronite is lost, and a residue of goethite and hematite may develop (Trecases 1975). Similarly Smith et al. (1987) observe that with increased weathering, smectite is lost from the olivine rim leaving a porous aggregate of goethite. In this situation it is very difficult to distinguish optically between original iddingsite and the residual goethite, because the micromorphological features of both phases are the same (Delvigne et al. 1979).

In a study of the weathering of forsterite (Mg-olivine) in ultramafic rocks of the western Ivory Coast, Nahon and Colin (1982) noticed that under humid tropical conditions, intermediate Mg-smectites or Fe$^{3+}$-smectites appear prior to the widespread formation of iron oxyhydroxides. They also observed that in forsterite, the smectite varies from an Mg-trioctahedral variety near the centre of the altered crystal to an Mg, Fe$^{3+}$, Al-dioctahedral/trioctahedral variety near the edge. The Al content of the latter smectite is provided by dissolution of adjacent minerals. This rim may be compared with the interlayered iron hydroxide and saponite (iddingsite) rim on olivine (Brown & Stephen 1959, Eggleton 1984, Smith et al. 1987).

Chemistry

Ni and Cr are commonly present in Mg rich olivines. The chromium usually occurs in minute exsolved plates of chromite, while the nickel is enclosed within the silicate. Fe$^{3+}$ is usually present and may be related to small exsolved grains of magnetite but more frequently to an oxidation rim formed during the dissolution of olivine. Relatively small amounts of Ca are present in olivine and P$^{5+}$ is present in trace amounts replacing Si$^{4+}$. In order to maintain charge balance there is an empty site elsewhere in the structure when P$^{5+}$ substitutes. There is some replacement of Mg and Fe in olivine by Mn and Ca but this is more common for Fe-rich olivines (Deer et al. 1992).

3.1.4 Pyroxene

Pyroxenes are essential constituents of basic igneous rocks, and augite is the common pyroxene enclosed within basaltic lava. Pyroxenes are chain silicates and have a structure
of tetrahedra arranged in chains bonded together by metallic ions. The most common metallic ions incorporated are those which enter into octahedral coordination with oxygen, such as Mg$^{2+}$, Fe$^{2+}$, Fe$^{3+}$, and Al$^{3+}$. Some Al may replace Si in the tetrahedra. A pronounced cleavage, with planes approximately normal to each other, parallels the silica chains. Access of water by way of the cleavages promotes solution of the weakly bonding cations.

Craig and Loughnan (1964) during a study of the weathering of basic volcanic rocks in New South Wales, found that the pyroxenes weathered directly to saponite. Loughnan (1969) suggested that chains of silica tetrahedra are released from the weathering pyroxenes and polymerise into sheets incorporating free Al and Mg, thereby forming chlorite or smectite or both. Free ferrous iron is stabilised by oxidation to the ferric state, while Ti combines with oxygen to crystallise as anatase.

If excess Ca results from the breakdown of the pyroxene, calcite may form. With increase in weathering intensity Ca, Mg and Si are lost and the remaining soil forming material becomes enriched in kaolinite, anatase, and oxides and hydroxides of ferric iron. This corresponds with earlier findings by Craig and Loughnan (1964) that montmorillonites are rendered unstable by the more intense weathering conditions (better drainage) near surface, leading to the formation of halloysite, kaolinite and poorly crystallised montmorillonite. In addition, iron as goethite, hematite, or an amorphous precursor of these is concentrated in the oxidised parts of the weathering zone. Subsequent intense weathering may cause the desilicification of clay minerals and the formation of bauxite minerals.

However, in north east Scotland, Basham (1974) recorded the gradual alteration of pyroxene to vermiculite pseudomorphs, the c-axis of the vermiculite being normal to that of the pyroxene, indicating topotaxial growth of the secondary vermiculite. Velde (1985) discusses the presence of vermiculite as a secondary mineral and observes that it forms as a result of continued weathering and oxidation. The formation of vermiculite reflects the loss of Ca and Mg from earlier formed trioctahedral phases, incorporation of Al into the clay, and oxidation of iron within the clay from Fe$^{2+}$ to Fe$^{3+}$.

In a discussion of the alteration of orthopyroxenes under lateritic conditions, Nahon and Colin (1982) described a three stage dissolution of orthopyroxene due to weathering. The first stage is the appearance of amorphous products with a similar chemical composition to the parent material, the second stage is the formation of smectites and ferruginous talc-like minerals, and the third stage features the appearance of iron oxyhydroxides in which well crystallised goethite is observed. Eggleton and Boland
Chapter 3: Basalt Mineral Dissolution and Element Mobility  

(1982) acknowledge the formation of a talc-like mineral as an intermediate stage in the weathering of enstatite (Mg, Fe orthopyroxene) to smectite.

Augite dissolution and subsequent smectite precipitation in the resulting voids leads to the formation of pseudomorphs. The pseudomorphs after augite may have similar compositions to plagioclase pseudomorphs (Eswaran 1979, Glassmann 1982, Glassmann & Simonson 1985).

Chemistry

The clinopyroxenes augite and titanaugite are the typical pyroxenes of basic alkaline rocks but the orthopyroxene enstatite may be present in olivine tholeiites. Ca poor augites are present in quick chilled basalts. Al, Fe$^{3+}$ and Na are present in most augites. In most augites Si and Al fill all the tetrahedral sites, but where there are vacancies, Fe$^{3+}$ is usually taken in. Clinopyroxene with a high Ti content and violet to purple/pink pleochroism is titanaugite. Ti content is usually relatively low, but in titanaugite the concentration of Ti is greatly increased. Cr is an important minor constituent in Mg-rich augites and the highest Mn concentrations are in Fe-rich augites. K is not present and Na has very low concentrations (Deer et al. 1992).

3.1.5  Opaque Oxides

Magnetite, titanomagnetite and ilmenite are the more common opaque accessory minerals of basaltic rocks. These minerals oxidise during weathering to yield hematite, maghemite, or goethite, simultaneously releasing titanium, which may have limited mobility, but is ultimately oxidised to anatase (Loughnan 1969). However, in a more arid environment, magnetite and ilmenite are very stable and show only slight decomposition, as a result of physical and chemical weathering. Magnetite and ilmenite therefore, persist into the weathering crust (Singer 1984).

Chemistry

The ideal formula for ilmenite is FeTiO$_3$ but generally some Mg and Mn substitute for Fe resulting in the composition (Fe,Mg,Mn)TiO$_3$. If magnetite and ilmenite coexist the Mn is always partitioned into the ilmenite. Ilmenite weathers to rutile, $\pm$ pseudorutile, hematite, anatase and secondary Fe-oxyhydroxides. Exsolution lamellae of hematite may form during the dissolution. Ilmenite is a common accessory mineral in many igneous rocks and is often associated with orthopyroxene in tholeiitic basalts. Ilmenite has a hardness of 5-6, is relatively resistant to weathering and is a common detrital mineral (Deer et al. 1992).
In magnetite small amounts of Al may substitute for Fe$^{3+}$ and Ca, Mn and Mg substitute for Fe$^{2+}$. A considerable amount of Ti can enter the magnetite structure forming titanomagnetite. Other substitutions are Cr and V for Fe$^{3+}$ and Ni, Co and Zn for Fe$^{2+}$. Magnetite is one of the most abundant oxide minerals in igneous rocks, typically an accessory mineral and is commonly titaniferous in more basic rocks. Magnetite has a hardness between 7.5 and 8, hence it resists weathering and is a common detrital mineral (Deer et al. 1992).

Magnesiochromite contains some Fe$^{2+}$, also Cr may be replaced by Al and Fe$^{3+}$. Chromite contains some Mg$^{2+}$ and may substitute Zn$^{2+}$ also. Chromite may occur as finely disseminated flakes in olivine. It is a common detrital mineral with a hardness of 7.5 to 8 and is commonly concentrated in deep weathering profiles (Deer et al. 1992).

### 3.1.6 Iron Oxidation and Weathering of Ferromagnesian Minerals

The effect of iron on weathering rates is complex (Colman & Dethier 1986). Wilson (1975) has suggested that oxidation of structural ferrous iron is important in the early weathering stages of ferromagnesian minerals. Iron is not always completely oxidised early in weathering as some Fe$^{2+}$ can be taken into trioctahedral clays. The rapidity of appearance of Fe$^{2+}$ in solution of experimentally weathered ferromagnesian minerals suggests that dissolution of the iron precedes its oxidation (Seiver & Woodford 1979), rather than oxidation in situ in the silicate structure as suggested by Huguenin (1974) for the oxidation of magnetite. Because Fe$^{3+}$ is more stable in the oxic weathering profile we find that there may be a transition from tri- to dioctahedral minerals when oxidation occurs, as Fe$^{2+}$ is replaced by Fe$^{3+}$ within the clay. Serpentine and ferruginous saponite in weathered basic rocks may be transformed into nontronite due to the oxidation of iron. In basic rocks where no phyllosilicates are initially present nontronite forms directly, that is, the initial Fe$^{2+}$ bearing rock produces an Fe$^{3+}$ silicate assemblage when weathered (Velde 1985).

The dissolution of fayalite (Fe-olivine), hypersthene (Mg, Fe orthopyroxene), basalt and obsidian (rhyolitic glass) have been modelled in the laboratory under varying conditions of pH and atmospheric gas (air, N$_2$, O$_2$) by Siever and Woodford (1979). Each sample dissolved more rapidly initially, followed by slower dissolution. In oxygenated atmospheres they observed the precipitation of Fe(OH)$_3$, including stages of nucleation, crystal growth, and spontaneous dehydration forming a coating on the surface of minerals. This rind of hydrated oxide Fe(OH)$_3$ on the silicate surfaces controlled further dissolution by requiring diffusion of silica, cations and oxygen through a surface barrier. There is evidence from weathering in arid regimes that mafic minerals develop an
Chapter 3: Basalt Mineral Dissolution and Element Mobility

Fe-oxide rind (Walker 1967) which may partly explain why mafic minerals weather more slowly in this setting.

Siever and Woodford (1979) also found that Mg$^{2+}$ and other cations are only marginally affected by the presence or absence of oxygen suggesting that the primary break-up and dissolution of the silicate structure by Mg$^{2+}$ for H$^+$ exchange is unaffected by oxidation. This is in agreement with the work of Luce et al. (1972) who suggest that a layer is formed on the silicate surface, aside from any hydroxide precipitate, controlling kinetics by diffusion. Many authors have discussed the development of a layer at mineral surfaces and diffusion of ions and fluids through that layer (Helgeson 1968, Helgeson 1971, White & Claussen 1980). However, one study of olivine, pyroxene, amphibole and feldspar grain surfaces has shown no such layer (Holdren & Berner 1979).

In the experiment of Siever and Woodford (1979), the exchange of metal ions for H$^+$ ions is affected by the pH of the weathering solution, confirming that solution pH influences silicate dissolution as earlier suggested by Grandstaff (1977). Dissolution rates in the absence of oxygen proceed unhampered by the Fe(OH)$_3$ precipitate. In reducing zones of temperate climate soils, particularly in poorly drained, waterlogged soils, mafic minerals weather at maximum rates. They infer that the absence of an oxidised iron-rich rind contributes to this rapid rate (Seiver & Woodford, 1979).

3.1.7 Chemistry of Accessory Minerals

**Zircon**

Zircon always contains Hf, and P$^{5+}$ is present in some varieties replacing Si$^{4+}$ in the structure. In order to maintain electrostatic neutrality REE, may enter the structure of the mineral. Many zircons contain appreciable U and Th. Zircon is colourless to pale brown in thin section, but the optical properties may be affected by metamictisation, the effect of radioactivity on the lattice, hence zircon grains may have a surrounding pleochroic halo when enclosed in or by other minerals. Zircon is a common accessory mineral of igneous rocks, generally present as early formed crystals enclosed in other minerals. Zircon is resistant, has a hardness of 7.5 and often survives more than one cycle of weathering and sedimentation (Deer et al. 1992).

**Apatite**

Apatite is a common accessory mineral in igneous rocks, and the most abundant P bearing mineral. Ca, F, OH or Cl are the principal elements that partition into apatite. Ca may be substituted for by Mn, Sr or REE especially LREE in particular Ce and some La.
Apatite may also contain $\text{CO}_2$ where $\text{CO}_3^{2-}$ and $\text{F}$ substitute for $\text{PO}_4^{3-}$. Synthetic substitutions include $\text{Sr}$, $\text{Ba}$, $\text{Pb}$ and $\text{Y}$ for $\text{Ca}$ and $\text{Si}$ and $\text{SO}_4$ for $\text{PO}_4$. Fluorapatite is the dominant igneous apatite and sometimes has (OH) added forming hydroxy-fluorapatite (Deer et al. 1992). Apatite occurs as a detrital mineral and has a hardness of 5, but dissolves rapidly in acid fluids.

Titanite

Titanite is not a common accessory mineral in basalts, but if it is present it may cause significant variation in the concentration of trace elements in the rock. Substitutions include $(\text{Al}, \text{Fe}^{3+}) + (\text{F,OH}^-)$ for $\text{Ti}^{4+} + \text{O}^{2-}$. Al and Fe enter octahedral sites and REE substitute for Ca. In addition, Ca, Mg, Na, K and Fe$^{2+}$ can be located in a seven fold site. Titanite is rich in trace elements especially Nb, Ta and V, plus Th and U. Titanite alters to anatase $\pm$ quartz $\pm$ rutile. It is relatively resistant, with a hardness of 5, and forms detrital grains in sediments (Deer et al. 1992).

Rutile

Rutile occurs as a resistant primary mineral but may form as a secondary mineral after other Fe-bearing phases such as ilmenite (Loughnan 1969). It may contain Nb and Ta, and Cr and V may substitute for Ta in rutile. It is commonly a detrital mineral and has hardness around 6 to 6.5 (Deer et al. 1992).

Feldspathoids

Nepheline characterises alkaline igneous rocks, leucite forms in K-rich basic lavas and analcite may be present in the groundmass of basalts. Feldspathoids weather more rapidly than feldspar (Wang, 1988).

Zeolites

Zeolites are formed readily from volcanic materials in alkaline conditions where fluids have concentrated carbonate-bicarbonate by evaporation. Hence they are more common in arid to semi-arid environments. Smectites may also be formed by the hydrolysis of vitric material. Zeolites form well developed crystals in the vesicles of basalts, considered to be precipitated from late stage fluids that permeated the basalts after their extrusion (England & Sutherland 1988).
Calcite

CaCO$_3$ may form crystals in amygdales either as a result of late phase precipitation from warm fluids or as a result of Ca remobilisation in bicarbonate fluids during the weathering of basalt.

3.2 ELEMENT MOBILITY DURING THE DISSOLUTION OF BASALT MINERALS

3.2.1 Potassium, Sodium, Calcium and Magnesium

A considerable depletion (50%-90%) of the alkaline earth and alkali metals occurs during the transition from rock to secondary products in basalt weathering (Tedrow & Wilkerson 1953, Hendricks & Whittig 1968, Mohr et al. 1972, Singer 1978, Noack et al. 1990) Experimental weathering of basalt for more than two years by Pedro (1961) showed that alkaline cations and some Si and Al had been removed, whereas iron and titanium were not. Comparable effects were found from profiles on basic volcanic rocks in Australia (Craig & Loughnan 1964). As a general observation, Ca, Mg, K and Na are mobilised early in the weathering of a basalt. Elements with similar ionic radii and valency characteristics such as Rb and Sr may also be mobilised at this time (Yaalon et al. 1974, Eggleton et al. 1987). The loss of these cations can be correlated with the devitrification of volcanic glass to palagonite, the formation of alteration rims on olivine grains and the early dissolution of ferromagnesian minerals and plagioclase.

Singer (1970) in a study of thin weathering crusts formed on basalt, observed a similar depletion of Ca, Mg and Na early in weathering of basalt from the Galilee, Israel. He attributed the smaller initial loss of K compared with Na and Ca, to the greater relative stability of K-feldspars and the more rapid weathering of Na and Ca bearing plagioclase feldspars. In a later study of weathering profiles on vesicular basalt, with thick saprolite development, Singer (1973) observed a similar but smaller depletion of Mg, Ca, Na and K. He proposed that this decrease in the depletion of chemical constituents could be explained by a decrease in the intensity of weathering because of impeded permeability in the basalt. Small losses of Ca are attributed to the reprecipitation in pores of Ca in the form of calcium carbonate. White and Sarcia (1978) experimentally weathered a fresh glass bearing olivine basalt. Deamineralised water dissolved small amounts of Si, Na and Ca from the basalt which parallels natural weathering in a semi arid climate. Reifenberg (1952) found a similar depletion in Ca and Mg, but only a weak depletion in Na and an enrichment in K in a strongly decomposed basalt boulder in Syria.
Potassium (K)

K together with Na and Ca, is an important cation in several silicate groups. Alkali feldspar and micas are the principal K-bearing phases but as these are not abundant in basaltic rocks the largest control on the K concentration in basalt weathering products is the dissolution of plagioclase feldspar and basaltic glass. Once mobilised, K either enters illite if this clay is present in the secondary material, is adsorbed onto other clays, or is removed in percolating fluids. K generally shows a strong decrease in abundance in weathering materials with increase in weathering. In arid regions the K content of groundwater increases.

Chemical relationships between K and Ba are very similar to those between Na and Ca, but as Ba is much less abundant in nature, K minerals usually contain Ba as a minor constituent. K and Rb have similar ionic radii which allows mutual substitution but Rb is relatively scarce (Heier & Billings 1978a). Pb has an ionic radius close to K which leads to the presence of traces of Pb in K-bearing minerals. K⁺ is also a similar size to H₃O⁺ and NH₄⁺. K⁺ is an element that has preferential fixation in cation exchange with clay minerals therefore K has lower affinity for hydration than Na⁺ and Ca²⁺ in competition with surface charge of minerals (Cocco et al. 1978a).

Sodium (Na)

Na is present in plagioclase feldspars, and to a lesser extent in pyroxenes and basaltic glass. Na is highly soluble during weathering and is more mobile during weathering than K. Hence, the Na/K ratio in the weathering mineral decreases during ion exchange. The Na content of groundwaters is a function of the weathering of Na-plagioclase from the bedrock and exchange of Ca for Na on the surfaces of neoformed clay minerals (Heier & Billings 1978c).

Calcium (Ca)

The most common Ca bearing phases in basalt are plagioclase feldspars, clinopyroxenes and basaltic glass. The rate of dissolution of Ca from silicate rocks during weathering is usually intermediate between Na and K and that of Al, Si and Fe. The concentration of calcium in groundwaters is controlled mainly by the dissolved carbonate, phosphate and sulphate species (Usdowski 1978a). Ca is released as a by-product of the reaction of carbonic acid with Ca-bearing phases in the basalt. Sr commonly shows similar chemical behaviour to Ca.
Magnesium (Mg)

Olivine and pyroxene readily release Mg during weathering of basalt. Forsteritic olivine is the species most common in basalts. Clay minerals adsorb cations in the approximate sequence Na<K<Ca<Mg<NH₄ therefore Mg will more easily replace Ca than vice versa (Usudowski 1978b). The ion exchange capacity of minerals other than clays and Fe- or Mn-oxides is usually small (Usdowski 1978b).

3.2.2 Silica

Because of the much lower solubility of silica, it is not as rapidly mobilised as a result of weathering. During hydrolysis Si is released from primary minerals, partly removed from the weathering environment and partly re-engaged in the neoformation of clay minerals (Singer 1970). A very minor fraction may also reprecipitate in the form of cryptocrystalline secondary silica, particularly chalcedony. White and Sarcia (1978) found that dissolved silica was reprecipitated as a gel which in nature would probably dehydrate to form opal. Spherulites of chalcedony rimmed with opal have been preserved on samples from weathering profiles developed on basalt (Craig & Loughnan 1964). When weathering occurs on more porous vesicular basalts the dissolution of silica is further reduced because of the weaker intensity of leaching (Singer 1973). The removal rate of Si may be accelerated by an acid weathering environment (Hendricks & Whittig 1968) but acid conditions are not likely to be produced during the early stages of basalt weathering (Navrot & Singer 1976).

Silica (Si) and silicates

As silicates hydrolyse in water they release silica into solution. There are three principle groups of silicates: those that dissolve congruently, those that dissolve incongruently and those that are so slightly soluble that they may be considered resistant. In basalts olivine and pyroxene are the first silicate minerals to disappear from the weathering rock, however, they do not necessarily dissolve congruently. Olivine alters under reducing conditions to ferrous Mg-vermiculite and smectite with loss of silica and Mg, and may oxidise to goethite with loss of silica and Mg. Pyroxenes alter through pyroboles to clays (Wang 1988). These reactions are incongruent.

Feldspars dissolve incongruently and form clay minerals. K-feldspars are more resistant to weathering than plagioclase feldspars and of the plagioclase feldspars, Na-bearing (albite) phases are more resistant than Ca-bearing (anorthite) phases. Quartz is resistant, it has low solubility and slow kinetics of dissolution (Siever 1978). When precipitating
from solution amorphous silica is produced rather than quartz. The presence of opaline silica in tropical soils implies that the profile must have periods of supersaturation with respect to amorphous silica. In the soil environment, acidity enhances the hydrolysis of silicates. Dissolved silica concentrations in natural waters vary widely as they are affected by meteoric water and rain dilution.

### 3.2.3 Manganese, Lead, Copper and Zinc

Mn, Pb, Cu, and Zn are more slowly removed than Mg, Ca, Na and K (Eggleton et al. 1987). Yaalon et al. (1974) working in the Galilee, describe Mn as being relatively immobile during basalt weathering. However, Navrot and Singer (1976) discuss the release of manganese from the host ferromagnesian minerals during weathering, and the subsequent mobilisation of Mn in solution as divalent manganese bicarbonate, suggesting that under reducing conditions this reaction may become significant. Copper may be retained in a basalt weathering profile because of its incorporation in neoformed clays, or adsorption onto clays and iron oxides. Zinc is also readily mobilised in solution unless it is enclosed within a relatively resistant phase.

**Manganese (Mn)**

Because of some similarities in chemical properties of Mn$^{2+}$ with Fe$^{2+}$ and Mg$^{2+}$ (and Ca$^{2+}$), Mn substitute for these elements in igneous minerals (Peacor 1978). Mn may be present in olivine, pyroxene and to a lesser extent, feldspar. In common ferromagnesian silicates the structural preference for Mn decreases from orthopyroxene and olivine to Ca rich pyroxene. Therefore the Mn in basalt is mostly enclosed in the olivine. During weathering Mn is released as soon as olivine starts to break down, and may become partly oxidised to Mn$^{4+}$ which forms oxides of very low solubility. A small fraction of Mn$^{2+}$ will be transported out but the low concentration of Mn in surface waters indicates that the mobility of this element is limited (Wedepohl 1978c).

**Lead (Pb)**

Pb and K are both large ions, and may substitute for each other. Olivine contains almost no Pb as there are no structural sites for this cation, and pyroxene, plagioclase and magnetite enclose only extremely small trace amounts of lead. Pb may sometimes substitute for Na and Ca in plagioclase. K-feldspar and micas are the main hosts for Pb. These phases are not common in basalts, and are relatively resistant to weathering. With weathering there is an overall depletion of Pb in derived sediments and soils but it may be concentrated in the clay fraction (Wedepohl 1978b).
**Copper (Cu)**

The Cu concentration in basalts is very low. Cu in basalts may be incorporated in very fine grained Cu-sulphides (chalcopyrite). During weathering the Cu is released when the sulphides are oxidised. The concentration of Cu in solution is controlled by adsorption onto clays and Fe-oxides and the presence of anions in solution. A low concentration of Cu in fresh waters indicates the restricted mobility of Cu during chemical weathering. Cu may be strongly adsorbed onto ferric iron oxides, giving a positive correlation of Cu and Fe-oxides, and clay minerals (Wedepohl 1978a). Often Cu is relatively concentrated in basalt weathering profiles.

**Zinc (Zn)**

Zn$^{2+}$ substitutes for Fe$^{2+}$ and Mg$^{2+}$ in silicates and oxides. Some Zn may occur as sphalerite in basalts but this is not common. Zn occurs more commonly in magnetite and chromite with lesser amounts in olivine and pyroxene and trace amounts in plagioclase. The Zn content of basaltic rocks is mainly contained in relatively resistant magnetite. If this host mineral breaks down Zn may be released and subsequently adsorbed onto clay minerals, iron oxides and organic compounds. There is a low concentration of Zn in surface water, suggesting that there is restricted mobility of this element from weathering. In general Zn concentration increases with weathering (Wedepohl 1978f).

### 3.2.4 Strontium, Barium, Rubidium, Nickel and Chromium

The dissolution of minor elements from weathered basalt rocks in Israel, followed the sequence: Sr, Ba > Mn, Cu > Co, Ni > Zn > Cr (Singer 1978). Sr and Ba appear to be the most mobile and the depletion intensity of Sr is very close to that of Ca indicating a similar instability.

Rare earth elements (REE) and Ba were diminished initially in the weathering of basalt corestones from eastern Australia, but appear to be slightly concentrated in the outer rind of the corestones (Eggleton *et al.* 1987) suggesting that they are incorporated into weathering products before being removed from the system.

Chromium is extremely immobile and frequently accumulates in weathering products. Within basalt profiles the immobility of Cr can be attributed to the stability of its host minerals, magnetite, ilmenite and chromite. Nickel and cobalt have ionic radii similar to those of Mg and Fe and can be retained in octahedral positions within the clay mineral lattice. They can also be retained in the adsorbed form.
Strontium (Sr)

The distribution of Sr is controlled by its size, intermediate between Ca and K as it can substitute for both, but will preferentially substitute for Ca (Fischer 1978b). In plagioclase feldspars there is an increase in Sr content with decrease in Ca content. Clinopyroxene much prefers Ca but will substitute Sr. Orthopyroxene and olivine have very little Sr substitution because of the lack of structural sites for the cation and therefore can only contain Sr in structural defects or adsorbed onto their surface. Hence, in basalt weathering Sr is predominantly released from plagioclase feldspar. Sr is generally mobilised less than Ca because it is more tightly held on clay minerals and more weakly hydrated than Ca. The original Sr concentration is usually maintained during the early stages of weathering then decreases with increase in plagioclase decomposition (Wedepohl 1978e).

Barium (Ba)

Ba$^{2+}$ has a large ionic radius and is commonly replaced by, and substitutes for, Pb$^{2+}$ and Sr$^{2+}$ and less commonly for K$^{+}$ and Ca$^{2+}$ (Fischer 1978a). In igneous rocks Ba is usually enclosed in feldspars. Ca substitution is observed in plagioclase and pyroxene. Apatite is an important non-silicate Ba-bearing phase. Pure plagioclase end members albite and anorthite contain less Ba than intermediate types. Experimental weathering of K-feldspar in water preferentially released Ba. Apparently Ba is relatively easily removed, and may even be more easily leached than K. However, on the presence of sulphate, BaSO$_4$ precipitates. Ba is adsorbed from solutions by clays and organic matter, Fe-oxides and especially by Mn oxyhydroxides (Puchelt 1978).

Rubidium (Rb)

Rb is generally enclosed in K-bearing minerals (Cocco 1978b) but because these are not commonly found in basalts the Rb concentration is extremely low. In weathering Rb is closely linked to K. Adsorption may play an important role in the concentration of Rb relative to K in the late stages of weathering, as Rb is held more firmly in adsorption positions than K (Heier & Billings 1978b). This may be because Rb has a similar ionic radii to H$_3$O$^+$. 

Nickel (Ni)

Nickel is taken into olivine early in magmatic crystallisation. Ni substitutes for Mg in olivines, and forsteritic olivines are most common in basalts. Spinels (magnetite and chromite ± ulvospinel) are also important sites for Ni incorporation. Ni is easily
mobilised during weathering, however, it is co-precipitated with Fe and Mn oxides so there is generally a relative concentration of Ni in soils (Turekian 1978) and Ni-silicates.

Chromium (Cr)

The major proportion of Cr in basaltic magmas is incorporated early into Cr-rich spinel. When magnetite and ilmenite co-exist the Cr is preferentially found in the magnetite. Olivine is low in chromium but may have small spinel inclusions which will increase the Cr concentration. Cr content in pyroxene is also quite low but generally clinopyroxene has more Cr than orthopyroxene. Because Cr$^{3+}$ resembles Al$^{3+}$ and Fe$^{3+}$ in its crystallochemical properties, it behaves similarly to these ions during weathering and ultimately concentrates in secondary products. The Cr present in chromite, magnetite and ilmenite concentrates in residual weathering products. Cr is fixed in weathering products without appreciable loss to surface runoff. Ferric (Fe$^{3+}$) iron-rich secondary minerals and clays become enriched in Cr with weathering. Mn$^{4+}$ oxide adsorbs Cr most effectively. Under progressive oxidation Cr goes to the chromate (CrO$_4^{2-}$) which is a readily soluble anion (Shiraki 1978).

3.2.5 Titanium, Zircon, Niobium and Aluminium

Titanium (Ti)

Ti occurs as an essential element in the minerals: rutile, titanaugite, titanomagnetite and ilmenite and rarely in phases such as titanite. Ti will substitute for Al$^{3+}$, Fe$^{3+}$, Nb$^{5+}$, Ta$^{5+}$, Mn$^{3+}$ in silicates, particularly pyroxenes (Tillmans 1978). If fine grains of ilmenite are enclosed in feldspars they will be residual when the feldspar weathers. Ti is more abundant in basalts than in felsic rocks.

The Ti-oxides and ilmenite are very resistant to weathering. If Ti bearing silicates are decomposed, the Ti will be dissolved but is converted to anatase which is retained in the profile as a stable mineral. Pedro (1961) showed experimentally that Ti was stable during the weathering of basalt. Consequently, there is usually an accumulation of Ti in weathering profiles (Correns 1978).

However, Ti can migrate in soils, and organic acids are probably the transporting agent. The highest solubility of anatase (and rutile) is in oxalic acid and citric acid hence the link between migration of Ti in soils and the presence of organic acids. Ti has been related with Zr, Y, Nb and Sr (Bloxham & Lewis 1972) and Zr and Cr (Chazen & Vogel 1974) in order to characterise specific magma types.
Zirconium (Zr)

Zr has a similar ionic radii to the lanthanide mineral Hf and they are almost always found together. The most important Zr-bearing mineral is zircon (ZrSiO4) (Bayer 1978). Zr forms minute inclusions in rock forming minerals and may be residual in weathering. Zr can replace Ti, Nb, Ta, rare earth elements (REE) and Fe. Amongst the oxides the highest concentrations of Zr are found in minerals containing Ti, Y, Nb and Ta, that is, titanomagnetite and ilmenite. The more common magnetite and spinels do not contain much Zr. The silicate minerals feldspars, feldspathoids, olivine and orthopyroxene contain trace amounts of Zr only (Erlank et al. 1978). There are more significant amounts in clinopyroxene, in particular titanaugite.

*Zircon* is most readily attacked under alkaline conditions. Metamictisation, damage caused by radioactive isotopes included in the lattice, reduces the stability of *Zircon*. Other factors that contribute to the breakdown of *Zircon* are zoning, inclusions, fractures and small grain size. Zr, once mobilised, may be incorporated into clay forming minerals and accumulate in the weathering profile as dissolved Zr is readily hydrolysed to colloidal particles of oxides, hydroxides or phosphates, which may be trapped in the profile or washed away (Erlank et al. 1978).

Niobium (Nb)

Nb and Ta form a solid solution, and because of the geochemical similarity, they commonly coexist in pyroxene, ilmenite and magnetite (Wedepohl 1978d).

Nb, Y, and Zr show low mobilisation during metamorphism and weathering and Nb and Zr are unaffected by seawater alteration of basalt. Nb and Ta are either released through the destruction of host species (Ti-bearing minerals) or concentrated in resistant minerals (ilmenite, titanite, zircon). Nb may occur in metamict minerals (zircon) which may facilitate its release. Nb is chemically unique as most of its compounds are almost insoluble in acid and alkaline media, hence the soluble Nb compounds require high concentrations of acid or alkali for their formation and stabilisation. Nb is depleted in proportions intermediate between Al and Si. Once released Nb may occur in clay minerals (Heinrich 1978).

Aluminium (Al)

Al is present in feldspars, pyroxenes, and layer silicates and comprises up to 14 wt% in basalts. Al released principally during feldspar break-down, is hydrated immediately and incorporated into layer silicates. Clay minerals and Al-hydroxides, form a sink for H+ ions. In general the solubility of Al in weathering processes is low and it is retained in
the weathering products, however, the element does actively participate in chemical reactions (Hem 1978).

3.2.6 Yttrium, Lanthanum, Cerium, Thorium and Uranium

Yttrium (Y), Lanthanum (La) and Cerium (Ce)

Y, La and Ce have broadly similar chemical behaviour. Acid conditions favour the solution and removal of lanthanides and they are removed from intensely weathered rock. In basalt the light lanthanides partition into plagioclase and heavy lanthanides into pyroxene, and the accessory phase apatite may be rich in REE. La and Ce are present in clinopyroxene with very minor amounts of Ce in olivine (Herrmann 1978). Y may be fixed in a resistant phase as it remains relatively immobile during weathering. Ce fractionates from the balance of the REE during weathering because it oxidises from Ce$^{3+}$ to Ce$^{4+}$ and is thereby fixed, while other REE are readily removed from the profile (Marker & de Oliveira 1994, Braun & Pagel 1994).

Thorium (Th)

Th is similar in size and has a close relationship with Ce, U and Zr, and is most abundant in the accessory phases apatite, titanite and zircon. Hence the concentration of Th in basalt is very low. Th is relatively immobile and is concentrated in residual minerals in soil and weathered basalt. If Th is mobilised during weathering it may accumulate in hydroxide minerals and clays (Rogers & Adams 1978a).

Uranium (U)

The concentration of U in basalts is extremely low, with U most abundant in apatite and zircon. U is readily oxidised to the comparatively soluble uranyl ion, therefore U is mobilised easily in surficial processes, unlike Th. This leads to a fractionation of U and Th during weathering. Any U that remains in the soil is retained in resistate phases such as zircon (Rogers & Adams 1978b).

3.2.7 Iron, Vanadium, Sulphur and Phosphorus

Iron (Fe)

In basalt iron is present in olivine, pyroxene and in Fe-Ti oxides. Olivine is the first iron bearing mineral to weather, followed by pyroxene. Magnetite is much more resistant to chemical weathering but can oxidise to hematite. Atmospheric oxygen reacts with ferrous
iron (Fe$^{2+}$) and converts it to (Fe$^{3+}$) ferric oxides which precipitate within the weathering profile (Berner 1978).

**Vanadium (V)**

V is found as a minor constituent in magnetite and pyroxene (Taylor *et al.* 1969, Evans 1978). Very small amounts occur in plagioclase, olivine, apatite and ilmenite. Although the concentration of V in basalts is low, it is greater than in more felsic rocks. If V is not enclosed in a resistant phase the major proportion of V will disperse in the clay fraction during weathering. In the clay fraction V can be adsorbed and incorporated into the clay mineral structures or be present in Fe-oxide coatings (Landergren 1978).

**Sulphur (S)**

The sulphur content in basaltic rocks is very low, and although S is analysed as a major element, it is usually present in parts per million levels. During weathering S participates extensively in redox processes but is influenced by solution pH. S forms volatile compounds with light elements, especially water. Aqueous solubility of oxidised sulphur compounds with metals is generally much higher than for the corresponding reduced sulphur compounds. S content is also influenced by a great number of biochemical processes. Ba may fix S forming BaSO$_4$ in the secondary weathering products. Sulphur in basalts may be enclosed in mafic phases, for example within fine disseminated chalcopyrite and secondary sulphates.

**Phosphorus (P)**

In basalt small amounts of P are present in augite and olivine, because of the substitution of some P$^{5+}$ for Si$^{4+}$, but the greatest abundance is in the accessory phase apatite. The solubility of apatite in the alkaline region is very small, and increases with the acidity of the solutions. In an acidic environment apatites are more soluble. P may be fixed in smectite and kaolinite by adsorption. P is capable of forming highly insoluble secondary compounds of the crandellite group which very strongly control the behaviour of P in natural processes.

P may complex with a number of elements during weathering including Sr, Ba, Pb, Ca and REE. REE may be retained in the incipiently weathered volcanic rocks (Melfi *et al.* 1990) but in more intensely weathered rock, where kaolinite is the dominant phase, REE are relatively depleted. The early enrichment in REE is attributed to sorption processes and/or the formation of slightly soluble hydroxides. The later depletion possibly results from the loss of cation exchange capacity accompanied by changes in pore water

3.3 PRINCIPAL SECONDARY BASALT WEATHERING PRODUCTS

3.3.1 Hematite and Goethite

The ideal hematite composition is Fe$_2$O$_3$, but some Ti, Al and Mn may be present. Hematite is characterised by a blood red streak (powder). In igneous rocks it is found as a weathering product of iron-bearing minerals. The presence of hematite is the most common cause of red colouration in rocks (Deer et al. 1992).

Goethite is the most widespread Fe-oxide in soils and mineral weathering environments and commonly is the only Fe-oxide (oxyhydroxide) in soils of cool and temperate zones. In warmer areas it is most frequently associated with hematite (Schwertmann et al. 1982). Lower temperatures, higher H$_2$O activity and higher organic matter contents favour the formation of goethite.

Goethite (FeO.OH) is yellow brown to red in colour and gives a yellow streak. Most goethite analyses show some SiO$_2$ impurity, and enclose some Fe$_2$O$_3$ and H$_2$O. Mn$^{3+}$ may substitute for Fe$^{3+}$ and Al may be a major substituent in soil goethite (up to 30 Mol%). It occurs as a weathering product of Fe-bearing minerals, under oxidising conditions (Deer et al. 1992). When goethite dehydrates it gives hematite.

Hematite and goethite are produced during the dissolution of Fe-bearing silicates and oxides in basalts. Hydrated minerals (goethite) may appear at the bottom of weathering profiles, close to the groundwater table or downslope where the unsaturated layer is reduced. They also appear again close to the surface in areas where they are temporarily hydrated during the wet season. Dehydrated minerals appear preferentially in the intermediate part of the unsaturated zone (Tardy et al. 1988). Hematite and goethite may exhibit a high variability of structural and crystal chemical characters which reflect the initial weathering conditions, but depend also on subsequent processes of dissolution and crystallisation which affect the minerals (Muller & Boudeulle 1990).

In soil materials the formation of goethite at the expense of hematite is enhanced by a variety of factors such as low temperatures, high water activity, low rates of Fe release from parent materials, high organic matter concentrations and relatively low pH.
The high activity of Al in the micro-environment favours goethite formation relative to hematite (Taylor 1987). Soil temperature is regulated by climatic factors such as latitude, altitude and continentality. The relative humidity of the soil atmosphere, that is, the thermodynamic activity of water, is controlled by rainfall, evaporation, permeability, pore size and depth of ground water table (Tardy et al. 1990b).

The chemical potential of water plays an important role in the transformation of goethite to hematite (Tardy & Nahon 1985). Dehydration reactions of the type goethite to hematite can be induced by a decrease in the thermodynamic activity of water (at constant temperature), by an increase in temperature (at constant activity of water), or by activity of water decreasing and temperature increasing at the same time. A decrease in water activity has a similar effect to an increase in temperature (Tardy et al. 1990b).

It also is possible that hematite may be hydrated to form goethite. Muller and Boudeulle (1990) suggest that in a deep weathering profile in Cameroon, hematite forms after nucleation from X-ray amorphous Fe(III) hydroxides in an aqueous system, and that goethite may be formed from hematite in this environment.

The chemical nature and high specific surface area of sub-microscopic Fe-oxide particles make them efficient sorbents and therefore sinks for inorganic anions (silicate, molybdate, phosphate), organic molecules (citrate, fulvic and humic acids and biocides), and cations such as Al, Cu, Pb, V, Zn, Co, Cr and Ni. The cations can be adsorbed onto the surface or incorporated into the oxide structure (Dixon & Weed 1989). In addition, Fe hydroxides are strong sorbers of U and other radionuclides.

### 3.3.2 Anatase

The low temperature polymorph of TiO2, anatase, is an alteration product of titanite and rutile, and may be neoformed during weathering as a result of concentration of Ti from the dissolution of ferromagnesian phases. Minor substitution of Fe and Sn may occur and Nb and Ta varieties are known. Anatase is a relatively common soil mineral (Deer et al. 1992), and often forms in close association with kaolinite in intensely weathered profiles. Much of the anatase present in weathered basalts may be sub-microscopic in size (pers. comm. Le Gleuher 1994).

### 3.3.3 Gibbsite

Gibbsite Al(OH)3 forms small tabular crystals with a pseudohexagonal outline. Gibbsite contains few substituent ions, mainly Fe3+ up to 1-2%. Gibbsite is one of the main
constituents of bauxites and is usually the product of intense weathering associated with halloysite, goethite and hematite, but it can be formed hydrothermally. Proportions of kaolinite and gibbsite are inversely related with gibbsite the dominant mineral in highly weathered material (Dixon & Weed 1989).

3.3.4 Kaolinite and Halloysite

Kaolinite has a low cation exchange capacity (CEC) up to 10 meq/100 g (compared with illite ~20 meq/100 g, smectite 100+ meq/100 g) and for halloysite the value is up to 40 meq/100 g. By contrast kaolinite has high anion exchange capacity, greater than for most clays, because of the presence of exchangeable (OH)⁻ ions on the outside of the structural layers. Small amounts of Fe, Cr, Ti, and Mg may be in impurities in kaolinite. Kaolinite may form massive blocks, vermiliform or granular aggregates, or piles of platelets, and rarely fibrous forms. Kaolinite platelets are flexible but inelastic. Kaolinite occurs in residual deposits formed by weathering or low temperature hydrothermal alteration of all Al-rich silicates. For example; the chemical reaction feldspar to kaolinite follows a two step process:

\[ 2.3\text{KAlSi}_3\text{O}_8 + 2\text{H}_2\text{O} \rightarrow \text{K}_0.3\text{Al}_2\text{Si}_3.7\text{Al}_0.3\text{O}_{10}(\text{OH})_2\cdot 4\text{H}_2\text{O} \]

\[ \text{feldspar} \quad \text{smectite} \]

\[ \text{K}_0.3\text{Al}_2\text{Si}_3.7\text{Al}_0.3\text{O}_{10}(\text{OH})_2 + 1.45\text{H}_2\text{O} \rightarrow 1.15\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 1.4\text{SiO}_2 + 0.3\text{KOH} \]

\[ \text{smectite} \quad \text{kaolinite} \]

the silica and the KOH is leached away. Under water saturated conditions illite rather than smectite may form. In the weathering of olivine phenocrysts, dioctahedral smectite crystallises on the margins of fissures, and with further weathering halloysite is formed away from the fissure walls (Smith et al. 1987), indicating local Al mobility.

Halloysite generally forms fibrous, spheroidal or irregular shapes. Halloysite fibres appear tubular or scroll-like with elongation parallel to \( b \) but there are some platey halloysites. Robertson and Eggleton (1991) describe the transition from kaolinite to halloysite and mechanism of halloysite tube formation. Halloysites show more variable compositions than kaolinites, may contain 1-2% Fe³⁺ and have a higher Al/Si ratio. The water in halloysite is so loosely held that even at room temperature in an unsaturated environment, most of the interlayer water is lost.

There is a relationship between kaolinite crystallinity and Fe content of kaolinites (Mestagh et al. 1980). If the kaolinite has good crystallinity, then it generally has low associated total iron and it gives a poorly crystalline external electron spin resonance
(ESR) signal. Poorly crystalline kaolins have approximately half internal and half external ESR Fe signals and the internal Fe-bearing material is crystalline while the external Fe-bearing material is poorly crystalline. Intermediate kaolinites show a combination of Fe location and crystallinity (Mestagh et al. 1980).

In a study of tropical weathering of recent basalts from Cameroon, Sieffermann and Millot (1969) describe two types of weathering profile and relate the variation in clay mineral assemblage to changes in climate environment. In the region with equatorial tropical climate, which was always humid, the parent basalt yielded allophane, kaolinite and gibbsite. In the regions with a climate that had a definite dry season the weathering sequence was from parent basalt through allophane then halloysite and metahalloysite to gibbsite.

3.3.5 Interstratified Kaolin-Smectite Clays

Eggleton et al. (1991) propose ways which the cation exchange capacity (CEC) of kaolinite can be elevated: the rock may contain discrete smectite, possibly in such thin packets that it is not detected by X-ray diffraction (XRD); the mineral may contain interstratified smectite; the kaolinite may have coupled ionic substitution (i.e. Al and Ca replacing Si and a vacant site); or if the kaolinite is fine grained, the exchange capacity arises from edge sites. Because the X-ray diffraction (XRD) identification of smectite phases present in kaolinite-smectites is difficult, especially when there is a high content of kaolinite (Cradwick & Wilson 1972, Srodon 1980) and because elevated CEC may be attributed to other features in clay-rich sequences, interstratified kaolin-smectites were often not recognised in early clay mineralogy work.

Interstratified kaolin-smectite clays have, since 1980, been found to be more common in weathering profiles (Norrish & Pickering 1983, Yerima et al. 1985, Herbillon et al. 1981, Quantin et al. 1984, Wilson 1987, Delvaux et al. 1990a, Churchman & Lowe 1993) especially those developed on basic volcanics. Herbillon et al. (1981) describe interstratified kaolinite-smectite minerals from basalt weathering profile in Africa, and relate a smectite-rich clay assemblage to areas of poorer drainage and the kaolinite-smectites to areas where drainage is better.

Tazaki (1982) noticed the relation between Fe content and the morphological variety of halloysites. Quantin et al. (1984) recognised Fe rich kaolinite-smectite, from Vanuatu and believed the smectite phase in the interstratified clay was a dioctahedral hisingerite. However, Wilson (1987) concluded that most of the smectites in kaolinite-smectites have the characteristic composition of the beidellite-nontronite series.
A direct correlation between K\(^+\) selectivity and halloysite content of weathered volcanics was recognised from weathered profiles in Cameroon and in the Caribbean (Delvaux et al. 1988, Delvaux et al. 1989a, Delvaux et al. 1989b, Fontaine et al. 1989). This occurred because the mineral was in fact interstratified halloysite-smectite. In addition the interstratified clays account for a higher cation exchange capacity (CEC) of the clay fraction (Delvaux 1989a, Delvaux et al. 1989b, Delvaux et al. 1990a). Delvaux et al. (1989c) experimentally altered Al-nontronite through kaolinite-smectites to kaolinite and Fe-oxides. Using ESR spectroscopy they detected Fe-rich smectite in kaolinite and Fe smectite-bearing interstratified clays. Further work on basalt pyroclastics from Cameroon allowed the identification of the Fe smectite phase as belonging to the beidellite to nontronite series (Delvaux et al. 1990b), as suggested by Wilson (1987) and later confirmed by other workers (Buhmann & Grubb 1991).

With an increase in weathering and the consequent reduction of interstratified smectite in halloysite, variations caused by the nature of the exchangeable cation are reduced, and the particle morphology changes from spheroids to tubes to platelets (Delvaux et al. 1992). There are two observed pathways for the formation of interstratified kaolin-smectite clays. In general soil halloysite-smectites preferentially form in base-rich volcanic ash soils from pyroclasts, whereas soil kaolinite-smectite forms in silica and base depleted environments from smectite clays (Delvaux & Herbillon 1993). Hence, the interstratified mineral is an intermediate phase in the conversion of smectite to kaolinite. Moore (1993) suggested that a continuum exists from a smectite-rich kaolin-smectite end member in moderately weathered material to a kaolin-rich kaolin-smectite end member in intensely weathered material and soils. In basalts with limited weathering the smectite rich end member dominates but because the CEC is already elevated and the interstratified clay is difficult to distinguish using XRD, this end member is often overlooked and the kaolin-rich phases are more commonly recognised.

### 3.3.6 Smectite Clays

The most common smectites in weathered basalts are beidellite, nontronite and saponite, with some montmorillonite. Beidellite and montmorillonite are present in bentonite deposits formed from the alteration of volcanic ash. Also montmorillonite is found in Fuller's earth formed from the weathering of basic volcanic rocks. Nontronite, an iron rich dioctahedral smectite, is a weathering product of basalts and volcanic glass (Eggleton 1977). Saponites form from basic volcanic material, sometimes filling amygdales in basalt. Smectites, especially beidellite and nontronite are widely found (sometimes mixed with illites) in soils derived from the weathering of basic rocks.
Diocahedral

(Pyrophyllite)  
Montmorillonite  
Beidellite  
Nontronite  

Dioctahedral

(Talc)

Saponite  
(Hectorite)  
(Sauconite)

Triocahedral

Table 3.1
Cation location within the common smectite clay minerals and comparable layer silicate phases (talc and pyrophyllite). Beidellite, nontronite and saponite, with some montmorillonite are the most common smectites formed in weathered basalts (after Dixon & Weed 1989).

3.3.7 Vermiculite

Vermiculite is generally derived from the weathering of biotite or chlorite (Evans 1992). Chlorite is not a common phase in basalt but may be present if the basalt has experienced deuteric alteration (Baker & Haggerty 1967). Chlorite may form small veinlets of chlorite in the olivine and pyroxene and fill amygdales in lavas. The chlorite is then readily broken down in the weathering process to vermiculite.

Chemically vermiculite is similar to micas and triocahedral smectites, especially saponite, but vermiculite generally has a larger grain size, a higher cation exchange capacity and greater substitution of Al for Si. In vermiculite the deficiency of positive charge lies mainly in the tetrahedral component. Vermiculites take up at most one layer of glycerol giving a 14 Å peak whereas smectite can take up a double layer giving a 17Å peak. Smectites dehydrate more readily and vermiculites rehydrate more readily. Vermiculites are formed mainly by the weathering of large flakes of biotite or chlorite whereas smectites form in basalts from the dissolution of ferromagnesian silicates, plagioclase feldspars and basaltic glass (Deer et al. 1992).
CHAPTER 4

CAINOZOIC CLIMATE EVOLUTION

4.1 INTRODUCTION

Considerable changes in the geographical configuration of the land and sea around Australia have taken place during the Cainozoic era (65 Ma to present) as a result of global and regional tectonic events. The opening of the Tasmanian Seaway in the latest Cretaceous to mid-Eocene and northward migration of the Indo-Australian plate thereafter (Veevers, 1991), led to significant changes in Australian paleoclimate through time (Figure 4.1). An overall change to a drier cooler climate through the Cainozoic resulted in expansion of the deserts of the Australian landmass. Two lines of evidence for this trend are; the reduction in rainforest pollen assemblages in terrestrial and marine cores with a concurrent increase in abundance of grass and sclerophyll woodland species, and the greater flux of eolian dust from the land to the sea. However, the evolution of climate has not been constant throughout the Cainozoic but has been punctuated by distinct cooler periods.

**Figure 4.1**

Successive positions of Australia relative to Antarctica as Australia moved northward during the Cainozoic (Kennett 1982).

General scenarios of climatic evolution, largely based on analysis of marine cores, have been put forward (Shackleton & Kennett 1975, Kennett 1982, Haq 1984, Kennett & von der Borch 1986, Frakes et al. 1987) providing a framework from which an interpretation
of on-land climatic change through the Cainozoic can be made. Techniques used in marine core analysis include interpretation of changes in the abundance of O and C isotopes, evaluation of sediment character (grain size, provenance), identification of pollen, observation of changes in sediment flux, identification of microfossils and their living environments and interpretation of clay mineralogy. Terrestrial stable isotope, pollen, microfossil and macrofossil studies, as well as shallow marine carbonate reef development studies provide further evidence of Australian paleoclimate in the Cainozoic.

4.2 CAINozoic CLIMATE EVOLUTION

4.2.1 Paleocene (65 to 58 Ma)

Fig 4.2
Reconstruction of the Southern Ocean 65 Ma ago, about the time of the Cretaceous Tertiary boundary (Kennett 1982).

Terrestrial climate for the Australia-Antarctica landmass, from the late Paleocene to early Eocene was equable. Warm marine temperatures conform with reconstructions of climate on the continents, where high-latitude regions were inhabited by temperate to sub-tropical species of vertebrates and plants (Zachos 1994). Sluiter (1991) in his study of palynoflora at Lake Eyre, central New South Wales, describes the vegetation as simple closed forest with conifers and evaluates annual mean temperature to be approximately 18-19°C and annual mean precipitation to be 1,400 mm. Although slightly cooler, similar conditions prevailed along the south East Australia coast and in north east Tasmania in the Paleocene as the rainfall was sufficiently high to sustain rainforest (Kemp, 1978). Yim (1991) suggests that this might represent a period favourable to deep weathering in north east Tasmania.
4.2.2 Eocene (58 to 36 Ma)

**Early Eocene**

Many studies confirm that equable climates persisted for most of the Australian landmass in the Eocene (Wolfe & Hopkins 1967, Wolfe 1971, Frakes & Kemp 1973, Frakes 1979, Brass *et al.* 1982, Kennett & von der Borch 1986, Caulet 1986, Murphy & Kennett 1986). At this time no cool circum-Antarctic ocean current existed. Instead a south flowing subtropical east Australia current was active (Kennett 1977). Because of this ocean current warm temperatures occurred throughout the south west Pacific during the Eocene, as indicated by low δ18O isotope values (Murphy & Kennett 1986) with the warmest conditions existing around 55 Ma (Zachos 1994). However, temperate climates persisted in higher latitudes (Cranwell *et al.* 1960, Taylor *et al.* 1990, Bird *et al.* 1990).

By the early Eocene the centre of the Australian landmass was humid, with peat-forming swamps and coarse clastic sediments in the Birdsville and smaller basins, and pollen studies showed assemblages characterised by floras that indicate high rainfall and considerable warmth (Truswell & Harris 1982). The study of pollen (Kemp 1981) from Nerriga, near Canberra and early Eocene leaf fossils (Christophel 1981) indicate that subtropical rainforest was present.

A change to Myrtaceae dominated vine forest in the Lake Eyre region (Sluiter 1991) implies that temperature and precipitation were slightly higher than in the Late Paleocene. By the Middle Eocene simple closed forest once again predominated, the estimated annual mean temperature was 17-18°C and annual mean precipitation was approximately 1,500 mm. When the Lake Eyre sequence is compared with those from the Gippsland and Otway Basins (Victoria), the southern basins are found to be slightly cooler (Truswell 1987, Sluiter 1991).

In southern New South Wales the climate was cool, wet and thermally seasonal throughout the Eocene (Taylor *et al.* 1990). At this time the Monaro region was at relatively high latitude, ~57.5°S (Idnurm 1985). Oxygen isotope studies of kaolinite from the Monaro and elsewhere in southern Australia show that cool conditions prevailed (Bird *et al.* 1990).

McGowran (1979) describes the late Paleocene to early Eocene as a major period of intense deep weathering in the high southern latitudes.
Middle Eocene

Fig 4.3
Reconstruction of the Southern Ocean and suggested surface water circulation 53 Ma ago (Kennett 1982).

A long term gradual cooling of the Southern Ocean took place over the middle and late Eocene from about 54 Ma to 36 Ma (Zachos 1994). The suggested paleoceanographic changes put forward to explain this mid-Eocene oceanic cooling, based on marine $\delta^{18}O$ isotope patterns and faunal evidence, include the partial opening of the sea-way between Australia and Antarctica around 53 Ma (Figure 4.3) (Weissel and Hayes 1974, Kennett et al. 1975, McGowran 1977, McGowran & Beecroft 1985) and decoupling of the warm-subtropical gyre from the north (Kennett 1977, 1978). The deep ocean basin that formed to the SW of the South Tasman Rise during the Eocene had highly restricted deep water circulation with the South Tasmania Rise blocking the development of the circum-Antarctic current (Andrews et al. 1975, Kennett et al. 1975).

Gill (1972) describes a change in the Australian vegetation at this time from Mesozoic fern/conifer flora to Tertiary conifer/Nothofagus flora. An increase in the pollen of the Nothofagus brassii group and drop in abundance of more tropical forms is noted as well (Partridge 1976a, 1976b). The development of grasslands in central Australia (Truswell & Harris 1982) corresponds with a predicted increase in aridity (McGowran 1979, Stein & Robert 1986).
Late Eocene

River valleys of the Murray Basin, central New South Wales, maintained rainforest cover from the late Eocene through to Mid Miocene (Martin 1991) and rainforest continued to grow through a wide area of central and southern Australia across to the south west and up into the north west of western Australia (Truswell & Harris 1982) implying that, at least initially, Australia’s vegetation was not as strongly affected by the temperature drop that coastal Australia experienced in the mid- to late Eocene.

Davies et al. (1991) note that there was a change in northern Queensland climate from subtropical/tropical to cool temperate in the late Eocene. Sea levels were high throughout the Eocene but dropped suddenly in the late Eocene to early Oligocene resulting in the deposition of subtropical carbonate material in the north, with temperate fluviodeltaic and carbonate sedimentation further south.

In Tasmania a rapid temperature drop in the late Eocene to early Oligocene is reflected in the marine δ18O isotope and faunal information from marine cores (Shackleton & Kennett 1975), and has been correlated with a period of on-land erosion (Yim, 1991).

4.2.3 Oligocene (36 to 24 Ma)

Fig 4.4
Reconstruction of the Southern Ocean and suggested surface water circulation 36 Ma ago (Kennett 1982).
By the late Eocene to early Oligocene high latitude climate had cooled sufficiently for Antarctic glaciation. The oldest high latitude glacial sediments observed in ocean floor cores, were deposited in the late Eocene, around 40 Ma (Zachos 1994).

A distinct change in temperature from moderate to cold, commencing around 38 Ma, has been termed the Terminal Eocene Cooling Event (Wolfe 1978, Corliss et al. 1984, Kennett & von der Borch 1986, Murphy & Kennett 1986, McGowran & Beecroft 1986, McGowran 1987, McGowran 1991). This event is characterised in the marine environment by rapid distinct $\delta^{18}O$ enrichment in both planktonic and benthic foraminifera (Kennett & von der Borch 1986), followed by lower $\delta^{18}O$ values later in the Oligocene (Corliss & Keigwin 1983). This cooling event is related to the complete opening of the Tasmanian sea-way at this time (Figure 4.4) and the formation of the circum-Antarctic current, and development of the circulating deep cold ocean currents (psychrosphere) (Kennett 1982, Frakes et al. 1987).

The cooling climates of the late Eocene persist into the early Oligocene (Kemp 1978), with $\delta^{18}O$ values from marine cores west of Australia imply that temperatures may have remained cool through to early mid-Oligocene (Shackleton & Kennett 1975, Murphy & Kennett 1986, Kennett & von der Borch 1986). Aridity spread widely across the country and where it was wet, floras were less diverse but better adapted for cooler climate than late Eocene species (Kemp 1978, Truswell & Harris 1982, Frakes et al. 1987). On Tasmania's central plateau, cold adapted floras prevailed at this time (MacPhail et al. 1991).

The mid- to late Oligocene was a period of climate change as the Indo-Australian plate migrated northward to lower latitudes and the circum-Antarctic current became established (Kennett 1977, Kvasov & Verbitsky 1981). The circum-Antarctic current reduced the northerly flow of cold water into the Tasman Basin. A warm east Australian current could once again flow down from the north, and on-land a moderate warming of climate was observed through the late Oligocene.

A broad monitor of climate changes on the Australian landmass is the changes in the composition of eolian dust blown from land to sea. During the Oligocene the terrestrial clay fraction of marine cores west of Australia are dominated by pedogenic smectite (Stein & Robert 1986). Smectite is principally associated with weathering of volcanics and by pedogenic processes in humid to semi-arid climatic regimes. The abundance of this mineral suggests relatively warm climatic conditions on-land in central and northern parts, with alternating periods of humidity and aridity. Toward the end of the Oligocene a gradual increase in the abundance of kaolin group clays is interpreted to result from more
intense weathering implying higher rainfall and possibly warmer climates in northern Australia (Stein & Robert 1986).

This pattern is also reflected in the shallow marine sequences of northern Queensland which show that, in the mid- to late Oligocene, the climate was initially relatively cool resulting in the formation of red algal bioherms instead of reefs. However, as Australia moved north the climate became more tropical and carbonate reefs started to form on top of the more temperate shallow marine bioherms and sediments (Davies et al. 1991).

In Tasmania, the Late Oligocene was a period of relative climatic stability (Shackleton & Kennett 1975, Yim 1991) and of floristic complexity (Hill & MacPhail 1983).

4.2.4 Miocene (24 to 6 Ma)

Early Miocene

Fig 4.5

Reconstruction of the Southern Ocean and suggested bottom water circulation 21 Ma ago (Kennett 1982).

The early Miocene (Figure 4.5) is characterised by warm climates (Vail & Hardenbol 1979, Kennett & Srinivasan 1983, Loutit et al. 1983, Woodruff & Savin 1985, Heusser 1986, Boersma 1986) with a climax of oceanic warmth, as defined by low δ18O values, around 19.5 Ma to 16.5 Ma (Kennett & von der Borch 1985, Wolfe & Poore 1982). The terrestrial Australian climate was again warm and moist over substantial parts of the continent, including the interior (Truswell & Harris 1982).
Dudgeon (1982) describes an early Miocene (22-24 Ma) palynoflora and macrofossil (ferns) assemblage from the Main Range, south east Queensland, which is dominated by rainforest species that prefer a warm humid climate. A similar study at Chalk Mountain, Warrumbungles, northern New South Wales, details the presence of similar rainforest species, around 16 Ma, implying a warm moist climate in this area also (Holmes et al. 1983).

Late Oligocene - early Miocene marine incursions in the Gippsland Basin (Holgate & Sluiter 1991) broadly compare with those suggested by Haq et al. (1987), and confirm that this is a time of high sea stand. The maximum onlap of marine sediments in the Gippsland Basin occurs in the early mid-Miocene (Webb et al. 1991).

**Middle Miocene**

McGowan (1979) states that deep weathering is well established by early-middle Miocene whereas the mid- to late Miocene appears to be a cooler period during which silcrete formation is more dominant.

There is a cooling event around the mid-Miocene (16.5 to 13.5 Ma) which corresponds to a time when it is likely that much of the east Antarctic ice sheet accumulated (Kennett & von der Borch 1986). In Tasmanian waters there is an early mid-Miocene temperature drop (Shackleton & Kennett 1975).

Slightly later (~14 to 13 Ma) on-land, the transition from a dominantly humid climate to more semi-arid and arid climate, caused reduced vegetation cover, and an increase in the amount of eolian material transported into the sea west of Australia (Stein & Robert, 1986). In central New South Wales *Nothofagus brassii* was lost from the river valley forests of the Murray Basin (Martin, 1991) reflecting a diminishing abundance of rainforest species.

From the late Middle Miocene to the earliest late Miocene there was a prolonged cool period (Shackleton & Kennett 1975, Kennett & von der Borch 1986). An increase in the abundance of illite around 12.5 Ma corresponds with an expansion of the deserts in north and central Australia, while southern Australia was still dominated by alternating humid and arid conditions (Stein & Robert 1986). At this time an increase desertification in north and north west Australia is also inferred from pollen (Kemp 1978) and from investigations of ancient drainage systems (van de Graff et al. 1977).
Late Miocene

In the Late Miocene (9 to 6.5 Ma) the Australian climate was warmer than the middle Miocene (Kennett & von der Borch 1986, Haq et al. 1980). Desertification of central Australia continued (Kemp 1978, Stein & Robert 1986) with an associated increase in grassland development and corresponding increase in opal phytolith abundance in marine cores (Locker & Martini 1986).


This period of increased cooling and aridity of Australia (Bowler 1982) corresponds with increased accumulation rates of wind blown terrigenous sediments in offshore cores (Stein & Robert 1986).

In northern Queensland, late Miocene sea level fall restricted reef growth and in places the reef was exposed. The sediments were dominated by terrigenous material at this time, despite being in tropical latitudes (Davies et al. 1991). In the river valleys of the Murray Basin, central New South Wales, wet sclerophyll forest superseded rainforest implying a drier climate in the late Miocene (Martin 1991). In the Gippsland Basin, Bolger (1991) describes a change from an equable humid climate during the late Miocene to a cooler more seasonal climate in late Miocene-Pliocene, based on change in energy of deposition, oxidation, and flux of sediment.

4.2.5 Pliocene (6 to 2 Ma)

Early Pliocene (5 to 4 Ma) climates were slightly warmer than the late Miocene (Kennett 1967, Ingle 1967, Loutit & Kennett 1979, McKenzie et al. 1984). Evidence for this warming includes high calcareous nannofossil diversity (Lohman 1986), the occurrence of marine transgressions (Kennett 1967, Kennett & Watkins 1974, Vail & Hardenbol 1979) and relatively low $\delta^{18}O$ values in benthic foraminifera (McKenzie et al. 1984, Kennett & von der Borch 1986).
The river valleys of the Murray Basin support *Nothofagus* rainforest in the early Pliocene, indicating a definite increase in precipitation compared with the late Miocene (Martin 1991).

A cooling event in the mid-Pliocene (3.4 Ma) based on relatively high $\delta^{18}O$ values in foraminifera (Kennett & von der Borch, 1986) corresponds with an increase in sediment accumulation rates in offshore cores, and hence a period of continued aridity on-land. Enhanced atmospheric circulation at this time may account for the transport of larger eolian particles into the sea (Stein & Robert 1986).

At Lake George, southern New South Wales, mid- to late Pliocene rainforest communities have been described (McEwan Mason, 1991), however these forests may have been established prior to the mid-Pliocene cooling.

A cool period in the late Pliocene (2.6 to 2.4 Ma) coincides with large ice sheets forming in the northern hemisphere and further ice accumulation over Antarctica (Kennett & von der Borch, 1986). The tectonic stability of Australia, and the fact that extensive ice sheets, such as those which formed in North America in the late Pliocene and through into the Pleistocene, did not occur in Australia, have facilitated the preservation of evidence of terrestrial paleoclimatic events not preserved in the northern hemisphere.

There is a change in the late Pliocene to wet sclerophyll forest in the Murray Basin river valleys, which means the climate was considerably drier than in the early Pliocene (Martin 1991). A dramatic vegetation change is also observed at Lake George where late Pliocene-Pleistocene open canopied assemblages are identified (McEwan Mason 1991).

4.2.6 Quaternary (2 Ma to present)

The Quaternary was dominated by fluctuating glacial/interglacial events (Heussier 1986) which are very complex and have been studied in considerable detail by many authors (see Chappell & Grindrod 1981, Bowler 1982, Imbrie et al. 1984, Williams et al. 1991). The use of carbon dating of organic material has facilitated better understanding of geologic and anthropogenic activity in the latter 30,000 years.

In periods corresponding with glacial maxima throughout the Quaternary terrestrial climates are considerably cooler and drier than present, but contemporary climate is a reasonable analogue for most interglacial periods.
4.3 CONTEMPORARY CLIMATE

4.3.1 Radiation

Annual mean radiation shows a progressive change with latitude, ranging from approximately 20 MJ/m²/yr in north Queensland to 14 MJ/m²/yr in Tasmania. This trend might be expected as the angle at which incident radiation from the sun strikes the earth's surface in low latitudes is much less oblique than in high latitudes. Small variations in radiation for some localities relate to aspect, for example the south facing outcrop at Archers Creek has lower recorded radiation than at the central Queensland localities. The highest monthly radiation at all localities is relatively uniform but higher latitudes have a much greater reduction in incident radiation in the winter months because of the cloud cover.

![Radiation vs Latitude for Sample Sites](image)

**Figure 4.6**
Change in radiation (MJ/m²/yr) with latitude (°S) for the sample sites in this study

4.3.2 Temperature

Inland sites generally have warmer temperatures for the warmest month and cooler temperatures for the coldest month than sites closer to the coast. The capacity for a large body of water to hold its warmth results in a buffering of temperatures for localities closer to the sea. Hence, the severity of seasonal variations is reduced for localities nearer the coast. This is reflected in the average annual temperature for inland sites (approximately 17°C) which is higher than those for the coastal sites (approximately 15°C). There is a general decrease in average annual temperature with latitude and this can be related to the general decrease in radiation with latitude previously observed.
When the mean temperature for the wettest quarter and the mean temperature for the driest quarter are compared for each site, an evaluation can be made about whether the contemporary regime has winter dominant precipitation or summer dominant precipitation. In order to do this, the assumption that summer usually has warmer temperatures than winter, is made. Most of the localities have a summer dominant rainfall, with only the Tasmanian sites showing strongly winter dominant rainfall.

Figure 4.7
Change in temperature (°C) with latitude (°S) for sites in this study greater than 150 km from the coast.

Figure 4.8
Change in temperature (°C) with latitude (°S) for sites in this study less than 150 km from the coast.
This implies that north of approximately 40°S sample sites within the east Australian basalt provinces are likely to experience warm moist spring-summer months which may be a period of more intense weathering, and cooler drier winter-autumn months, when the rate of chemical weathering slows. Further south most of the rain falls in the winter.

**Figure 4.9**
Change in mean temperatures (°C) for the wettest and driest quarters with latitude (°S) gives an indication of whether the region has summer or winter dominant rainfall.

### 4.3.3 Precipitation

**Figure 4.10**
Change in annual precipitation (mm) with distance from the coast (km) for the samples sites studied.
Precipitation does not show a clear relationship with latitude as it is affected, to a certain extent, by elevation and more strongly by proximity to the coast. Localities closer to the coast generally have greater rainfall than inland sample sites.

4.3.4 Seasonality

The seasonality of radiation, temperature and precipitation, reflects the degree to which each of these parameters vary (coefficient of variation) in a year. The seasonality of precipitation shows a strong negative correlation with increase in latitude. Hence, in low latitude tropical regions the seasonality of precipitation is large because almost all of the rainfall occurs over a short period of time, in the form of tropical storms, and for the rest of the year the rainfall is low by comparison. At progressively higher latitudes the precipitation becomes more evenly spread throughout the year.

Because air temperature is, in part, dependent on the amount of radiation that reaches the earth's surface, both temperature and radiation have a similar trend in seasonality with latitude. This positive trend is opposite to that exhibited by precipitation, and the seasonality is not as pronounced. At lower latitudes there is less year-round variation in radiation and temperature than at higher latitudes.

![Seasonality of Radiation, Temperature and Precipitation vs Latitude for Sample Sites](image)

Figure 4.11

Change in seasonality of radiation, temperature and precipitation with latitude (°S) for the sample sites studied.
4.4 PALEOCLIMATE, CONTEMPORARY CLIMATE AND CAINOZOIC BASALT WEATHERING

Throughout the Cainozoic, Australian terrestrial climates have become cooler and the landmass increasingly arid. This transition has not been progressive and rather has been punctuated by cooler and warmer episodes. Warm moist conditions enhance the processes of terrestrial weathering and regolith development, although these processes may take place in cooler environments over longer periods of time. For this reason, extended periods of warm humid climate identified in the:

(i) mid- to late Paleocene,
(ii) the mid-late Eocene and
(iii) late Oligocene to early Miocene

might be expected to be periods when accelerated deep weathering occurred on the Australian landmass (Frakes et al. 1987). In addition, the Quaternary, with equable climates in the interglacials, may be another period when accelerated deep weathering might take place.
5.1 LOCATION

Three localities were sampled in the island state of Tasmania (Figure 5.1) (Appendix 1). On the remnant basalt plains in the north west of Tasmania, near the settlement of Guildford, a profile was sampled in a road cutting adjacent to the Hellyer River (41.26°S 145.41°E, 617 m asl). Further east on the central Tasmanian highland plateau, the Monpeelyata canal drains Little Pine Lagoon. In the south wall of the canal a basalt sequence 6 m thick is exposed (42.00°S 146.37°E, 1007 m asl). Near the town of Branxholme in north west Tasmania, a deeply weathered basalt showing spectacular secondary iron staining is exposed in a road cutting near the crest of a hill (41.10°S 147.44°E, 176 m asl).

![Map of sample localities in north west, north east and central Tasmania.](image-url)
5.2 CONTEMPORARY CLIMATE

The annual mean radiation is least at Hellyer River Bridge in north west Tasmania, slightly higher at the Monpeelyata canal site and highest in Branxholme in the north east (Table 5.1). Because the weather is influenced by the prevailing wind which blows from the west, cloud cover is greatest in the western part of the island, and this cloud impedes passage of radiation to the land surface.

<table>
<thead>
<tr>
<th></th>
<th>TAS17 NORTH WEST TASMANIA</th>
<th>TAS27 CENTRAL TASMANIA</th>
<th>TAS9 NORTH EAST TASMANIA</th>
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<tr>
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<td>159.98</td>
<td>188.12</td>
</tr>
</tbody>
</table>

Table 5.1

Contemporary climate information for the Tasmanian sample localities (BIOCLIM).

The annual mean temperatures are greater in the north east than in the north west, and considerably lower again on the central plateau. They do not follow the radiation trend because of the influence of altitude on temperatures in central Tasmania. Hence, because Monpeelyata canal is at higher altitude than the other two localities, temperatures are cooler. North west Tasmania is next coolest because, the westerly and south westerly winds carry cool moist air from the west. By the time the winds reach north east Tasmania they may be warmer. In addition, the Branxholme locality receives a greater annual mean radiation, so temperatures are higher in the north east.
Chapter 5: Basalt Weathering Profiles from Tasmania  75

The cool moist air carried by the westerly and south westerly winds drops rain on the western part of Tasmania, and consequently the Hellyer River Bridge locality receives almost twice the annual rainfall as north east Tasmanian localities. The rainfall on the central plateau is less than half that recorded for the north west Tasmania locality, because the plateau is in an area of rain shadow. The rainfall in the north east of the island is relatively high, because of the proximity to the sea. From the mean temperatures of the wettest and driest quarters all three localities are seen to have winter dominant rainfall (Chapter 4).

Three quite different contemporary climate regimes are identified at these localities. In the north west climates are cool and relatively wet, in central Tasmania a sub-alpine cool/cold dry climate prevails and in the north east a warm moist climate dominates.

5.3 PALEOCLIMATE AND VEGETATION

Early Eocene to Oligocene *Nothofagus* temperate rainforest species are described from Cethana in north west Tasmania (Hill 1984) and temperate to subtropical species of late Oligocene age from Little Rapid River in north west Tasmania (Hill 1987b). However, there are some *Nothofagus* species identified at the latter locality for which extant species show a broad latitudinal distribution, implying that present climate may not be an adequate analogue for the climate of this period (Hill 1987b). Despite this observation, it appears that cool temperate rainforest, somewhat like that present in Tasmania today, was present in the Eocene and Oligocene in north west Tasmania. It follows that rainfall was relatively high but temperatures quite cool.

Macfossils and pollen described from mudstone underlying basalt flows in Monpeelyata canal indicate that the Central Tasmanian plateau in the late Oligocene to early Miocene supported diverse riparian rainforest with proto-alpine/subalpine flora (MacPhail et al. 1991). A humid climate may be indicated by the presence of some *Nothofagus* species. Because taxa which can be associated with temperate to tropical conditions are absent, and because of the small leaf size of rainforest and other species (MacPhail et al. 1991, Hill & Gibson 1986), the climate was likely to be cool to cold.

Hill and MacPhail (1983) describe pollen and macrofossils of Oligocene age from fine sediment lenses in a braided fluvial fan at Pioneer in the Ringarooma Valley, north east Tasmania. The vegetation represented was closed temperate rainforest with an assemblage floristically more complex than modern Tasmanian rain forest from the same area. The Oligocene climate at this locality is interpreted as cool with high rainfall (Hill & MacPhail 1983).
Chapter 5: Basalt Weathering Profiles from Tasmania

5.4 GEOLOGY - NORTH WEST TASMANIA

In north west Tasmania basalt forms extensive plains which cover approximately 250 km$^2$ (Johnson et al. 1989). The lavas infilled the paleotopography ultimately forming an elevated plain approximately 100 m above sea level near Wynyard on the Tasmanian north coast, and reach 750 m altitude, 70 km inland (Burns 1964, Barton et al. 1966, Sutherland 1969, Gee 1971, Gee 1977, Brown & Forsyth 1984, Johnson et al. 1989, Seymour 1989). Drilling has shown that in places the basalt pile is over 360 m thick and may consist of 50 or more flows (Seymour 1989, Guilline 1967, Gee 1971), often with intercalated or underlying layers of Eocene to early Oligocene sediment (Brown & Forsyth 1984). These thick stacks of flows indicate significant pre-basalt relief (Burns 1964).

Subsequently the plains forming basalts have been dissected, leaving a remnant plateau with large thicknesses of basalt eroded through in river valleys, and outliers of basalt capping hills (Prider 1948, Brown 1986, Seymour 1989). These outliers indicate that the basalt plains were much more extensive in the past. Other geomorphological features recognised include twinned, displaced and diverted drainages (Sutherland 1989).

Many valleys along the north coast became blocked with basalt before the marine high-stands of the Miocene (Sutherland 1973a). In the far north-western part of the island lavas are less extensive but are notable for the high proportion of aquagene basalts erupted into mid-Tertiary seas (Sutherland & Corbett 1974, Quilty 1972, Sutherland 1969, 1973a, 1980, Sutherland & Wellman 1986). In the southern part of the basalt-covered area the flows form several distinct topographic steps and the margins of multiple sheets form step-like features on the valley sides (Collins et al. 1981). A pink- or red-brown alteration at the top of some flows is due to weathering and probably indicates subaerial extrusion of the basalt, follow by an appreciable time interval before burial beneath the succeeding flows (Seymour 1989). Intercalated soil between lava flows can be distinguished from a baked flow top on the lower flow on the basis of: the presence of fossilised vegetation or rootlet traces, preservation of soil horizons, and/or the intercalation of aeolian sediment. Evidence of baking may be difficult to find but may include the presence of charred vegetation.

The spectrum of basalt compositions represented include basanite, alkali basalt, nepheline hawaiite, hawaiite, olivine and quartz tholeiite (Sutherland & Wellman 1986, Sutherland 1989, Johnson et al. 1989).

Most of the documented dates on the north west Tasmanian basalts are from localities near the north coast. The basalts in the Wynyard region include late Oligocene or older alkaline rocks (>26.3 Ma) and early Miocene olivine tholeiite and middle Miocene nephelinite basanites (>13.3 Ma) (Sutherland & Wellman 1986). Between Wynyard and
Somerset, limburgitic basalts are overlain by latest Oligocene to earliest Miocene marine sediments (Gee 1971, 1977, Sutherland 1973b).

The basalt pile in the main area centred on Guildford, near the Hellyer River Bridge sample site of this study, is a "highly complex, interdigitating and laterally variable sequence of overlapping flows, sediments and pyroclastics" (Seymour 1989). In the Guildford area a borehole has been drilled, the uppermost basalt is olivine tholeiite and palynology and paleomagnetism provide a date for the basalts of 35.3 Ma to 36.5 Ma (Seymour 1989).

5.5 HELLYER RIVER BRIDGE, NORTH WEST TASMANIA VOLCANIC PROVINCE

5.5.1 Nature of the Exposure

At this locality two quite different flows are represented in a road cutting through the plains basalts, adjacent to the Hellyer River (Figure 5.2, Plate 5.1, Appendix 1). This profile lies within the subdued topography of the plains basalts, and the water table lies below the level of the lower flow. The lowermost vesicular basalt flow is more pervasively weathered than the overlying, more massive basalt. The contact between the basalts is irregular and there has been some injection of the overlying lava into depressions in the lower basalt. There is a very dense red brown oxidised layer at the contact, about 2-3 cm thick, which may be an incipient soil preserved between the two flows, and may have been baked.

Beneath a brown skeletal soil with remnant corestone fragments, the upper basalt is massive and is cut by at least two large vertical joint sets. The joints are approximately perpendicular to each other, forming rectangular, prismatic blocks (up to 1.2 m in width and depth, and up to 2.5 m in height). Underlying the moderately weathered basalt prisms (TAS17/1) is a zone of smaller (10-15 cm diameter), more intensely weathered corestones (TAS17/2) surrounded by rubbly weathered basalt material. The upper basalt has flowed along a depression or channel in the underlying basalt.

Massive, pervasively weathered vesicular basalt (TAS17/3) forms the top of the lower flow. Pore spaces in the weathered rock, mostly vesicles and small fractures, are partially filled by chabazite. A spheroidal weathering texture is vaguely preserved in the moderately weathered vesicular basalt (TAS17/5) near the base of the lower flow.
Figure 5.2
Sample points in the Hellyer River Bridge profile, north west Tasmania.

Plate 5.1
Hellyer River Bridge profile.

5.5.2 Geochemistry

For the basalt samples (TAS17/1, TAS17/2, TAS17/3, TAS17/5) the isocons are best fit lines through representative points Y and Al which are believed to be the least mobile
element pair. At this locality most elements appear to have been mobile to some degree and the interpretation derived from the isocon diagrams gives a broad indication of the likely element pathways, and the overall mass balance. The fresh basalt used for isocon construction is nepheline hawaiite from north west Tasmania (sample number DR1180, Appendix 2).

Upper

TAS17/1: \( \frac{C_i^W}{C_i^O} = 1.24 \) \( \Delta M = -19\% \)
TAS17/2: \( \frac{C_i^W}{C_i^O} = 1.30 \) \( \Delta M = -23\% \) INCREASE IN

Lower

TAS17/3: \( \frac{C_i^W}{C_i^O} = 1.75 \) \( \Delta M = -43\% \) WEATHERING
TAS17/5: \( \frac{C_i^W}{C_i^O} = 1.59 \) \( \Delta M = -37\% \) ↑

The slopes \( \left( \frac{C_i^W}{C_i^O} \right) \) of the isocon lines reflect the progressive increase in mass loss \( (\Delta M) \) and hence increase in intensity of weathering of the basalt samples outward from joint bounded blocks in the upper flow and up profile in the lower flow. A decrease in the intensity of weathering along joint planes from the base of the upper flow implies that waters have been ponded in this region, which has resulted in more intense weathering in this zone (TAS17/2).

Figure 5.3

Isocon diagrams and corresponding histograms for TAS17/3 and TAS17/5. Histograms show relative mass change (%) for analysed elements.
This is reflected in the greater calculated mass loss ($\Delta M$) value for this interval. Mass loss ($\Delta M$) values for the lower flow show that this basalt is more intensely weathered than the overlying flow and the permeable vesicular flow top is more weathered than the lower, more massive, part of the flow. Hence, these values reflect the field observations.

**Lower Basalt**

The trace elements Ba and Zn show slight enrichment with weathering. La, Fe (total), Th, Ni, Cu, Mn and Ti are moderately depleted (-30%-60%) early in weathering while Pb, Rb and V are progressively depleted as weathering proceeds. Cr, Si, S and Zr show major depletion (-60%-90%), and Ce, Nb, Mg, K, Na, P and Ca show high to extreme depletion ($<<-60\%$) in all samples (Figure 5.3).

![Figure 5.4](image)

*Figure 5.4*

Isocon diagrams and corresponding histograms for TAS17/1 and TAS17/2. Histograms show relative mass change (%) for analysed elements.
Upper Basalt

The elements Pb, La are slightly enriched in the least weathered samples and maintain a relatively constant elevated concentration throughout the more weathered samples. **Zn** is progressively enriched while all other elements show significant depletion. S, V, Si and Ti are moderately depleted in the weathered samples while Fe (total), Ni, Ca and Th are progressively removed. Cr, Cu, Mg, Mn, Zr and Na show major depletion and Ce, Nb, K, P, Rb and Sr extreme depletion throughout the weathered basalt (Figure 5.4).

5.5.3 Clay Mineralogy

Lower Basalt

The lowermost vesicular basalt sampled, TAS17/5, has an X-ray diffraction (XRD) trace that reflects the relatively intense weathering that has taken place at this level (Figure 5.5). The principal primary mineral preserved in this trace is etched plagioclase feldspar. Magnetite and ilmenite may be present but their traces are largely obscured by those of other minerals. The clay separate has relatively high concentrations of Fe and Mg (Appendix 4) and the XRD trace indicates that there is dioctahedral smectite and possibly some trioctahedral smectite present.

The smectite clay assemblage is probably dominated by the dioctahedral clay nontronite with some dioctahedral Al-smectite, and small amounts of the trioctahedral saponite preserved. The cation exchange capacity (CEC) for the clay separate is 36 meq/100 g and the Si:Al ratio is 1.38. The CEC is in the normal range for smectite but the Si:Al ratio is low implying that there has been considerable Si removal. Hematite is observed in this trace and is probably responsible for the red colouration of the lower vesicular basalt. Vesicle fill materials were analysed and found to be chabazite in some vesicles, and a resinous clay mixture, probably saponite, nontronite and Al-smectite in others.

The sample taken from higher in this flow, TAS17/3, has an XRD trace almost identical to that of TAS17/5, except that there has been a greater development of smectite clay, corresponding to the greater degree of weathering at this level. There are peaks for dioctahedral smectite and a minor amount of trioctahedral smectite, implying that the clay assemblage is the same as that lower in the profile. The CEC is 42 meq/100 g and the Si:Al ratio 1.47. The red colouration of this sample can be attributed to hematite. Two vesicle fill materials were analysed and once again were chabazite (TAS17/4) and smectite. The smectite is trioctahedral and is probably saponite.
The red clay layer separating the two flows was not sampled, but based on the mineralogy of the lower basalt, from which the clay layer is derived, it is likely to be composed of smectite clays and the red colouration may be attributed to hematite.

**Figure 5.5**
Stacked X-ray diffraction (XRD) traces for samples TAS17/1, TAS17/2, TAS17/3 and TAS17/5.

*Upper Basalt*

Peaks for many primary minerals occur in the XRD trace for TAS17/2 from the base of the upper flow (Figure 5.5). Plagioclase feldspar and pyroxene (augite) are represented, with no peaks for olivine observed. Primary Fe-Ti oxides may be present but their traces are not clearly defined. Smectite is the dominant clay, and from the clay separate and XRD information, dioctahedral nontronite and Al-smectite are most abundant with a lesser amount of saponite. Although the CEC is relatively low at 17 meq/100 g, the Si:Al ratio of 1.88 is more typical of the values for smectite clays. Minor hematite and goethite may be present. The vesicle fill analysed was trioctahedral smectite and because the iron content in the clay separate is high, this clay may be Fe-saponite.
The freshest basalt in the profile (TAS17/1), outcrops in the main body of the upper flow. This material is only moderately weathered and so has many primary minerals represented in its trace. These include plagioclase feldspar, pyroxene (augite), olivine, magnetite and ilmenite. The clay assemblage is dominated by a mixture of trioctahedral and dioctahedral smectites, probably Fe-saponite, saponite, nontronite and Al-smectite. The Al smectite may be an iron bearing beidellite. This smectite rich assemblage accounts for the CEC of 47 meq/100 g but the high Si:Al ratio implies finely ground silicates in the separate.

The overlying skeletal soil is dark red-brown and has abundant float from the upper basalt within it. The soil is smectitic with a predominantly dioctahedral clay assemblage of nontronite and Al-smectite.

**Summary**

The principal neoformed clays present are smectites including Fe-saponite, saponite, nontronite and probably beidellite formed during the dissolution of ferromagnesian silicate minerals, especially olivine, and montmorillonite formed during the breakdown of plagioclase feldspar. Trioctahedral smectites are formed early in the breakdown of olivine, and are preserved in the centres of the large olivine phenocryst pseudomorphs. With increased weathering these clays progressively breakdown to dioctahedral forms. At the base of the upper flow where weathering fluids may have ponded, trioctahedral and dioctahedral smectites preferentially form because abundant cations are available for incorporation into clays. The vesicle fill materials throughout the profile are rich in trioctahedral smectites, implying that percolating fluids were rich in cations.

The zeolite mineral, chabazite was recognised as a vesicle fill in the lower basalt, and may be a phase precipitated in equilibrium with the fluids percolating through the weathering basalt. The precipitation of zeolites in equilibrium with weathering fluids is discussed in Chapter 11.

The lower basalt is significantly more hematite rich, but the vesicular basalt may have been partially oxidised at the time of eruption, as well as during weathering. Within the upper basalt goethite is the primary neoformed Fe-bearing secondary phase, but adjacent to fractures, vesicles and in weathering rinds, hematite is more prevalent.

**5.5.4 Petrography**

The basalt at the base of the upper flow (TAS17/2) has abundant fine grained plagioclase feldspar comprising the bulk of the groundmass with small grains of pyroxene in inter-
Plate 5.2
TAS17/2 (crossed polars)
Goethite and clays replace ferromagnesian silicates and basaltic glass

Plate 5.3
TAS17/1 (crossed polars)
Large olivine phenocrysts are intensely weathered to hematite, goethite and stained smectite clays
lath spaces (Plate 5.2). Groundmass plagioclase is largely weathered to poorly oriented clays, but the primary basaltic texture is well preserved. Very fine grained angular opaque oxides infill spaces between plagioclase laths. Pockets of basaltic glass have completely altered to secondary clays which are goethite stained.

Occasional clots of slightly larger plagioclase microphenocrysts occur in the groundmass. Rare large plagioclase feldspar phenocrysts are present but show rounded resorbed shapes and the outer zones are intensely etched. Olivine phenocrysts are completely weathered to secondary clays, and in places trioctahedral saponite is present in the cores of these pseudomorphs. Hematite is only concentrated in the basalt adjacent to microfractures and near exposed faces, elsewhere goethite predominates. Vesicles are completely filled with clays which are very similar in appearance to those replacing olivine.

The more massive upper part of the overlying basalt (TAS17/1) has a very similar groundmass although the plagioclase feldspars are not as intensively weathered (Plate 5.3). Fine grained groundmass pyroxene grains are preserved, as are angular extremely fine grained opaque oxides, probably magnetite and ilmenite. All basaltic glass and groundmass olivines have weathered to secondary goethite, hematite and stained clays, imparting a dark brown-orange colouration to the rind areas of the hand specimen. Goethite is more pervasive in the groundmass than hematite, but hematite is more prevalent near fractures and close to exposed faces, implying that some dehydration of goethite has taken place due to drying of the profile.

Most of the large euhedral olivine phenocrysts are intensely weathered and have been replaced by hematite and goethite stained smectite clays. Olivine microphenocrysts are not as intensely weathered, and show well preserved cores of unweathered olivine within rims of secondary products. These fresher olivine grains are not as intimately associated with micro-fractures, and the weathering rind, as the more intensely weathered ones. In addition they are relatively unfractured, so weathering fluids cannot penetrate the mineral as easily as larger more fractured grains. Scattered plagioclase feldspar microphenocrysts are not chemically etched.

5.5.5 Profile Summary

The lower basalt is more intensely weathered near the top and notably more weathered than the overlying basalt. Because the intensity of weathering increases upward through the flow, the basalt may have been exposed at the land surface, allowing weathering fluids to percolate downward. The contact between the two flows is irregular and reflects the surface on the lower flow prior to extrusion of the upper flow. When the upper basalt
flowed over the older basalt, it preserved the clay rich material formed at the top of the lower flow, and may have baked it. Later this clay-rich zone formed a low permeability layer. Subsequent weathering of the lower basalt has probably occurred as a result of lateral movement of fluids through the flow.

The enrichment of Pb, La and Ba in moderately weathered basalt may be attributed to the formation of secondary carbonate or phosphate phases. The mass loss (ΔM) values for the samples for the upper basalt reflect the moderate weathering of the upper basalt and confirm the field observation that the small corestones near the base of the flow are more weathered than the large jointed blocks forming the body of the flow. Hence, it appears the upper basalt has weathered near the base, at the same time as weathering from the top down.

This phenomenon has been observed at a number of other localities in the eastern Australian basalt provinces, for example at Native Dog Creek in the Monaro Province, southern New South Wales. It seems to occur where the joint sets cutting the basalt flow are quite widely spaced (i.e. greater than approximately 40 cm), where the joints are initially quite open, and most importantly, where the basalt overlies a relatively impermeable layer. Weathering fluids percolate preferentially down the open joints but passage is limited at the impermeable layer at the base of the flow. The fluids are then ponded and weathering of the lowermost parts of the flow can take place at the same time as weathering due to percolation of fluids near the land surface.

5.6 GEOLOGY - CENTRAL TASMANIA VOLCANIC PROVINCE

The Central Tasmania Volcanic Province sits atop Tasmania's resistant dolerite central plateau, with some flows descending off the plateau, down the ancestral Derwent River channel. The plateau has an elevation of approximately 1,000 m but higher points are up to 1,400 m above sea level (Banks 1973, Sutherland & Hale 1970, Johnson et al. 1989). Large outpourings of basalt lava form low relief plains around Great Lake, and a number of other lakes on the plateau. This implies that many of the lakes were originally formed as a result of basalt damming of watercourses, and in some localities there is evidence of the eruption of basalt into water (Spry 1962, Sutherland & Hale 1970, Sutherland 1973b, 1980, Sutherland & Wellman 1986). The flows range in thickness from a few metres on the basalt plains to over 100 m in the valley fill sequences (Forsyth & Guilline 1979). Inverted topography is pronounced where basalts overlie softer sedimentary Triassic and Tertiary beds, more prevalent in the surrounding Midlands and Derwent Valley regions (Sutherland 1989). Farther east Tertiary basalts have been extruded into fault controlled valleys (Forsyth & Guilline 1979).
There is a variety of basalt types represented in this province but the principal compositions are olivine tholeiitic basalts and transitional basalts, with some thick flows of quartz tholeiitic basalt. Alkali basalt, basanite and nephelinite underlie and cap some sequences (Sutherland & Hale 1970, Forsyth & Guilline 1979, Sutherland 1980, Sutherland & Wellman 1986, Johnson et al. 1989).

Ages on flows around Great Lake lie within the range 24.2 Ma to 22.4 ± 0.6 Ma (Sutherland et al. 1973b, Sutherland & Wellman 1986). Other undated basalts are assumed to be approximately the same age as they are dissected to a similar extent. Hence, the diversion of the Derwent River to a southerly course, because of the infilling of the upper Derwent by lavas flowing down its tributaries from the north, must have taken place at some time during the upper Oligocene to lower Miocene (Johnson et al. 1989). Rare plugs of olivine (monticellite) melilitite crop out at Shannon Tier (35.4 ± 0.4 Ma) (Edwards 1950, Johnson et al. 1989) and melilite nephelinite at Laughing Jack Marsh (30.1 Ma) (Sutherland 1973b, Brey & Green 1975, Frey et al. 1978, Johnson et al. 1989), and are older than the dated plains and valley fill basalts.

5.7 MONPEELYATA CANAL, CENTRAL TASMANIA VOLCANIC PROVINCE

5.7.1 Nature of the Exposure

Two basalt flows crop out in this profile in the south wall of the Monpeelyata canal (Figure 5.1, Figure 5.6, Plate 5.4, Appendix 1). In this area the basalt forms an area of subdued topography south and east of Little Pine Lagoon, and the canal is excavated through them to depth of about 6 m. The incipiently to slightly weathered, sparsely vesicular basalt at the base of the profile (TAS27/5), forms a layer of large subangular blocks up to 1.2 m in width, depth and height. There are some relatively sharp joint planes preserved but weathering has commenced wherever fluids have been able to percolate, forming rubbly onionskins surrounding smaller blocks and weathered material along the joint planes bounding larger blocks. Further up-profile the large basalt blocks become more weathered and are overlain by a highly vesicular basalt (TAS27/4), possibly a flow top layer.

The upper basalt is slightly vesicular, generally has smaller block development than the lowermost basalt, and stacks of corestones roughly preserve the original columnar jointing of this flow. Sample TAS27/2 is a small corestone formed adjacent to a block, about 25 cm across, from which TAS27/3 was sampled. The rubbly weathered basalt material, TAS27/1, immediately adjacent to the blocks and corestones forms an onionskin
texture about them. The sequence culminates in a poorly developed, gravelly, olive coloured skeletal soil.

Figure 5.6
Sample points in the Monpeelyata profile, central Tasmania.

Plate 5.4
Monpeelyata profile
5.7.2 Geochemistry

For the basalt samples (TAS27/1, TAS27/2, TAS27/3, TAS27/4, TAS17/5) the isocons are best fit lines through the representative points (Y), Zr, Al and Ti which are believed to be the least mobile elements. The fresh basalt used for isocon construction is quartz-tholeiitic basalt from north Tasmania (sample number DR11808, Appendix 2).

The slopes ($C_i^W/C_i^O$) of the isocon lines reflect the progressive increase in mass loss ($\Delta M$) and hence increase in intensity of weathering of the basalt samples outward from corestones.

Upper

- TAS27/1: $C_i^W/C_i^O = 1.12$ $\Delta M = -11%$
- TAS27/2: $C_i^W/C_i^O = 1.10$ $\Delta M = -09%$
- TAS27/3: $C_i^W/C_i^O = 1.10$ $\Delta M = -09%$

Lower

- TAS27/4: $C_i^W/C_i^O = 1.15$ $\Delta M = -13%$
- TAS27/5: $C_i^W/C_i^O = 1.05$ $\Delta M = -05%$

Figure 5.6

Isocon diagrams and corresponding histograms for TAS27/4 and TAS27/5. Histograms show relative mass change (%) for analysed elements.
Figure 5.7
Isocon diagrams and corresponding histograms for TAS27/1, TAS27/2 and TAS27/3.
Histograms show relative mass change (%) for analysed elements.
Chapter 5: Basalt Weathering Profiles from Tasmania

Lower Basalt

Th shows a consistent, relatively large enrichment in the lower basalt. K shows a change from moderately depleted near the base of the flow to slightly enriched in the vesicular layer. This enrichment is most unusual as K is not very abundant in basalts and is generally readily removed during weathering. Zn and Fe (total) lie on the isocon and in this profile have remained immobile during weathering. Cu, V, Mn, Si, Na, Ca and Sr show only slight depletion, but become more depleted with increase in weathering. P is slightly depleted in both the massive and vesicular layers of the flow. Pb shows major depletion lower in the flow but is less depleted in the more weathered material. Ba and Mg follow the opposite trend, showing significant depletion with weathering. Cr, La, Ce and Nb all show major depletion, Rb is severely depleted initially but less depleted in the vesicular layer. Si and Ni are strongly depleted throughout (Figure 5.7).

Upper Basalt

As in the lower basalt, all samples show a large enrichment in Th. Again K and Rb show enrichment with weathering. Fe (total) and Zn plot near the isocon. Pb, Ba, Cu, V, Si, Na, P, Ca and Sr are moderately depleted in all samples. La and Ce are progressively enriched while Mn and Cr are depleted with weathering. Nb and Mg show major depletion, and S and Ni, severe depletion throughout the upper basalt (Figure 5.8).

5.7.3 Clay Mineralogy

Lower Basalt

Sample TAS27/5 is only moderately weathered and this is reflected in the X-ray diffraction (XRD) pattern which shows a small amount of secondary clay development (Figure 5.9). The dominant clay present is a trioctahedral smectite, probably Fe-saponite, with lesser amounts of the dioctahedral smectites nontronite and Al-smectite making up the balance. Accordingly the cation exchange capacity (CEC) is 38 meq/100 g and the Si:Al ratio in the clay separate is 3.00. The Si:Al ratio is a little high implying that there may be some free silica in the system, perhaps in fine sediment introduced by fluids percolating through the profile, or as a result of precipitation of amorphous silica in the profile. The diffraction trace has peaks for a number of primary minerals including plagioclase feldspar, pyroxene (augite), olivine, magnetite and ilmenite. Minor goethite and hematite may be present.

The XRD trace for TAS27/4 shows an increase in weathering compared to TAS27/5. Although the primary minerals plagioclase feldspar and pyroxene (augite and possibly
some orthopyroxene) are represented in the trace, olivine no longer occurs. Magnetite and ilmenite are present in this sample. There has been a greater development of smectite clays and goethite is present, with minor hematite. This may reflect the breakdown of olivine to iddingsite, a composite of smectite clays and goethite. The smectites present are mostly dioctahedral nontronite and Al-smectite but small amounts of saponite may occur. In the clay separate an anomalous very large peak at approximately 10Å reflects the presence of a small amount of crystalline mica. This mineral is not primary in the basalt so must have been introduced from elsewhere. Again the Si:Al ratio is high reflecting the incorporation of this sediment but the CEC is 56 meq/100 g which is typical for a smectite dominated clay separate. Vesicle fill material from this sample was analysed and found to be trioctahedral smectite, probably saponite.

Figure 5.9
Stacked X-ray diffraction (XRD) traces for samples TAS27/1, TAS27/2, TAS27/3, TAS27/4 and TAS27/5.

Upper Basalt

Sample TAS27/3 appears less weathered than TAS27/4, perhaps because this material is less vesicular, and hence has been subjected to less fluid throughflow (Figure 5.8), or because TAS27/4 was in a zone of incipient soil formation prior to influx of the overlying
basalt. The XRD trace for TAS27/3 has peaks for many primary minerals including plagioclase feldspar, pyroxene (augite and orthopyroxene), olivine, magnetite and ilmenite. The secondary products are dominated by dioctahedral smectite clays. The clay separate is mostly composed of nontronite with some Al-smectite and possibly minor saponite present. The CEC for the clay separate is 47 meq/100 g which reflects the smectite dominance but the Si:Al ratio is 3.13 indicating that excess Si is present, perhaps contributed from fine grained canal sediments entering pore spaces. Secondary iron oxides and oxyhydroxides may be present but were not clearly represented on the XRD trace, possibly because some of their peaks are partially obscured by the patterns for primary minerals.

For sample TAS27/2 the XRD trace is very similar to that of the adjacent weathered basalt. Once again the primary minerals preserved include plagioclase feldspar, pyroxene (augite and possibly some orthopyroxene), magnetite and ilmenite. Olivine peaks were not evident on the XRD trace. The secondary minerals are composed primarily of dioctahedral smectite clays dominated by Al-smectite and nontronite. Trioctahedral saponite probably does not occur (Mg content is low), or is present in very minor amounts. The CEC is in keeping with the dominantly smectite clay assemblage at 52 meq/100 g. The Si:Al ratio is 2.83, again slightly high to be explained by smectites alone. Peaks for iron oxides and oxyhydroxides are not clear, but these minerals are likely to be present.

The rubbly onionskin material, TAS27/1, is more weathered than the materials underlying it. However, the weathering has proceeded sufficiently slowly in this environment that primary minerals are still preserved. The intensity of the peaks for the primary minerals are much reduced but plagioclase feldspar, pyroxene (augite and possibly orthopyroxene), magnetite and ilmenite are observed. Olivine is no longer represented on the trace. Secondary minerals are again dominated by dioctahedral smectite clays. Nontronite is probably the most abundant clay, with some Al-smectite present also. The CEC is 45 meq/100 g which corresponds with values for smectite rich clays, but the Si:Al ratio is 3.48, indicating an abundance of silica material in the clay separate.

The overlying rubbly skeletal soil was not sampled but has basalt gravel forming a large part of its bulk. This gravel material probably has a composition very similar to TAS27/1 from which it forms. The dominant secondary minerals would be dioctahedral smectites, probably nontronite and Al-smectite. Hematite is not abundant in these samples, and goethite formation is not well advanced. This explains why the soil has a dusty pale olive colouration (Munsell 5Y 5/4), rather that red colours observed on basalt weathering profiles elsewhere.
Summary

The materials produced as a result of basalt weathering at this locality are dominated by smectite clays (Plate 5.5, 5.6, 5.7, 5.8). Trioctahedral clays are relatively prevalent implying that neoformed smectites have not completely broken down to dioctahedral smectites. Because there has been only limited mass loss from these samples and the weathering is moderate, trioctahedral smectites might be expected to be preserved. The Si:Al ratios for the clay separates are elevated in all samples implying that there is additional silica incorporated in the clay fraction. This silica is either derived from crushed primary silicates incorporated from the parent material during sample preparation, or from fine sediment introduced to pore spaces in the profile from the canal waters.

Goethite is the dominant secondary phase within coherent basalt corestones, but hematite is more prevalent near exposed faces and adjacent to joints and fractures.

Plate 5.5 (A), Plate 5.6 (B), Plate 5.7 (C), Plate 5.8 (D)
Scanning electron micrographs (SEM) of smectite clays in the basalt from the Monpeelyata canal profile. (A) and (B) show smectite clays forming mamillary shaped aggregates. (C) shows typical smectite morphology. (D) shows smectite coating exposed mineral faces.
5.7.4 Petrography

Lower Basalt

The lowermost basalt at this site (TAS27/5) is incipiently weathered and the only indication of weathering is the devitrification of basaltic glass in pockets between the groundmass plagioclase feldspar laths (Plate 5.9). Olivine is not a phenocryst phase in this basalt, and clinopyroxene, probably augite, is abundant in the groundmass. Angular, elongate opaque oxides, most likely magnetite and ilmenite, are scattered throughout the groundmass. Elongate prismatic orthopyroxenes, with well developed reaction rims of clinopyroxene (augite), are the principal phenocryst phase. In places narrow elongate orthopyroxene phenocrysts have been completely replaced by clinopyroxene. Rare larger clinopyroxene grains may be described as micro-phenocrysts. Vesicles have poorly developed, goethite stained, clay linings.

The overlying vesicular material (TAS27/4) has a similar composition with essentially the same assemblage, but the basalt is more intensively weathered with the plagioclase feldspar pervasively altered to clays and the groundmass pyroxene completely weathered to secondary goethite, hematite and stained clays (Plate 5.10). Cores of orthopyroxene phenocrysts are preserved and are surrounded by hematite rich zones where the augite rich reaction rims have completely weathered to secondary products. In weathering rinds near exposed faces, adjacent to vesicles and close to micro-fractures, some orthopyroxene phenocrysts have completely weathered to secondary smectite clays. This basalt is more vesicular than the material lower in the flow, and clay linings of goethite and hematite stained clays are well developed. A clear crystalline phase fills the centres of some vesicles, most likely a zeolite. In other vesicles there is a residue of fine grained sediment that is composed primarily of clay minerals, but may contain crystalline phases.

Upper Basalt

The sample taken from a large, slightly weathered basaltic block higher in the profile (TAS27/3) is almost identical in primary mineralogy to the lowermost basalt (TAS27/5). This basalt is marginally more weathered and correspondingly basaltic glass has completely devitrified to poorly oriented clays, and groundmass clinopyroxene has commenced weathered to goethite, hematite and stained clays (Plate 5.11). Plagioclase feldspar laths are etched but are largely intact and the primary basaltic texture is well preserved. Unweathered elongate, angular opaque oxides are present. Vesicles close to exposed faces have well developed goethite and hematite stained clay linings, but zeolite precipitation is not as apparent as in the lower basalts. Orthopyroxene phenocrysts are unweathered.
Plate 5.9
TAS27/5 (crossed polars)
the basalt is incipiently weathered with devitrification of glass the most obvious manifestation

Plate 5.10
TAS27/4 (crossed polars)
Orthopyroxene phenocrysts are etched along fractures and cleavage planes. vesicles are lined with goethite and clays

Plate 5.11
TAS27/3 (crossed polars)
This basalt has almost identical primary mineralogy to TAS27/5. Groundmass phases are more weathered but orthopyroxene phenocrysts are less so

Plate 5.12
TAS27/1 (crossed polars)
Hematite precipitation is prevalent proximal to microfractures
TAS27/2 is weathered to a similar degree as TAS27/3 but has thicker goethite stained clay linings in voids, and clay/goethite mixtures are slightly more apparent in the groundmass (Plate 5.12). Inner parts of the rubbly weathered basalt (TAS27/1) are very similar texturally to TAS27/2, but micro-fractures are much more prevalent in the former, and hence hematite precipitation therein is much greater. Primary plagioclase feldspar laths with groundmass clinopyroxene and angular magnetite and ilmenite are clearly distinguishable in the groundmass, but the plagioclase and pyroxene grains have experienced partial dissolution. Orthopyroxene phenocrysts are strongly etched, especially those close to micro-fractures, exposed faces and vesicles. The goethite and hematite stained clay linings in vesicles are well developed and in places opaque coatings, possibly composed of Mn-oxides, are present.

5.7.5 Profile Summary

The basalts are moderately weathered throughout the profile, but the vesicular material is more intensely affected, hence the vesicular top of the lower flow (TAS27/4) is more weathered. This layer forms a recess in the face of the exposure because the interlocking vesicles (pores) make the basalt from this layer more permeable than the underlying basalt. This permeability contrast facilitates the preferential percolation of fluids through the vesicular layer and hence, there is a greater susceptibility of the vesicular basalt to physical weathering (abrasion, erosion). This is because it has a more brittle original structure, and because it is more intensely weathered than, and hence softer than, the basalt below it. Consequently, the recess is formed due to the frittering of friable material from the face at this level in the profile.

All basalts at this locality are periodically subjected to saturation when the canal is full, but this is a relatively recent phenomenon. However, the enrichment of K, Rb and Th, the elevated Si:Al ratio values and the presence of mica in XRD traces, implies that some fine sediment deposition in pore spaces in the basalt, has taken place.

Despite appearing progressively more weathered in the sequence TAS27/3, TAS27/2, TAS27/1 in hand specimen, the mass loss shows that they do not show much chemical difference in degree of weathering. There may have been some addition of elements to the rubbly weathered basalt, and onionskin material associated with the more weathered corestones. This occurs either by precipitation or neoformation of secondary minerals, with element flux from elsewhere, or by eluviation or introduction of of minerals from outside the profile.
5.8 GEOLOGY - NORTH EAST TASMANIA VOLCANIC PROVINCE

The basalts of the North East Tasmania Volcanic Province can be divided into two groups on the basis of age and distribution. The Blue Tier basalts are dated at approximately 47 Ma (Sutherland & Wellman 1986, Yim et al. 1985) and lie between 500 m and 800 m above sea level. The younger basalts, are dated at approximately 16 Ma, and lie in the Ringarooma Valley. The younger ages of these basalts compared to the Blue Tier basalts confirm the physiographic interpretations of two ages by Nye (1925), Nye and Blake (1938) and Edwards (1939).

Blue Tier Basalts

Flows overlie pyroclastics and river sediments and are up to 230 m thick (Sutherland & Wellman 1986). They descend northward as eroded remnants of flows that follow paleo-drainage depressions and channels. Eruptive centres are thought to be at Weldborough Pass and possibly under Mt Littlechild. The principal rock types are alkali basalt, hawaiite and transitional basalt (McClenaghan et al. 1982, Johnson et al. 1989).

K-Ar ages from the Weldborough Basalt at Mt Littlechild gave dates of 46.2 Ma ± 0.6 Ma, 47.4 Ma ± 0.5 Ma and 47.2 Ma ± 0.6 Ma (Sutherland & Wellman 1986) which correspond, to within experimental error, with an early Eocene age between 46.3 Ma ± 1.8 Ma and 47.1 Ma ± 1.4 Ma derived from fission track dates on zircons (Yim et al. 1985). Electron spin resonance (ESR) work has come up with similar dates (Yim 1991). This is the oldest Tertiary volcanism identified in Tasmania (Sutherland & Wellman 1986). Because the basalts are deeply dissected, considerable erosion has taken place to form the present day relief features (Yim et al. 1985). Uplift associated with basaltic volcanic activity would help account for the considerable degree of erosion (Yim 1991).

Ringarooma Basalts

The basalts in the Ringarooma Valley extend over 40 km following paleo-channels trending north and north-east and are composed of nephelinite, basanite and alkali basalt (McClenaghan et al. 1982, Johnson et al. 1989). The basalts are Miocene in age and a date of 16 Ma ± 0.3 Ma for a sample of porphyritic alkali olivine basalt overlying Mathinna Beds sediments agrees very well with dates of 15.9 Ma ± 0.6 Ma and 15.6 Ma ± 0.3 Ma obtained from samples overlying Tertiary sediments (Brown 1977) and ages of 16.0 Ma, 16.3 Ma and 16.4 Ma ± 0.3 Ma from dissected flows (McClenaghan et al. 1982).
Because the older basalts are located at higher elevation and a prolonged subsequent period of erosion has given rise to considerable dissection of these flows, the major landforms seen today, were most likely already well established at the time of the eruption of the middle Miocene basalts. The eruption of the Ringarooma Basalts had significant physiographical implications in the area, as they apparently blocked a number of north west flowing rivers originating in the Blue Tier, causing them to join up and flow north east along a course similar to that of the present Ringarooma River. Formerly these north west flowing rivers were tributaries of the Boobyalla River (Yim et al. 1985). The Branxholme locality in this study, lies within the Ringarooma basalts.

5.9 BRANXHOLME, NORTH EAST TASMANIA VOLCANIC PROVINCE

5.9.1 Nature of the Exposure

The relatively deep weathering profile at this locality is formed at the crest of a hill, and is exposed in a road cutting near the town of Branxholme, in the Ringarooma Valley (Figure 5.10, Plate 5.13, Appendix 1). Two basalt flows overlie sediment (TAS9/8) and there is a brownish olive clay-rich layer (TAS9/7) near the top of the sediment which resembles a paleosol. The contact between the sediment and the basalt is irregular and it appears the uppermost part of the sediment was soft and wet when the basalt flowed over it. Irregularities have formed due to variable load and fluid release at the time of emplacement of the basalt. As a by-product of this interaction of fluid (water/steam) with the basalt, clay materials (TAS9/6, TAS9/5) have formed near the contact.

The lower basalt is intensely weathered and is largely altered to clays, iron oxides and iron oxyhydroxides. In many places spheroidal weathering can only be recognised by colour changes where concentric rings of alternating white and orange clay materials (TAS9/4b) surround extremely weathered remnant corestones (TAS9/4) (Plate 5.14). Very little of the original rock texture is preserved.

The upper basalt is less weathered and has clearly defined, massive blocky corestones (TAS9/3) up to 80 cm in diameter. Red, crumbly, soil-like weathered basalt (TAS9/2) has formed between the corestones. Despite the proximity of this material to its moderately weathered parent, significantly alteration has already taken place. A skeletal (red) brown soil (TAS9/1) is derived from this material and has substantial corestone rubble incorporated in it.
Figure 5.10
Sample points in the Branxholme profile, north east Tasmania.

Plate 5.13
Branxholme profile.
Plate 5.14
Spectacular alternating colour bands preserve the corestone - onionskin texture.

5.9.2 Geochemistry

For the basalt samples (TAS9/2, TAS9/3, TAS9/4, TAS9/4b) the isocons are best fit lines through the representative points Nb and Zr which are believed to be the least mobile element pair. At this locality most elements appear to have been mobile to some degree and the interpretation derived from the isocon diagrams gives a broad indication of the likely element pathways, and the overall mass balance. The fresh basalt used for isocon construction is alkali basalt from north east Tasmania (sample number DR11804, Appendix 2).

The slopes \( C_{1W}/C_{1O} \) of the isocon lines reflect the progressive increase in mass loss \( (\Delta M) \) and hence increase in intensity of weathering of the basalt samples outward from corestones.

<table>
<thead>
<tr>
<th></th>
<th>( C_{1W}/C_{1O} )</th>
<th>( \Delta M )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper</td>
<td>TAS9/2:</td>
<td>-72%</td>
</tr>
<tr>
<td></td>
<td>TAS9/3:</td>
<td>-65%</td>
</tr>
<tr>
<td>Lower</td>
<td>TAS9/4b:</td>
<td>-73%</td>
</tr>
<tr>
<td></td>
<td>TAS9/4:</td>
<td>-70%</td>
</tr>
</tbody>
</table>

↑ INCREASE IN WEATHERING
Figure 5.10
Isocon diagrams and corresponding histograms for TAS9/4 and TAS9/4b.
Histograms show relative mass change (%) for analysed elements.

Lower Basalt

Y and P show major enrichment in less weathered samples, but are depleted in the more weathered basalt. Th shows progressive enrichment with weathering. In contrast Zn is slightly enriched early in weathering but is subsequently removed, ultimately showing major depletion. Fe (total) and Ti show an early moderate depletion and then retain relatively constant concentrations. La displays major depletion in the corestone material but is much less depleted in the weathered onionskin material. Ni shows progressive depletion while Ce and Mn are significantly depleted early in weathering. Cr, Cu, Al and V exhibit major to extreme depletion while Pb, Ba, Mg, Si, K, Na, Rb, Ca and Sr show extreme depletion throughout the basalt (Figure 5.10).
Chapter 5: Basalt Weathering Profiles from Tasmania

Figure 5.11
Isocon diagrams and corresponding histograms for TAS9/2 and TAS9/3. Histograms show relative mass change (%) for analysed elements.

Upper Basalt

Th becomes enriched as weathering proceeds. Although P shows major enrichment in the least weathered samples, its concentration is depleted with weathering. Fe (total) shows major depletion in the least weathered sample and moderate enrichment in the most weathered sample.

Ti and Zn show moderate depletion, but there is a slight relative enrichment in Zn with weathering. La, Ce, Ni, Cu and Mn display major depletion in the samples while Y and V become progressively depleted with increase in degree of weathering. Al, Pb, Ba, Cr, Mg, Si, K, Na, Rb, Ca and Sr are all extremely depleted in this weathered basalt (Figure 5.11).
5.9.3 Clay Mineralogy

Underlying Sediments

The sediment sample TAS9/8 has medium to fine sand sized clasts in a white clay matrix. Quartz crystals, up to 0.5 mm in diameter, were the predominant clasts observed. Mica flakes were not apparent in hand specimen. This material has an X-ray diffraction (XRD) trace dominated by quartz and to a lesser degree mica. These primary minerals appear to be sitting in a matrix of kaolinite clay, identified by a sharp principal peak at 7.12Å and corresponding subsidiary peaks. In addition, some illite clay may be present, formed as a secondary product after the weathering of muscovite. The cation exchange capacity (CEC) of 21 meq/100 g reflects the mixture of kaolin group clay which generally has a low CEC, and illite which has a higher CEC. The Si:Al ratio of 1.55 is intermediate between the 1:1 expected for kaolin group clays and the 2:1 ratio for mica.

The paleosol layer near the top of this sediment (TAS9/7) is a pale brown-olive (Munsell 2.5Y 5/4) sandy clay-rich material with relatively high porosity. The XRD trace is almost identical to that of the underlying sediment but with more advanced clay development. The kaolin group clays represented are a mixture of kaolinite and halloysite. There is a well developed 10Å peak which is attributed to mica/illite. Corresponding subsidiary peaks were observed for these minerals. The CEC for the clay separate is 28 meq/100 g and the Si:Al ratio 1.33. The brown colouration may be attributed to the inclusion of disseminated organic material.

Green (TAS9/6) and white (TAS9/5) clay materials have formed as a result of the interaction of the basalt with the sediment and its pore water, at the basalt sediment interface. The green material (TAS9/6), has an elevated plateau on the bulk XRD trace from the 7.2Å position back toward the halloysite clay position (around 10Å), and there is a subsidiary peak at 4.43Å. For the clay separate there is a kaolinite peak at 7.24Å but the subsidiary peaks are mostly lost, because mixtures of kaolinite and halloysite are less ordered than kaolinite. The CEC for this material, 32 meq/100 g, suggests the presence of a moderate amount of smectite clay (~20%). However, the Si:Al ratio for the clay separate is 1.17, a value close to that expected for a kaolin group clay dominant assemblage.

Sharp peaks occur for the mineral magnetite showing that this mineral is present in the sample. Observation of the hand specimen under binocular microscope reveals that fine sand size grains of magnetite are disseminated throughout this clay-rich sediment. It is possible that this horizon may have basaltic pyroclastic material associated with it,
however, it is so intensely weathered/altered that no primary sedimentary texture is preserved.

Sample TAS9/5 is a white clay-rich material with some secondary iron staining giving it a patchy yellow-white appearance. The XRD trace for this material once again shows a poorly developed plateau from the 7Å position beyond the 10Å position. The CEC is 22 meq/100 g which is within the range of values for a kaolin-smectite mixture. A best-fit comparison with NEWMOD (Reynolds 1985) kaolinite - dioctahedral (Fe) smectite, suggests that kaolin group clay would account for approximately 80%, and smectite 20%, of the interstratified clay. Subsidiary peaks for smectite are present but partially obscured by other minerals. The Si:Al ratio is 0.90 confirming that the kaolin group clays are dominant in this sample. Minor magnetite is present, probably from the same source as TAS9/6, but not as concentrated as in the green sample. The high Ti value in the clay separate suggests that anatase may be present in the weathered material, but anatase is difficult to distinguish on the XRD trace.

Lower Basalt

The extremely weathered corestones in the lower basalt are surrounded by concentric rings of secondary products (TAS9/4b) with alternating colours (white and orange), which once were "onionskins". The XRD traces for both the orange and the white bands reflect the same mineralogy, although the orange bands contain slightly more goethite and hematite (Figure 5.13). The principal clay mineral is halloysite, with some kaolinite as well. The trace for the orange material shows an elevated plateau from the 7Å position beyond the 10Å position, but the white material shows a clearly defined peak at 7.24Å which has a tail toward 10Å. The CEC for the clay separate is 13 meq/100 g and the Si:Al ratio is 0.96, which both confirm the presence of kaolin group clays. Minor magnetite is present and may be a relict phase from parent basalt.

The corestone material is not as intensively weathered as the surrounding banded material, but the XRD trace indicates that only relict primary minerals are preserved in sample TAS9/4. The clay mineral assemblage includes vermiculite as the principal neoformed clay. Vermiculite is here identified by a principal peak that occurs around the 14.4Å position that is not affected by glycolation and collapses to 11.8Å with heating. There may be minor kaolin group clays present, but the small peak at 7.14Å is more likely to be a subsidiary peak for vermiculite. All of the peaks for vermiculite are clearly displayed in the traces for both the corestone and its closest onionskin. It is possible that the elevated plateaus in the XRD traces of the more intensely weathered material surrounding these corestones, are in part the result of a mixture of vermiculite and kaolin group clays present. The clay separate gives a low CEC, 12 meq/100 g, typical of kaolin
group clays despite the presence of vermiculite, suggesting that the vermiculite has flocculated during clay separation, or that the vermiculite is high charge vermiculite (which has a relatively low CEC). The Si:Al ratio is 0.74 for this sample. Magnetite is detected in the XRD traces.

![XRD traces](image)

**Figure 5.13**
Stacked X-ray diffraction (XRD) traces for samples TAS9/2, TAS9/3, TAS9/4 and TAS9/4b.

**Upper Basalt**

Above a gradational contact, more resistant massive corestones crop out, sitting in a matrix of weathered onionskin material. This sequence forms the main body of the upper flow. The corestones at this level are considerably fresher than the underlying material and this is apparent in the XRD trace for sample TAS9/3 (Figure 5.13). This resistant corestone has a trace with some primary phases still recognisable, including minor plagioclase feldspar and pyroxene, probably augite. A peak for olivine was not present on the XRD trace suggesting it had already been altered to secondary products. Peaks for magnetite were observed although they were partially obscured by those of other minerals. Once again the clay mineral assemblage was dominated by vermiculite, identified by a principal peak at 14.26 Å as well as subsidiary peaks.

Three onion skins out from the corestone were analysed by X-ray diffraction (XRD). These traces show the lack of olivine, the progressive but quite rapid loss of plagioclase feldspar, the persistence but progressive alteration of pyroxene (augite), the presence of magnetite and the increase in vermiculite from corestone outward. A resinous clay mineral formed in a void near the outer corestone was smectite. Hence, no smectite has
formed within the matrix of weathering onionskin material, but rather has been precipitated in voids, at this sample point.

The traces for the more intensely weathered crumbly soil-like material TAS9/2 show kaolin group clays as the predominant secondary clays. The minerals are probably a mixture of kaolinite and halloysite as the asymmetry of the peaks present show a moderate degree of disorder in the kaolin group clay assemblage. Peaks for vermiculite are no longer present in the trace, suggesting that vermiculite has broken down to kaolinite. One small sharp quartz peak is recognised, but because quartz is not observed in any other weathered basalt traces in this profile, it is likely that this is material that has been eluviated down profile from the soil zone.

The red, skeletal soil material capping this sequence, TAS9/1 has the same mineralogy as the intensely weathered onionskin material, TAS9/2, with kaolin group clays, probably a mixture of kaolinite and halloysite, predominating and vermiculite no longer present. Free quartz grains were observed in the soil zone and are attributed to an aeolian source.

Summary

The clay mineralogy at this site is dominated by kaolin group clays reflecting the intense weathering that has taken place at this locality. Vermiculite present in the basalts (Plate 5.15, 5.16, 5.17) may have formed from the breakdown of chlorite no longer preserved in the samples. The chlorite probably formed as a result of slight deuteritic alteration of the basalt around the time of emplacement, as chlorite is not a common primary mineral in most basalts. Because this locality has always had a cool climate (Chapter 4), the weathering reactions may have proceeded relatively slowly and this would have enhanced vermiculite formation, as cations would be available for incorporation into this phase. Scanning electron microscope work confirms the juxtaposition of pyroxene and vermiculite, with some kaolinite in the lower basalt and provides evidence that pyroxene may be breaking down directly to vermiculite. Smectite clays have been precipitated in voids implying that recent percolating fluids have been cation rich (Plate 5.18). The cations may be derived from weathering of the younger overlying basalt.
5.9.4 Petrography

Lower Basalt

The corestone material from this basalt (TAS 9/4) is intensively weathered and is almost entirely composed of secondary products. The primary basaltic texture is not well preserved but the corestone - onionskin relationships can be recognised. The only primary minerals present are fine grained opaque oxides which retain their angular shapes (Plate 5.19, 5.20, 5.21). These oxides are abundant and have been concentrated as a result of collapse of the basalt structure during weathering, and in fractures due to eluviation. The groundmass phases have completely weathered to goethite and hematite stained clays but in areas more proximal to veinlets and exposed surfaces hematite is the dominant secondary Fe-bearing phase. A black coating on exposed faces and in larger open fractures may be Mn-oxide.
Plate 5.19
TAS9/4 (crossed polars)
The basalt is intensively weathered and almost entirely composed of secondary products. The primary basaltic texture is not well preserved.

Plate 5.20
TAS9/4 (crossed polars)
Groundmass phases have completely weathered to goethite, hematite and clays. Proximal to microfractures hematite is dominant.

Plate 5.21
TAS9/4 (crossed polars)
Pseudomorphs after orthopyroxene are composed of vermiculite clays. Former augite reaction rims have weathered to Fe stained clays.

Plate 5.22
TAS9/3 (crossed polars)
Pseudomorphs of olivine and pyroxene are replaced by goethite and clays whereas groundmass material is dominantly weathered to hematite.
Large elongate phenocryst pseudomorphs formed after orthopyroxene, are infilled with vermiculite clays and many have rims of Fe-stained clays, which may formerly have been reaction rims of clinopyroxene. Smaller pseudohexagonal microphenocrysts, now completely replaced by goethite, hematite and Fe-stained clays, were formerly olivine.

**Upper Basalt**

The most indurated basalt at this locality (TAS9/3) is an extremely fine grained glassy basalt with an orange-red coloured weathering rind. The least weathered groundmass is pervasively altered to goethite stained clay minerals with very small relict feldspar laths poorly preserved (Plate 5.22). The more intensely weathered basalt in the weathering rind and close to micro-fractures is dominated by hematite and stained clays. Fine grained primary angular opaque oxides, probably magnetite with some ilmenite, are abundant in the groundmass and appear to have been physically concentrated.

Phenocrysts are almost entirely weathered to secondary products, predominantly goethite and hematite with some stained clays, including vermiculite. It is extremely difficult to distinguish the nature of the original phenocryst phases. Many pseudomorphs are elongate and sub-rectangular and relict cores appear to have straight extinction, so the original mineral was most likely orthopyroxene. Smaller pseudomorphs have the pseudohexagonal shape of olivine, but no olivine is preserved.

The corestone material from the lower basalt (TAS9/4) is extremely weathered with groundmass phases completely altered to secondary goethite, hematite and stained clays. Angular, opaque oxides appear to be concentrated in the groundmass, and may be breaking down to secondary Fe-bearing phases, but it is difficult to observe clearly because of the fine grained nature of these minerals. Pseudomorphs after phenocrysts are recognisable and the larger examples have neoformed clays preserved in their cores. Some pseudomorphs after pyroxene appear to have cores of vermiculite. Most of the groundmass is goethite-stained clays, with hematite more dominant closer to micro-fractures. Small pseudohexagonal weathered microphenocrysts, now completely weathered to Fe-stained clays, were formerly olivine crystals.

5.9.5 **Profile Summary**

The lower basalt samples (TAS9/4, TAS9/4b) show large mass losses and are extremely weathered to the point that the primary basaltic texture is no longer preserved. However, spheroidal weathering textures are observed and the concentric banding of former onionskins is clearly preserved. The pattern of internal variation in degree of weathering
of the basalt, becoming more weathered outward from corestones, can be recognised even in this extremely weathered basalt.

Y and P enrichment may be associated with localised secondary phosphate neoformation during weathering, however, Ce, La, Pb and Ba did not show similar enrichment. Progressive Th enrichment may be attributed to its adsorption onto and incorporation into weathering products. Ti and Fe depletion in the intensely weathered lower basalt may be associated with the percolation of acid fluids.

The overlying blocky basalt (TAS9/3) is considerably less weathered, although the red, crumbly material (TAS9/1) between the blocks is intensely weathered, and has a similar mass loss (ΔM) to the underlying basals. The contrast in weathering between flows implies that: either the upper basalt is younger than the lower basalt, or the lower basalt has been affected by water table ponding. Because this outcrop is at the crest of a hill, the former explanation is more likely.
6.1 LOCATION

The Monaro Volcanic Province stretches from just north of Cooma south almost to Bombala, on the South-eastern Highlands of New South Wales (Figure 6.1). Two localities were sampled in this province, one north of Cooma on the Big Willow property (36.06°S 149.05°E) and one south west of Nimmitabel, on the Sherwood property (36.36° S 149.07°E) (Appendix 1).
6.2 CONTEMPORARY CLIMATE

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Table 6.1

Contemporary climate information for the Monaro sample localities (BIOCLIM)

Both Big Willow and Sherwood localities receive similar radiation and the annual mean temperature at both localities is comparable, although slightly warmer at Big Willow (Table 6.1). Winter temperatures at both localities are very cold and frequently a few degrees sub-zero. The most notable difference between the two localities is that Sherwood, in southern Monaro has a greater annual precipitation than Big Willow. Both localities receive most of their precipitation in the spring and early winter months and are relatively dry in late summer and winter, with some of the winter precipitation occurring as snow. There is a rain shadow effect in this area as the Volcanic Province lies to the east of the Snowy Mountains.
6.3 **PALEOCLIMATE AND VEGETATION**

According to studies of oxygen isotopes in kaolinite from weathering profiles in the Monaro (Bird *et al.* 1990b) the climate in the early Tertiary was cool to cold. Fossil pollen, spores and wood indicate that the Monaro was covered in cool-temperate rainforest at this time (Taylor *et al.* 1990). Work on fossil leaves of a similar age support this interpretation (pers. comm. Hill 1990). The presence of rainforest implies that the area was cool and wet, and possibly had seasonal variation in temperature and rainfall. This cool climate is in keeping with the predicted high latitude, approximately 57.5°S, for the Monaro at this time (Idnurm 1985).

6.4 **GEOLOGY - MONARO VOLCANIC PROVINCE**

In the Monaro Volcanic Province multiple basalt flows with an aggregate thickness of up to 400 m overlie Paleozoic metasediments and granitoids of the Lachlan Fold Belt (Brown *et al.* 1993). Roach (1991) recognised that lineaments in the basement influence the positioning of the volcanic plugs which sit on or near the intersections of two or more lineaments. Hence, fracture intersections are zones of preferred migration along which magmas were channelled to the surface. There is evidence for early phreatomagmatic events in this large lava field (4,200 km²), but most of the eruptions were relatively passive effusive events issuing lava from a number of small vents. This formed a layered lava sequence, with intercalated lacustrine and alluvial sediments, which ultimately filled deep paleo-valleys (Taylor *et al.* 1985, Veitch 1987, Brown *et al.* 1988). Volcanism occurred episodically from the early Tertiary approximately 57.5 Ma to the middle Tertiary around 34 Ma (Wellman & McDougall 1974). The flow basalts are mainly alkali basalts and basanites with minor nephelinite. Plug rocks types include alkali olivine basalts, olivine nephelinites and nepheline basanites (Kesson 1973, Roach 1991).

Interbasaltic bauxites have been recorded from this province (Brown *et al.* 1992, Taylor *et al.* 1992). Past climate environment information from the fossil record in the Monaro, indicates that it was cool in the early Tertiary (Taylor *et al.* 1990). Despite many authors suggesting that bauxites only form under tropical conditions (Bardossy 1974, McFarlane 1983, Ollier 1984, Nahon 1986, Frakes *et al.* 1987, Chapman 1989, Tardy *et al.* 1990a, Bardossy & Aleva 1990), because that is the environment in which we commonly see them forming and preserved today, Taylor *et al.* (1992) argue that cool climate bauxite development occurred in the Monaro. They propose that in an area of relative tectonic stability, where there is sufficient rain and good drainage, bauxites may develop despite the cool temperatures. Bauxite development would take place over a longer period than in more tropical regions (Bird & Chivas 1988, Eggleton *et al.* 1987, Taylor *et al.* 1989, Taylor *et al.* 1990).
6.5 BIG WILLOW, MONARO VOLCANIC PROVINCE

6.5.1 Nature of the Exposure

Sample points in the BigWillow profile, Monaro Volcanic Province.

Plate 6.1
Big Willow profile
Chapter 6: Basalt Weathering Profiles from Southern New South Wales

At the spring mouth massive, moderately weathered, indurated basalt (BW3, BW4) crops out, with a more intensely weathered basalt (BW2), apparently part of the same flow, above (Figure 6.2).

Approximately 20 m above the natural point of issue of the spring, a dam has been constructed which taps the same aquifer. Adjacent to the dam rubbly weathered basalt is exposed, with well developed moderately weathered corestones apparent. Surrounding these corestones concentric onionskins of weathered basalt have formed (BW-1, BW-2) (Plate 6.1). Yellow coloured, goethitic, clay-rich material has deposited in cracks between adjacent corestones. The whole sequence is overlain by a black basaltic soil which has largely been transported downslope. Samples were taken from a upper mid-slope position, except for those near the mouth of the spring.

6.5.2 Geochemistry

For the basalt samples (BW4, BW3, BW2, BW-1, BW-2) the isocons are best fit lines through the representative points Nb, (Zr) and Ti which which are believed to be the least mobile elements. The fresh basalt used for isocon construction is alkali basalt from the Monaro Volcanic Province (sample numbers K65 & R3, Appendix 2).

The slopes \( C_i W/C_i O \) of the isocon lines reflect the progressive increase in mass loss \( \Delta M \) and hence increase in intensity of weathering of the basalt samples outward from corestones and upward through the profile.

\[
\begin{array}{lllll}
Upper & BW-1: & C_i W/C_i O = 3.14 & \Delta M = -68\% & \uparrow \\
 & BW-2: & C_i W/C_i O = 1.85 & \Delta M = -46\% & \text{INCREASE IN} \\
Lower & BW2: & C_i W/C_i O = 1.83 & \Delta M = -45\% & \text{DEGREE OF} \\
 & BW4: & C_i W/C_i O = 1.27 & \Delta M = -21\% & \text{WEATHERING} \\
 & BW3: & C_i W/C_i O = 1.15 & \Delta M = -13\% & \uparrow 
\end{array}
\]

Based on field relationships alone it is not clear whether these weathered basalt samples and those lower in the sequence are from the same flow or whether two separate flows are represented. The fact that the absolute mass loss \( \Delta M \) values for these samples continue a broad trend first observed in the lower exposure (greater mass loss with observed increase in weathering), provides some evidence that all samples were taken from a single flow.
Chapter 6: Basalt Weathering Profiles from Southern New South Wales 117

Lower Basalt

Ba is anomalously enriched in the slight to moderately weathered basalts, BW3 and BW4, but sits on the isocon in the more weathered sample BW2 (Figure 6.3). Fe₂O₃ is strongly enriched in all samples. Mn, V and Sr show a moderate enrichment initially, but in the most weathered material they are moderately depleted. Cr, Ni and K show significant depletion with increase in weathering. They are all moderately enriched to start with, but show major to extreme depletion in the more intensely weathered sample (BW2). In contrast P shows a change from slight to major enrichment with weathering.

Figure 6.3
Isocon diagrams and corresponding histograms for BW2, BW3 and BW4.
(Histograms show relative mass change (%) for analysed elements.)
Ce and La are slightly depleted to start with but show a relative enrichment with weathering. Th, Zn and Al are constantly slightly depleted in this profile. Y is slightly depleted initially, but plots adjacent to the isocon in the more weathered samples. Cu, Si, Ca, S, Mg, Na and Rb become more depleted with increased weathering. Pb shows major depletion.

**Upper Basalt**

![Figure 6.4](image)

Isocon diagrams and corresponding histograms for BW-2 and BW-1.

Histograms show relative mass change (%) analysed elements

Mn and Ba are extremely enriched in the moderately weathered basalt corestone, but then both are depleted with increased weathering, Mn remaining moderately enriched and Ba showing major depletion. Ce sustains a major enrichment in all samples. Ni, although slightly enriched at first, shows extreme depletion in more weathered samples.

V plots near the isocon, and Th maintains a constant slight depletion in all samples. La shows an increase in concentration with weathering. Zn follows an opposing trend with a
change from slightly to extremely depleted as weathering proceeds. Pb, Cr, S, Cu and Si show major depletion early in weathering, with S Cu and Si becoming progressively more depleted with increase in weathering. In contrast, P and Y both show relative enrichment after early depletion. Mg, Fe\(^{2+}\), K, Na, Rb, Ca, and Sr are extremely depleted throughout the profile (Figure 6.4).

### 6.5.3 Clay Mineralogy

*Lower Basalt*

![X-ray diffraction traces for BW4, BW2, BW-1 and BW-2](image)

**Figure 6.5**

Stacked X-ray diffraction (XRD) traces for BW4, BW2, BW-1 and BW-2

Peaks for primary minerals are abundant in the bulk X-ray diffraction (XRD) analyses for BW3 and BW4 (Figure 6.5). The traces are dominated by peaks for plagioclase feldspar,
with olivine and minor pyroxene, but the feldspar peaks tend to obscure some peaks for the ferromagnesian silicate minerals. Magnetite and ilmenite are represented and small sharp quartz peaks indicate the presence of minor amounts of quartz. The principal clay phase is smectite. The clay separate has relatively high Fe and Mg, and from XRD the smectite present is identified as predominantly trioctahedral, probably saponite and possibly Fe-saponite. Some dioctahedral smectite is present, probably nontronite with minor Al-smectite. The CEC for the clay separates range from 36 meq/100 g to 47 meq/100 g and the Si:Al ratio lies between 1.74 and 2.81 which are compatible with smectite dominating the clay assemblage. Minor hematite and goethite are present.

The primary minerals represented in the XRD trace for BW2 are dominated by plagioclase feldspar. Peaks for primary ferromagnesian silicate minerals are not clear although some pyroxene peaks are still present. This suggests that olivine has been more strongly affected by early weathering than pyroxene. Magnetite and ilmenite peaks appear on the trace and minor proportions of quartz persist in this sample. The dominant clays present are kaolin group clays, kaolinite and possibly some halloysite. Minor smectite may be present, but it is not forming a well defined peak. The presence of a diffuse smectite peak and a kaolinite peak (~7Å) which tails off toward the 10Å position might suggest that some interstratified kaolinite-smectite phases are present. A best-fit comparison with NEWMOD (Reynolds 1985) kaolinite - dioctahedral (Fe) smectite, suggests that kaolin group clay would account for approximately 60-70%, and smectite 30-40%, of the interstratified clay.

**Upper Basalt**

Higher in the sequence a pervasively weathered basalt has been sampled (Figure 6.5). BW-1 still retains an onionskin texture, but is almost totally weathered to secondary products. The XRD trace shows evidence of relict feldspar, magnetite and ilmenite. The balance of primary minerals have been weathered away. The clay separate for this sample has relatively high Fe, but low Mg, and the smectite is dioctahedral (XRD). Most Fe would probably be present as iron oxyhydroxides in this grain-size fraction, however the balance may be incorporated into nontronite, an iron bearing dioctahedral smectite. Gibbsite and Al-smectite (beidellite) are also be present. The CEC for this sample is 56 meq/100 g. The Si:Al ratio is 1.09, which is consistent with a mixture of beidellite (Si:Al = 3.7:2.3) and gibbsite (Si:Al = 0:1). Peaks for the zeolite mineral natrolite are present in the trace and it is probably precipitated in voids in the weathering basalt.

Only minor plagioclase feldspar, magnetite and ilmenite are represented in the XRD trace for BW-2 and no quartz peak was found. Smectite is the dominant clay in this soil, with gibbsite and goethite also present. The smectite is dioctahedral and the presence of
abundant iron, evident in the clay separate chemistry, would facilitate the formation of nontronite. Because the structural model for nontronite does not account entirely for the clay chemistry there is probably another dioctahedral smectite occurring, most likely a small amount of Al-smectite, (beidellite). The CEC for the clay separate is 43 meq/100 g and the Si:Al ratio is 1.29. Again the Si:Al ratio is intermediate between that expected for smectite and gibbsite because of the mixture of the two.

A paler coloured more weathered rind on the fragments of weathered basalt adjacent to cracks in the weathered basalt was dominantly gibbsitic. Hence gibbsite (and goethite) are residual in vein-like zones of intensely weathered material between basalt corestones. Continued weathering in the soil zone may lead to concentration and further formation of these minerals in zones of preferred fluid flow. A discussion of the formation of gibbsite and the chemistry of the prercolating fluids is discussed in Chapter 11.

Summary

Lower Basalt

In the freshest samples (BW3, BW4) the dominant clay present is trioctahedral smectite, principally formed from the break down of olivine and groundmass ferromagnesian silicates. Dioctahedral smectite may be formed from the break down of trioctahedral smectite with continued weathering. Plagioclase feldspar may weather to dioctahedral Al-smectite and basaltic glass may weather to smectite clays. Secondary Fe-oxyhydroxides are dominated by goethite with minor hematite.

In the slightly more weathered material (BW2) kaolin group clays are more dominant in the XRD trace than smectite clays. Although the principal peak for smectite is not apparent, there may be some smectite present in interstratified kaolin-smectite clays, formed as intermediate products in the breakdown of smectite to kaolinite and halloysite. The principal secondary Fe-bearing phase is goethite with some hematite present.

Upper Basalt

The clay fraction mineralogy for BW-2 is unusual because smectite and gibbsite occur together. Gibbsite Al(OH)₃ is a residual product, generally associated with extremely intense leaching of elements. This mineral is not usually found in sequences that have had little or no kaolin group clay development taking place as the chemical pathway for gibbsite formation from smectite clays usually has kaolin group clays as an intermediate stage. Closer inspection shows that the gibbsite is concentrated in more intensely weathered rinds along cracks and strongly weathered vein-like zones between corestones.
Concentrations of goethitic material are also observed in these zones. It appears that smectite is the first formed secondary phase, and with continued weathering may be replaced by the kaolin group minerals, kaolinite and halloysite, especially along marginal zones of fluid percolation. With continued throughflow of weathering fluids along these zones, the kaolin group minerals may be further leached to form gibbsite.

BW-1 has essentially the same mineral assemblage as BW-2 but there is no primary plagioclase feldspar preserved and the primary basaltic texture has started to collapse. Again the gibbsite is associated with the zones of intense weathering between corestones, which are also sites of significant secondary iron oxide and oxyhydroxide and Mn-oxide precipitation, as observed petrographically. These zones are pathways of preferred fluid percolation and have either formed as a result of considerable throughflow of water, or have formed as a result of periodic saturation of the profile. The former scenario is preferred as in the latter case leached cations would be concentrated in the ponded fluids and would be available for re-incorporation into secondary products.

6.5.4 Petrography

Lower Basalt

The least weathered basalt (BW3) is relatively massive with micro-phenocrysts of olivine in a groundmass of fine grained plagioclase laths, devitrified glass, and angular inter-lath shaped opaque oxides (Plate 6.2). All of the groundmass material between the feldspar laths has weathered to clay minerals, and pockets of goethite between laths indicate the former presence of a groundmass ferromagnesian silicate phase, probably olivine and pyroxene. Some small grains of groundmass pyroxene are preserved. Within the basalt sample the olivine phenocrysts are only incipiently weathered to smectite clays and goethite, but in the weathering rind secondary goethite and minor hematite are abundant and olivine phenocrysts are wholly altered to secondary products. Small opaque minerals within the olivine phenocrysts are identified as Cr-spinel. Scattered vesicles are lined with fine grained, yellow goethite-bearing clays.

Although BW4 appears relatively indurated in hand specimen, with a well preserved primary basalt texture, the fine grained groundmass plagioclase feldspar is almost entirely weathered from this sample (Plate 6.3). Micro-fractures cross-cut BW4 and secondary Fe-oxide and oxyhydroxide precipitation is concentrated around these fractures (Plate 6.4, 6.5). Geothite stains the clays of the groundmass in a band with intensity of colouration decreasing outward from the micro-fractures. Many weathered olivine phenocrysts are replaced with clay minerals, possibly trioctahedral phases, with very little Fe-staining. The formation of goethitic rims on olivine grains is much better developed.
Plate 6.2
BW3 (crossed polars)
Olivine phenocrysts are incipiently weathered to ameite clays and goethite along fractures

Plate 6.3
BW4 (plane polarised light)
Secondary Fe oxyhydroxides replace groundmass phases.

Plate 6.4
BW4 (plane polarised light)
Fe oxyhydroxide precipitation is concentrated around microfractures

Plate 6.5
BW4 (crossed polars)
Some goethitic material in this fractures is dehydrating to hematite
Plate 6.6
BW2 (crossed polars)
the groundmass is pervasively weathered to clay minerals with small angular opaque oxides disseminated throughout.

Plate 6.7
BW2 (plane polarised light)
Euhedral olivine microphenocrysts have weathered to goethite and clays.

Plate 6.8
BW2 (crossed polars)
Microfractures are infilled with goethite stained clays and hematite. Close to fractures olivine phenocrysts are intensely weathered.

Plate 6.9
BW-1 (crossed polars)
Voids are infilled with a zeolite showing radiating acicular habit.
proximal to the microfractures (Plate 6.4, Plate 6.5). Very small primary opaque oxides, probably magnetite and ilmenite, and some small fragments of pyroxene are preserved unweathered in the groundmass (Plate 6.3).

The groundmass in BW2 is pervasively weathered to clay minerals with tiny fragments of etched plagioclase feldspar, and small angular magnetite and ilmenite grains scattered throughout the clay matrix. Small fragments of groundmass pyroxene are preserved. All olivine phenocrysts are completely weathered, with paler coloured cores and more clearly defined thick goethitic rims. Goethite and hematite are also concentrated in cross cutting microfractures (Plate 6.8). The smectite originally formed during the breakdown of olivine may be further weathered to kaolin group clays. A thick goethite rich rim surrounds these clays. The primary basaltic texture is poorly preserved and is starting to break down.

*Upper Basalt*

BW-1 is completely weathered to a goethite- (and hematite-) bearing clay plasma. The breakdown of primary opaque oxides has commenced and very dense concentrations of Fe- and probably Mn-bearing secondary phases are associated with cross-cutting microfractures. Voids, which are possibly relict vesicles, but which show flattened and distorted shapes, and former micro-fractures, are infilled by a clear crystalline mineral with radiating acicular habit and straight extinction, that resembles a zeolite (Plate 6.9). The presence of zeolites in voids supports the suggestion that there has been episodic drying of the profile.

### 6.5.5 Profile Summary

The trend in absolute mass loss (-ΔM) values, together with field observations, suggests that the sequence represented at this locality is a single flow, which has been weathered dominantly from the top downward. The secondary mineral assemblage is dominated by smectite clays although interstratified kaolin-smectite phases may be present, and in zones of extreme weathering, between near-surface corestones, some gibbsite has formed. Kaolin group clays form only a minor proportion of the secondary mineral suite. The juxtaposition of gibbsite and smectite during weathering is quite unusual and is discussed in more detail in Chapters 11 and 12.

The elevated concentrations of Ba, P, Ce and La are attributed to the localised neoformation of secondary phases, most likely phosphates, in the weathering profile. However, Pb does not show similar enrichment. Some Ce enrichment may be associated
with the oxidation of Ce\(^{3+}\) to Ce\(^{4+}\), as Mn and Fe also show similar enrichment patterns.

### 6.6 SHERWOOD, MONARO VOLCANIC PROVINCE

#### 6.6.1 Nature of the Exposure

This outcrop (Figure 6.6, Plate 6.10, Appendix 1), has a similar topographic setting to Big Willow, in an upper mid-slope position on the side of a stream gulley. Spheroidal weathering has led to the formation of well developed corestones at this locality. Low in the profile corestones up to 20 cm in diameter are preserved (SW6), but intense weathering forming onionskins of weathered basalt surround these. In the upper parts of this lower flow, the weathering is more pervasive, corestones are smaller, and the basalt more intensely weathered (SW5). Between the flows there is a lacustrine deposit (SW2, SW4) which contains leaf fossils (Dansie 1993). The upper flow is weathered similarly to the material underlying the lacustrine deposit, and where the sediment pinches out, it is difficult to distinguish between the two flows. The upper flow has corestones 15-20 cm in diameter (SW1) becoming more rubbly and more intensely weathered up-profile, until it is overlain by a transported black soil.

![Diagram of Sherwood profile](attachment:image.png)

**Figure 6.6**
Sample points in the Sherwood profile, Monaro Volcanic Province.
6.6.2 Geochemistry

For the basalt samples (SW1, SW5, SW6) the isocons are best fit lines through the representative points Y, (Zr), Al and Ti which are believed to be the least mobile elements. The fresh basalt used for isocon construction is alkali basalt from the Monaro Volcanic Province (sample numbers K65 & R3, Appendix 2).

The slopes \( \left( \frac{C_{i}^{W}}{C_{i}^{O}} \right) \) of the isocon lines reflect the progressive increase in mass loss (\( \Delta M \)) and hence increase in intensity of weathering of the basalt samples outward from corestones and upward through the profile.

\[
\begin{array}{l|lll}
\text{Upper} & \text{SW1:} & C_{i}^{W}/C_{i}^{O} = 1.31 & \Delta M = -24\% & \text{INCREASE IN} \\
\text{Lower} & \text{SW5:} & C_{i}^{W}/C_{i}^{O} = 1.83 & \Delta M = -25\% & \text{DEGREE OF} \\
& \text{SW6:} & C_{i}^{W}/C_{i}^{O} = 1.27 & \Delta M = -04\% & \text{WEATHERING} \\
\end{array}
\]

\text{Lower Basalt}

Ba is extremely enriched in the lower basalt samples. Likewise, Cr and Ce both show a relatively constant large enrichment. Cu, V, Ni, and Mn are all moderately enriched in the corestone but become more depleted with weathering until they show major depletion in
the rubbly weathered onionskin material. In contrast Zn exhibits a slight enrichment with weathering.

Si, P, Ca, Na and Sr plot on the isocon for the corestone sample but all are depleted in the rubbly weathered basalt. Si and P become moderately depleted, Fe (total) shows major depletion and Ca, Na and Sr show extreme depletion with increase in the degree of weathering. Pb, La and Th show a moderate early depletion and thereafter their concentration remains constant. Nb, Mg, K and Rb are removed early in weathering but K and Rb show secondary enrichment. S is extremely depleted throughout the weathering sequence (Figure 6.7).

Figure 6.7
Isocon diagrams and corresponding histograms for SW1, SW5 and SW6.
Histograms show relative mass change (%) for analysed elements
Upper Basalt

Zn and Cr are both enriched during weathering of this basalt. Ba, La, Cu, V and P lie on the isocon. All other elements analysed show relative depletion with respect to unweathered basalt. Pb, Fe (total), Th, Si and Ni are slightly to moderately depleted, while Ce, Nb, Mg and Sr all show major depletion, and S, Mn, K, Na, Rb and Ca are extremely depleted as a result of weathering (Figure 6.7).

6.6.3 Clay Mineralogy

Lower Basalt

The lowermost weathered corestone sampled, SW6, has abundant primary minerals represented in the trace (Figure 6.8). Plagioclase feldspar is most abundant with olivine and pyroxene peaks present also. There is a clear principal smectite peak on the XRD trace and both trioctahedral and dioctahedral smectite phases are present. The clay separate has high Fe and Mg concentrations, so the trioctahedral clay is probably Fe-saponite, with associated saponite. The dioctahedral phases are probably nontronite and Al-smectite. The presence of smectite clays is reflected in the cation exchange capacity (CEC) for the clay separate which is 71 meq/100 g and the Si:Al ratio which is 2.61. There may be minor iron oxyhydroxides in these samples but the peaks are small and partially obscured by the feldspar traces.

The sample from higher in this flow, SW5, is more intensely weathered. Accordingly there are little or no primary mineral peaks present in the trace, but there is a concentration of quartz in this sample. Because this sample lies so close to the siliceous lake sediments in the outcrop, either some of the fine quartz material has been eluviated down-profile, or siliceous fluids have percolated through the weathering basalt. Smectite is the dominant clay type present. The clay separate for this sample has a moderate amount of Fe and high Mg and the XRD trace indicates that both trioctahedral and dioctahedral smectite phases are present. Because the Mg content is relatively high, the trioctahedral smectite is probably saponite. The dioctahedral smectite clays present are likely to be a mixture of nontronite and Al-smectite. Accordingly the CEC is 89 meq/100 g and the Si:Al ratio is 2.14.

There is a small 10Å peak present in the bulk XRD trace that is not affected by glycolation. The presence of minor halloysite is indicated by a major peak at 7.18Å, as well as minor peaks. Although the 10Å peak may be associated with the kaolin group clays, the peak is very sharp, and it is more likely that it is associated with micas derived from the lacustrine sediments.
Chapter 6: Basalt Weathering Profiles from Southern New South Wales

Figure 6.8
Stacked X-ray diffraction (XRD) traces for sample SW1, SW5, and SW6.

Lacustrine Sediments

Two samples were taken of siliceous lacustrine sediments at this site, SW4 and SW2. The lake sediments have XRD traces that are dominated by quartz peaks, however peaks for some other primary minerals and secondary products are observed. Phyllosilicates present in the samples include smectite, kaolinite and mica. The clay separate has moderate to low concentrations of Fe and Mg, and on the XRD trace there are peaks for both trioctahedral and dioctahedral smectite. The trioctahedral clay is probably saponite but the dioctahedral clays are likely to be more abundant with Al-smectite forming in excess of nontronite. The kaolin group clay is identified as kaolinite.

The XRD trace shows a peak at 9.95 Å and subsidiary peaks of muscovite. Observations of the hand specimen SW4 under binocular microscope revealed white mica flakes within the siliceous matrix of the lacustrine sediment. Provenance for this mica is not known but one possibility is that it is derived from the low grade metamorphosed Ordovician-Silurian sandstones and shales that form the basement in this area. An outcrop of this rock type may have been eroded in the catchment area feeding this lake. The white mica
The range of CEC values for these samples is 36 meq/100 g to 57 meq/100 g and the Si:Al ratios are between 1.66 and 1.70, reflecting the mixture of phases in the clay separate.

**Upper Basalt**

A single weathered corestone, SW1, has been sampled from the upper flow (Figure 6.9). This corestone is intensely weathered but feldspar peaks are still clearly recognised in the XRD trace. All other primary minerals have weathered, largely to smectite, which is the predominant mineral present. The 06l peaks for smectite indicate that both trioctahedral and dioctahedral phases are present. Fe content is high in the clay separate but Mg content only moderate, so the trioctahedral smectite is probably Fe-saponite with minor saponite present and the dioctahedral clays are probably a mixture of nontronite and Al-smectite. The CEC for the clay separate is 76 meq/100 g and the Si:Al ratio is 1.90, both of which are in keeping with a clay assemblage dominated by smectite. SW1 has a resinous coating lining cracks in the sample. The XRD trace indicates that this is also smectitic. This crack-lining material is probably a mixture of the dioctahedral clays nontronite and beidellite ± hematite and minor goethite.

**Summary**

The clay mineralogy of the weathered basalt throughout the profile is dominated by smectite which forms as a by-product of the breakdown of basaltic glass, olivine, pyroxene and plagioclase feldspar. Olivine is very susceptible to dissolution and goethite bearing smectite-rich rims form early in weathering. Olivine weathers initially to trioctahedral smectite and goethite ± hematite which may, in turn, breakdown to dioctahedral smectite, goethite and hematite, with increased weathering. Plagioclase feldspar weathers to an Al-smectite, probably montmorillonite and possibly kaolinite. Goethite is the dominant secondary Fe-bearing phase present, and it imparts a brown colouration to the profiles.

Muscovite does not occur in these basalts. Muscovite found in the upper parts of the lower basalt has almost certainly been translocated down-profile from the overlying lacustrine sediments which are rich in muscovite. Likewise there is an enrichment in quartz which is likely to have been introduced by eluviation also. The muscovite is not clearly observed in thin section suggesting that it has been partially weathered. The presence of even a small amount of mica would explain the 9.95Å peak on the XRD trace and the anomalously enriched K and Rb values in sample SW5.
6.6.4 Petrography

Plate 6.11
SW6 (crossed polars)
Large cubedral olivine phenocrysts pseudomorphs are entirely composed of smectite clays in particular Fe-saponite (showing interference colours), nontronite and beidellite (brown poorly orientated clays)

Plate 6.12
SW1(crossed polars)
Small cubedral Cr-spinels are residual in weathered olivine pseudomorphs

Plate 6.13
SW1 (crossed polars)
Open microfractures are lined with oriented clays which in turn are coated by Fe-Mn oxides
Chapter 6: Basalt Weathering Profiles from Southern New South Wales 133

Lower Basalt

This basalt (SW6) has relatively large plagioclase feldspar laths forming the bulk of the groundmass with most of the interstitial basaltic glass, olivine and pyroxene weathered to secondary products (Plate 6.11). Sufficient fragmented pyroxene grains are preserved to show that this mineral originally had a sub-ophitic to ophitic texture with the groundmass plagioclase feldspar penetrating the pyroxene. Where groundmass pyroxene is completely weathered, goethite and hematite material is preserved in many small adjacent pockets, forming a mosaic similar to the original ophitic texture of the primary mineral.

Very large olivine phenocrysts are completely weathered to secondary smectite clays probably trioctahedral Fe-saponite and saponite at the centre of some of the larger grains, with dioctahedral clays surrounding them. Many of the smaller olivine phenocrysts are entirely weathered to dioctahedral smectite clays, probably nontronite and an Al-smectite. Well developed goethite rich rims enclosed the olivine derived smectite clays. Within the weathered olivine phenocrysts, extremely small opaque minerals can be recognised and these are identified as Cr-spinel. Primary opaque oxides, probably magnetite and ilmenite, are extremely fine grained in this basalt, and are not abundant in the groundmass.

Upper Basalt

The upper corestone material (SW1) is extremely weathered with the groundmass feldspar intensely etched and much of it weathered to clays. Primary mafic groundmass minerals are completely weathered as are the euhedral olivine phenocrysts (Plate 6.12, 6.13). These phenocrysts are entirely replaced by secondary clays, probably dioctahedral smectites including nontronite and an Al-smectite (beidellite). With continued weathering, smectite clays within the olivine pseudomorphs break down to kaolin group clays. Fine, euhedral blocky grains of Cr-spinel are observed within weathered olivine grains. While goethite is the dominant secondary Fe-bearing phase in the weathering basalt, hematite is concentrated along micro-fractures. Some goethite bearing clays infill micro-fractures in the weathered basalt.

6.6.5 Profile Summary

Both basalts at this locality are weathered from the top down, hence the more weathered material lies at the top of the flows. Corestones features are well developed and fluid percolation along former joint planes leads to enhanced weathering in the zones between the corestones. Unusual cation enrichment in the zone below the lacustrine deposit can be attributed to down-profile translocation of muscovite and quartz. In particular, the
presence of micas provides an explanation for the elevated concentrations of K and Rb. Enrichment of Ba and Ce may be attributed to the neoformation or precipitation of a secondary phase (phosphate, sulphate, carbonate).
CHAPTER 7

BASALT WEATHERING PROFILES FROM NORTHERN NEW SOUTH WALES

7.1 LOCATION

The Warrumbungles Volcanic Province of northern New South Wales (Figure 7.1), is located approximately 500 km NW of Sydney, immediately west of the township of Coonabarabran. Profiles were sampled at two localities, one in a small diatomite quarry on Chalk Mountain (31.07°S 149.04°E) and another exposed in a road cutting on the Newell/Oxley Highway (31.27°S 149.00°E)(Appendix 1).

Figure 7.1
Warrumbungle and Ebor Volcanic Provinces showing sample localities

The Ebor Volcanic Province forms an arcuate highland, the Dorrigo plateau, in the New England region of northern New South Wales (Figure 7.1), and lies mid-way between the coastal township of Coffs Harbour and the large inland town of Armidale. The settlements of Dorrigo and Ebor sit atop Ebor Volcano. The sample site is west of Dorrigo (30.19°S 152.41°E).
7.2 CONTEMPORARY CLIMATE

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<th>WFT10 DORRIGO EBOR</th>
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</tbody>
</table>

|                       |                                  |                                    |                   |
| TEMPERATURE (°C)      |                                  |                                    |                   |
| ANNUAL MEAN TEMPERATURE | 15.06                        | 16.36                              | 11.86             |
| MAXIMUM TEMPERATURE WARMEST MONTH | 30.30                  | 31.87                              | 23.67             |
| MINIMUM TEMPERATURE COLDEST MONTH | -0.02                    | 0.81                               | -0.29             |
| ANNUAL TEMPERATURE RANGE | 30.32                        | 31.06                              | 23.96             |
| SEASONALITY OF TEMPERATURE | 38.74                       | 36.81                              | 39.87             |
| MEAN TEMPERATURE WETTEST QUARTER | 22.14                     | 23.64                              | 17.44             |
| MEAN TEMPERATURE DRIEST QUARTER | 11.47                    | 16.61                              | 9.09              |

|                       |                                  |                                    |                   |
| PRECIPITATION (mm)    |                                  |                                    |                   |
| ANNUAL PRECIPITATION  | 590.42                         | 620.74                             | 875.85            |
| PRECIPITATION WETTEST MONTH | 79.24                     | 73.72                              | 105.49            |
| PRECIPITATION DRIEST MONTH | 33.58                     | 39.81                              | 45.86             |
| RANGE OF PRECIPITATION | 45.67                        | 33.91                              | 59.64             |
| SEASONALITY OF PRECIPITATION | 28.06                     | 18.10                              | 25.86             |
| PRECIPITATION WETTEST QUARTER | 207.45                    | 192.18                             | 289.22            |
| PRECIPITATION DRIEST QUARTER | 116.24                    | 131.73                             | 161.88            |

Table 7.1

Contemporary climate information for the Warrumbungle and Ebor sample localities (BIOCLIM)

Although all three localities receive similar incident radiation, the Warrumbungles localities are further inland and so average slightly higher air temperatures, and are slightly drier than the Ebor locality. Winter temperatures are equally cool at all three localities.

7.3 PALEOCLIMATE AND VEGETATION

The Miocene (~16 Ma) flora and pollen assemblages from Chalk Mountain, Warrumbungles Volcanic Province, suggest that this area supported a rainforest cover, with drier area species less abundant (Holmes et al. 1983), and this is compatible with the high rainfall in this area (Kemp 1978) at that time. This was followed by generally cooler climates and increasingly drier conditions (Stein & Robert 1986).

Two subsequent periods of slight warming probably occurred, one in the early Late Miocene and another in the Early Pliocene. These periods coincide with oceanic warming.
which correlates with glacial melting in polar regions, and hence slightly warmer terrestrial climates. In addition these warmer times may have been periods of greater precipitation (Kennett & von der Borch 1986).

The Quaternary was dominated by fluctuating glacial-interglacial events and variable temperatures (Williams et al. 1991, Chappell & Grindrod 1981, Williams et al. 1993).

Pollen and macrofossils (ferns) from a succession of sub-basaltic sediments in the Dorrigo region, Ebor Volcanic Province, give an early Miocene age (Hill 1987a, Sluiter 1987), which is consistent with the age of the Ebor basalts. Palynology indicates that a moist, swampy environment prevailed at that time (Sluiter 1987).

Farther inland pollen and macrofossils (ferns) within diatomite deposits in the Main Range (Stevens 1970, Beckmann & Stevens 1978, Johnson et al. 1989) are derived from Early Miocene flora (Dudgeon 1982). Two different forest assemblages have been identified in this area, one with abundant rainforest species and only a few open forest forms and the other an open eucalypt-type forest. Nutrient deficiency rather than climate control is probably responsible for the diversity of the two ecosystems, as the closed forest developed on rich basaltic soil, whereas the open forest grew on nutrient poor, well drained, sandstone soils.

The presence of the rainforest community suggests that the climate may have been more humid than at present. The structure and general composition of forests in this region have remained much the same since the Miocene (Stover and Partridge 1973, Martin 1973, Kemp 1978, Dudgeon 1982) although the distributions have changed.

Basalts overlying the diatomites are deeply weathered suggesting that the climate changed from stable to seasonal in the Mid- to Late Miocene.

7.4 GEOLOGY - WARRUMBUNGLES VOLCANIC PROVINCE

Warrumbungles Volcano is a deeply dissected continental alkaline shield volcano of Middle Miocene age (17 Ma to 13 Ma) (Dulhunty & McDougall 1966, McDougall & Wilkinson 1967, Dulhunty 1973, Wellman & McDougall 1974). The central part of the shield is dominated by a trachytic complex (Duggan 1988) which erupted through, and intruded trachytic pyroclastics, around 16 Ma and 15 Ma (McDougall & Wilkinson 1967, Wellman & McDougall 1974). Quartzose Pilliga Sandstone crops out near the central complex and is tilted indicating that there has been some updoming of the basement (Wellman 1986, Johnson et al. 1989). The felsic, central complex is surrounded by relicts of a thin outer apron of predominantly mafic lavas. Hawaiiite basalt and mugearite
are the most common mafic rock types especially to the north and south of the shield with some rare alkali basalt and benmoreite (Duggan et al. 1993).

The large shield volcano may have risen up to 1,000 m above surrounding basement (Wellman 1986) and covered an area in of almost 2,000 km² (Duggan et al. 1993). It has subsequently been dissected by a well developed radial drainage system, with resistant plugs, domes and dykes in the central complex forming spectacular peaks. Outliers of layered lava sequences with intercalated pyroclastics and lacustrine sediments occur in areas that would formerly have been the outer flanks of the volcano.

Newell/Oxley Highway

A thin plateau covering sequence of hawaiite and mugearite extends southward from the flanks of the Warrumbungle shield (Duggan et al. 1993). These basalts have been dated at two localities approximately 16 kilometers apart on the Oxley Highway between Coonabarabran and Gilgandra, at 13.8 Ma ± 0.3 Ma and 13.5 Ma ± 0.4 Ma (Dulhunty & McDougall 1966). Flows in the Castlereagh River Valley, south of the Warrumbungles are Middle Miocene (14.5 Ma and 17 Ma) in age, and are considered co-extrusive with the Warrumbungle shield volcano basalt flows that crop out along the Newell/Oxley Highway (Dulhunty 1973).

Chalk Mountain

Deposits of lacustrine sediments are preserved on the outer flanks of the volcano, in many cases an artifact of basalt lava flows damming water courses. At Chalk Mountain, north of the central complex of Warrumbungles, the diatomite deposits are underlain and capped by hawaiite flows. The lacustrine sediments are rich in fish, insect, bird and plant fossils (Johnson et al. 1989).

7.5 NEWELL/OXLEY HIGHWAY, WARRUMBUNGLES VOLCANIC PROVINCE

7.5.1 Nature of the Exposure

The sampled road cutting on the Newell/Oxley Highway is located at the crest of a rise and exposes a section through three flows (Figure 7.2, Plate 7.1, Appendix 1). The lowermost rock type at this site is a slightly to moderately weathered highly vesicular basalt (WFT4/1) which is cross-cut by chalky-textured veins and veinlets of calcium carbonate (WFT4/2). The upper part of this basalt is formed by rubbly red scoriaceous material (WFT4/3), a flow top breccia. Because of its higher porosity, which facilitates
greater fluid percolation, the scoriaceous basalt is more pervasively weathered than the underlying vesicular basalt.

**Figure 7.2**

Sample points in the Newell/Oxley Highway profile, Warrumbungle Volcanic Province.

**Plate 7.1**

Newell/Oxley Highway profile
Chapter 7: Basalt Weathering Profiles from Northern New South Wales

This sequence is overlain by a more massive weathered basalt which shows well defined onionskin weathering, surrounding indurated corestones of various sizes. Some large basalt blocks, in excess of 1 metre in diameter, are preserved between joint planes, with spheroidally weathered basalt between blocks, but most corestones are in the order of 15 to 20 cm in diameter. In the field, the basalt of the larger blocks (WFT4/5) appears only incipiently weathered, compared to the smaller weathered corestones (WFT4/4). In the upper part of this zone the onionskins grade into rubbly weathered vesicular basalt (WFT4/6), and this in turn grades into a less vesicular, orange-grey rubbly weathered basalt (WFT4/7).

Overlying the middle basalt there is a layer 1 to 2 m thick of white, fine grained, feldspar rich trachytic ash (WFT4/8).

The uppermost basalt sequence is represented by an intensely weathered basalt with moderately weathered corestones (WFT4/9). The corestones are quite small, usually less than 10 to 15 cm in diameter. The intensely weathered onionskin material from above and below the white trachytic ash is difficult to tell apart, and in places, where the ash layer pinches out or is obscured, the basalts appear continuous. The spheroidally weathered upper basalt grades into a dark yellowish brown soil (WFT4/10).

### 7.5.2 Geochemistry

For the basalt samples (WFT4/1, WFT4/3, WFT4/4, WFT4/5, WFT4/6, WFT4/7, WFT4/9) the isocons are best fit lines through the representative points (Y, Nb, Zr) Al and Ti, which are believed to be the least mobile elements. The fresh basalt used for isocon construction is hawaiite from the Warrumbungle Volcanic Province (sample number EAV30, Appendix 2).

The slopes \( \frac{C_i^W}{C_i^O} \) of the isocon lines reflect the progressive increase in mass loss (\( \Delta M \)) and hence increase in intensity of weathering of the basalt samples outward from corestones and upward through the profile.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Sample</th>
<th>( C_i^W/C_i^O )</th>
<th>( \Delta M )</th>
</tr>
</thead>
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<tr>
<td>Upper</td>
<td>WFT4/9:</td>
<td>( C_i^W/C_i^O = 1.31 )</td>
<td>( \Delta M = -24 % )</td>
</tr>
<tr>
<td></td>
<td>WFT4/7:</td>
<td>( C_i^W/C_i^O = 1.36 )</td>
<td>( \Delta M = -26 % )</td>
</tr>
<tr>
<td></td>
<td>WFT4/6:</td>
<td>( C_i^W/C_i^O = 1.15 )</td>
<td>( \Delta M = -13 % )</td>
</tr>
<tr>
<td></td>
<td>WFT4/4:</td>
<td>( C_i^W/C_i^O = 1.03 )</td>
<td>( \Delta M = -03 % )</td>
</tr>
<tr>
<td></td>
<td>WFT4/5:</td>
<td>( C_i^W/C_i^O = 1.01 )</td>
<td>( \Delta M = -01 % )</td>
</tr>
<tr>
<td>Middle</td>
<td>WFT4/3:</td>
<td>( C_i^W/C_i^O = 1.24 )</td>
<td>( \Delta M = -19 % )</td>
</tr>
<tr>
<td></td>
<td>WFT4/1:</td>
<td>( C_i^W/C_i^O = 1.08 )</td>
<td>( \Delta M = -07 % )</td>
</tr>
<tr>
<td>Lower</td>
<td>WFT4/7:</td>
<td>( C_i^W/C_i^O = 1.36 )</td>
<td>( \Delta M = -26 % )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>( C_i^W/C_i^O )</th>
<th>( \Delta M )</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>WFT4/7:</td>
<td>( C_i^W/C_i^O = 1.36 )</td>
<td>( \Delta M = -26 % )</td>
<td>↑</td>
</tr>
<tr>
<td>WFT4/6:</td>
<td>( C_i^W/C_i^O = 1.15 )</td>
<td>( \Delta M = -13 % )</td>
<td>INCREASE IN</td>
</tr>
<tr>
<td>WFT4/4:</td>
<td>( C_i^W/C_i^O = 1.03 )</td>
<td>( \Delta M = -03 % )</td>
<td>DEGREE OF</td>
</tr>
<tr>
<td>WFT4/5:</td>
<td>( C_i^W/C_i^O = 1.01 )</td>
<td>( \Delta M = -01 % )</td>
<td>WEATHERING</td>
</tr>
<tr>
<td>WFT4/3:</td>
<td>( C_i^W/C_i^O = 1.24 )</td>
<td>( \Delta M = -19 % )</td>
<td></td>
</tr>
<tr>
<td>WFT4/1:</td>
<td>( C_i^W/C_i^O = 1.08 )</td>
<td>( \Delta M = -07 % )</td>
<td>↑</td>
</tr>
</tbody>
</table>
Lower Basalt

Fe (total), Zn and P plot very close to the isocon throughout weathering. La, Ce, Cu, V, Si and Na show a slight depletion. Ba, Cr, Ni, Mg, Mn and Ca all become notably more depleted with weathering. K, Rb, Pb, Th and Sr show major depletion (Figure 7.3).

Middle Basalt

Fe (total) shows slight enrichment but lies close to the isocon. V, Cu, P and Zn are moderately enriched with weathering, but there is a drop in V, Cu, P and, to a lesser extent, Zn concentrations, in the most weathered sample. Si is depleted progressively during weathering.

La, Ce, Ba, Ni, Mg, Ca and Rb show an early moderate depletion in the least weathered samples, followed by slower, progressive depletion with weathering, but Mn, Na and Sr show depletion commencing a little later. Cr, Th and K show major depletion in moderately weathered samples, but with increase in degree of weathering, Cr becomes
slightly enriched, while Th and K continue to be removed at a slower rate. Pb shows a
similar pattern to Th and K, but is extremely enriched in the most weathered sample. S is
depleted during weathering (Figure 7.4).

*Upper Basalt*

Ba is extremely enriched in the sample from the upper flow. Fe (total), P, Zn, V and Mn
plot adjacent to the isocon. Si, Na and Sr show moderate depletion, Pb, La, Ce, Th, Cu,
K, Rb and Ca show major depletion and Cr, Ni and Mg extreme depletion from this
sample.
Figure 7.4

Isocon diagrams and corresponding histograms for WFT4/4, WFT4/5, WFT4/6, WFT4/7 and WFT4/9. Histograms show relative mass change (%) for analysed elements.
Figure 7.5

Lower Basalt

Sample WFT4/1 from the base of the lowermost flow is moderately weathered but peaks for primary plagioclase feldspar are observed in the XRD trace (Figure 7.5). All of the primary ferromagnesian silicate minerals appear to have been completely altered as peaks for them do not occur on the trace. Minor peaks are present for magnetite and possibly
ilmenite. Dioctahedral smectite clay is the most abundant secondary product. Because the clay separate has a relatively high Fe concentration, nontronite is the most abundant smectite with lesser amounts of Al-smectite. Minor amounts of goethite are also present. The cation exchange capacity (CEC) for the clay separate is 69 meq/100 g which is relatively high and in keeping with a clay assemblage dominated by smectite, as is the Si:Al ratio of 2.69. Two vesicle fill materials were analysed for this sample. Both were identified as dioctahedral smectite, predominantly nontronite with some Al-smectite present.

Veins of white chalky calcite (WFT4/2) cross-cut this weathered basalt. Resinous green dioctahedral smectite (XRD) infills small voids in the carbonate vein likely to be a mixture of nontronite and Al-smectite based on the Al:Si ratio of 2.31 and high Fe in the clay separate. This material had a CEC of 103 meq/100 g which is within the range for smectite clays.

Higher in the same flow the basalt is scoriaceous, red coloured and more intensely weathered (WFT4/3). The XRD trace shows that some relict plagioclase feldspars, as well as magnetite and possibly ilmenite, are preserved. The principal secondary mineral formed is dioctahedral smectite, probably nontronite and some Al-smectite. Some hematite is present and minor goethite. The CEC is 52 meq/100 g, and Si:Al ratio 2.4. Two vesicle fill materials were analysed from this sample. Once again both were found to be smectite. It is unclear from the traces whether these clays are trioctahedral or dioctahedral. The assemblage could therefore be a mixture of saponite, nontronite and Al-smectite clays.

Middle Basalt

The middle flow has blocky massive basalt, that is incipiently weathered (WFT4/5), near its base (Figure 7.5). Peaks for primary minerals are still clearly identifiable in the XRD trace for this sample, and include plagioclase feldspar, pyroxene (augite), ilmenite and magnetite. Incipient weathering has produced a small amount of trioctahedral and dioctahedral smectite. The clay assemblage is most likely a mixture of saponite with minor Fe-saponite, nontronite and Al-smectite. The CEC for this sample is 31 meq/100 g and the Si:Al ratio is 2.49. Some contamination of the clay separate with crushed primary minerals may have occurred in this sample.

A coating has formed on a joint face on this sample, which may formerly have bounded a small vein. The XRD trace for the coating identified it as dioctahedral smectite, probably a mixture of nontronite and Al-smectite. In addition there were peaks for a number of zeolites including thomsonite \([\text{NaCa}_2(\text{Al,Si})_{10}\text{O}_{20}.6\text{H}_2\text{O}]\), natrolite
Chapter 7: Basalt Weathering Profiles from Northern New South Wales 146

[Na2Al2Si3O10.2H2O] and chabazite [Ca2Al4Si8O24.12H2O]. One vesicle fill was analysed for this sample and the XRD trace identified the enclosed minerals as smectite, some relict feldspar and zeolites, an assemblage similar to that coating the joint face.

The smaller weathered basalt corestone, WFT4/4, has an XRD trace with a well developed principal smectite peak, and a limited amount of primary minerals represented, predominantly plagioclase feldspar, ilmenite and magnetite. Minor amounts of pyroxene may occur in the sample and olivine appears to have weathered away. Both trioctahedral and dioctahedral smectite clays are present, including saponite, nontronite and Al-smectite. Secondary iron oxides and oxyhydroxides have been precipitated but do not register significant peaks on the XRD trace. The CEC is 45 meq/100 g for this sample and Si:Al ratio 2.62.

Two successive onionskins were sampled out from the corestone. The minerals represented in these traces are similar to those of the corestone but show the progressive decrease in the amount of plagioclase feldspar and pyroxene, depletion of olivine to the point that it is no longer detectable, persistence of the oxide minerals magnetite and ilmenite, and an increase in the relative proportions of hematite with some goethite. The smectite clays are a mixture of saponite, nontronite and Al-smectite, although the dioctahedral phases are more dominant. An orange clay coating, lining the cracks between successive onionskins, was analysed and found to be smectite.

The rubbly vesicular basalt WFT4/6 shows pervasive alteration of the ferromagnesian silicate minerals from the protolith. Primary minerals still represented in the XRD trace are plagioclase feldspar, magnetite and ilmenite. Pyroxene and olivine have been completely weathered. Secondary minerals include hematite and minor goethite, but are dominated by dioctahedral smectite clays, probably nontronite and Al-smectite, and this is reflected in the high CEC of the clay separate, 53 meq/100 g. The Si:Al ratio is 2.54, which is appropriate for a smectite clay assemblage. Vesicle fill material analysed by XRD was found to be trioctahedral smectite, probably saponite with some Fe-saponite. A dark reddish brown clay coating on this sample had a similar assemblage.

Sampled at the top of the middle flow, the grey weathered vesicular basalt WFT4/7 gave an XRD trace with very few primary minerals represented. These include plagioclase feldspar and Fe-Ti oxides, probably magnetite and ilmenite. The secondary clay formed is dioctahedral smectite, most likely a mixture of nontronite and Al-smectite. The CEC for this sample is 71 meq/100 g and the Si:Al ratio 2.4. In addition some goethite and minor hematite are present. One vesicle fill analysed was found to be smectite, but the distinction between dioctahedral, trioctahedral or a mixture, is uncertain. A coating on
this sample is primarily composed of nontronite clay with some Al-smectite. It also contained very minor amounts of quartz, which may have had an eluvial origin.

**Intercalated Sediment**

Sample WFT4/8 has a different composition to the balance of the profile. This material is formed from clay to silt sized euhedral albite crystals that appear relatively unweathered. The XRD trace shows only very little clay development which confirms the freshness of these feldspars. In addition there is a small amount of quartz present in some samples and this is observed as sand sized grains in hand specimen. Smectite was present lining fractures in the sediment which explains the Si:Al ratio value of 2.26, despite an extremely low CEC, 18 meq/100 g, for this clay separate dominated by fine grained primary feldspar.

This white layer is a trachytic ash horizon. Laminations and other lacustrine sedimentary structures were not apparent in the field, supporting the idea that this is fall material from a trachytic eruption. It is not immediately clear why the basalts above and below this layer are so intensely weathered and the feldspars in this material are not. Sufficient weathering has taken place to remove all evidence of volcanic glass but the feldspars are only incipiently weathered. It seems that the overlying basalt must have been emplaced very shortly after the deposition of the ash, sealing it from the elements. Weathering of the ash horizon would be retarded until the overlying basalt had weathered considerably.

**Upper Basalt**

The moderately weathered corestone WFT4/9, sampled from the flow overlying the trachytic ash material, has a very similar composition to the weathered basalt beneath the ash (Figure 7.5). The primary minerals present, are plagioclase feldspar, magnetite, possibly some titanomagnetite and ilmenite. Primary ferromagnesian minerals, olivine and pyroxene, are not well preserved. Peaks for hematite and goethite occur in the XRD trace, with a mixture of trioctahedral and dioctahedral smectite clays forming the bulk of the secondary products. Fe content is high in the clay separate, so the dominant clay mineral is probably nontronite with a lesser amount of Al-smectite. Some saponite is also present with minor amounts of Fe-saponite. The CEC for the clay separate is 67 meq/100 g and the Si:Al ratio is 2.94, both in keeping with the presence of smectite clays. The high Si:Al ratio suggests that there may be some excess silica present in the clay separate, possibly associated with weathering, but more likely associated with eluviated material.

The first onionskin has an XRD trace similar to the corestone. Peaks for olivine and pyroxene do not occur, plagioclase feldspars are represented but are slightly less
abundant and the Fe-Ti oxides magnetite and ilmenite, persist. Smectite clay abundance increases slightly and hematite and goethite are recognised on the trace. A coating, lining cracks between the onionskins, was identified as smectite.

XRD analysis of the overlying soil WFT4/10 shows that it is smectitic with some relict feldspar incorporated from the weathering profile and some introduced quartz present. The smectite is mostly dioctahedral nontronite with some Al-smectite. The CEC for the clay separate is 67 meq/100 g and Si:Al ratio is 2.05, which both support the presence of smectite clays. The feldspar is plagioclase and most likely derived from the weathered basalts. Quartz is thought to be introduced from elsewhere as this mineral was not apparent in XRD traces from samples lower in the basalt profile.

Summary

The principal secondary weathering products were smectite clays. Primary ferromagnesian silicates breakdown initially to trioctahedral smectites, saponite and Fe-saponite, which then convert to dioctahedral phases nontronite and beidellite. Montmorillonite and beidellite may be formed during the breakdown of plagioclase feldspar but Fe-rich dioctahedral clays are apparently more abundant than montmorillonite. Because ferromagnesian silicate minerals weather readily, Fe is available to be incorporated into nontronite clays, and some Al is present for iron-rich beidellite formation. Ca and Na incorporated into the smectites are probably derived from the breakdown of basaltic glass or plagioclase feldspar.

Secondary Fe-oxyhydroxides, hematite and goethite, are prevalent in the weathered basalts. Goethite is apparently more abundant early in weathering and is produced as soon as olivine commences dissolution. Hematite is formed throughout weathering.

7.5.4 Petrography

Lower Basalt

Plagioclase feldspar laths, disseminated small opaque minerals perhaps ilmenite and clots of slightly larger opaque minerals, probably magnetite, are the only primary phases preserved in WFT4/1. There does not appear to have been a ferromagnesian phenocryst phase in this basalt. The pockets of secondary clays between feldspar laths were most likely originally groundmass ferromagnesian silicate minerals and/or glass. Vesicles are lined with clays and these have been stained with secondary iron oxyhydroxides. In WFT4/1 this staining is bright yellow in colour, implying that goethite is present (Plate 7.2, Plate 7.3).
Plate 7.2
WFT4/l (crossed polars)
Etched groundmass plagioclase feldspar laths with interstitial fine grained angular opaque oxides and clays

Plate 7.3
WFT4/l (plane polarised light)
Voids are lines with goethite stained clays

Plate 7.4
WFT4/3 (crossed polars)
Groundmass phases pervasively weathered to hematite stained clays

Plate 7.5
WFT4/3 (crossed polars)
Voids are infilled with a mixture of Fe oxyhydroxides, predominantly goethite, and clays
Plate 7.6
WFT4/5 (crossed polars)
Titanaugite forms a subophitic texture with groundmass plagioclase laths.

Plate 7.7
WFT4/4 (crossed polars)
Groundmass ferromagnesian silicate and basaltic glass weather to Fe oxyhydroxides and clays

Plate 7.8
WFT4/6 (crossed polars)
Secondary products proximal to vesicles contain hematite. Void fill materials are goethite rich

Plate 7.9
WFT4/7 (crossed polars)
The basalt is pervasively weathered to clays but the primary texture is largely preserved
WFT4/3 is noticeably more iron oxide stained with a strong red (hematite) colouration. Fine grained, primary Fe-Ti oxides are disseminated throughout the groundmass, but have irregular shapes suggesting that dissolution of these phases may have commenced. Some relict plagioclase laths can be recognised but the groundmass has almost entirely been altered to secondary clays and iron oxides. Despite this fact the primary basalt texture is still preserved and the vesicles largely maintain sub-spherical shapes. Once again vesicles show clay linings with some goethite (yellow) and hematite (red) present. The clays are fine grained and form botryoidal or mamillary coatings on the vesicle walls, which may also partially infill the vesicles. The clay linings are cracked and have started to curl and this may in part be responsible for the rounded shapes observed in thin section (Plate 7.4, 7.5).

**Middle Basalt**

In WFT4/5 quite a large amount of clinopyroxene (titanaugite - pink pleochroic) is preserved although many of the relict crystals are surrounded by clay minerals that show interference colours, probably saponite or Fe saponite. There is no olivine or glass preserved and it appears that these are entirely weathered to secondary clays and iron oxyhydroxides. Plagioclase feldspar is abundant but all laths are etched. Almost all of the clays show considerable iron staining, apparent in both plane polarised light and under crossed-nicols. The opaque oxides show sharp grain boundaries and many preserve the shape of the space between plagioclase laths that they originally infilled, but now the plagioclase is mostly weathered away. Where opaques have had room to grow they show rhombic and pseudohexagonal shapes (Plate 7.6).

The onionskin material from the smaller weathered corestone WFT4/4 shows titanaugite forming rare relict cores amidst secondary products (Plate 4.7). The plagioclase feldspar laths are more intensely weathered than in WFT4/5, but the primary magnetite and ilmenite grains preserve their original inter-lath, shapes and appear to be considerably more resistant than the silicate minerals. Dull brown secondary clays infill spaces between relict crystals, and in many places are iron oxide stained. Secondary Fe-oxyhydroxides, mostly hematite, have precipitated in localised zones, around veinlets and cracks and in pockets in the groundmass, associated with clays. This has led to an orange colouration of the onionskin material in handspecimen.

WFT4/6 is vesicular and the formation of secondary products appears to be more advanced close to the vesicles, indicating that they may form interlocking zones through which fluids may flow. The only primary minerals preserved in this sample are abundant relict plagioclase feldspar laths and disseminated resistant Fe,Ti-oxides. Brown clays, possibly nontronite or Al-smectite, are ubiquitous throughout the sample and secondary
iron oxides are present in localised areas, possibly the former sites of ferromagnesian silicates. Greater concentrations of hematite occur along micro-fractures in the basalt, and surrounding vesicles (Figure 7.8).

Upper Basalt.
The uppermost basalt is pervasively weathered to clay, with primary Fe,Ti-oxides, and fine grained, almost completely weathered plagioclase laths, the only remaining primary minerals. Some of the primary magnetite and ilmenite is starting to etch in this sample. Overall the section is dark coloured because of the abundance of brown clays, and the colouration caused by fine grained secondary Fe-oxides (hematite) and Fe-oxyhydroxides (goethite) disseminated throughout the sample. The texture of the parent basalt is largely preserved (Figure 4.9).

7.5.5 Profile Summary

In the lower basalt, increase in weathering up-profile reflects the greater ease of fluid percolation through the rubbly, more vesicular materials near the top of the flows. This is supported by the observation in thin section that there is greater development of secondary weathering products adjacent to vesicles. There can therefore be a greater intensity of weathering in layers that have a high interlocking porosity and hence high permeability, allowing enhanced fluid flow. The broad increase in intensity of weathering up profile occurs because most of the water introduced to this profile is rainwater which filters downward from the land surface. All lavas are more weathered away from corestones as there is preferred fluid percolation down cracks and joints in the basalt, between the corestones.

Secondary veins, infilled with Ca(Mg) carbonate and minor smectite clays, crosscut the basalt in places. This is in keeping with bicarbonate rich fluids percolating through the joints in the basalts, ultimately sealing themselves by precipitating carbonate material. Bicarbonate is a by-product of hydrolysis reactions during the weathering of basaltic minerals and the cations, principally Ca and Mg, are removed during these same reactions. These processes are discussed further in Chapter 11.
7.6 CHALK MOUNTAIN, WARRUMBUNGLES VOLCANIC PROVINCE

7.6.1 Nature of the Exposure

![Diagram showing sample points in the Chalk Mountain profile, Warrumbungle Volcanic Province.]

**Figure 7.6**
Sample points in the Chalk Mountain profile, Warrumbungle Volcanic Province.

**Plate 7.10**
Chalk Mountain profile - dotted lines show profile level
The basalt at this locality sits high in the topography, capping a thick diatomite deposit (Figure 7.6, Plate 7.10, Appendix 1). Two basalts overly buried paleosols that appear to be derived from a mixture of basaltic pyroclastic material and quartzofeldspathic sediment. The upper flow is an extremely fresh hawaiite (WFT2 1/1), and immediately underlying it is a more weathered basalt, showing well developed spheroidal weathering. In places the zone of corestones (WFT2/8, WFT2/7) grades down into grey vesicular basalt (WFT2/6). This in turn overlies two layers of extremely weathered material, an upper black soil (WFT2/5) and a lower red soil (WFT2/4). Beneath this is a sandy layer (WFT2/0) underlain by a thick sequence of lacustrine sediments, largely comprised of diatomite. The latter have been commercially exploited at this locality.

### 7.6.2 Geochemistry

For the basalt samples (WFT2 1/1, WFT2/6, WFT2/7) the isocons are best fit lines through the representative points \( Y \), Al and Ti, are believed to be the least mobile elements. The fresh basalt used for isocon construction is hawaiite from the Warrumbungle Volcanic Province (sample number EAV30, Appendix 2).

The slopes \( C_i^{W/C_i^O} \) of the isocon lines reflect the progressive increase in mass loss \( \Delta M \) and hence increase in intensity of weathering of the basalt samples outward from corestones. This is most clearly observed in the middle flow at this locality.

| Upper  | WFT2 1/1: \( C_i^{W/C_i^O} = 1.00 \) \( \Delta M = 0\% \) |
| Middle | WFT2/6: \( C_i^{W/C_i^O} = 1.45 \) \( \Delta M = -31\% \) |
|        | WFT2/7: \( C_i^{W/C_i^O} = 1.10 \) \( \Delta M = -9\% \) WEATHERING |
| Buried | WFT2/5: COMPLETELY WEATHERED |
| Paleo | WFT2/4: COMPLETELY WEATHERED |

**Middle Basalt**

Mn and V are enriched in the moderately weathered corestone material, WFT2/7, but as weathering proceeds both are removed from the profile. V maintains a slight enrichment in the more weathered basalt, WFT2/6. Fe (total) and Zn show slight enrichment early in weathering but, while the total Fe concentration diminishes with increased weathering, Zn is further enriched. Y and Ce are enriched with weathering Y is generally considered relatively immobile so this enrichment is unusual. P plots close to the isocon (Figure 7.7).
Na, Ba, Cu, and Ca show an early moderate depletion and continue to be progressively lost from the weathering basalt. La, Si and Rb are depleted at a much slower rate, after initial moderate depletion. Pb, Th, Nb, Zr and K show major depletion in the least weathered samples, but thereafter are released more slowly. The depletion of the normally relatively immobile elements Nb and Zr is unusual. Mg and Sr show major depletion and continue to be progressively weathered from the basalt, while Cr and Ni are almost completely lost from all weathered samples (Figure 7.7).

**Upper Basalt**

The isocon for this basalt lies within error of the 1:1 line for fresh rock (Figure 7.8). The histogram shows that most elements are depleted in this incipiently weathered rock. There is minor concentration of Fe (total) reflecting the early fixation of Fe$^{3+}$ in the outer rind of the sample, and at the same time, slight enrichment in Cu, V and Al takes place. The most noticeable enrichment is that of Rb.
7.6.3 Clay Mineralogy

Buried Paleosols

The red soil-like layer, WFT2/4, which overlies quartzose sediments, is composed of smectite, a kaolin group mineral, possibly halloysite, and minor quartz (Figure 7.9). There is some elevation of the trace between the halloysite peak and the broad smectite peak, implying that this layer contains halloysite-smectite interstratified clays. The CEC for the clay separate is 40 meq/100 g, which is in the range for smectite clays, and is too high to be accounted for by kaolin group clays alone. The Si:Al ratio is 1.26, which is intermediate between the values expected for kaolin group, and smectite clays.

The dark coloured extremely weathered material WFT2/5 that overlies the red clay-rich layer, has an unusual XRD trace with an elevated plateau around the principal smectite peak region (17 Å) and a 10 Å peak. This pattern suggests that this material is largely composed of halloysite-smectite interstratified clays. The CEC for this material is 34 meq/100 g and the Si:Al ratio is 1.23, and both values support the presence of halloysite-smectite interlayer clays. A best-fit comparison with NEWMOD (Reynolds 1985) kaolinite - dioctahedral (Fe) smectite, suggests that kaolin group clay would account for approximately 70-80%, and smectite 20-30%, of the interstratified clay. The white mineral present throughout the profile in cracks forming a network within the the black material, was found to be chabazite, Ca$_2$Al$_4$Si$_4$O$_{24}.12$H$_2$O, a zeolite mineral.

The mineralogy of these two clay-rich layers suggests that they represent basaltic material that has been intensely weathered to the point where the primary rock texture is no longer
Chapter 7: Basalt Weathering Profiles from Northern New South Wales 157

preserved. These layers are much more weathered than the overlying basalt (WFT2/6, WFT2/7, WFT2/8), and apparently predate it (Figure 7.9). Although these weathered horizons do not appear to have formed on the underlying quartz and kaolin rich sediments, quartz is incorporated in them.

Middle Basalt

The XRD trace for the corestone WFT2/8 incorporates peaks for plagioclase feldspar, very minor amounts of pyroxene (augite), olivine, and magnetite with some ilmenite. The secondary minerals hematite and goethite are represented but some of their peaks are partially obscured by the peaks of primary minerals. A mixture of trioctahedral and dioctahedral smectite clays make up the bulk of the secondary products and are dominated by nontronite, saponite, and possibly Fe-saponite, as both Fe and Mg contents are high in the clay separate. Lesser amounts of Al-smectite probably occur with the nontronite (Figure 7.9). The CEC for the clay separate is 47 meq/100 g and the Si:Al ratio is 3.04. The high Si:Al ratio may be attributed to the presence of crushed primary silicates in the clay separate of this slightly weathered basalt.

Four onionskin layers were analysed out from this corestone. Essentially the XRD traces look the same, however, olivine and pyroxene are progressively lost, and secondary iron oxyhydroxides are more clearly defined.

Figure 7.9
Stacked X-ray diffraction (XRD) traces for samples WFT2/4, WFT2/5, WFT2/7 and WFT2/6.
Chapter 7: Basalt Weathering Profiles from Northern New South Wales

The XRD trace for WFT2/7 is dominated by peaks for plagioclase feldspar, magnetite and ilmenite. Pyroxene is represented in the trace but not in large proportions, and peaks for olivine were absent. The smectite assemblage is a mixture of saponite, possibly Fe-saponite and nontronite with lesser amounts of Al-smectite. The weathered basalt layers surrounding this corestone showed the same trends observed for WFT2/8. The cation exchange capacity (CEC) for this sample is 30 meq/100 g and the Si:Al ratio is 2.90. Again crushed primary silicates in the clay separate are probably elevating this value.

WFT2/6 has an XRD trace with peaks for only a few primary minerals. These include plagioclase feldspar, magnetite and ilmenite. Olivine and pyroxene are completely weathered away as peaks do not appear on the trace. Secondary hematite and goethite occur in small amounts, but the most abundant secondary minerals are the smectite clays. The clay assemblage for this sample is mostly dioctahedral smectite, dominated by nontronite, as Fe is high in the clay separate, with some Al-smectite. The CEC of this intensely weathered basalt is 61 meq/100 g which is in the range for smectite clays. The Si:Al ratio for this sample is 1.95 which is in keeping with smectite clays dominating the assemblage. Vesicle fill material analysed for this sample was identified as smectite.

Upper Basalt

The upper basalt WFT2 1/1 is relatively fresh with the earliest processes of weathering, for example the incipient weathering of olivine to iddingsite, and devitrification of pockets of glass in the groundmass, commencing. The primary minerals represented in the X-ray diffraction (XRD) trace include plagioclase feldspar, pyroxene (augite), olivine, and Fe,Ti-oxides, probably magnetite and ilmenite. There are no clays or secondary iron oxides or hydroxides evident on the trace at all.

Summary

Buried Paleosols

The buried paleosols were weathered to smectitic clays, hematite and minor goethite. Subsequent weathering has enhanced the breakdown of smectite clays to kaolin group clays, and as a consequence interstratified halloysite-smectites have formed as intermediate products in the breakdown.

The presence of zeolite minerals in a network of cracks cross-cutting the black coloured weathered basalt layer, near the exposure face, may be associated with seasonal drying of the profile. This drying causes cracking and enhances the precipitation of zeolites as pore
fluids are progressively evaporated and ions therein are concentrated. The percolating fluids would be alkaline, under these circumstances.

**Middle Basalt**

The dominant secondary products in the middle basalt are smectite clays with hematite and goethite. The trioctahedral clays, saponite and Fe-saponite, are formed as the first weathering products when olivine and pyroxene breakdown. These clays are subsequently converted to dioctahedral clays, nontronite and Al-smectite, with increased removal of ions. Goethite is also formed early in the weathering of ferromagnesian minerals, especially olivine, but may be dehydrated to hematite if the profile dries out. Hematite is also produced directly as a product of the breakdown of ferromagnesian silicates.

Trioctahedral clays are more apparent in the XRD traces for this basalts than for the basalts analysed from WFT4. This is because the lava at this locality is more porphyritic lava than the lava considered from the Newell/Oxley Highway. For example, if a weathered olivine phenocryst has a relict olivine core, surrounded by saponite which in turn is surrounded by nontronite and Al-smectite, the trioctahedral smectite is preserved for longer than in the WFT4 localities where the olivines are smaller to start with and the conversion of trioctahedral to dioctahedral clays takes place more rapidly.

Plagioclase feldspar weathers along defects and zones of weakness in its structure. Although weathering commences earlier in plagioclase feldspar than pyroxene, the pyroxene is wholly weathered before the plagioclase is. This suggests that the rate of weathering of feldspar is slower than for pyroxene.

Plagioclase feldspar may weather to the dioctahedral smectite clay montmorillonite, but montmorillonite is not a dominant phase on the XRD trace for these samples. It is possible that ions released during the weathering of ferromagnesian silicates, especially iron, are incorporated in the smectites produced during the breakdown of plagioclase feldspar, resulting the production of a more nontronite-like smectite. Overall there is less Al available in basaltic rocks than, for example, in granitic rocks, for the formation of Al, Mg rich smectites like montmorillonite. However, Al-smectite may be present as a minor phase associated with nontronite.
7.6.4 Petrography

Middle Basalt

This basalt is porphyritic with plagioclase feldspar (albite-oligoclase) An7-30 as the principal phenocryst phase and lesser amounts of Fe-Ti oxides, olivine and clinopyroxene (augite), in a plagioclase-phyric groundmass. Corestone materials (WFT2/7, WFT2/8) are moderately weathered with groundmass olivine completely lost, scattered tiny grains of pyroxene almost entirely weathered away and basaltic glass completely devitrified to secondary clays. Groundmass plagioclase feldspars maintain lath shapes, but twinning cannot be clearly resolved on many grains because they are chemically etched. Groundmass plagioclase feldspar is considerably more weathered than phenocryst plagioclase feldspar.

Phenocryst phases show distinct effects of weathering with olivine almost totally weathered to secondary smectite clays, mostly nontronite and Al-smectite but with some saponite close to the relict olivine cores (Plate 7.14). The plagioclase feldspar phenocrysts show preferential dissolution along micro-fractures, twin planes and zone boundaries, but are not as pervasively weathered as the olivine phenocrysts (Plate 7.13). Pyroxene phenocrysts are not as common and appear to be relatively resistant to weathering initially, compared to the plagioclase feldspar and olivine. Large rhombic and pseudohexagonal Fe-Ti oxides maintain their euhedral shape and do not appear to be etched during the initial stages of weathering (Plate 7.11).

Accessory phases enclosed within phenocrysts include Fe-Ti oxides, most commonly associated with the ferromagnesian silicates, but also enclosed in plagioclase feldspars. Rare very fine grained, rod shaped, apatite crystals were observed within plagioclase feldspars along with occasional small dark rings which may be pleochroic haloes associated with zircon grains.

Brown-yellow (goethite) stained clays replace basaltic glass in less weathered portions of the sample, reflecting an early phase in weathering. Concentrations of secondary Fe-oxyhydroxides are associated with the breakdown of olivine or pyroxene, or with cross-cutting veinlets (Plate 7.12).

The more intensely weathered sample, WFT2/6, has only strongly etched plagioclase feldspar laths, and fine grained, disseminated Fe-Ti oxide grains as primary phases in the groundmass (Plate 7.15, 7.16). Clays are more widely distributed throughout, probably associated with the more advanced weathering of the plagioclase feldspars. In addition to
Plate 7.11
WFT2/7 (crossed polars)
Pseudohexagonal opaque microphenocrysts show little evidence of weathering

Plate 7.12
WFT2/7 (crossed polars)
Concentrations of secondary Fe oxyhydroxides are associated with crossed-cutting microfractures

Plate 7.13
WFT2/8 (crossed polars)
Plagioclase phenocrysts show preferential dissolution along microfractures, twin planes and zone boundaries

Plate 7.14
WFT2/8 (crossed polars)
Olivine phenocrysts pervasively weathered to nontronite and beidellite with saponite close to relict cores
Plate 7.15
WFT2/6 (crossed polars)
Secondary weathering of groundmass phases to Fe oxides amidst etched feldspar laths

Plate 7.16
WFT2/6 (crossed polars)
Plagioclase feldspar phenocryst are strongly etched and may be weathered around rims

Plate 7.17
WFT2 1/1 (crossed polars)
Relatively fresh porphyritic hawaiite with incipiently weathered olivine and pristine plagioclase feldspar

Plate 7.18
WFT2 1/1 (crossed polars)
Angular opaque oxides occupy inter-lath spaces. Olivine weathering to smectite clays and goethite
localised concentrations secondary Fe-oxides (hematite) are distributed throughout the sample imparting a dark colouration to the section.

Phenocryst phases are more intensely weathered with olivine and pyroxene completely lost, plagioclase feldspars showing intense dissolution around their edges, and deeply carved etch marks on feldspar surfaces. These etched zones follow former microfractures, and twin planes. One large primary opaque oxide phenocryst shows dissolution along a crack in the grain, and is breaking down to hematite, indicated by red colouration.

**Upper Basalt**

The uppermost, relatively fresh basalt (WFT2 1/1) at this locality is a hawaiite. Large clinopyroxenes (titanaugite) form an ophitic texture with groundmass plagioclase laths. The dominant phenocryst phase is plagioclase feldspar An7-30 with complex multiple twinning and zoning. Olivine phenocrysts show irregular fracture and incipient alteration to smectite clays and goethite has commenced along these cracks. Glass occupies only very small spaces between laths in the feldspar-phric groundmass, while ferromagnesian silicates, magnetite and ilmenite are abundant and are distributed throughout (Figure 7.17, 7.18).

### 7.6.5 Profile Summary

This outcrop reflects episodic emplacement of basaltic eruptives, with at least four layers represented. The lower two layers are now wholly weathered to secondary weathering products, dominated by halloysite-smectite clays, and it is difficult to distinguish whether these materials were originally lavas or pyroclastic in origin. The layers are in the order of 1.5 m thick and, if allowance is made for compaction during weathering, a considerable thickness of scoriaceous material would be required to form them. This locality is on the flanks of the shield, some distance from the eruptive centre so the build up of a thickness of pyroclastic material is unlikely by primary processes alone. It is possible that these soils are developed on aeolian material that was derived from both quartzofeldspathic and basaltic sources. The quartz in these samples precludes them being derived from flow basalts despite their burial beneath multiple thin lava flows forming a veneer over the landscape, in this locality.

In the Main Range, Dudgeon (1982) has described a deep weathering profile on basalts that overly early Miocene diatomite sequences and attributes this weathering to a change from a relatively constant equable, humid paleoclimate, to a more seasonal paleoclimate later in the Miocene. At Chalk Mountain, the lower basalts also overlie early Miocene
The middle basalt shows well developed spheroidal weathering which is characteristic for lavas that have been weathered as a result of percolation of water through cracks and joints in the basalt. The base of this basalt is a little more weathered because it is vesicular, and interlocking vesicles make it more permeable. In addition, weathering fluids may have found the underlying clay-rich layer relatively impermeable, and ponded near the base of the flow. The precipitation of zeolite phases provides some evidence for the percolation of alkaline fluids in this profile. This may explain why Nb and Zr have shown some mobility, when generally they are considered relatively immobile.

The overlying hawaiite lava is approximately 5 m thick, and is incipiently weathered at the base, where it was sampled.

7.7 GEOLOGY - EBOR VOLCANIC CENTRE

The Ebor Volcano has been severely eroded on its southern and eastern sides, forming steep cliffs which bound the arcuate Dorrigo Plateau to the west. The shield had an original height above basement of around 500 to 600 m (Johnson et al. 1989). Headward erosion by the rivers on the seaward side of the volcano have exposed a sequence of thick flows (Ollier, 1982). There is a well developed radial drainage pattern on the remnants of the shield, at the centre of which lies a small gabbroic intrusion 2 km in diameter, surrounded by a hornfels ridge. This was probably the central feeder for the volcano (Brownlow 1972, Gleadow & Ollier 1987).

The volcano was active approximately 19 Ma to 18 Ma ago (McDougall & Wilkinson 1967, Wellman & McDougall 1974, Gleadow & Ollier 1987) and this is supported by a date for the central intrusion of around 18 Ma (Wellman & McDougall 1974, Gleadow & Ollier 1987).

7.8 DORRIGO PLATEAU, EBOR VOLCANIC CENTRE

7.8.1 Nature of the Exposure

In an upper-slope position on a small hill on the Dorrigo Plateau a very deep red-brown weathering profile has developed on free draining weathered basalt (Figure 7.10, Plate 7.19, Appendix 1). The materials from the zone of deep weathering, WFT10/7 and WFT10/6 can be distinguished on the basis of colour, and are red-brown and grey-brown respectively with red-brown coloured soil (WFT10/1), capping the sequence. A resinous dull yellow clay (WFT10/4) locally infills voids and cracks in weathered materials.

![Image of Dorrigo Plateau profile](image)
There is a lens of mottled, pale gold coloured material (WFT10/5), that lies between the upper soil-like layers, at one side of the outcrop. This material is now almost completely altered to clay minerals, retains little of the structure of the original rock, and is thought to be the weathered remnant of a fine-grained or glassy sediment that was deposited in a depression adjacent to, and overlying, the basalt. Grey clay-rich weathered material (WFT10/8) forms a prominent base to the deeply weathered profile.

The least weathered material sampled at this locality, WFT10/2, is a weathered porphyritic basalt, found protruding through the soil apron. Large relict euhedral plagioclase phenocrysts are now completely altered to clays in this saprolitic material.

### 7.8.2 Geochemistry

For the basalt samples (WFT10/1, WFT10/2, WFT10/6, WFT10/7, WFT10/8) the isocons are best fit lines through the representative points Nb, Zr and Ti, which are believed to be the least mobile elements. The fresh basalt used for isocon construction is quartz-tholeiitic basalt from Ebor Volcanic Centre (sample number EAV214, Appendix 2).

The slopes \( C_i^{W}/C_i^{O} \) of the isocon lines reflect the progressive increase in mass loss (\( \Delta M \)) and hence increase in intensity of weathering of the basalt samples upward through the profile.

<table>
<thead>
<tr>
<th>Weathering Zone</th>
<th>Sample</th>
<th>( C_i^{W}/C_i^{O} )</th>
<th>( \Delta M )</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deep</td>
<td>WFT10/6</td>
<td>2.95</td>
<td>-66%</td>
<td>( \uparrow )</td>
</tr>
<tr>
<td>Weathering</td>
<td>WFT10/7</td>
<td>2.64</td>
<td>-62%</td>
<td>INCREASE IN</td>
</tr>
<tr>
<td>Saprolite</td>
<td>WFT10/8</td>
<td>2.21</td>
<td>-55%</td>
<td>DEGREE OF</td>
</tr>
<tr>
<td>Saprolite - Deep</td>
<td>WFT10/2</td>
<td>1.13</td>
<td>-12%</td>
<td>WEATHERING</td>
</tr>
</tbody>
</table>

Pb, La, Ni and Al show large enrichments in the saprolitic material, but while Ni and Al show progressive depletion as they are mobilised in the more weathered materials, La concentrations remain high and Pb concentrations fluctuate. Ce is enriched in the weathered material which is similar to the behaviour of La. Cu is not as enriched in the saprolite as Ni, but thereafter the depletion pattern for Cu parallels that for Ni. Th is slightly enriched in the saprolite and then lost from the soil-like material. S is enriched in the more weathered material. Fe (total) is enriched is progressively enriched with weathering, but then concentrations drop nearer the land surface. Ba, Y and P show large fluctuations in concentration, but their enrichment/depletion is similar. There is a drop in abundance of Si, V and Zn from the saprolite to the deeply weathered material, and then
they maintain a constant low concentration. Cr, K, Na, Rb, Ca, Sr, Mg and Mn are all depleted early in weathering (Fig 7.11).

Figure 7.11

Isocon diagrams and corresponding histograms for WFT10/2, WFT10/8, WFT10/7 and WFT10/6

Histograms show relative mass change (%) for analysed elements
7.8.3 Clay Mineralogy

![Stacked X-ray diffraction (XRD) traces for samples WFT10/2, WFT10/8 and WFT10/7.](image)

Saprolite

Weathered basalt with well preserved primary texture WFT10/2 protrudes through the soil apron (Figure 7.12). Plagioclase feldspar peaks are barely discernible on the X-ray diffraction (XRD) trace, implying that this saprolitic material has been weathered almost entirely to a mixture of kaolinite and halloysite clays. The cation exchange capacity (CEC) for this sample is 1 meq/100 g, which is very low, and the Si:Al ration is 0.92 which is compatible with the dominant clays belonging to the kaolin group.

Zone of Deep Weathering

The lowermost material sampled (WFT10/8) has an XRD trace that is dominated by a kaolin group clay peaks, probably halloysite, with secondary hematite and some goethite represented (Figure 7.12). No primary minerals are preserved indicating that this material is already intensely weathered. WFT10/8 has a CEC of 8 meq/100 g and an Si:Al ratio of 0.99, which are within the range for kaolin group clays.

The red-brown coloured saprolite (WFT10/7) is predominantly composed of a mixture of kaolinite and halloysite clays, and hematite. The CEC for the clay separate is 9 meq/100 g and the Si:Al ratio is 0.90. The hematite accounts for the red colouration of the material. The clay separate contains some gibbsite, which occurs as small white nodules in hand specimen.
Sample WFT10/6 is dark yellowish brown coloured and has the same dominant mineralogy as the materials underlying it, but hematite is not as abundant. The clay separate for this sample has a CEC of 9 meq/100 g and the Si:Al ratio is 0.97.

The lens of pale gold coloured clay-rich material (WFT10/5), that sits between grey-brown coloured soil-like material (WFT10/6) and the overlying soil WFT10/1, is predominantly composed of kaolin group clays. The clay assemblage is either a mixture of kaolinite and halloysite. The CEC for this clay rich material is 10 meq/100 g and the Si:Al ratio is 0.99. There is a small peak indicating the presence of minor quartz in this sample.

The soil WFT10/1 is halloysite bearing, with hematite present, giving it a red colour. Gibbsite occurs in small nodules, throughout the soil and dominates the bulk trace, although halloysite is apparent in the clay separate trace. The CEC for this sample is 10 meq/100 g and the Si:Al ratio is 0.35, which is low, reflecting the dominance of gibbsite in the clay separate.

Summary

Plate 7.20 (A), Plate 7.21 (B), Plate 7.22 (C), Plate 7.23 (D). Scanning electron micrographs (SEM) of kaolin group clays from the Dorrigo Plateau profile. (A) and (B) kaolinite occurs as well formed stacked sub-hexagonal plates. (C) and (D) halloysite (H) has a tubular morphology.
The mineral assemblage is dominated by kaolin group clays, probably a mixture of kaolinite and halloysite. High in the profile gibbsite is identified, becoming increasingly more abundant up-profile. Kaolinite is increasingly less dominant up-profile, and the gibbsite appears to be formed at the expense of the kaolinite. Hematite is the Fe-oxide responsible for most of the red-brown colouration of the weathered material.

The lens of orange weathered basaltic sediment has a clay mineral assemblage dominated by halloysite and kaolinite (Plate 7.20, 7.21, 7.22, 7.23), which is very similar to that of the enclosing weathered lava. The gibbsite bearing, halloysitic soil (WFT10/1) overlies both the sediment lens and the weathered basalt lava.

### 7.8.4 Profile Summary

The basalt profile at this locality is deeply weathered and predominantly composed of secondary kaolin group clays, sesquioxides of Fe and Al, and Fe-oxyhydroxides. The texture of the parent basalt is only well preserved in the saprolite sample (WFT10/2), which is porphyritic with large weathered feldspar phenocrysts apparent in hand specimen. The enrichment of Pb, La and Ce may be attributed to the presence of secondary neoformed minerals, including phosphates and carbonates.
8.1 LOCATION

Figure 8.1
Sample localities in the Tweed Volcanic Province.

The Tweed Volcano straddles the border between north east New South Wales and south east Queensland, and lies immediately west of the town of Murwillumbah (Figure 8.1). Two profiles were sampled, one in the north at Beechmont (28.08°S 153.11°E) and another in the south at East Lismore (28.50°S 153.20°E).
8.2 CONTEMPORARY CLIMATE

Annual mean radiation is similar at both localities but temperatures are slightly different with Beechmont a little cooler because it is located at higher elevation. Precipitation is very high in both localities but there is marginally greater rainfall in East Lismore on the southern flanks of the volcano (Table 8.1).

<table>
<thead>
<tr>
<th></th>
<th>TFT6 East Tweed</th>
<th>TFT12 Beechmont</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>RADIATION (MJ/m²/yr)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annual Mean Radiation</td>
<td>17.86</td>
<td>17.92</td>
</tr>
<tr>
<td>Highest Monthly Radiation</td>
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<td>23.89</td>
</tr>
<tr>
<td>Lowest Monthly Radiation</td>
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<td>11.07</td>
</tr>
<tr>
<td>Range of Radiation</td>
<td>14.04</td>
<td>12.83</td>
</tr>
<tr>
<td>Seasonality of Radiation</td>
<td>26.79</td>
<td>25.03</td>
</tr>
<tr>
<td>Radiation of the Wettest Quarter</td>
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<td>20.24</td>
</tr>
<tr>
<td>Radiation of the Driest Quarter</td>
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<td>15.28</td>
</tr>
<tr>
<td><strong>TEMPERATURE (°C)</strong></td>
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<td></td>
</tr>
<tr>
<td>Annual Mean Temperature</td>
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<td>16.83</td>
</tr>
<tr>
<td>Maximum Temperature Warmest Month</td>
<td>28.31</td>
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<td>Minimum Temperature Coldest Month</td>
<td>6.39</td>
<td>6.07</td>
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<td>Annual Temperature Range</td>
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<td>20.58</td>
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<tr>
<td>Mean Temperature Driest Quarter</td>
<td>14.41</td>
<td>12.81</td>
</tr>
<tr>
<td><strong>PRECIPITATION (mm)</strong></td>
<td></td>
<td></td>
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<tr>
<td>Annual Precipitation</td>
<td>1631.28</td>
<td>1528.22</td>
</tr>
<tr>
<td>Precipitation Wettest Month</td>
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</tr>
<tr>
<td>Precipitation Driest Month</td>
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<td>50.14</td>
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<td>Range of Precipitation</td>
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<td>Precipitation Driest Quarter</td>
<td>235.20</td>
<td>188.56</td>
</tr>
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</table>

Table 8.1
Contemporary climate information for the Tweed sample localities (BIOCLIM)

8.3 PALEOCLIMATE AND VEGETATION

Dudgeon (1982) describes an Early Miocene (22 Ma to 24 Ma) palynoflora and macrofossil (ferns) assemblage from the Main Range, south east Queensland, which is dominated by rainforest species that prefer a warm humid climate. A comparable study at Chalk Mountain, Warrumbungles, northern New South Wales, details the presence of similar rainforest species, around 16 Ma, implying a warm moist climate in this area also (Holmes et al. 1983).
Thin sedimentary beds, largely shales and diatomite, are intercalated in the lowermost unit of at least 10 thin flows on Mount Tamborine, and also near Beechmont, but fossils have not been described from these localities.

8.4 GEOLOGY - TWEED VOLCANIC PROVINCE

The Tweed shield volcano sits on a basement high (Wellman 1986) formed during intrusion of the central plutonic complex, Mt Warning (Paterson 1970, Smart 1970, Gould 1970, Bruce 1978, Johnson et al. 1989). Much of the eastern part of the volcano has been removed by erosion and precipitous cliffs, largely of basaltic lava flows with interlayered rhyolites, border the erosion caldera on the north, south and western sides. The caldera is around 30 km in diameter and preserved eruptives reach a maximum thickness of 900 m in the northern wall. The original shield volcano was approximately 100 km in diameter with an original estimated height of approximately 1,900 m above sea level and an original volume of lava 3,200 km³ (Solomon, 1964). Mafic lavas were the first erupted, followed by rhyolitic units which, in turn, were overlain by a younger mafic sequence (McTaggart 1962, Ewart et al. 1971, Duggan & Mason 1978, Ewart et al. 1980).

The lowermost basalt on the south side of the shield, the Lismore Basalt, is at the same stratigraphic level as the Beechmont Basalt in the north. The Nimbin Rhyolite and, in the north, Binna Burra and Springbrook Rhyolites conformably overlie the Lismore and Beechmont Basalts respectively. The uppermost basalt, the Blue Knob Basalt caps high areas on the irregular topography formed by the rhyolites and the Hobwee Basalt correlates with the Blue Knob Basalt on the north side of the shield (Ewart et al. 1987).

The Lismore Basalt is very extensive and underlies large areas of low relief on the southern flanks of the shield around Lismore (Wilkinson 1969). The basalt is predominantly tholeiitic, with occasional alkaline types. The lavas, which are rarely thicker than 10 metres, probably flowed from the central complex (Duggan & Mason 1978, Ewart et al. 1987). The Beechmont basalt is the equivalent unit on the northern side of the shield where it forms the Beechmont Plateau. When the Beechmont and overlying Hobwee basalts are juxtaposed they are difficult to distinguish from each other. The underlying Albert basalt, which is derived from the adjacent Focal Peak centre, is also very similar to the Beechmont basalt (Green 1964). In the past the whole sequence has been referred to as the Lamington volcanics (Exon 1972).

The Hobwee Basalt, overlie the Binna Burra Rhyolite formation and reaches a maximum thickness of nearly 600 m at Mount Hobwee (Ewart et al. 1987). Correlative pyroclastics are also recorded at this level in the stratigraphy (Watt 1979, Uttley 1972). The Blue
Knob Basalt is stratigraphically highest, on the south side of the shield and correlates with the Hobwee Basalt in the north. It occupies depressions in the underlying Nimbin rhyolite. At Blue Knob, this basalt reaches its maximum thickness (350 m) (Wilkinson 1969, Duggan & Mason 1978). The units on the northern and southern side of the shield may not directly correlate. The rhyolite groups are discontinuous, and where the upper and lower basalts are juxtaposed they are difficult to distinguish from one another because many flows show extensive chemical and mineralogical overlap (Ewart et al. 1980, Ewart et al. 1977).

The Albert and Kyogle Basalts are associated with the slightly older Focal Peak Volcano to the west of the Tweed Volcano (Ross 1977). These basalts have been intruded and cross-cut by alkali basalt and hawaiite lavas from Tweed Volcano (Duggan & Mason 1978, Ewart et al. 1987).

The Tweed volcano was active from about 23.5 Ma to 20.5 Ma (Webb et al., 1967, McDougall & Wilkinson 1967, Wellman and McDougall 1974) and ages derived for the sampled basalts support the suggested stratigraphic succession (McTaggart 1962, Ewart et al. 1971, Duggan & Mason 1978, Ewart et al. 1980) for the shield. The Beechmont basalt is dated at 22 Ma, while older remnant coastal basalt outliers, at Fingal Point and Burleigh Heads, are dated at 22.6 Ma and 22.9 Ma respectively (Wilkinson 1969, McDougall and Wilkinson 1967). These tholeiitic outliers are chemically and mineralogically (McDougall & Wilkinson 1967) similar to the Beechmont and Lismore basalts, but are older and their emplacement precedes the eruption of the Kyogle and Albert basalts around 22.5 Ma (Wellman & McDougall 1974) from the Focal Peak centre and may relate to later tholeiitic eruptives interspersed through these Focal Peak basalts (Mason 1969).

The northern, Beechmont and Hobwee basalts are dominantly quartz-normative grading into olivine-normative types (Ewart et al. 1977, Ewart et al. 1980, Ewart 1981, 1982). The southern Lismore and Blue Knob basalts are composed predominantly of tholeiitic andesite with minor icelandite and sporadic flows of mildly alkaline rocks (Duggan & Wilkinson 1973). Duggan and Mason (1978) show the occurrence of nepheline-normative basalts within the Lismore and Blue Knob basalts. Tholeiitic andesites contain high pressure megacrysts which is unusual as they are customarily interpreted as the products of low pressure fractional crystallisation of tholeiitic magma (Duggan & Wilkinson 1973). In this case they appear to have a high pressure origin. Similar rare aluminous augite megacrysts have been found in a single olivine-normative Beechmont lava.
Chapter 8: Basalt Weathering Profiles from Southern Queensland/Northern NSW 175

8.5 EAST LISMORE, TWEED VOLCANIC PROVINCE

8.5.1 Nature of the Exposure

At this locality a single weathered basalt flow is exposed in a road excavation (Fig 8.2, Plate 8.1, Appendix 1), in an upper slope position in the topography. There is significant vertical and lateral variation in the degree of weathering of this basalt, with a general increase in weathering.

Figure 8.2
Sample points in the East Lismore profile, Tweed Volcanic Province

Plate 8.1
East Lismore profile
away from corestones and, on a broader scale up-profile. Apart from the deep orange soil (TFT6/10) that caps the sequence, the most weathered material in this profile forms pale coloured intensely weathered zones that, in some cases, still partly preserve a basalt rock texture (TFT6/2, TFT6/7, TFT6/9). These pale zones represent relict pathways of preferred fluid flow through the profile, and may be sites of secondary precipitation.

Other samples, characterised by strong deep orange to yellow-brown colouration (TFT6/5, TFT6/6), show significant secondary iron oxide and oxyhydroxide precipitation. The more indurated corestone materials range from incipiently to moderately weathered basalt (TFT6/4, TFT6/3) with the replacement of small plagioclase phenocrysts by secondary minerals, apparent in some hand specimens.

8.5.2 Geochemistry

For the basalt samples (TFT6/3, TFT6/4, TFT6/5, TFT6/6, TFT6/7, TFT6/9) the isocons are best fit lines through the representative points Nb, Zr and Ti which which are believed to be the least mobile elements. The fresh basalt used for isocon construction is olivine-tholeiitic basalt from Tweed Volcano (sample numbers OR21 & 33037, Appendix 2).

The slopes (C_i^W/C_i^O) of the isocon lines reflect the progressive increase in mass loss (ΔM) and hence increase in intensity of weathering of the basalt samples outward from corestones.

<table>
<thead>
<tr>
<th>Pale Zone</th>
<th>TFT6/9: C_i^W/C_i^O = 0.75</th>
<th>ΔM = +33%</th>
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<tbody>
<tr>
<td>Weathered</td>
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<td>ΔM = -37%</td>
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<tr>
<td>Basalt</td>
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<td>ΔM = -31%</td>
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<tr>
<td></td>
<td>TFT6/3: C_i^W/C_i^O = 1.13</td>
<td>ΔM = -12%</td>
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<tr>
<td></td>
<td>TFT6/4: C_i^W/C_i^O = 1.03</td>
<td>ΔM = -03%</td>
</tr>
</tbody>
</table>

Weathered Basalt

S, Cr and Th are extremely enriched in all samples. Ni and Zn show strong enrichment in the least weathered samples, but both are depleted with continued weathering. V shows major enrichment and thereafter maintains this level of concentration. Pb shows a similar pattern but is enriched with increase in degree of weathering. Al maintains a major enrichment throughout the profile until some Al is lost in the most weathered sample. Fe (total) is slightly enriched in almost all samples although shows major enrichment in the most weathered material. Si, Ca, Sr, Cu and Ce are all slightly depleted in the corestone material and show significant depletion with increase in weathering. Ba, La, Mn, Na, Y,
Mg and P all show major depletion to start with and are extremely depleted in the most weathered material. K and Rb are strongly depleted early in weathering.
Pale Zone

The pervasively weathered basalt material represented by the pale coloured sample TFT6/9 has experienced a mass gain (positive ΔM), when compared with unweathered basalt. This material is completely altered to secondary products and is also cross-cut by small veinlets. In addition, features that would have been vesicles or voids in the original basalt are now infilled by secondary weathering products. The mass gain implies that elements from outside this zone have been introduced to this zone.

Al, S, Cr, Th and Ni are all significantly enriched in these intensely weathered zones. Fe₂O₃ and V show enrichment in the rest of the profile but are moderately depleted in TFT6/9. Zn and Si are slightly enriched and maintain relatively constant concentrations. Cu and P are moderately depleted in the pale coloured material and become more depleted.
with weathering. Ba, La, Ce, Y, Mg, Mn, K, Na, Rb, Ca and Sr are all readily removed from this material.

8.5.3 Clay Mineralogy

![Figure 8.4](image)

Stacked X-ray diffraction (XRD) traces for samples TFT6/4, TFT6/3, TFT6/6, TFT6/5, TFT6/9 and TFT6/10

Weathered Basalt

The X-ray diffraction (XRD) trace for the rind on TFT6/4 shows a small smectite peak and peaks for a number of primary minerals (Figure 8.4). Peaks for plagioclase feldspar are observed on the XRD trace, however the feldspar traces tend to obscure other minerals. Pyroxene and some magnetite and ilmenite peaks are detectable. The presence
of hematite peaks is noted. Peaks for both dioctahedral and trioctahedral smectite clays are present. Chemistry from the clay separate for TFT6/4 has relatively high values for Fe and Mg suggesting that the smectite assemblage is probably composed of early formed trioctahedral Fe-saponite and saponite with some Fe-bearing dioctahedral nontronite. A dioctahedral Al-smectite may be present also. The CEC is relatively low for this material, 18 meq/100 g and the Si:Al ratio is 1.20, but kaolin group clays are not apparent in the XRD trace.

The weathered corestone from TFT6/3 gives similar traces to TFT6/4, however peaks are not as clear for pyroxene. The clay coating occurring on faces of these samples is smectitic. Peaks for trioctahedral smectites are no longer observed, and although Fe concentration is still relatively high for the clay separate, Mg concentration has dropped, suggesting that nontronite is the dominant clay present, with some Al-smectite. Because of the mixtures present, it is extremely difficult to fit structural models to the clays.

The bulk XRD traces for samples TFT6/6 and TFT6/5 no longer have many peaks representative of primary minerals, apart from magnetite and ilmenite. In addition, the clay mineral dominantly represented in the traces is a kaolin group mineral, probably halloysite. Accordingly the CEC for these samples is in the range 10 meq/100 g to 15 meq/100 g and the Si:Al ratios lie between 0.88 and 0.95. Poorly defined peaks are present for the hematite, and minor goethite, in these samples.

Pale Zone

Pale coloured, intensely weathered irregular zones occur within the basalt saprolite material at this locality (Figure 8.4). In places these zones almost appear to ring corestones, following fractures between the onionskins. X-ray diffraction traces for this sample TFT6/9 indicate the presence of kaolin group clays. The CEC for the clay separate is 5 meq/100 g and the Si:Al ratio 0.98, implying that kaolinite is the dominant kaolin group clay present.

Soil

The soil material (TFT6/10) has an XRD trace that is dominated by a kaolin group clay peaks (Figure 8.4). The asymmetry and position of the peaks suggest that the clay may be halloysite. The red colouration comes from hematite. The CEC for this material is extremely low, 9 meq/100 g, and the Si:Al ratio is 0.95, reflecting the presence of kaolin group clays in the more weathered parts of the profile.
Summary

Weathered Basalt

Weathering basalt is initially replaced by an assemblage dominated by smectite clays. This assemblage is composed of saponite, nontronite and Al-smectite formed during the breakdown of ferromagnesian silicates, montmorillonite and kaolinite formed during the dissolution of plagioclase feldspar and the smectite clays formed during the alteration of basaltic glass.

As weathering proceeds kaolin group clays become dominant and in intensely weathered zones kaolin is the principal phase present. Kaolin is principally derived from smectite clays in an intensely leaching environment as well as directly from the breakdown of relict plagioclase feldspar.

Goethite is the principal Fe-bearing secondary mineral neoformed during primary mineral dissolution in the weathering basalt, but it is rapidly converted to hematite in this profile. Hematite is also concentrated in weathering rinds and close to micro-fractures and voids. Goethite is mostly preserved within the weathered basalt away from exposed surfaces.

Pale Zone

Because of the simple kaolin group clay assemblage, it appears that these are zones of high fluid throughflow, and secondary neoformation of clays, as well as sites of preferred precipitation. The loss of primary basaltic texture is associated with the microstructural collapse of the intensely weathered material.

In thin section, some of the oriented kaolin clays observed in olivine pseudomorphs in this material, have a similar appearance to the smectite clays that first formed when the silicate was weathered. Apparently the kaolin group clays are preserving the initial texture.

8.5.4 Petrography

Weathered Basalt

Corestone materials (TFT6/3, TFT6/4) from the weathered basalt clearly retain primary basaltic texture. Etched plagioclase feldspar laths are the most prevalent groundmass mineral with interstitial pyroxene, magnetite and ilmenite preserved. The opaque oxides have elongate shapes which reflect the shape of the inter-lath site they originally
Plate 8.2
TFT6/3 (crossed polars)
Groundmass augite forms a sub-ophitic texture with plagioclase feldspar. Hematite is concentrated in microfractures and olivine phenocrysts are thoroughly weathered.

Plate 8.3
TFT6/4 (crossed polars)
Plagioclase phenocrysts are fractured, strongly etched and weathered to clays along fractures, twin planes and around their edges.

Plate 8.4
TFT6/9 (plane polarised light)
The basalt is intensely weathered to secondary Fe oxyhydroxides and clays. Goethite causes yellow colouration of some clays.

Plate 8.5
TFT6/9 (crossed polars)
Elongate opaque oxides preserve primary inter-lath shape. Otherwise primary basaltic texture is poorly preserved.
occupied. Pockets of neoformed clays and goethitic material in the groundmass are former sites of basaltic glass and small olivine and pyroxene grains. Where micro-fractures cross-cut the basalt, and near the exposed face, the concentration of secondary hematite is greater than goethite. Goethite is more dominant away from the micro-fractures (Plate 9.2, 9.3).

The basalt is porphyritic with large plagioclase feldspar and olivine phenocrysts. The plagioclase phenocrysts, andesine An33-38, are fractured and strongly etched and altered to clays along fractures and twin planes and around their edges. These clays are mostly orange in colour due to staining by secondary Fe-bearing minerals. The olivine phenocrysts in weathering rinds and proximal to cross-cutting micro-fractures are wholly weathered to secondary hematite and goethite and Fe-stained clays.

**Pale Zone**

The primary basaltic texture of this material (TFT6/9) is very poorly preserved and has commenced breakdown. Secondary weathering products dominate the samples which are wholly weathered to a clay-rich plasma with a small amount of secondary hematite and minor goethite disseminated throughout. Locally hematite is enriched, around voids and adjacent to micro-fractures (Plate 8.4, 8.5). Fine grained elongate primary opaque oxides preserve the morphology of the original inter-lath space which they filled. Angular areas devoid of primary or secondary iron minerals are former sites of plagioclase phenocrysts, now entirely weathered to clays. Rare pseudomorphs after olivine phenocrysts are preserved. They have a very clearly defined rim of hematitic material with a clay core, and clays arrayed in growth orientation giving them a different appearance to the randomly oriented matrix clay. Voids are also infilled with growth oriented clays.

**8.5.5 Profile Summary**

This profile may be described as a transitional weathering profile as the secondary mineral assemblage is dominated by smectite clays immediately adjacent to the corestones, but the bulk of the more intensely weathered basalt in the exposure, the pale zone and the soil zone are dominated by a kaolin group clay suite. The pale zone has formed as a result of the focus of fluid percolation along joint planes between corestones. Because of this, the material in this zone is cation depleted, kaolin-rich, and may be the site of precipitation from percolating fluids. This is supported by the positive mass change ($\Delta M$) for this material. The enrichment of Th and Pb may be related to the precipitation of secondary carbonate minerals, and the elevated Al values are attributed to the concentration of this element in secondary clays.
8.6 BEECHMONT, TWEED VOLCANIC PROVINCE

8.6.1 Nature of the Exposure

A single basalt flow, exhibiting well developed spheroidal weathering, is represented at this locality, on the elevated Beechmont Plateau (Figure 8.5, Plate 8.6, Appendix 1).

Figure 8.5
Sample points in the Beechmont profile, Tweed Volcanic Province.
Chapter 8: Basalt Weathering Profiles from Southern Queensland/Northern NSW

Corestones (TFT12/7) are generally larger, up to 30 cm in diameter, nearer the base of the flow, suggesting that this profile has principally been weathered from the top down. Many of the smaller corestones (TFT12/4) appear to be more intensely weathered than the larger blocks. In addition there are small areas of massive weathered basalt (TFT12/5) with poorly developed jointing, which do not have well developed corestones. Whereonionskin material (TFT12/6, TFT12/3) has developed between corestones weathering is advanced, and rubbly brown weathered basalt material (TFT12/2, TFT12/1) grades vertically into the overlying crumbly deep orange soil.

8.6.2 Geochemistry

For the basalt samples (TFT12/1, TFT12/2, TFT12/3, TFT12/4, TFT12/6) the isocons are best fit lines through the representative points Nb, Zr and Ti which are believed to be the least mobile elements. The fresh basalt used for isocon construction is olivine-tholeiitic basalt from Tweed Volcano (sample numbers OR21 & 33037, Appendix 2).

The slopes ($C_i^W/C_i^O$) of the isocon lines reflect the progressive increase in mass loss ($\Delta M$) and hence increase in intensity of weathering of the basalt samples outward from corestones.

<table>
<thead>
<tr>
<th></th>
<th>$C_i^W/C_i^O$</th>
<th>$\Delta M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil TFT12/1</td>
<td>1.53</td>
<td>-35%</td>
</tr>
<tr>
<td>Soil TFT12/2</td>
<td>1.56</td>
<td>-36%</td>
</tr>
<tr>
<td>Basalt TFT12/3</td>
<td>1.68</td>
<td>-40%</td>
</tr>
<tr>
<td>Basalt TFT12/6</td>
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<td>-38%</td>
</tr>
<tr>
<td>Basalt TFT12/4</td>
<td>1.51</td>
<td>-34%</td>
</tr>
</tbody>
</table>

There is a decrease in slope between weathered basalt and the overlying soil which reflects a mass increase associated with the collapse of the microstructure as soil forms. A relative mass gain such as this may also occur as a result of the addition of material from elsewhere, and the soil zone is the part of the profile likely to be affected in this manner.

Weathered Basalt

Pb, Y and Th are extremely enriched in all samples. La and Zn are strongly enriched in the corestone samples but are rapidly depleted in the more weathered samples. S shows extreme enrichment, while Ce has fluctuating concentration but is always moderately enriched. V maintains a very constant concentration after an slight initial enrichment but becomes depleted in the soil zone. Fe (total) lies on the isocon initially but becomes more concentrated with increase in weathering. Cr is depleted early in weathering and is subsequently strongly enriched. Ba, Mn, P, Cu, Rb and Si are all progressively depleted.
with weathering. Of these Cu is the only element that might be expected to concentrate in the weathered material. Ni, Mg, K, Na, Ca and Sr are readily removed early in weathering of the basalt (Figure 8.6).
Figure 8.6
Isocon diagrams and corresponding histograms for TFT12/1, TFT12/2, TFT12/3, TFT12/4 and TFT12/6. Histograms show relative mass change (%) for analysed elements.

8.6.3 Clay Mineralogy

The X-ray diffraction (XRD) trace for the moderately weathered basalt corestone, TFT12/4, showed limited kaolin group clay development (Figure 8.7). Primary minerals represented by peaks in the trace include plagioclase feldspar, minor olivine and pyroxene, magnetite and ilmenite. The onionskin material surrounding this sample exhibits has a greater kaolin group clay development, and the primary mineral peaks are lost from the trace.

The clays are a mixture of halloysite and kaolinite, and there is a minor amount of quartz present. The cation exchange capacity (CEC) for the clay separate is 9 meq/100 g and the Si:Al ratio is 1.24, values which are in keeping with a dominantly kaolin group clay assemblage.
Chapter 8: Basalt Weathering Profiles from Southern Queensland/Northern NSW

The bulk XRD trace for the rubbly weathered basalt sample TFT12/6 shows that the dominant clay type kaolinite, and halloysite is present. Accordingly the CEC is 10 meq/100 g and the Si:Al ratio is 1.15. Hematite has contributed to the red colouration of the coating on this sample.

![Figure 8.7](image)

Stacked X-ray diffraction (XRD) traces for samples TFT12/1, TFT12/2, TFT12/3, TFT12/6 and TFT12/4.

A slightly more weathered rubbly onionskin material, TFT12/3, gives an XRD trace showing definite halloysite clay peaks. The CEC for the clay separate is 7 meq/100 g which is a low value typical of kaolin group clays and the Si:Al ratio is 0.92, close to the model value of 1. There is no evidence of any primary phases, apart from magnetite and ilmenite. Small sharp peaks indicate the presence of hematite, and this sample also has red coloured material coating joint faces.

The pervasively weathered sample TFT12/2 has a similar red earthy coating to TFT12/6 but hematite peaks are not as apparent for this sample. Once again the bulk XRD analysis shows an elevated plateau with the main peak at 7.38Å. However, the cation exchange capacity (CEC) for the clay separate is low, 9 meq/100 g, so these are not interstratified clays, rather they are partially hydrated kaolin group clays, probably halloysite and some kaolinite. The Si:Al ratio is 1.01 which is in the range for kaolin group clays.

TFT12/1 is truly soil material, with a strong red colouration (Munsell, moist, 5YR 3/4). The XRD trace indicates that the dominant clays are halloysite and kaolinite. The CEC for
this sample is 8 meq/100 g and the Si:Al ratio is 0.97. Small quartz peaks occur in this trace. Quartz was also detected in one trace lower in the profile so, although it appears this mineral has been introduced from elsewhere, possibly by aeolian transport, there must also have been some eluviation of extremely fine grained material (<4 µm), down cracks in the profile. Hematite is present in the sample, with minor goethite.

**Summary**

XRD shows that weathering is sufficiently intense for kaolin group minerals to form relatively early in weathering. This may, in part, be because olivine generally weathers rapidly to smectite clays, but olivine is not a dominant primary phase in this basalt. It appears that the pyroxene present has largely weathered to goethite and hematite. Plagioclase feldspar weathers to kaolin group clays, and the small amount of glassy mesostasis present devitrifies and is weathered to kaolin group clays also. Some of the XRD traces appear to have some smectite clays present, but the CEC are consistently low, confirming the dominant presence of kaolinite and halloysite clays.

**8.6.4 Petrography**

In the more consolidated weathered corestone samples (TFT12/4, TFT12/6) fine grained laths of plagioclase feldspar comprise the bulk of the groundmass with relatively large inter-lath primary opaque oxides, and scattered small angular grains of pyroxene preserved. Groundmass olivine and basaltic glass is completely weathered to clays and goethite with some hematite. The primary basaltic texture is preserved. Phenocryst phases are sparse but are dominantly euhedral augite and plagioclase feldspar, albite-andesine An33-38. Plagioclase feldspars are deeply etched along fractures. Weathering rinds are well developed and hematite is extremely abundant therein (Plate 8.7, 8.8).

**8.6.5 Profile Summary**

The single flow represented at this locality has weathering products distributed throughout the profile with scattered corestones supported in rubbly saprolite material. The secondary mineral assemblage for this profile is dominated by kaolin group clays, kaolinite and halloysite, despite a number of corestones being preserved in the profile almost to the soil zone. Where smectite occurs it is immediately adjacent to the corestones, and it is apparently rapidly converted to kaolin group clays with continued weathering. Elevated values for Pb, Y, Th, Ce and La are attributed to the localised neoformation of phosphates during weathering.
Plate 8.7 (crossed polars)
Plate 8.8 (plane polarised light)

TFT12/4  Groundmass olivine and basaltic glass is completely weathered to clays and goethite with some hematite. Unweathered opaque oxides preserve their original inter-lath morphology.
The Springsure and Peak Range Volcanic Provinces are located in the Emerald District, approximately 250 km from the coast, in central Queensland (Figure 9.1). Two profiles were sampled, one west of Springsure township, on the Dawson Developmental Road (24.07°S 147.59°E), and one east of Clermont township, on the Stock Route Rd (22.47°S 147.47°E).
9.2 CONTEMPORARY CLIMATE

<table>
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<tr>
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<th>EFT9 STOCK ROUTE PEAK RANGE</th>
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Table 9.1
Contemporary climate information for the West Springsure and Stock Route sample localities.

The Springsure and Peak Range Volcanic Provinces have tropical to subtropical temperatures, but, because of their distance from the coast, precipitation is relatively low and hence, they experience a sub-humid to semi-arid climate (Table 9.1).

The annual mean radiation is similar at both sample localities and is relatively high. Accordingly evaporation rates are high with estimated annual pan evaporation values for Springsure of 1,806 mm, Emerald 1,891 mm and Clermont 1,881 mm (Fitzpatrick 1967a, 1967b). The highest rates of evaporation occur from October to January inclusive (Webb & Dowling 1990). Because the annual mean precipitation is in the order of 600 to 700 mm, these high evaporation rates cause considerable drying of basalt weathering profiles, resulting in desiccation fracturing and frittering of fragmented material.

Annual mean temperature at both sites is very similar with high temperatures (>33°C) common during early summer and cool temperatures (>5°C) in the winter. Overnight frosts can be expected in winter, and diurnal temperature ranges may be high, especially in winter and spring.
As mentioned, mean annual precipitation in this area is relatively low. Rainfall patterns are summer dominant but are highly variable with greater rainfall in the south of the area. Greater rainfall at higher latitude may correspond with slightly more winter rain in the south, reflected in the values for precipitation of the driest month.

9.3 PALEOCLIMATE AND VEGETATION

Deeply weathered profiles within the volcanic pile at Peak Range indicate localised breaks in volcanic activity and have been related to a period of warm humid climate in the late Oligocene to early Miocene (Grimes, 1980). This deep weathering is not observed on basalts at the present land surface which are, at the youngest, 27 Ma implying that either weathered material has been stripped from the plains basalts, or the preserved deeply weathered profiles relate to earlier periods of higher, or more sustained, rainfall.

Bird et al. (1990) found that alunite from a weathering profile underlying the basalt in Springsure Province gave a late Paleocene age, within error of the age inferred by paleomagnetism (60 Ma ± 10 Ma) for a major period of deep weathering in Queensland (Idnurm and Senior 1978), and this is consistent with the field evidence that deep weathering predates the basalt extrusion in this area.

Remnants of the original vegetation are characterised by an open savannah woodland with a dense ground cover of grasses. However, now the land is largely used for grazing and in the south, on the basalt downs, fodder crops and grain are cultivated. Dense brigalow scrub occurs along watercourses in the district.

9.4 GEOLOGY - SPRINGSURE VOLCANIC PROVINCE

Approximately 7,000 km² of rolling basaltic plains up to 330 m thick surround the township of Springsure, with a central cluster of felsic volcanic centres at Minerva Hills (Veevers et al. 1964, Mollan et al. 1969, Olgers et al. 1966, Johnson et al. 1989). The plains basalts of the Springsure Volcanic Province thin out over the Springsure anticline and the underlying gently folded Permian beds crop out in an eroded window through the basalts, along the fold hinge of of the anticline (Johnson et al. 1989).

For most of the basalts there were apparently three stages of extrusion (i) older mafic rocks (ii) interbedded mafic and felsic rocks of the Minerva Hills Volcanics and (iii) younger mafic rocks. Older basalts are dated at 33 Ma to 34 Ma and 27 Ma 28.7 Ma (Webb & McDougall 1967) which may broadly correspond to the older and the interbedded volcanics. Younger basalt flows range in age from approximately 26 Ma to
24 Ma (Mollan et al. 1969, Ewart, 1982). The older basalts are predominantly hawaiites (Veevers et al. 1964a) but include tholeiitic basalts (Bird et al. 1990). The interbedded basalts are more K-rich basalts and mugearites. Younger basalt flows cap hills east of Springsure and Mount Boorambool. These rocks are predominantly hawaiites but include tholeiitic basalts (Johnson et al. 1989).

South west of Springsure township a K-Ar age determination on basalt gave an age of 27.8 Ma (Bird et al. 1990), which is consistent with other ages obtained from basalts of the Springsure Province (Webb and McDougall 1967, Ewart 1982) and is close to the sample locality for this study.

9.5 WESTERN SPRINGSURE, SPRINGSURE VOLCANIC PROVINCE

9.5.1 Nature of the Exposure

This basalt outcrops at the crest of a small rise in the basalt plains. The main flow represented at this locality shows well developed spheroidal weathering (Figure 9.1, Plate 9.1, Appendix 1). Because of the semi-arid environment, the clay-bearing onionskin material dries and becomes a crumbly gravel which flakes away from the face and forms a rubble apron at the base of the profile. Hence, the corestones (EFT22/4, EFT22/3a) form resistant knobs in the face with the more weathered material (EFT22/3,
EFT/2) about them less prominent. Incipiently weathered corestones persist to the land surface and it is not apparent that weathering occurred preferentially from the surface down. The black/brown dusty skeletal soil (EFT22/1) that caps this sequence is comprised of crumbly gravel material of disaggregated onionskins with some pebbles of less weathered basalt and in places corestone float.

To the east of the main profile vesicular basalt (EFT22/6, EFT22/5) crops out, at a similar depth to the massive basalt sampled, and may represent the flow top. Corestone development in this vesicular material is not as apparent, despite it being moderately to intensely weathered in hand specimen. White chalky calcium carbonate veins pass through the profile generally following the zones of more weathered material between corestones.
9.5.2 Geochemistry

For the basalt samples (EFT22/2, EFT22/3, EFT22/3a, EFT22/4, EFT22/5, EFT22/6) the isocons are best fit lines through the representative points (Y), Nb, Zr, Al and (Ti) which are believed to be the least mobile elements. The fresh basalt used for isocon construction is hawaiite from Springsure Volcanic Province (sample numbers 38747 & AK71, Appendix 2).

The slopes \( \frac{C_i^W}{C_i^O} \) of the isocon lines reflect the progressive increase in mass loss \( \Delta M \) and hence increase in intensity of weathering of the basalt samples outward from corestones. The scoriaceous material is more weathered because of ease of fluid flow through the more permeable material.

\[
\begin{align*}
\text{Vesicular} & \\
EFT22/5: & \quad C_i^W/C_i^O = 1.25 \quad \Delta M = -20\% \\
EFT22/6: & \quad C_i^W/C_i^O = 1.22 \quad \Delta M = -18\% \\
\text{Massive} & \\
EFT22/2: & \quad C_i^W/C_i^O = 1.16 \quad \Delta M = -14\% \\
EFT22/3: & \quad C_i^W/C_i^O = 1.12 \quad \Delta M = -11\% \quad \text{INCREASE IN} \\
EFT22/3a: & \quad C_i^W/C_i^O = 1.10 \quad \Delta M = -09\% \quad \text{DEGREE OF} \\
EFT22/4: & \quad C_i^W/C_i^O = 1.10 \quad \Delta M = -09\% \quad \text{WEATHERING}
\end{align*}
\]

Cr, Fe\(_2\)O\(_3\) and Ni show strong enrichment in these samples. La, Zn, V all show major enrichment, Zn is enriched early and thereafter maintains an elevated concentration, while La and V are progressively enriched with weathering. Mn is also progressively enriched, but is depleted from the vesicular samples. Pb, Ba and Cu are depleted early in weathering then progressively increase in abundance as weathering proceeds (Figure 9.3).

Ce, Th, P, Ca and Sr maintain relatively constant concentrations but become slightly enriched in the most weathered samples. This is most unusual for Ca and Sr which are usually removed early in the weathering of basalt. In contrast Mg maintains a relatively constant concentration and then is lost from the most weathered samples. Si, K, Rb and Na all show relatively constant values throughout weathering which is unusual as K and Na are usually mobilised early in weathering. FeO and S are strongly depleted early in weathering (Figure 9.3).
Chapter 9: Basalt Weathering Profiles from Central Queensland
Figure 9.3
Isocon diagrams and corresponding histograms for EFT22/2, EFT22/3, EFT22/3a, EFT22/4, EFT22/5, EFT22/6.
Histograms show relative mass change (%) for analysed elements.
9.5.3 Clay Mineralogy

Samples EFT22/4 and EFT22/3a have peaks for most primary basalt minerals in their XRD traces including plagioclase feldspar, magnetite, ilmenite and very minor amounts pyroxene (Figure 9.4). Peaks for olivine are not observed. Dioctahedral nontronite and an Al-smectite are the dominant secondary minerals, with a minor amount of trioctahedral clay, and goethite and hematite are present. Minor amounts of kaolinite may be present. The cation exchange capacities (CEC) for the clay separates lie within the range 25 meq/100 g to 37 meq/100 g, and the corresponding Si:Al ratios are 2.44 to 2.85. These values are within the range characteristic for smectite clays, although the silica content is a little high. Elevated silica content can be attributed to the presence of a small amount of crushed primary silicate minerals in the clay separate. Minor amounts of calcite are present.

Further out from the corestones, more intensely weathered samples EFT22/3 and EFT22/2 show the loss of pyroxene peaks from the XRD trace, with progressive increase in weathering. Plagioclase feldspar, magnetite and ilmenite peaks persist in the traces, but the peak intensities for plagioclase are reduced. Secondary goethite and hematite are more
abundant in the samples. Smectite clay minerals are abundant in these weathered basalts and the assemblage includes a mixture of nontronite and Al-smectite, with a minor amount of trioctahedral saponite. Minor amounts of kaolinite may be present. The CEC for these clays are between 43 meq/100 g to 58 meq/100 g and the Si:Al ratios are within the range 2.07 to 2.62. The values are typical for an assemblage dominated by smectite clays. Vesicle lining material is identified as a mixture of nontronite and Al-smectite, and there may be some calcite present.

The more intensely weathered vesicular basalts, EFT22/5 and EFT22/6, have primary plagioclase feldspar, magnetite and ilmenite peaks preserved in their XRD traces but pyroxene and olivine peaks are absent (Figure 9.4). Secondary iron oxyhydroxides are present in the samples, and in the case of EFT22/5, hematite gives the sample a red colouration in hand specimen. Smectite clay is the dominant secondary product and the assemblage is probably a mixture of nontronite and Al-smectite. Accordingly the CEC for the clay separates are within the range 43 meq/100 g to 50 meq/100 g and the Si:Al ratios are 2.85 to 2.88. The silica values are elevated. The same mixture of smectite clays, with the possible addition of minor saponite, was found as vesicle lining material in both samples. Goethite peaks were present in the XRD traces for material lining the vesicles.

Summary

The secondary products at this locality are dominated by dioctahedral smectites, most likely a mixture of nontronite, beidellite and montmorillonite. Nontronite and beidellite are mostly neoformed during the breakdown of olivine and pyroxene, and basaltic glass. Montmorillonite is likely to be the clay derived from the breakdown of plagioclase feldspar as there was no evidence of alteration of this phase to kaolin group clays in the XRD traces.

Trioctahedral smectite phases are not abundant at this locality. Although these clays are likely to be those first formed during the weathering of olivine and possibly pyroxene, these silicates are present as groundmass phases only, and as olivine breaks down very early in weathering, little trioctahedral smectite (saponite), is preserved. Small amounts of saponite are preserved in vesicle linings, perhaps implying that they have formed more recently.

Goethite seems to be the dominant secondary Fe-bearing phase initially released during the breakdown of groundmass ferromagnesian silicates, as observed in thin section, but it is rapidly dehydrated to hematite during periods of drying of the profile. Hematite is present adjacent to microcracks, voids and exposed basalt surfaces, while goethite is
better preserved within the less weathered material. Goethite is present with clays lining vesicles, but these linings may have formed much later in weathering.

9.5.4 Petrography

The least weathered samples, EFT22/4 and EFT22/3a, have a well preserved primary pilotaxitic texture with abundant fine grained feldspar laths forming 70 to 80% of the groundmass. All groundmass olivine and basaltic glass have weathered to secondary clays, with some goethite staining apparent. In many places where glass has weathered, there is a rim of clays formed at the edge of the secondary products and this preserves the shape of the inter-lath pocket the glass originally filled (Plate 9.2).

In weathering rinds on these basalt samples, and adjacent to microfractures the clays combine with goethite and hematite. Occasional fine veinlets in this material are infilled with calcite. Groundmass pyroxene is present and partially preserves a sub-ophitic texture with the plagioclase feldspars. The pyroxene is pink-pleochroic titanaugite. Clusters of euhedral opaque oxides, some up to microphenocryst size, are probably magnetite with some ilmenite and are well preserved between the feldspar laths. The only obvious phenocrysts observed are sparsely distributed olivine crystals that are wholly weathered to secondary clays, probably dioctahedral smectites. Less obvious are rare blocky microphenocrysts of alkali feldspar present within the plagioclase feldspar material.

Within the more weathered samples of massive basalt, EFT22/3 and EFT22/2, hematite and goethite are much more widespread staining clays throughout the groundmass. Few groundmass pyroxene grains are preserved and plagioclase laths are etched, weathered to clays. Opaque oxides preserve their euhedral shape and are not affected by chemical dissolution. Cracks are more common in these materials, and adjacent to cracks weathering is much more intense with secondary Fe-bearing phases abundant in the weathering products (Plate 9.3).

The vesicular material, EFT22/6, is more intensely weathered but does not have as many micro-fractures cross-cutting it so does not have as much hematite and goethite throughout the groundmass. Instead the plagioclase feldspar laths have largely weathered to clays. Hence, the only groundmass phases preserved are etched relict plagioclase feldspars and euhedral opaque oxides. All voids, even very small ones, are infilled with secondary clays and the larger ones have calcite filling the centre of the amygdales (Plate 9.4, Plate 9.5).
Plate 9.2
EFT22/4 (crossed polars)
This moderately weathered basalt has a well preserved primary pilotaxitic texture. Titanaugite forms a subophitic texture in the groundmass.

Plate 9.3
EFT22/3 (crossed polars)
Ferromagnesian silicates and basaltic glass have weathered to goethite stained clays. Angular opaque oxides are preserved unweathered.

Plate 9.4
EFT22/5 (crossed polars)
Poorly oriented clays are replacing groundmass plagioclase. Angular opaque oxides are preserved unweathered.

Plate 9.5
EFT22/5 (crossed polars)
Etched plagioclase feldspar laths lie within hematite stained clays. Angular opaque oxides persist. There appear to be two populations of opaque minerals.
EFT22/5 is pervasively weathered with relict plagioclase feldspar laths and euhedral opaque oxides the only identifiable primary minerals. The balance of the sample is hematite stained clays and voids are lined by yellow (goethite stained) clay minerals. In some vesicles fragments of clay coated feldspar laths are preserved. A single small blocky alkali feldspar microphenocryst was observed, and is probably more apparent in this material because it is slightly more resistant to weathering than plagioclase feldspar.

9.5.5 Profile Summary

Physical frittering of weathered basalt from the face as a result of profile desiccation is a very active contemporary process. The soil is very thin and primarily comprised of rubbly fragments of weathered basalt indicating that throughflow of fluids at this locality is episodic and there is insufficient time when the profile is wet for any depth of clay-rich soil to form. This basalt does not preserve an older deep weathering profile despite its emplacement around 27.8 Ma, prior to the warm humid late Oligocene-early Miocene and Quaternary interglacial periods, implying that the climate of these inland localities has been semi-arid for a considerable period of time, or that evidence of older weathering has been stripped off at this site. Carbonate is present as a secondary precipitate at this locality and this may explain why there is an enrichment in La, Ba and Pb. The dryness (reduced fluid throughflow) of the profile may the explanation for the longer retention of alkali and alkaline earth cations in the profile.

9.6 GEOLOGY - PEAK RANGE VOLCANIC PROVINCE

The Peak Range Volcanic Province is an 100 km long chain of residual volcanic peaks, a number with ponded lava caps, that trend approximately north-west, south-east and cover an area of approximately 2,500 km² (Olgers 1969, Johnson et al. 1989). They are composed of trachyte, rhyolite and basalt (Veevers et al. 1964, Mollan 1965, Wellman 1978) and rise up to 450 m above the surrounding lava plains. The clear alignment of peak forming centres in this province suggests that volcanic activity is related to a major structural feature. A basement high of Upper Devonian to Lower Carboniferous volcanic rocks underlies the Peak Range and Mollan (1965) suggests that magma has risen along a pre-Permian fault.

Because of the close spatial arrangement between basaltic dykes in central Peak Range, and remnants of flat lying basalts, the most intense activity is likely to have been focussed in this area. However, there are multiple centres, distributed over a wide area, that may have contributed lava to the plains basalts (Johnson et al. 1989). Alkaline basalts (hawaiites) are predominant in the south of the Province, and have been dated at 30 Ma to
27 Ma (Wellman & McDougall 1974). Tholeiitic basalts are more common in the north and have been dated at 40 Ma to 34 Ma (Wellman & McDougall 1974).

9.7 STOCK ROUTE, PEAK RANGE VOLCANIC PROVINCE

9.7.1 Nature of the Exposure

The weathered basalt profile is exposed in the wall of a small quarry in the plains basalts (Figure 9.5, Plate 9.6, Appendix 1). There are two basalt flows represented at this locality. The lower basalt shows well developed spheroidal weathering and is cross-cut by chalky calcium carbonate veins. Intensely weathered, massive, basalt (EFT9/10) forms the body of the flow, and the upper part is vesicular (EFT9/9). The red coloured vesicular flow top basalt is weathered in hand specimen but is indurated, and vesicles are lined with pale blue-grey smectite clays and calcite. This basalt is separated from the overlying flow by a 30 cm thick layer of secondary chalky calcium carbonate material EFT9/8.

Vesicular material (EFT9/5) at the base of the overlying basalt is weathered and has considerable precipitation of secondary carbonate within vesicles and voids in its structure, and other secondary products have replaced primary minerals. The body of the upper intensely weathered basalt (EFT9/4) is more massive than the base and has well developed corestones.
The basalts have veins cross-cutting them with concentrations of clay minerals and carbonates (EFT9/6, EFT9/7). The basalt sequence is overlain by a gravelly dusty brown-olive skeletal soil (EFT9/1) formed largely from frittered onionskin material. Some clays (EFT9/2) have formed in depressions in the basalt, and nodular carbonate material is recognised in the soil zone (EFT9/3).

Plate 9.6
Stock Route profile

9.7.2 Geochemistry

For the basalt samples (EFT9/4, EFT9/5, EFT9/9, EFT9/10) the isocons are best fit lines through the representative points Y and Ti are believed to be the least mobile element pair. At this locality most elements appear to have been mobile to some degree and the interpretation derived from the isocon diagrams gives a broad indication of the likely element pathways, and the overall mass balance. The fresh basalt used for isocon construction is basanite from Peak Range province (sample number EAV87, Appendix 2).

<table>
<thead>
<tr>
<th>Upper</th>
<th>EFT9/4: $C_1^W/C_1^O = 0.56$</th>
<th>$\Delta M = +79%$ (Massive)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EFT9/5: $C_1^W/C_1^O = 0.73$</td>
<td>$\Delta M = +37%$ (Vesicular)</td>
</tr>
<tr>
<td></td>
<td><strong>CHALKY CALCIUM CARBONATE</strong></td>
<td></td>
</tr>
<tr>
<td>EFT9/9:</td>
<td>$C_1^W/C_1^O = 0.83$</td>
<td>$\Delta M = +20%$ (Vesicular)</td>
</tr>
<tr>
<td>EFT9/10:</td>
<td>$C_1^W/C_1^O = 0.66$</td>
<td>$\Delta M = +52%$ (Massive)</td>
</tr>
</tbody>
</table>
Lower Basalt

The slopes (CiW/CiO) of the isocon lines are less than 1 showing that there has been a mass gain for these samples. At this locality the samples have been flushed with calcium carbonate rich fluids and the mass gain can be attributed to the secondary precipitation in veins and veinlets and infilling of voids with calcite. In addition there has been enhanced clay formation. If it is assumed that approximately similar amounts of calcite have been added to all of the samples then the sample with the largest mass gain (ΔM) was originally the least weathered basalt, and the sample with the smallest mass gain was originally the most weathered basalt.

Fe₂O₃, Cr, Si and Al are all extremely enriched, but Si and Al slightly less so in the more vesicular material (Figure 9.6). Ni shows progressive enrichment with weathering. Pb, Cu and Zn are all significantly enriched but show a slight depletion with increase in weathering and carbonate precipitation. V shows a similar trend but is much more depleted with weathering than Pb, Cu and Zn. Na and Ca have values that straddle the isocon implying that their overall concentration has remained relatively stable. Mn and Rb
are progressively depleted from the massive to the vesicular material and La, Th, Mg and Zr all show major depletion throughout the basalt. Ba, K, P and Sr show an increase in depletion from major to extreme with increase in weathering, and S, Nb, Ce and FeO are extremely depleted in both samples.

**Upper Basalt**

![Isocron diagrams and corresponding histograms for EFT9/4 and EFT9/5](image)

Histograms show relative mass change (%) for analysed elements.

Cr, Fe₂O₃, Ni, Al and Si all show extreme enrichment in both samples. Pb, Cu and S show progressive enrichment with weathering and increased carbonate precipitation (Figure 9.7). Zn, Mg and Mn show progressive depletion from the massive basalt (EFT9/4) to the vesicular basalt (EFT9/5). V, Na and Ca have values that remain relatively constant. This is unusual for Na and Ca as they are readily mobilised during basalt weathering. Ba, La, Ce, Th, Zr, K, Rb, Sr, P, Nb and FeO all show major depletion with increased weathering. Th might normally be expected to be slightly enriched and Nb and Zr generally remain relatively immobile during basalt weathering, so this strong depletion is unusual.
9.7.3 Clay Mineralogy

The four basalt samples from this locality (EFT9/4, EFT9/5, EFT9/9, EFT9/10) are all very intensely weathered and the only primary mineral peaks apparent in their traces are for plagioclase feldspar and minor magnetite and/or ilmenite (Figure 9.8). Secondary products are dominant with smectite clay peaks clearly defined and goethite and hematite peaks present on the XRD traces. The smectite clay assemblage is composed of a mixture of saponite, nontronite and Al-smectite. CEC values between 47 meq/100 g and 91 meq/100 g are typical for a smectite clay dominant assemblage, and the Si:Al ratios for the clay separate, between 2.04 and 2.66, are also within the smectite range. Two principal types of vesicle fill material are identified including the same assemblage of smectite clays, and calcite. Calcite peaks are present on all four traces and calcite has precipitated in veinlets as well as in voids in the weathering basalt.

![Figure 9.8](image)

**Figure 9.8**
Stacked X-ray diffraction (XRD) traces for samples EFT9/10, EFT9/9, EFT9/5 and EFT9/4.

Sample EFT9/8 is taken from a 30 cm thick white layer cross cutting the exposure parallel to, and separating, the two flows. It is composed of chalky calcite and is thought to represent a ground water/water table carbonate deposit.

Clays sampled from a vein cutting the upper flow (EFT9/6, EFT9/7) show accumulations of secondary clay minerals mixed with calcite. EFT9/6 is mostly composed of a mixture
of nontronite and Al-smectite. The adjacent sample, EFT9/7, is composed of a similar assemblage with associated chalky, fine grained calcite. The CEC for the relatively pure clay separates are 102 meq/100 g and 104 meq/100 g respectively and the corresponding Si:Al ratios are 2.40 and 2.45.

At the base of the soil a pocket of clay-rich material (EFT9/2) and a mottled zone with nodular white material (EFT9/3) are preserved. The clay-rich material, EFT9/2, is a mixture of nontronite, Al-smectite and has a CEC of 106 and a Si:Al ratio of 2.02. The white nodular material is fine grained calcite.

The overlying skeletal soil EFT9/1, is brown-olive in colour and is dominated by the smectitic clays nontronite and Al-smectite. The CEC for the clay separate is 95 meq/100 g and the Si:Al ratio is 2.05. A minor amount of relict feldspar is preserved in the soil and peaks for goethite and calcite are recognised in the XRD traces.

Summary

The mass gains (ΔM) for the basalt samples can be accounted for by secondary calcite precipitated in veinlets and vesicles, in addition to secondary iron oxyhydroxides precipitated throughout the weathered rock and neoformed clay minerals replacing primary minerals. Largely the processes of basalt weathering that might be expected at this locality have taken place and are only slightly affected by the secondary carbonate precipitation. Smectite clays are the dominant neoformed clays but kaolin group clay has formed in some of the veins cross-cutting the basalts. The kaolin group clays probably formed due to the continued leaching of cations from smectite clays in these zones of preferred fluid flow. Alternatively this could be an overprinting of weathering by more acid fluids. Fe-oxyhydroxides are abundant and their distribution is generally associated with open cracks, exposed faces and vesicles. Goethite stains neoformed clays within the basalt and clay linings within vesicles. Hematite dominates elsewhere, implying that goethite is dehydrated to hematite in exposed areas, when the profile dries out.

9.7.4 Petrography

The weathered massive basalt samples (EFT9/4, EFT9/10) have preserved plagioclase feldspar laths and rare grains of pyroxene. In areas of the sample distant from microcracks, basaltic texture is well preserved. Euhedral opaque oxides which preserve their angular inter-lath shape are preserved largely unweathered. Calcite has precipitated in voids in the weathering basalt (Plate 9.6, Plate 9.7). Large areas of the matrix are occupied by oriented secondary clays. Former areas of glass groundmass have been replaced with oriented clays but the original shape of the inter-lath space is preserved, and
Olivine pseudomorphs with goethite rims have calcite precipitating in place of clays in their core.

Calcite infills vesicles, voids within weathered minerals and microfractures throughout this basalt. Hematite is the dominant Fe oxide in the groundmass.

Pseudomorphs of ferromagnesian silicates have oriented clays enclosed within a goethite rich rims.

Clays replace weathered groundmass phases and preserve the inter-lath morphology. Concentric banding can be observed within these clays.
Plate 9.10
EFT9/10 (crossed polars)
Convolute textured hematite, goethite and stained clays infill voids adjacent to microcracks. Within this material secondary calcite has precipitated.

Plate 9.11
EFT9/10 (crossed polars)
Pseudomorphs of euhedral olivine have goethitic rims which enclose orientated clays.

Plate 9.12
EFT9/4 (crossed polars)
Vesicles are infilled with hematite, goethite and stained clays. Weathering is more intense proximal to microfractures.

Plate 9.13
EFT9/5 (crossed polars)
Hematite is the dominant Fe oxide replacing groundmass phases.
there is an internal concentric banding in the clays. Pseudomorphs of olivine phenocrysts have goethitic rims preserved but the enclosed areas, which were first weathered to poorly oriented smectite clays, have been replaced by convolute textured oriented clays (Plate 9.8, Plate 9.9).

Large areas (2 to 3 mm diameter) adjacent to cracks, are completely infilled with convolute textured hematite, goethite and stained clays, and in voids within this material calcite is precipitated (Plate 9.10, Plate 9.11). The groundmass surrounding these areas has been preferentially weathered to secondary products, most obvious because of the Fe-staining (Plate 9.12, Plate 9.13). Proximal to open veinlets Fe-staining and secondary poorly oriented clay mineral formation is more prevalent. Calcite is also precipitated in micro-veinlets cross-cutting the basalt.

The weathered vesicular basalts (EFT9/5, EFT9/9) have relatively pervasive hematite staining of the groundmass, which imparts a red colouration to the hand specimen. The groundmass plagioclase feldspar laths have suffered greater dissolution than those in the massive basalts and no primary ferromagnesian silicates are preserved. Feldspars are weathering to poorly oriented clays and may be replaced by cryptocrystalline calcite. Euhedral opaque oxides are present, but etching of the grains and alteration to hematite may have commenced. Oriented clays line interlath pockets and concentric textures are present within the clays. Vesicles are lined with hematite and goethite stained clays, and many are infilled by calcite. Occasionally calcite has precipitated in the voids within the goethite rims of olivine pseudomorphs, replacing the clay minerals that were formerly present.

EFT9/3, a carbonate nodule from the soil zone, is composed of cryptocrystalline calcite and has very little internal structure. There is some dendritic manganese on the surface and within the nodular material. Pockets, up to 2 mm diameter, of relict minerals and secondary products from the weathered basalt, are enclosed within the nodule.

9.7.5 Profile Summary

The vesicular basalts were subject to greater weathering because they are more permeable, and they are closer to an obvious zone of fluid throughflow. The vesicular basalts were more intensely weathered prior to calcite precipitation than the massive basalts because of the greater porosity and permeability. So, when the calcite precipitated into the weathered materials, the massive basalts show a greater mass gain than their vesicular equivalents. Veins cross-cutting the basalts are fine grained calcium carbonate and smectite clays. The formation of discrete areas of quite large amounts of clay may be attributed to the very high throughflow of fluids at this locality. The central interbasaltic
chalky-calcite horizon is greater than 30 cm thick and the volume of fluids required to deposit such a vein is considerable. The most notable change in element mobility patterns is reflected by Nb and Zr which have apparently been mobile in this profile, in the alkaline fluids.
CHAPTER 10

BASALT WEATHERING PROFILES FROM NORTHERN QUEENSLAND

10.1 LOCATION

The Atherton Volcanic Province (Figure 10.1) covers most of the Atherton Tableland, approximately 40 km south west of Cairns (De Keyser & Lucas, 1968). Some flows roughly parallel the path of the Palmerston Highway and extend down to, and spread across, the coastal plain in the Innisfail area. Some younger eruptives in the Innisfail area are derived locally. Three profiles were sampled in this province at Archers Creek, Millaa Millaa and near Innisfail (Figure 10.1, Appendix 1).

Figure 10.1
Sample localities in the Atherton, McBride and Nulla Volcanic Provinces, Northern Queensland.

At the first sample site weathered basalt is exposed in a road cutting where the Kennedy Highway cuts Archers Creek (17.39°S 145.20°E), west south west of Ravenshoe. At the
Chapter 10: Basalt Weathering Profiles from Northern Queensland

southern end of the Atherton Tableland, a profile was sampled just east of Millaa Millaa on the Palmerston Highway (17.31°S 145.38°E). The third profile was sampled inland of Innisfail (17.33°S 145.58°E) where a deep weathering profile has developed on basalt that is being quarried for road aggregate.

The McBride Volcanic Province (Figure 10.1) lies approximately 150 km south west of Atherton and is bisected by the Kennedy Highway which truncates the Murronga Basalt approximately 12 km north of Conjuboy (18.35°S 144.44°E). A weathered profile on the Murronga Basalt was sampled in this road cutting.

Approximately 150 km inland from Townsville, the Nulla Volcanic Province (Figure 10.1) lies to the south and south west of the Burdekin River. A profile was sampled in a small road aggregate quarry on the western side of Fletcher Vale Road (19.50°S 145.42E).

### 10.2 CONTEMPORARY CLIMATE

<table>
<thead>
<tr>
<th>LMAC</th>
<th>ARCHERS CREEK</th>
<th>QFT11</th>
<th>QFT8</th>
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<tr>
<td></td>
<td>MILAA MILAA</td>
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<td>70.55</td>
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Table 10.1

Contemporary climate information of the Atherton Volcanic Province.
Chapter 10: Basalt Weathering Profiles from Northern Queensland 216

This region is situated between the latitudes 17° to 20° south, so the climate is tropical to sub-tropical (Table 10.1, 10.2). Although annual mean radiation at all localities is very similar, inland sites have marginally higher average radiation and correspondingly have higher recorded pan evaporation rates. Average annual pan evaporation for a locality immediately west of Nulla Volcanic Province ranges from 1,700 to 2,000 mm, while for Atherton evaporation is in the order of 1,300 to 1,400 mm (Isbell et al. 1976). The Innisfail locality has the lowest annual mean radiation, because it is affected by coastal cloud cover.

Atherton Tableland localities have the coolest annual mean temperatures, Innisfail has higher average temperatures and the inland localities are warmer in the summer time but as cool as Atherton in the winter time.

<table>
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<td>Lowest Monthly Radiation</td>
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<tr>
<td>Precipitation Driest Quarter</td>
<td>26.18</td>
<td>39.41</td>
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Table 10.2

Contemporary climate information for the McBride and Nulla Volcanic Provinces.

Rainfall is considerably greater at Innisfail than at the other localities because this area is affected by the coastal weather regime. In the tropics, coastal regions are prone to summer cyclones and rainfall is largely associated with high intensity, short duration thunderstorms. Atherton Tableland localities are sufficiently close to the coast to be influenced by the higher rainfall but, the annual precipitation for the Atherton localities is
less than half that of coastal region. McBride and Nulla provinces receive considerably less precipitation, and the region can be considered semi-arid.

Rainfall is very seasonal with the greatest precipitation in summer months. Winter precipitation (driest quarter) is less than 20% of the summer rainfall, hence water deficits occur in many Atherton and most Nulla and McBride weathering profiles in winter. Isbell et al. (1976) suggest that in areas where mean annual rainfall is greater than 1,600 mm, weathered profiles are likely to dry out for periods of days, while at sites with lower annual rainfall profiles are likely to be dry for periods of a few months or more. The hydrological balance analysis carried out by Lepsch (1989) for the Innisfail area, using the method of Thornthwaite and Mather (1955), shows that the seasonality of rainfall does not cause any apparent water deficit periods for this area. This implies a very high rate of fluid percolation and an absence of periods where the soil is dry for more than several days (Lepsch 1989). Increased throughflow allows for a greater amount of element mobilisation because of enhanced dissolution of primary minerals.

10.3 PALEOCLIMATE AND VEGETATION

Paleoclimate

Fluvial and lacustrine sediments are often preserved beneath and within the basalt sequences. Floral and faunal fossils are found in such sediments, but in the deposits near Nulla (Archer & Wade 1976) and McBride (White & Crespin 1959, McNamara 1990, Gaffney and McNamara 1990) vertebrate fossils are the most studied. Vertebrate fossils give only a broad indication of the climatic regime, however, the presence of terrestrial and arboreal mammals in the Allingham Creek deposits (Archer & Wade 1976), underlying Nulla Basalt, give an indication that the surrounding area supported savannah woodland around 4.5 to 4 Ma ago (Wyatt and Webb 1970). This forest type implies that climatic conditions were relatively dry in the Pliocene.

On the Atherton Tableland, a comprehensive palynological study of lake sediments preserved in Lynch's Crater and Strenekoff's Crater (Kershaw et al. 1991), has provided evidence for climatic periods wetter and drier than the present during the Quaternary. In particular Kershaw et al. (1991) detail two considerably drier periods, where rainfall was between 500 and 1,500 mm, one between 9,000 to 78,000 years B.P. and another about 170,000 to 126,000 years B.P.
Vegetation

On the Atherton Tableland rainforest originally predominated, with schlerophyll woodland to open woodland developing in more arid areas (Webb 1959, Webb 1968, Tracey and Webb 1975, Tracey 1982). Areas of open forest or woodland have an associated moderately dense grass or sedge ground cover (Isbell et al. 1976). Around the turn of the century, forest on gentler slopes was cleared for agricultural purposes (Laffan 1988). Today a complex mosaic of rainforest and woodland is preserved on the ranges, while improved pastures have been developed on rolling country, and crops are grown on the gently undulating and fertile weathered lava flows (Laffan 1988).

In the Innisfail area most of the original rainforest has been cleared from the coastal plain and the land cultivated for improved pasture and sugar cane, with some small banana and tea plantations (Lepsch 1989).

Inland, the soils of the Nulla and McBride provinces, support open woodland and, in areas of higher precipitation, woodland communities (Isbell and Murtha 1972). The grass cover is moderately dense in the open woodland-woodland forests (Isbell et al. 1976). Large areas are cleared and form open grasslands.

10.4 GEOLOGY - ATHERTON VOLCANIC PROVINCE

The Atherton Volcanic Province can be divided into two portions, the flat to rolling country of the Atherton Tableland which is more deeply dissected in the south (Isbell et al. 1976, Laffan 1988, Warrell et al. 1987), and the younger eruptives that stretch south east, to the coastal plain near Innisfail (Lepsch 1989).

Atherton Tableland

The Atherton Tableland is an elevated plateau approximately 30 km inland from the coast, which lies between 700 m and 900 m above sea level, with a maximum elevation of 1,370 m at Mt Fisher in the south. The geology and soils of the region have been described and mapped by a number of workers (Best 1962, Isbell et al. 1968, Isbell et al. 1976, Isbell et al. 1977, Isbell 1980, Laffan 1988). The most extensive rock type is basalt which extends from Rocky Creek on the northeastern boundary of the region, to Ravenshoe in the west, and beyond Millaa Millaa on the southern boundary of the Atherton Tableland (Laffan 1988). The composition of basaltic rocks in the Atherton Volcanic Province range from basanite and alkali basalt to tholeiitic basalt (Isbell et al. 1976, Johnson et al. 1989), and the age range of the basalts is 3.1 Ma to 10,000 yr B.P (Stephenson & Coventry 1986). In the Archer’s Creek area, flows from the Ravenshoe
volcano follow the Millstream for 20 kilometers and are dated at 1.2 Ma (Stephenson & Coventry 1986). The basalts sampled in this study may be of similar age.

**Innisfail and the Coastal Plain**

Laffan (1988) correlates the greater dissection and relief in the south of the Atherton Tableland with higher rainfall. The basalts in this southern area of the Atherton Tableland are younger than the topographic features and in places lavas have followed valleys towards the coast (Isbell et al. 1976). On the coastal plain strongly dissected remnants of these valley fill flows, are perforated by younger vents and overlain by preserved scoria cone materials and associated minor lava flows (Lepsch 1989).

The age range of the basalts in the Innisfail area is 3.3 Ma to 1.6 Ma for the flows that have descended from the southern Atherton Tableland and 0.8 Ma to 0.645 Ma for eruptives originating on the coastal plain (Lepsch 1989, Stephenson & Coventry 1986). The lava being quarried inland of Innisfail may be of similar age to a lava sampled just below Crawford's Lookout on the Palmerston Highway (1.61 Ma).

**10.5 ARCHERS CREEK ATHERTON VOLCANIC PROVINCE**

**10.5.1 Nature of the Exposure**

This profile is in an upper slope position, is extremely thick and incorporates at least two basalt flows (Figure 10.2, Plate 10.1, Appendix 1). At the base the lower basalt is massive and blocky (LMAC25), but becomes more weathered and red coloured up-profile (LMAC24, LMAC23).

Higher in the stratigraphy an unconsolidated conglomerate with rounded pebbles (LMAC21) is overlain by weathered gravelly quartzose sediment (LMAC20) which grades into a fining upward sequence of weathered sediments (LMAC19, LMAC18, LMAC17, LMAC16). A well developed mottled zone has formed as a result of the leaching of these materials, which appear to have been preferentially weathered from the top down. A yellow coloured firm clay (LMAC15) layer lies at the top of the mottled zone and above this a layer of gleyed grey clay material (LMAC14, LMAC13, LMAC11) crops out.

The base of the upper basalt appears quite vesicular (LMAC12), however higher in the sequence blocks of relatively fresh to incipiently weathered massive basalt (LMAC22) are exposed. Despite being lower in the profile, LMAC12 is marginally more weathered than LMAC22. Basalt corestones (LMAC8, LMAC10), surrounded by onionskins of more
intensely weathered basalt (LMAC9), are well developed in the middle and upper parts of the flow.

Higher again in the sequence, corestones appear to be more vesicular (LMAC6) and more intensely weathered, with rubbly clay-rich material (LMAC7, LMAC 5) surrounding them. A red and grey mottled clay (LMAC4) overlies the basalt sequence, and above this again lies a layer of orange-brown gravel to pebble sized, goethite coated, nodular material (LMAC3). This material is in turn overlain by a yellow-brown coloured goethite-rich soil (LMAC2, LMAC1).

**Figure 10.2**
Sample points in the Archers Creek profile, Atherton Volcanic Province.
10.5.2 Geochemistry

For the basalt samples (LMAC5, LMAC6, LMAC7, LMAC8, LMAC9, LMAC10, LMAC12, LMAC22, LMAC23, LMAC24, LMAC25) the isocons are best fit lines through the representative points Y, (Nb), Zr and Ti, which are believed to be the least mobile elements. The fresh basalt used for isocon construction is basanite from Atherton Volcanic Province (sample number EAV234, Appendix 2).

The slopes ($C_i^{W}/C_i^{O}$) of the isocon lines reflect the progressive increase in mass loss ($\Delta M$) and hence increase in intensity of weathering of the basalt samples outward from corestones and upward through the profile.
Chapter 10: Basalt Weathering Profiles from Northern Queensland

Upper

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</tr>
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</tr>
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<td>WEATHERING</td>
</tr>
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</tr>
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Lower

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<tr>
<td>LMAC25</td>
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<td>-01%</td>
<td>WEATHERING</td>
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INTERBASAL SEDIMENTS

Lower Basalt

Fe₂O₃, Zn, Ni and Th are enriched in all samples. La shows an initial moderate enrichment and then maintains a relatively constant concentration with increase in degree of weathering. Pb, Ce and P plot very close to the isocon for all samples, hence have not been lost or gained in this basalt. Ba and Cr show a slight depletion, after which no further Cr is lost, and Ba is progressively enriched, as weathering proceeds. K, Ca, Sr, Mg, V, Cu, Mn, Si, Na, Rb and Al are all progressively lost from the weathering basalt. Sr shows an enrichment in the most weathered sample implying that it has been incorporated into a secondary weathering product. V and Cu might normally be expected to become enriched in weathered material. S and FeO are depleted very early in weathering but iron is fixed in the profile by oxidation of FeO to Fe₂O₃ (Figure 10.3).

Upper Flow

For the less weathered samples in the lower part of this basalt (LMAC8, LMAC9, LMAC10, LMAC12, LMAC22) Cr, Fe₂O₃, Ni and Zn all show significant enrichment. Sr is enriched initially, but is progressively depleted with weathering. Th shows moderate enrichment with increase in weathering. Many elements, including K, Si, Ba, La, Ce, Cu, Mn, P and Al maintain relatively constant concentrations, reflecting the largely incipient nature of weathering of these samples, as indicated by their low net mass losses (ΔM). Ca and V are progressively lost with weathering. Pb shows a major concentration drop initially, but is slightly enriched again in the more weathered samples. S and FeO are mostly removed from the profile (Figure 10.4).
Figure 10.3
Isocon diagrams and corresponding histograms for LMAC23, LMAC24 and LMAC25.
Histograms show relative mass change (%) for analysed elements.
Figure 10.4

Isocon diagrams and corresponding histograms for LMAC7, LMAC5, LMAC6, LMAC9, LMAC10, LMAC8, LMAC12 and LMAC22. Histograms show relative mass change (%) for analysed elements.

The upper, more weathered samples in this basalt (LMAC5, LMAC6, LMAC7) show greater variation in element flux than the corestone materials. Pb, La, Ce, Ba and Y are all anomalously enriched in the weathered vesicular basalt (LMAC6). Pb maintains a high concentration in the more weathered equivalents, Y shows progressive depletion, and La, Ce and Ba show large fluctuations in concentration. Zn shows major enrichment with fluctuating concentrations in the more weathered material.

Fe2O3, Ni and Cr are significantly enriched initially and thereafter are retained in the weathered material, but Cr is depleted again in the most weathered sample (LMAC7). V is slightly depleted, but thereafter maintains a constant concentration. K, Mg, Si, Cu, Mn and P all show a progressive depletion as weathering proceeds, although the rate of depletion of Si is slower than other cations. Al is relatively readily removed, however, locally shows enrichment. Rb, S, FeO, Na, Ca, and Sr all show strong depletion with weathering.
10.5.3 Clay Mineralogy

Lower Basalt

LMAC25 is a relatively fresh basalt with very limited clay and secondary iron oxyhydroxide development apparent from the X-ray diffraction (XRD) trace (Figure 10.5). The primary minerals identified include plagioclase feldspar, olivine, a small amount of pyroxene (augite and some orthopyroxene), magnetite and ilmenite. The coating on this sample was identified as smectite, and a vesicle fill was found to be smectite with very minor kaolin group clays present also. In both cases it was unclear whether the smectites were trioctahedral or dioctahedral. The cation exchange capacity (CEC) for this sample, 12 meq/100 g, is very low reflecting the lack of clay mineral development for this sample.

More intensely weathered basalt from this flow (LMAC24) is composed of the same suite of minerals, however, the relative abundance of them has decreased and secondary products are beginning to occur in the trace. Smectite clays have formed and some secondary iron oxyhydroxides are present in the sample, but their representative peaks are partially obscured by peaks of primary minerals. The smectites are: minor saponite and Fe-saponite, with nontronite the predominant clay present and some Al-smectite occurring. The CEC for the clay separate is 68 meq/100 g and the Si:Al ratio is 2.14, both in keeping with an assemblage dominated by smectite clays. A resinous crack coating-vesicle lining taken from this sample is identified as smectite, with a small amount of kaolin group clay.

The most weathered sample from the lower basalt LMAC23, is more vesicular than the underlying materials. Peaks for all primary minerals, except pyroxene, are preserved in this trace, although the peaks for olivine have decreased in intensity. Because olivine is still present in this strongly weathered sample, it most likely occurs as a phenocryst phase. The further development of secondary minerals is observed in the XRD trace with smectite and kaolin group clay peaks present. The smectite assemblage is dominated by dioctahedral clays, nontronite with some Al-smectite. The corresponding CEC is 72 meq/100 g and the Si:Al ratio is 1.79, which are within the range for smectite clays. In addition, hematite and minor goethite may be present. A coating on the faces bounding this sample is found to be a mixture of smectite and kaolin group clays, similar to the coating-vesicle fill material on LMAC24.
Interbasaltic Sediments

Samples LMAC21 through LMAC11, excluding LMAC12 and LMAC22, represent a sedimentary sequence which lies between the two basalts that outcrop at this locality. The lowermost samples (LMAC21, LMAC20) are fluviatile sediments with clasts up to pebble and cobble size. Overlying these are fining upward, quartz rich gravelly sands which also contain some weathered feldspar, apparently K-feldspar because samples LMAC17-19 are rich in potassium. A dioctahedral smectite, possibly montmorillonite, is the predominant secondary mineral. The cation exchange capacity (CEC) for the clay separates lie between 53 meq/100 g and 58 meq/100 g and the Si:Al ratios are in the range 2.04 to 2.54, values typical for smectite clay assemblages. A weathering profile has developed on these sediments giving them a mottled appearance. LMAC16 is the uppermost clay-rich material which has a CEC of 85 meq/100 g and a Si:Al ratio 2.16, implying that the dominant clay present is smectitic. This interval has been coloured orange by secondary Fe-oxides.

Overlying this sequence is a slightly more indurated clay-rich layer (LMAC15) which in turn is overlain by a layer of grey clay (LMAC11, LMAC13, LMAC14). This interval is rich in the dioctahedral smectite, montmorillonite. The CEC for the four clay separates range from 83 meq/100 g to 92 meq/100 g, and the Si:Al ratios are between 2.18 and
2.69, which are compatible with the clay assemblage being dominated by smectite clays. The clays are all quartz bearing and are therefore not derived from a basaltic parent. The sediments do not show laminations or other sedimentary structures characteristic of lacustrine sediments, and no diatoms were found. The massive fine grained nature of these sediments and the association with fluvial sediments in the outcrop suggests that these are overbank muds, or concentrated fluvial fines.

**Upper Basalt**

The upper basalt has a vesicular base LMAC12, however higher in the sequence blocks of relatively fresh basalt are exposed LMAC22 (Figure 10.6). These samples have very similar mineralogy, although LMAC12 is more weathered and consequently has a higher proportion of secondary minerals. Primary minerals preserved in both samples include plagioclase feldspar, olivine, pyroxene (augite), magnetite and ilmenite. No secondary clay mineral peaks are observed in the XRD trace for LMAC22 but some secondary iron oxyhydroxides may be present. LMAC12 has a small smectite peak and the clay assemblage present appears to be saponite and nontronite with some Al-smectite. Accordingly the clay separate for LMAC 12 has a CEC of 76 meq/100 g and the Si:Al ratio for this sample is 2.40. Coating and vesicle fill materials for both samples are smectitic.

Higher in the same flow weathered basalt corestones LMAC8 and LMAC10 crop out and slightly more weathered material, LMAC9, was sampled nearby. All three show roughly the same primary mineral assemblage, with the most notable difference being the loss of pyroxene from the more weathered material. Primary minerals preserved in the samples are plagioclase feldspar, olivine, magnetite, ilmenite ± pyroxene. Secondary products show an overall increase in abundance with the principal smectite peak becoming more pronounced as the basalt becomes more weathered. The CEC for the clay separates range from 17 meq/100 g to 42 meq/100 g. The Si:Al ratios range from 1.92 to 2.74. Hematite and goethite peaks become progressively more apparent, with increase in weathering. Coatings and vesicle fills analysed for these samples are all smectitic.

Higher again in the sequence the corestones become more vesicular (LMAC6) with moderately to intensely weathered rubbly material (LMAC5, LMAC7) surrounding them. LMAC6 is the freshest vesicular corestone sampled from this flow and is composed of plagioclase feldspar, olivine, magnetite and ilmenite. Secondary products are limited to minor development of kaolin group clays and the possible presence of some smectite clays. The clay separate for LMAC6 has a CEC of 15 meq/100 g which reflects the limited clay development and possibly the predominance of kaolin group clays over smectite clays. The Si:Al ratio is 2.37 which is a value more typical of smectite clays, but
silica may be elevated by the incorporation of finely crushed primary silicate phases during sample preparation. Goethite and hematite are present, but their peaks are largely obscured by those of the primary minerals. A coating on the outer surface of this corestone was identified as a mixture of dioctahedral smectite, probably nontronite with some Al-smectite, and a kaolin group clay, probably halloysite.

**Figure 10.6**
Stacked X-ray diffraction (XRD) traces for samples LMAC4, LMAC5, LMAC6, LMAC9, LMAC10, LMAC8 and LMAC12.

Soft clay-rich weathered basalt, that still maintains the original basalt texture (LMAC5), was sampled between the corestones at this level. Primary minerals have largely been weathered away with the only remaining phases being a very small amount of relict plagioclase and minor amounts of magnetite and ilmenite. Secondary products are
dominated by smectite with significant quantities of kaolin group clays forming also. An elevated plateau between the smectite and kaolin peaks (XRD) suggests that the latter is probably halloysite. It is possible that there is also some interstratified kaolin-smectite minerals formed here. This is supported by the CEC of 41 meq/100 g and Si:Al ratio of 1.46, values which are intermediate between those of discrete kaolin group clays and smectite clays. A best-fit comparison with NEWMOD (Reynolds 1985) kaolinite - dioctahedral (Fe) smectite, suggests that kaolin group clay would account for approximately 70-80%, and smectite 20-30%, of the interstratified clay. Secondary hematite and goethite are present.

More intensely weathered basalt LMAC7, shows a limited primary assemblage including plagioclase, magnetite and ilmenite. Secondary products are more apparent in the XRD trace for this sample and include halloysite and dioctahedral smectite, probably nontronite with some Al-smectite. The clay separate for this sample has a CEC of 20 meq/100 g and a Si:Al ratio of 1.64, which suggests that there may be some interstratified halloysite-smectite clays present. Small amounts of goethite with some hematite occur also. The outer coating on this sample was found to be a mixture of dioctahedral smectite, predominantly nontronite with some Al-smectite, and halloysite. This is almost identical to the material found coating the nearby corestone LMAC6.

LMAC4 is a red and grey streaky mottled clay that sits at the top of this basalt sequence. It has a very similar mineralogy to LMAC5 and LMAC7 but no longer preserves the primary basaltic texture. The grey and red streaks were analysed separately and both were found to have a similar composition dominated by a mixture of dioctahedral smectite clay, and kaolin group clays. The clay mineral assemblage is dominated by nontronite and halloysite with some Al-smectite present. The CEC of 27 meq/100 g and Si:Al ratio of 1.41 supports the suggestion that interstratified halloysite-smectite clays may be present. A best-fit comparison with NEWMOD (Reynolds 1985) kaolinite - dioctahedral (Fe) smectite, suggests that kaolin group clay would account for approximately 70-80%, and smectite 20-30%, of the interstratified clay. Minor amounts of quartz were apparent in the XRD trace. The quartz is thought to have been introduced from higher in the sequence as this mineral is not recognised in samples taken beneath this clay layer. The red colouration of some of this clay material is probably attributable to minor amounts of hematite, but peaks for this mineral are not well defined on the XRD trace for the clay separate.

Overlying Sediments and Soil

Immediately overlying the basalt sequence is a coarse gravelly sediment with small quartzose pebbles coated in yellow coloured, goethite stained, clay material. This is
superseded by a yellow sandy layer and ultimately a goethite stained kaolinitic soil. The soil material (LMAC3, LMAC2, LMAC1) is transported quartz rich sediment with strong secondary weathering to kaolin group clays and goethite. The CEC for the clay separate from these samples are in the range 9 meq/100 g to 11 meq/100 g and the Si:Al ratios are between 1.02 and 1.06, values within the range for kaolin group clay assemblages.

Summary

The clay mineralogy of the lower basalt is dominated by smectite clays. The least weathered sample has almost no clay content except that associated with the incipient formation of rims around olivine phenocrysts. Trioctahedral smectite clays, saponite and Fe-saponite, appear to be those first formed during the breakdown of olivine phenocrysts. These smectites in turn convert to dioctahedral phases, nontronite and beidellite with increased weathering. Plagioclase feldspar laths appear to be altering to an Al-smectite, possibly montmorillonite, but some kaolin group clays may be present also. Within the vesicles, where there is higher fluid throughflow, the clay assemblage is a mixture of smectite and kaolin group clays, implying that where there is sufficient leaching, smectite clays may breakdown to form kaolin group clays.

Secondary hematite and goethite are precipitated amidst clays formed during the dissolution of ferromagnesian silicate minerals, as well as along microfractures, adjacent to vesicles, and in thin weathering rinds on fresher basalts. Neoformation of goethite is apparently associated with the breakdown of olivine to a mixture of smectite and goethite.

The clay mineralogy of the upper basalt shows a transition from a smectite dominated assemblage near the base of the flow where indurated basalt is weathering, to a more kaolin rich assemblage near the top of the flow. Samples LMAC12, LMAC22, LMAC8, LMAC10 and LMAC9 are only incipiently weathered and as a consequence the limited amount of clays present in these samples are dominated by smectite. This smectite is derived from the early weathering of ferromagnesian silicates to Fe-saponite, saponite, nontronite and Fe-beidellite and plagioclase feldspar to Al-smectite.

Trioctahedral smectite is the phase adjacent to cores in weathered olivine phenocrysts with dioctahedral phases farther out from the weathering core. This implies that the olivine first breaks down to trioctahedral clays and they in turn form dioctahedral clays with continued weathering. As weathering proceeds some of these smectite clays are converted to kaolin group clays and, with increased leaching, some primary phases, in particular plagioclase feldspar, are able to weather directly to kaolin group clays.
In the most weathered samples LMAC5, LMAC7 and LMAC4, not only are smectite clays and kaolin group clays present as discrete phases, but intermediate interstratified clays formed during the breakdown of smectite to kaolin group clays may be present. The XRD traces are unusual in that there is an elevated plateau between the principal kaolin group clay peak and the principal smectite peak. Isbell et al. (1976) state that the cation exchange capacities of the clay fractions of some of the lower rainfall soils suggest that they contain small amounts of randomly interstratified material but that detection of these clays is difficult due to lack of positive diffraction effects. CEC in the range 20 meq/100 g to 50 meq/100 g and Si:Al ratios around 1.5, for LMAC5, LMAC7 and LMAC4, provide strong support for the presence of these interstratified clays. A best-fit comparison with NEWMOD kaolinite - dioctahedral (Fe) smectite, suggests that kaolin group clay would account for approximately 75-80%, and smectite 20-25%, of the interstratified clay. These intermediate kaolinite-smectites (or halloysite-smectites) may dominate the clay fraction in the transition zone. Gibbsite was not found at this locality.

Both hematite and goethite are present in the secondary products at this locality. Hematite is more abundant but is not as dominant over goethite as observed in many other profiles farther east on the Atherton Tableland. This may be because this profile is still actively weathering and goethite is neoformed during the breakdown of ferromagnesian silicate minerals, such as olivine and pyroxene. Hence at this locality goethite is still relatively abundant but in more deeply weathered profiles (e.g. Millaa Millaa) hematite is more prevalent, and imparts a deep red colouration to the profile.

### 10.5.4 Petrography

**Lower Basalt**

LMAC 25 is incipiently weathered basalt with some secondary hematite and goethite precipitation occurring in the narrow rind. Olivine phenocrysts in the rind and near microfractures in the basalt show the development of a thin rim of smectite clays and goethite (iddingsite). The groundmass ferromagnesian silicates and basaltic glass have commenced weathering also. Fine grained plagioclase feldspar comprises the bulk of the basaltic groundmass material which also has Fe,Ti-oxides disseminated throughout. Pyroxene, mostly clinopyroxene forming a sub-ophitic texture with plagioclase feldspar, is primarily a groundmass mineral, however, one orthopyroxene phenocryst was observed (Plate 9.2).

The olivine phenocrysts in LMAC 23 are almost entirely weathered to secondary iron stained smectite clays, with some small etched cores remaining. Only relict primary feldspar is preserved, as it is almost entirely weathered to secondary weathering
Plate 10.2
LMAC25 (crossed polars)
Largely unweathered porphyritic basalt with vitric mesostasis. Olivine phenocrysts have poorly developed weathering rims.

Plate 10.3
LMAC23 (crossed polars)
Olivine phenocrysts are almost entirely weathered but have well preserved goethite rims.

Plate 10.4
LMAC22 (crossed polars)
Large olivine phenocrysts are preserved with only limited development of weathering rims.

Plate 10.5
LMAC10 (crossed polars)
Although groundmass plagioclase and pyroxene are preserved olivine microphenocrysts have thick weathering rims.
Plate 10.6
LMAC10 (crossed polars)
Plagioclase phenocrysts are intensely etched along twin planes and microfractures to montmorillonite and/or kaolin group clays.

Plate 10.7
LMAC9 (crossed polars)
Groundmass ferromagnesian phases have weathered to hematite clays and fractured olivine phenocrysts have well developed weathering rims.

Plate 10.8
LMAC6 (crossed polars)
Groundmass pervasively weathered to clays. A resorbed olivine phenocryst weathers to goethite and clays.

Plate 10.9
LMAC7 (crossed polars)
Relict cores of olivine phenocrysts are preserved in extremely weathered groundmass that no longer preserves primary basaltic texture.
products. The groundmass is dark coloured, largely due to hematite precipitation throughout the groundmass which surrounds finely disseminated grains of relatively intact primary Fe,Ti-oxides. Locally secondary Fe-oxyhydroxides are concentrated where ferromagnesian silicates have weathered away, along microfractures and adjacent to vesicles. Vesicles are lined with fine grained goethite stained clays (Plate 10.3).

Upper Basalt

There is a vesicular base to the upper basalt (LMAC12) and because this overlies a relatively impermeable clay rich layer, percolating fluids have weathered this layer more than the overlying massive basalt (LMAC22). However, there has not been significant ponding of fluids at the base of this flow because the vesicular basalt is only slightly weathered. Euhedral olivine phenocrysts have well developed rims of secondary smectite clays and goethite, and more fractured grains are almost entirely weathered with some Fe-saponite and saponite present, adjacent to relict olivine cores. Groundmass basaltic glass and ferromagnesian silicate minerals are completely altered to secondary weathering products. Small plagioclase feldspar laths, all partly etched, comprise the bulk of the groundmass, with tiny relict clinopyroxene grains preserved occasionally. Secondary Fe-oxyhydroxides are more prevalent along microfractures in the basalt. Small primary Fe,Ti-oxides are widely distributed throughout the groundmass.

LMAC22 is incipiently weathered massive porphyritic basalt with euhedral phenocrysts of olivine in a groundmass of fine grained plagioclase laths, devitrified volcanic glass, scattered clinopyroxenes (augite), and abundant small opaque oxides. Secondary products are predominantly clays replacing groundmass phases, and glass. Hematite and goethite are precipitated along microfractures and associated with clays in rims forming around olivine phenocrysts (Plate 10.4).

LMAC 10 is weathered to a similar extent as LMAC12 near the base of the flow. Euhedral olivine phenocrysts have rims of smectite clays and goethite (iddingsite), and groundmass phases are mostly weathered with olivine and glass completely replaced and scattered tiny relict pyroxene grains preserved amidst etched plagioclase laths. Smaller and more fractured olivine crystals have been completely replaced by smectite clays, probably nontronite and an Al-smectite phase, with associated goethite and hematite giving a brown-red colouration to the secondary products. Occasional large plagioclase phenocrysts are intensely etched and have preferentially altered along twin planes and microfractures, to montmorillonite and/or kaolin group clays. Small euhedral magnetite and ilmenite grains are distributed throughout the groundmass (Plate 10.5, Plate 10.6).
Chapter 10: Basalt Weathering Profiles from Northern Queensland

The onionskin material immediately adjacent to this corestone (LMAC9) is only marginally more altered than weathered corestone material (LMAC10) and shows similar features, except that the groundmass pyroxene can no longer be identified, olivine phenocrysts are more intensely altered to secondary products, and hematite, goethite, and clays are more pervasive throughout the groundmass, especially near microfractures in the basalt. Etched feldspar laths comprise most of the groundmass, along with scattered small euhedral magnetite and ilmenite grains, and the primary basalt texture is well preserved (Plate 10.7).

Higher in the profile, the slightly vesicular weathered corestone material (LMAC6) has a fine grained groundmass with small plagioclase laths that are largely replaced by secondary clays. Large euhedral olivine phenocrysts with rhombic and pseudohexagonal shapes have well developed iddingsite rims, and more fractured examples have zones of secondary smectite clays and iron oxides (hematite) and hydroxides (goethite) cross-cutting remnant olivine cores. No mafic groundmass phases are preserved except magnetite and ilmenite which mostly resist chemical weathering. Basaltic glass is wholly devitrified and replaced by secondary clays. There are vein-like darker coloured zones in the groundmass material, thought to be localised areas of more intense weathering associated with fluid penetration (Plate 10.8).

LMAC7 is an extremely weathered sample with a groundmass that is almost completely altered to secondary clays. Small magnetite and ilmenite grains are the only primary phases that are well preserved. The primary basalt texture is retained but is starting to breakdown. Hematite with some goethite, is localised in areas where ferromagnesian silicate minerals weathered, especially former olivine phenocrysts, as well as along fractures in the basalt and adjacent to vesicles. Some of the larger olivine phenocrysts retain relict cores, but most are completely weathered to secondary products (Plate 10.9).

10.5.5 Profile Summary

The majority of weathering profiles on older basalts from the Atherton province are much more intensely weathered than that exposed at this locality. One reason for this is that the climate is slightly drier on the western margin of the province and fluid flow through the profile is not as great as for localities farther east. In addition, superposition of clastic materials that weather to relatively impermeable clay-rich assemblages may have hampered vertical percolation of water through the basalt, thereby retarding the rate of weathering in these basalts, until they were exposed.

The lower basalt is relatively massive near the base but more vesicular near the top. This lava flow structure, together with preferential percolation of fluids from the land surface
downward has led to more intense weathering nearer the top of the flow, and this is reflected in the calculated mass losses (ΔM) for the samples from this flow.

Similarly, the vesicular base of the upper flow (LMAC12) is slightly more weathered than the overlying massive basalt (LMAC22), as there is enhanced fluid flow through the more porous vesicular basalt. In addition, fluids flowing downward through the profile may be impeded by an impermeable layer immediately below the vesicular basalt. Thereafter the waters might pond at this level or move laterally through the vesicular material. The limited degree of weathering exhibited by this basalt implies that although this is a zone of enhanced flow, fluids reach this level in the profile sporadically. This is in keeping with the predicted hydrological balance of basalt regolith profiles in this rainfall zone, which suggest that sequences may dry out, especially near their base, for periods up to a few months a year (Isbell et al. 1976).

The massive joint bounded basalt blocks (LMAC22) and corestones (LMAC8, LMAC10) of the central portion of this flow are incipiently weathered, largely because fluids were unable to penetrate them as efficiently as the underlying and overlying more vesicular materials. Spheroidal weathering has commenced as a result of fluid percolation down joints from above.

The uppermost weathered part of this flow (LMAC4, LMAC5, LMAC6, LMAC7) has well developed corestones with surrounding concentric zones of rubbly weathered basalt and clays which have formed more readily than in the central part of the flow. This is because the upper portions of the flow are less prone to complete drying, as most of the incident weathering fluids flow from the land surface downward, and fluid flow is enhanced by the vesicular nature of the parent basalt. In addition, percolating fluids will gradually approach equilibrium with respect to the secondary phases formed in the weathered basalt and may no longer have the capacity to weather primary minerals as intensely as they do near surface. This observation is consistent with the distribution of kaolinite (more intense weathering) and smectite (less intense weathering) in this profile. The secondary formation of phases, for example phosphates, carbonates and sulphates, may explain elevated concentrations in Pb, La, Ce, Ba and La observed for localised parts of this profile.
10.6 MILLAA MILLAA, ATHERTON VOLCANIC PROVINCE

10.6.1 Nature of the Exposure

Figure 10.7
Sample points the Millaa Millaa profile, Atherton Volcanic Province.

Plate 10.10
Millaa Millaa profile.
This profile is located in a crest position in the topography, is deeply weathered and comprised largely of red coloured saprolite with a relict spheroidal weathering texture preserved near the base of the outcrop (Figure 10.7, Plate 10.10, Appendix 1). Generally the clay-rich materials do not preserve basaltic texture and indurated basalt was not encountered in this exposure. Samples were taken at approximately 70 cm intervals with QFT11/1 in the soil zone at the top and QFT11/7 at the base of the exposure.

10.6.2 Clay Mineralogy

The secondary products for all samples are dominated by kaolin group clays, a mixture of kaolinite and halloysite, with kaolinite dominant, as well as minor gibbsite. The colour of the samples changes from brown to red up-profile, and correspondingly hematite becomes more prevalent in X-ray diffraction (XRD) traces higher in the profile, with goethite more dominant lower down. A minor amount of quartz, which is introduced from elsewhere, is present in the upper two soil samples.

![Figure 10.8](image)

Stacked X-ray diffraction (XRD) traces for samples QFT11/1, QFT11/2, QFT11/3, QFT11/4, QFT11/5, QFT11/6 and QFT11/7.

10.6.3 Profile Summary

The soils of the Millaa Millaa locality are formed from well drained, very strongly weathered older basaltic lavas. This profile fits very well into the Maalan series of Laffan (1988) which is characterised by "a dark reddish brown clay loam A1 horizon overlying dark reddish brown light clay and medium clay B horizons. Dark brown medium and
Chapter 10: Basalt Weathering Profiles from Northern Queensland 241

heavy clay with a few strongly weathered basalt fragments occur at depths below 60-70 cm, with a strongly developed polyhedral structure throughout the profile”.

The observed gibbsite content is greater higher in the profile, and kaolinite (and halloysite) content decreases, suggesting that gibbsite is forming at the expense of kaolin group clays (Figure 10.8). Annual mean rainfall at the southern end of the Atherton Tableland may reach 2,600 mm in some years, which leads to considerable throughflow of weathering fluids and almost continual saturation of the profile.

10.7  PALMERSTON HIGHWAY, INNISFAIL, ATHERTON VOLCANIC PROVINCE

10.7.1  Nature of the Exposure

This deeply weathered profile overlies incipiently weathered basalt (QFT8/-1) exposed in a quarry face (Figure 10.9, Plate 10.11, Appendix 1). In localised areas weathered material (QFT8/0) cross-cuts the upper part of this basalt in vein-like zones. The contact between the relatively fresh indurated basalt and the overlying weathering profile is not exposed. Mottled grey and white clay-rich materials (QFT8/1, QFT8/2) that still maintain the large scale textural relationships of spheroidally weathered basalt (grey cores with more intensely weathered white clay material surrounding them) lie at the base of the profile.

Figure 10.9
Sample points in the Palmerston Highway profile, Atherton Volcanic Province.
Chapter 10: Basalt Weathering Profiles from Northern Queensland 242

This grades upward into rubbly weathered basalt (QFT8/3, QFT8/4, QFT8/5) with a red-orange soil profile (QFT8/6, QFT8/7) at the top of the sequence.

Plate 10.11
Palmerston Highway profile.

10.7.2 Clay Mineralogy

QFT8/-1 has abundant primary mineral peaks present in its XRD trace representing plagioclase feldspar, olivine (high Mg), pyroxene (augite), magnetite and ilmenite. No secondary products are observed in the trace but some hematite and/or goethite may be present (Figure 10.10).

The balance of the samples are dominated by kaolin group clays usually a mixture of halloysite and kaolinite, with secondary goethite and hematite. Some primary magnetite and ilmenite may be present but the peaks are not clear in the XRD traces. Gibbsite is present in the samples nearer the land surface (QFT8/6, QFT8/7).
Chapter 10: Basalt Weathering Profiles from Northern Queensland 243

Figure 10.10
Stacked X-ray diffraction (XRD) traces for samples QFT8/-1, QFT8/0, QFT8/1, QFT8/2, QFT8/3, QFT8/4, QFT8/5, QFT8/6 and QFT8/7.

10.7.3 Petrography

The least weathered (QFT8/-1) basalt is fine grained with olivine forming small euhedral phenocrysts. Within the basalt these phenocrysts are well preserved but in the rind formed near exposed surfaces, olivine grains are completely altered to secondary clays and goethite. Fine grained plagioclase feldspar laths, euhedral primary Fe,Ti-oxides, basaltic glass that has started to devitrify, relict olivine and very small etched pyroxenes comprise the groundmass.

The mesostasis in QFT8/0 is completely weathered to secondary clays, in places showing a yellow-brown goethite stain. Deep red coloured hematite is localised in areas where olivine phenocrysts have weathered away and along microfractures in the basalt. Fine grained, euhedral opaque oxides are distributed throughout the groundmass. No feldspar laths are preserved and have largely been replaced by kaolin group clays. The primary basalt texture has started to breakdown.

Rubbly weathered basalt (QFT8/4) from higher in the profile is very similar in composition to WFT8/0, but has retained a great deal more secondary Fe-oxyhydroxides,
impacting an orange colour to the sample. Hematite and to a lesser extent goethite, are concentrated in areas where ferromagnesian silicates minerals (especially olivine), have altered, along micro-fractures in the weathered basalt and adjacent to vesicles. Vesicles are lined by goethite stained clays.

10.7.4 Profile Summary

In this extremely high rainfall area most of the weathering profiles are very deep and the predominant clays present are kaolin group clays with some gibbsite nearer the land surface. This exposure has a relatively high content of halloysite lower in the profile (QFT8/1, QFT8/2, QFT8/3) with kaolinite becoming more dominant higher up (QFT8/4, QFT8/5, QFT8/6). Halloysite is not widely documented from this area, probably because most sampling takes place nearer the land surface, and the halloysite appears to be more prevalent deeper in the profile, closer to the parent basalt.

Plate 10.12
Scanning electron micrograph (SEM) of an Fe-Ti oxide (O) with goethite rich coating (G) surrounded by kaolinite clays (K).

Lepsch (1989) correlates the presence of halloysite and kaolinite (Plate 10.12) in the clay assemblage with the youth of the landform, and hence the steepness of the country, younger landforms being steeper than more stable older landforms. He also correlates the presence of kaolin group clays and gibbsite in the clay separate with landforms of intermediate age and hence intermediate slope. In the near surface layers of this profile where the most intense weathering takes place (QFT8/5, QFT8/6), gibbsite forms, and the kaolinite content drops implying that kaolinite clay is consumed in the formation of gibbsite. This sequence with a clay assemblage transitional from halloysite dominant through kaolinite dominant to gibbsite dominant, does not easily fit Lepsch’s landform model, but may be compared with the Pin Gin series detailed by Sleeman & Lepsch (1988).
No smectite clays were present in the samples from this locality, so it appears that the basaltic glass and plagioclase feldspar are altering directly to halloysite and kaolinite. Although Lepsch (1989) states that the olivine phenocrysts have weathering rims of iddingsite, which is described as a combination of smectite clays and secondary goethite (Eggleton 1984) and possibly some hematite (Banfield et al. 1990). Alternatively the weathering of the ferromagnesian silicate phases may produce a goethite (and hematite) rich rim material (Plate 10.12), which incorporates only a limited amount of clay, or a kaolin group clay. But earlier XRD studies on young basalt weathering profiles suggest that randomly interstratified halloysite-smectite may be present deeper in the sequence (Sleeman & Lepsch 1988, Lepsch 1989).

The weathered products lower in the profile (QFT8/0, QFT8/1, QFT8/2) are relatively pallid and this is due to the lesser secondary Fe-oxyhydroxide precipitation at this level. Nearer the land surface materials become more orange coloured because goethite and some hematite are present, and the overlying soil is red-orange, because of the hematite content.

10.8 GEOLOGY - MCBRIDE VOLCANIC PROVINCE

The lavas in McBride Volcanic Province have flowed radially outward from a central cluster of vents (Griffin 1977) covering a roughly circular about 80 km in diameter. The broad topographic doming in this area is probably not related to volcanism, but to late Cainozoic tectonic activity similar to that observed further south (Coventry and Stephenson 1985, Stephenson & Coventry 1986). Some of the flows in this province are very long, for example the Undara lava flow which extends for greater than 160 km (Atkinson et al. 1975, Stephenson & Griffin 1976). These long flows formed because of the favourable topography, because the lavas were highly fluidal, and because there was continuous extrusion for a sustained period. Ultimately broad lava plains were constructed. Pyroclastic activity localised about centres, formed scoria cones and composite cones. The range of basaltic compositions represented are nephelinite, alkali basalt, basanite, hawaiite and mugearite (Johnson et al. 1989). Volcanics in this province range in age from 7.9 Ma to approximately 50,000 yr B.P. (Johnson et al. 1989).

This study discusses a profile sampled in a road cutting on the Kennedy Highway through the Murronga Basalt. Basanite, alkali basalt and hawaiite are represented within this basalt which is dated at between 120,000 and 180,000 yr B.P. (Griffin 1977).
Chapter 10: Basalt Weathering Profiles from Northern Queensland 246

10.9 KENNEDY HIGHWAY, MCBRIDE VOLCANIC PROVINCE

10.9.1 Nature of the Exposure

Figure 10.11
Sample points in the Kennedy Highway profile, McBride Volcanic Province.

Plate 10.13
Kennedy Highway profile.
This dry rubbly profile has poor corestone (QFT7/1, QFT7/2) development near its base, but in a massive zone near the centre of the flow (QFT7/3), blocky spheroidal weathering is more apparent. Further rubbly weathered basalt overlies this (QFT7/4, QFT7/5), and the sequence is capped by a 20 cm thick, red-brown, dusty soil (QFT7/6, QFT7/7) with small pebbles of weathered rock material distributed through it (Figure 10.11, Plate 10.13, Appendix 1). Pebble sized fragments of weathered basalt fritters off the face and has formed a talus slope at the base of the exposure.

10.9.2 Clay Mineralogy

The freshest basalt corestones (QFT7/1, QFT7/2, QFT7/3) have primary plagioclase feldspar, pyroxene (augite), olivine (high Mg), magnetite and ilmenite peaks in the XRD traces. A progressive decrease in intensity for the olivine and pyroxene peaks with increased weathering was noted. Secondary products are dominated by iron oxyhydroxides, although the peaks for hematite and goethite are partially obscured by those of the primary minerals. No clay development is apparent in the bulk XRD traces for these samples but the clay separate XRD traces show that a small amount of halloysite clay is present in the samples (Figure 10.12).
Rubbly basalt samples QFT7/4 and QFT7/5 are considerably more weathered than the underlying corestone material. The primary minerals preserved in the samples are plagioclase feldspar, olivine (high Mg), magnetite and ilmenite. Pyroxene no longer occurs on the XRD trace. There is a definite decrease in the intensities of the plagioclase feldspar and olivine peaks compared with those analysed from lower in the profile. Peaks for secondary goethite with some hematite are more noticeable on the trace, and there is kaolin group clay development represented. The kaolin group clays are halloysite in sample QFT7/4 and a mixture of halloysite and kaolinite in sample QFT7/5 (Figure 10.12).

Float pebbles (QFT7/6, QFT7/7) in the brown dusty skeletal soil were analysed and found to have similar assemblages but with QFT7/6 much more intensely weathered. QFT7/7 has a primary mineral assemblage similar to that of the corestones including plagioclase feldspar, olivine (high Mg), magnetite and ilmenite. Secondary goethite with some hematite may be present. The clay separate XRD traces show that kaolin group clay has developed and this is dominated by kaolinite with minor halloysite. QFT7/6 has the same primary mineral assemblage but intensities of peaks for plagioclase and olivine are reduced. Goethite and hematite are present in the sample and the dominant clay present is kaolinite. The soil is composed of kaolin group clays with relict primary minerals from the weathering basalt, notably plagioclase feldspar, and goethite and hematite.

10.9.3 Petrography

The corestones (QFT7/1, QFT7/2, QFT7/3) low in this profile are fine to medium grained, massive, porphyritic basalts with euhedral olivine as the principal phenocryst phase. Etched plagioclase feldspar laths, with interspersed small euhedral opaque oxides, devitrified basaltic glass, and sparsely distributed weathered small olivine and pyroxene crystals, comprise the bulk of the groundmass. Olivine phenocrysts have well developed rims, which appear to be almost entirely goethite and some clays, surrounding relict cores. Smaller and fractured olivine grains are more intensely altered and some have been completely replaced by secondary products. Goethite and some hematite are also concentrated along microfractures in the moderately weathered basalts (Plate 10.14).

Higher in the profile rubbly weathered basalt (QFT7/4) has essentially the same texture but the groundmass is almost entirely weathered to secondary products. Olivine phenocrysts have largely been replaced by goethite, but there are some examples which retain relict cores. Clays are ubiquitous in the groundmass and secondary Fe-oxyhydroxides, which probably replaced groundmass ferromagnesian silicates, are scattered throughout and are locally concentrated in areas where olivine phenocrysts have
Plate 10.14
QFT7/2 (crossed polars)
Olivine phenocrysts have well developed weathering rims which are comprised of goethite.

Plate 10.15
QFT7/4 (crossed polars)
Clays are ubiquitous in the groundmass and secondary Fe oxyhydroxides are concentrated where pyroxene and olivine have weathered.

Plate 10.16
QFT7/5 (crossed polars)
Hematite and goethite dominate secondary products especially proximal to microfractures.

Plate 10.17
QFT7/6 (crossed polars)
Olivine phenocrysts are wholly weathered to secondary products and the groundmass has largely been weathered to clays.
weathered or along microfractures in the basalt. Fine grained primary opaque oxides are disseminated throughout the groundmass also (Plate 10.15).

Weathered vesicular basalt (QFT7/5) is exposed near the land surface. Similar material is incorporated in the skeletal soil as pebble float (QFT7/7). Both samples are pervasively weathered with the groundmass largely altered to secondary clays, goethite and hematite. Plagioclase laths are etched but retain their morphology, and primary basaltic texture is preserved. Opaque oxides are fine grained and are scattered throughout the groundmass. Olivine phenocrysts have well developed goethitic rims and where they lie close to zones of more intense weathering, for example in the basalt rind or adjacent to vesicles and microfractures, the phenocrysts are almost entirely weathered. In the central parts of the sample, the olivine phenocrysts are relatively well preserved. The secondary Fe-bearing phase appears to be a darker red colour in the samples that are closer to the land surface and there may be some conversion of goethite to hematite with desiccation of the profile. Vesicles are lined with red (hematite) coloured linings or are infilled by soil clay material (Plate 10.16).

The most weathered sample is a pebble from the soil zone (QFT7/6) which is slightly more massive than QFT7/5 and QFT7/7. Olivine phenocrysts are wholly weathered to secondary products and the only primary minerals preserved in the groundmass are a few skeletal plagioclase feldspar laths and disseminated opaque oxides. The groundmass has largely been weathered to secondary clays. Rare olivine cores occur amidst localised concentrations of goethite, hematite and clays, which have replaced the balance of the phenocryst. In many cases the outer rim is hematitic and the core is weathered to goethite (Plate 10.17).

10.9.4 Profile Summary

The most apparent anomaly at this locality is that despite the relatively dry climatic conditions, smectites are not the dominant minerals in the clay assemblage. Little or no smectite is recorded in the XRD traces for this profile. In a broad sense halloysite is more prevalent closer to unweathered basalt. Olivine weathering rims appear to be almost entirely goethite with minor kaolin group clays present. Hematite is relatively prevalent in this profile despite goethite being the initial alteration product of ferromagnesian silicates, implying that periodic desiccation of the profile leads to dehydration of goethite to hematite. Despite the low rainfall at this locality for most of the winter, summer rainfall although sporadic, may be relatively high, apparently allowing sufficient leaching of the profile for kaolin group clays to form. In addition, the basalt flow is younger than the surrounding lava field basalts and forms a subtle topographic high. So this basalt is uppermost in the weathering profile and well drained.
10.10 GEOLOGY - NULLA VOLCANIC PROVINCE

In the Nulla Volcanic Province quiet extrusion of low viscosity basalt formed a low relief lava plain, approximately 7,500 km², that gently slopes to the east and north-east toward the Burdekin River valley. Pyroclastic activity was virtually absent at the 46 vents that have been identified (Johnson et al. 1989) and effusive activity dominated. The range in ages for this province is 5.2 Ma to 13,000 yr B.P. (Wyatt & Webb 1970, Stephenson et al. 1978). As a result of weathering older lavas have had primary surface textures erased, marginal scarps have formed and an overlying skeletal soil has developed (Isbell et al. 1977). These weathering features are most pronounced in the north of the province, and may largely be related to a period of more intense weathering in this area, between 1.5 Ma and 3.9 Ma (Bird et al. 1990). Younger lavas (Toomba flow, 13,000 yr B.P.) have well preserved primary surface textures and almost no soil cover (Isbell et al. 1977). The lava type is predominantly hawaiite.

10.11 FLETCHER VALE ROAD, NULLA VOLCANIC PROVINCE

10.11.1 Nature of the Exposure

Weathered basalt crops out in the wall of a small quarry from which it is extracted for road aggregate (Figure 10.13, Plate 10.18, Appendix 1). A large scale, near vertical, rhombic, joint set forms jutting faces in the excavated exposure. Most of the weathered basalt is blocky in nature but spheroidal weathering is well developed, especially lower in the profile. Central portions of larger blocks are relatively fresh, hence this weathered basalt is useful road building material.
The least weathered material exposed (QFT1/10, QFT1/6) was sampled from the centre of large blocks. Slightly more weathered samples (QFT1/7, QFT1/8, QFT1/9) were taken from flakes and veneers adjacent to joint planes. Lower in the flow the basalt was sampled in progressive steps outward from a corestone (QFT1/2, QFT1/3, QFT1/4, QFT1/5) and more weathered onionskin material (QFT1/1) was sampled nearby.

Plate 10.18
Fletcher Vale Road profile.

10.11.2 Clay Mineralogy

Samples QFT1/10 and QFT1/6, then QFT1/7 through QFT1/9, are the least weathered basalts in this profile. They show a progressive increase in the intensity of weathering, but still retain the primary mineral assemblage plagioclase feldspar, olivine, pyroxene (augite), magnetite and ilmenite. Secondary products range from, a small amount of
dioctahedral smectite clay, minor kaolin group clays, and possibly goethite and hematite in QFT1/10, to a moderate amount of smectite clay, clearly defined kaolin group clays, goethite and hematite in QFT1/9. In all samples the smectite clays are probably nontronite with some Al-smectite, and the kaolin group clays, a mixture of kaolinite and halloysite (Figure 10.14).

![Stacked X-ray diffraction (XRD) traces for samples QFT1/1, QFT1/2, QFT1/3, QFT1/4, QFT1/5, QFT1/10, QFT1/6, QFT1/9, QFT1/8, QFT1/7, QFT1/12 and QFT1/11.](image)

**Figure 10.14**

Stacked X-ray diffraction (XRD) traces for samples QFT1/1, QFT1/2, QFT1/3, QFT1/4, QFT1/5, QFT1/10, QFT1/6, QFT1/9, QFT1/8, QFT1/7, QFT1/12 and QFT1/11.

Samples QFT1/2 through QFT1/5 and QFT1/1, show the progressive loss of a number of primary minerals and the development of secondary products. Most notably olivine is lost from even the freshest of these samples and the XRD peak intensities of plagioclase feldspar, and pyroxene are progressively reduced. Correspondingly the peak intensities for smectite, kaolin group clay, goethite and hematite increase. Magnetite and ilmenite persist in these samples. In all samples the smectite clays are dominated by nontronite and an Al-smectite and the kaolin group clay present is halloysite.
Dull orange yellow coloured dusty soil caps the sequence and has kaolinite as the principal clay mineral. The uppermost soil sample has minor gibbsite. Smectite clay peaks are absent from the XRD trace (Figure 10.14).

10.11.3 Petrography

The freshest weathered basalt (QFT1/10, QFT1/6) has a feldspar-phryic groundmass with elongate opaque oxides, possibly magnetite or titanomagnetite, sparsely distributed throughout. Groundmass olivine phenocrysts are completely weathered to secondary smectite and goethite. Large relatively unweathered titanaugite grains, form a sub-ophitic to ophitic texture with the plagioclase feldspar laths that form the bulk of the groundmass (Plate 10.19, 10.20). The feldspar laths are etched and have commenced alteration along zones of weakness such as twin planes. Olivine phenocrysts occur in two populations, one forming clusters of smaller phenocrysts and the other, scattered large phenocrysts. All of the olivine phenocrysts are completely weathered to secondary smectite clays, goethite and hematite.

Slightly more weathered material from this exposure (QFT1/7, QFT1/8, QFT1/9) show more intense weathering of groundmass feldspar to secondary clays. Olivine phenocrysts are almost entirely weathered and few relict cores are preserved. Some of the totally altered olivine phenocrysts have brown coloured clay preserved in their core surrounded by a red coloured goethite-hematite mixture. Pyroxene grains appear more fragmented, but this may occur as a result of the weathering of the enclosed plagioclase laths. Goethite staining of clays occurs near exposed faces, adjacent to micro-fractures and in linings of small vesicles. Sparsely distributed elongate opaque oxides are preserved intact (Plate 10.21, 10.22).

Lower in the profile the corestone material (QFT1/2) is weathered to a similar degree as QFT1/7 through QFT1/9, but there is considerably more Fe-staining of clays. The orange-yellow goethite staining appears to diffuse outward from the intensely weathered olivine phenocrysts. Plagioclase feldspar is etched and may laths have been replaced by secondary clays. Pyroxenes appear fragmented and have commenced weathering to goethite and possibly to clays, however these clays may be associated with the dissolution of enclosed feldspars (Plate 10.23).

The onionskin materials (QFT1/3, QFT1/4, QFT1/5, QFT1/1) have cross-cutting micro-fractures along which enhanced weathering of minerals has taken place. Plagioclase feldspars continue to progressively breakdown to clays. Although pyroxene is preserved in all samples, it appears to be continuous with pockets of goethitic material in many of
QFT1/6 Titanaugite shows clear pink pleochroism and plane polarised light and has a sub-ophitic to ophitic texture with plagioclase feldspar laths in the groundmass. The extreme contrast in rates of weathering of olivine and pyroxene are well represented.
Plate 10.21
QFT/7 (crossed polars)
Olivine microphenocrysts are completely weathered to Fe oxyhydroxides and clays

Plate 10.22
QFT/8 (crossed polars)
Fractures are lined with goethite, hematite and clays

Plate 10.23
QFT/2 (crossed polars)
Fe-staining of clays is closely associated with intensely weathered olivine pseudomorphs

Plate 10.24
QFT/4 (crossed polars)
Proximal to microfractures weathering of ferromagnesian silicates is more intense.
the more weathered examples, implying that this material is derived from the dissolution of titanauge. Goethitic and hematitic material, associated with former olivine phenocrysts, continues to diffuse outward from these areas of concentration. Scattered primary opaque oxides are preserved intact. Very small opaque oxides are observed within the weathered olivine phenocrysts in places, and these flakes may be Cr-spinel (Plate 10.24).

10.11.4 Profile Summary

The least weathered basalt shows incipient weathering to smectite clays (Plate 10.26), with minor kaolin group clay development (Plate 10.27, 10.28). As the basalt becomes increasingly more weathered the proportion of smectite clay progressively decreases and the proportion of kaolin group clay minerals increases, but smectite is the dominant clay type and persists in samples up to the soil zone. Formamide treatment indicates that the kaolin group clay present is dominantly halloysite. Within the shallow, 10-15 cm thick, skeletal soil, kaolin is the dominant clay type and smectite only a minor phase. Development of a small amount of gibbsite was observed in the uppermost soil sample.

Largely the weathering in the least weathered part of the flow is similar to weathering of basalts in higher latitudes. Olivine and pyroxene weather to secondary smectite clays, dominantly dioctahedral nontronite and an Al-smectite (beidellite) with goethite and hematite (Plate 10.25). Basaltic glass and plagioclase feldspars breakdown to secondary clays including Al-smectite with some kaolin group clays (Figure 10.29). Primary Fe-oxides are relatively resistant unless they are in an intensely leaching environment. Hence the alteration products in the fresher parts of the flow are dominated by smectite clays with minor kaolin group clays plus goethite with minor hematite and accessory magnetite and ilmenite.

However, at this locality there is a relatively rapid transition to a secondary assemblage in which smectite persists but kaolin group clays are prevalent and gibbsite forms in the upper soil zone. This assemblage tends toward that of an intensely leaching environment. Because the smectite content decreases in more weathered samples as kaolin group clay content increases, halloysite and kaolinite appear to form at the expense of some smectite. Another explanation for this trend is that the kaolinite is forming as a result of weathering of primary phases and is added to the smectite already present. However, if the former scenario holds, this is the environment in which kaolin-smectite interstratified clays may form. Because discrete kaolin group minerals and discrete smectites are present in the clay fraction, it is difficult to observe the presence of interstratified clays using the XRD technique.
Plate 10.25 (A), Plate 10.26 (B), Plate 10.27 (C), Plate 10.28 (D), Plate 10.29 (E)

Scanning electron micrographs (SEM) from the Fletcher Vale Road profile. (A) comb-like etched texture in pyroxene (Px). Mineral has Fe-rich smectite-bearing coating (S). (B) smectite coating (S) on etched minerals. (C) & (D) sub-hexagonal kaolin clay plates (K) on etched plagioclase (P). (E) apatite rods (A) projecting from etched plagioclase feldspar (P).

The unusual mixture of assemblages may be caused by the very seasonal nature of the contemporary climate at this locality. Almost all of the annual rainfall is introduced to the profile in the summer months because of tropical storms, and this is a period of high fluid throughflow in the profile. Because unweathered basalt cores are already surrounded by the early formed smectite rich weathering products, physical access of weathering fluids to the fresh basalt is impeded and greater leaching within the partially
weathered material may be the dominant process. Hence the weathered material becomes more kaolin rich, and gibbsite may form near the land surface, but within the least weathered basalt, smectite is the principal mineral neoformed.
11.1 INTRODUCTION

A twelve month water sampling program was carried out from November 1991, at the two Monaro localities, Big Willow and Sherwood (Figure 11.1). It was necessary to monitor the springs for a year in order to evaluate the effects of seasonal temperature, rainfall and vegetation changes. The Monaro sites were selected for sampling because they were the most proximal to Canberra. Sampling was carried out as near as possible to the middle of the month in order to provide regular sampling intervals.

Figure 11.1

Water sample localities in the Monaro Volcanic Province - Big Willow and Sherwood.
The bedrock is basalt lava which has been spheroidally weathered to a suite of secondary clays, dominated by smectite phases, with relict basalt corestones preserved. The weathering environment is characterised by low to moderate precipitation (500 - 700 mm/yr) the relief change along the aquifers is in the order of 50 metres, and natural stream erosion which exposes the aquifer mouth at both localities, is sufficient to produce exposures through the weathered basalt sequence.

Big Willow 1 (BW1) is an exploratory borehole which taps a basalt aquifer at depth and has a small cross section, about 15 cm in diameter, open to the surface. A polyethylene capped water sampler was inserted approximately 2 metres into the top of the borehole and water was sampled each month. Big Willow 2 is a naturally occurring spring that issues from fractured basalt approximately 400 m away from BW1. Each Big Willow sample site taps a different aquifer and BW1 may experience some surficial water contribution during heavy rain events. The Sherwood springs issue from the banks of a small tributary to Teapot Creek, and are separated by about 5 metres. It is possible that these springs tap the same aquifer. Both Sherwood 1 (SW1) and Sherwood 2 (SW2) flow naturally from weathered fractured basalt.

In addition to the sampling of water for analysis in the laboratory, measurements of water temperature, water pH, dissolved oxygen concentration and electrical conductivity were carried out using a HYDROLAB; independent water temperature was measured using a mercury bulb thermometer; independent pH was measured using a portable pH meter; and bicarbonate concentrations were derived in the field using a field titration technique. Cation and anion concentrations were derived in the laboratory, using Atomic Absorption Spectrophotometry (AAS) and Flow Injection Analysis (FIA) respectively (Appendix 6).

11.2 HYDROLAB MEASUREMENTS

Analyses carried out using the HYDROLAB multiprobe include measurement of water temperature, water pH, dissolved oxygen concentration and electrical conductivity.

11.2.1 Water Temperature

Water temperature adjusts much more slowly than air temperature as the water is insulated by the body of rock through which it is flowing. Hence, there is a time lag between the temperature changes in air and the corresponding changes for aquifer water (Figure 11.2). In addition, average groundwater temperature shows much less fluctuation as a result of the insulation effect of the rock.
Big Willow

Both BW1 and BW2 show a classic seasonal variation with warmer water temperatures in the late summer-early autumn months, and cooler temperatures in the late winter early spring months. This shows an offset with the air temperatures which are highest in summer and lowest in winter. However, BW1 appears to warm a little sooner than BW2, perhaps because it has a small opening to the atmosphere, and warm rains can enter the column. The water temperature range for BW1 is 11°C to 17°C, and for BW2 is 10°C to 16°C.

![Graphs showing average monthly water temperature for BW1, BW2, SW1 and SW2](image)

**Figure 11.2**
(1991/1992) Average monthly water temperature (°C) for sample localities BW1, BW2, SW1 and SW2
Sherwood

At Sherwood a clear seasonal variation in aquifer water temperature is observed with warmest temperatures in late summer-early autumn and coolest temperatures in late winter early spring, for both SW1 and SW2. Once again this is slightly out of phase with the air temperature seasonal variation. The temperature range for the Sherwood aquifer waters is 10 to 16 °C.

Water Temperature

The delay in the seasonal variations when the aquifer water temperatures, are compared with local atmospheric temperatures, reflects the time taken for cool waters to pass through the system. In this case there is a lag of approximately one month at BW2, SW1 and SW2. Because the sampling intervals are monthly, the change in the data may partly correspond with when sampling occurred. Despite this possibility the residence time of waters in the aquifers is likely to be between 3 to 5 weeks. BW1 has warmer temperatures early in the sampling period which may be correlated with the entry of rainwater into the borehole around this time, but later in the season the temperatures at BW1 are more or less in phase with the temperatures of waters issuing from the aquifers. In the Monaro air temperature changes from summer to winter and from night to day can be quite extreme, however, the waters sampled show limited temperature variation. This occurs because the fractured basalt through which the water flows insulates it from atmospheric temperature fluctuations, and only seasonal variations are observed in the aquifer water temperature data.

11.2.2 Water pH

Rain water in the Monaro region is a dilute acid (pH 5.13) but the fluids issuing from the aquifers are neutral to alkaline, and maintain a relatively constant alkalinity throughout the year despite changes in fluid throughflow.

Big Willow

At Big Willow pH values are very constant throughout the year, and are generally neutral to alkaline. At BW1 pH values range from 6.5 to 8 and at BW2 the pH values lie between 7 and 8.
Figure 11.3

Sherwood

Measured pH values at Sherwood show that the waters are alkaline with values in the range 7.5 to 8.5 at both SW1 and SW2.

Water pH

Rain water entering the system is slightly acidic (pH 5.13). This rain water may dissolve soil CO2 when percolating through the soil zone resulting in the formation of carbonic acid (H2CO3) and some solvated CO2. When these dilute acids interact with the basalt of
the aquifer wall the carbonic acid may dissociate to form bicarbonate, as a by-product of the weathering (hydrolysis) of silicate minerals (Figure 11.3). If bicarbonate is the dominant anion the pH will be neutral to alkaline (pH > 6.5). As the processes of weathering (hydration, hydrolysis, redox) proceed within the aquifer, the percolating waters approach equilibrium with the secondary mineral assemblage they are passing through. Because of this equilibration effect, the pH of the fluids issuing from the aquifers remains relatively constant throughout the study period.

11.2.3 Dissolved Oxygen Concentration

Rain is generally saturated with respect to oxygen as it is in direct contact with the atmosphere. Ponded water is able to interact with the atmosphere at its surface and has dissolved oxygen concentrations in the order of 9.5 to 11.5 mg/l. However, groundwater is usually depleted with respect to oxygen, as it is consumed in the reactions of rock weathering (oxidation reactions). Dissolved oxygen concentration is affected by temperature, that is, cold water holds more dissolved oxygen.

Big Willow

Dissolved oxygen concentrations at both localities (Figure 11.4) are less than 3 mg/l, which is relatively depleted with respect to rain water and show that these waters have interacted with the fractured basalt that they passed through. Concentrations are relatively low at the beginning of the sampling period and then show a peak around January/February, implying that there has been an influx of oxygenated waters at this time. Concentrations are low again in March but then steadily increase until they reach a peak in May of around 2.9 mg/l at both sites. In June, dissolved oxygen values drop slightly and thereafter plateau at values between 1.6 and 1.9 mg/l to the end of the sampling period.

Sherwood

Concentrations of dissolved oxygen at SW1 and SW2 are less than 4.5 mg/l, and generally less than 2 mg/l so are significantly depleted with respect to rainwater (Figure 11.4). There is a small peak in dissolved oxygen values at both sites in the January/February period, similar to that observed at Big Willow. Once again there is a progressive increase in dissolved oxygen concentrations from March through to a maximum of around 4.3 mg/l in May, which drops back to around 1.9 mg/l in June and for the rest of the sampling period maintains concentrations around 1.7 to 1.9 mg/l at both localities.
Figure 11.4
(1991/1992) Monthly dissolved oxygen concentration (mg/L) for the sample localities BW1, BW2, SW1 and SW2, compared with maximum and minimum monthly air temperature (°C) and total monthly rainfall (mm).
Dissolved Oxygen

The peak in dissolved oxygen concentrations around January/February at both Big Willow and Sherwood can be related to an influx of oxygenated rainwater. Much more significant in the concentration pattern for dissolved oxygen is the maximum, recorded in May at all sample sites. This coincides with a low rainfall period, and so the elevated oxygen content cannot be attributed to an anomalous throughflow of rainwater. Instead this may correlate with the first cold period for the year as May through July are the principle months when frost, and in some cases snow, occur. In May 1991 the first overnight sub-zero temperatures were recorded at these localities. This may also account for the more intense increase in dissolved oxygen concentration in May at the Sherwood sites because this locality is in a valley, on the south side of a large hill and experiences slightly cooler winter temperatures than Big Willow.

11.2.4 Electrical Conductivity (EC)

Electrical conductivity (EC) is the ability of a medium to conduct an electric current. In water it is a measure of the concentration of total dissolved salts in solution. For this reason, changes in the concentration of salts, reflected in the changes in ion concentrations will cause changes in electrical conductivity. EC is affected by temperature because of the reduced activity of cations in cooler water. That is, if there are less salts in solution because the water is cold, then the conductivity will be lower.

Big Willow

Electrical conductivity patterns lie within a limited range, 400 to 550 µseimens for BW1 and 300 to 450 µseimens for BW2, for most of the year, but there is a significant drop at both localities in the late summer (Figure 11.5). At BW1 this drop takes place in January, and the waters are poorly conductive through until March, whereas at BW2 the drop in conductivity does not occur until February and values are back within the normal range by March. In both cases the years peak electrical conductivity occurs directly after the low period.

Sherwood

Although there is some fluctuation, electrical conductivity values mostly lie between 350 and 450 µseimens for SW1 and between 250 and 400 µseimens for SW2 (Figure 11.5). There is a drop in conductivity, at both sites, in February, but by March the conductivity has risen again. The peak in conductivity at the Sherwood springs occurs directly after the period of low conductivity.
Figure 11.5

(1991/1992) Monthly electrical conductivity (µseimens) for the sample localities BW1, BW2, SW1 and SW2, compared with maximum and minimum monthly air temperature (°C) and total monthly rainfall (mm).
**Electrical Conductivity**

There appears to be a flushing event taking place, causing a dilution of the waters and because the concentration of dissolved salts is lower, the electrical conductivity is lower. The flushing event occurs earlier at BW1 than at the other three sites because borehole at BW1 is open to the atmosphere and rain can enter the hole. Hence, rains occurring in January, which affected BW1 directly, were not seen to affect the basalt aquifers BW2, SW1 and SW2 until a month later. This implies that the residence time for waters in the aquifers is in the order of one month (3 to 5 weeks), as previously suggested from observations of water temperature. The peak in conductivity after the main flushing event for the year may correspond with the mobilisation of ions released during the flushing event but not removed from the system at that time. Once water throughflow drops the relative concentration of ions in solution is greater until the system stabilises again.

### 11.3 TURBIDITY, COLOUR, ODOUR

**Big Willow**

BW1 waters show some turbidity and organic staining causing discolouration, for the months January, February and March but at all other times the samples were colourless and non-turbid. BW2 waters showed very slight staining in February only. All waters were odourless at the time of sampling.

**Sherwood**

No samples from the aquifer sites SW1 and SW2, were turbid, or showed any colour, indicating that almost no sediment or finely suspended material is transported from the aquifers in the waters, and no staining has taken place. All waters were odourless at the time of sampling.

**Turbidity, Colour, Odour**

The period of discolouration and turbidity corresponds with the period of heavy rain at BW1. This suggests that surface runoff was contributing some sediment and stained water, probably discoloured by organic material, to the borehole at this time. BW2 waters showed slight staining one month later, which approximately corresponds with the time it takes for the rain waters to pass through the aquifer. The staining most likely took place as rainwaters entering the aquifer passed through land surface vegetation. At both localities the discolouration is slight and there is no residual vegetable material observed in the waters.
11.4 ANION ANALYSES

11.4.1 Bicarbonate (HCO$_3^-$)

**Big Willow**

BW1 shows relatively constant bicarbonate concentrations, between 170 and 190 mg/l, throughout the sampling period, apart from a concentration drop in January to 75 mg/l which remains low through February (90 mg/l) and March (105 mg/l) and rises again to 180 mg/l in April (Figure 11.6). BW2 shows much more fluctuation in bicarbonate concentration with most analyses lying in the range 195 to 210 mg/l. There may be a relative depletion in the late summer months but this appears to be overprinted by an increase in bicarbonate from February (200 mg/l) through March (217 mg/l) until it reaches a peak in March (227 mg/l). From March bicarbonate concentrations drop down again until they lie within the range observed before the bicarbonate peak, but there is another small rise in concentration around July. The patterns for the two localities are quite different for this anion and it appears that the surficial influence at BW1 is affecting the bicarbonate balance.

**Sherwood**

Both SW1 and SW2 show similar pattern of bicarbonate concentration/depletion with relatively constant values, in the range 203 to 215 mg/l, showing a small drop in late summer then a definite increase in concentration from January through February reaching a peak concentration of 227 mg/l for SW1, and 218 mg/l for SW2 in March (Figure 11.6). In April the concentrations drop back down to between 205 and 215 mg/l for SW1, and between 203 and 212 mg/l for SW2, similar to those measured before the peak. There is a slight enrichment in bicarbonate again around July.

**Bicarbonate**

The borehole at BW1 shows a large reduction in concentration in January indicating that rainwater has entered the hole directly, and diluted the bicarbonate present. Local rainwater has bicarbonate concentrations of approximately 4.69 mg/l, which is much less than the measured concentrations in groundwater. In contrast, the peak in bicarbonate values, at BW2, SW1 and SW2, occurs in the February-March-April period which is shortly after the recorded maximum monthly rainfall in January, suggesting that this increase corresponds with the increase in the volume of water passing through the aquifers sampled.
Figure 11.6  
(1991/1992) Monthly bicarbonate concentration (mg/L) for the sample localities BW1, BW2, SW1 and SW2, compared with maximum and minimum monthly air temperature (°C) and total monthly rainfall (mm).
Chapter 11: Physicochemical Analysis of Basalt Groundwater 272

As mentioned above the bicarbonate concentrations in rain water are relatively low, so for the bicarbonate concentration to increase in the groundwater at this time, there must be enhanced mobilisation of the \( \text{CO}_2 \) from the organic matter, soils and weathering rock that the water passes through on its way into the aquifer, and enhanced formation of bicarbonate during weathering within the aquifer. The smaller peak in bicarbonate concentrations around July may be associated with a recorded increase in precipitation in June.

11.4.2 Chloride (Cl\(^-\))

Big Willow

The chloride concentrations at BW1, 60 to 75 mg/l for most of the year, are much higher, than at BW2 and show much greater variation (Figure 11.7). At BW1 there is a large drop in chloride concentration from January through March, with a concentration drop to below 10 mg/l. In April the chloride concentration stabilises again but there is a slight increase in concentration around June and a larger increase around late August and into September. BW2 has quite a different trace with much more constant chloride concentrations which lie in the range 18 to 40 mg/l. There is a very small reduction in chloride concentration around February and a small enrichment in chloride concentration from August to the end of the sampling period, but the large fluctuations observed at BW1 are not observed at BW2.

Sherwood

Both localities at Sherwood show extremely low chloride concentrations in the range 5 to 15 mg/l, and there is very little fluctuation throughout the sampling period (Figure 11.7). There is a slight drop in chloride concentration in the Sherwood spring waters from February through April.

Chloride

The chloride concentration in the local rainwaters is approximately 1.43 mg/l, so the measured groundwater concentrations show notable enrichment with respect to Cl\(^-\) in the aquifer samples BW2, SW1 and SW2 (up to 40 mg/l), and extreme enrichment in the borehole sample BW1 (up to 95 mg/l). It appears that following periods of intense rainfall such as occurred in January, Cl\(^-\) shows a decrease in concentration which is essentially a dilution effect. However, after smaller amounts of rain, for example in June, and again in September, there appears to be Cl\(^-\) enrichment. There may be a balance therefore between the amount of chloride released as a result of increased mineral
Figure 11.7

(1991/1992) Monthly chloride concentration (mg/L) for the sample localities BW1, BW2, SW1 and SW2, compared with maximum and minimum monthly air temperature (°C) and total monthly rainfall (mm).
weathering because of greater throughflow of water following rain events, and the rate at which chloride is removed from the system in the percolating waters. In the latter part of the sampling period, it appears that the rainfall events were small enough that chloride mobilised in the aquifer was concentrated in the waters rather than washed out in dilute solution. At BW1, a small chloride enrichment is observed around June and a greater chloride enrichment is noted around September, and both months are times of increased rainfall. These enrichments in chloride concentration may be associated with evaporation at BW1 because the mouth of the borehole is open to the atmosphere.

11.4.3 Nitrates and Nitrites (NO$_3^-$, NO$_2^-$)

Big Willow

The concentration of nitrates and nitrites in the measured groundwater samples are extremely low, generally <1 mg/l, and are present in approximately the same concentration as the local rainwater, 0.45 mg/l (Figure 11.8). Small enrichments in nitrate and nitrite concentration are observed at BW2 but this effect is not observed at BW1.

Sherwood

The waters of the Sherwood springs show concentrations of nitrate and nitrite that are greater than those measured at Big Willow (Figure 11.8). Even so, the concentrations are less than 1.5 mg/l and for most samples are less than 0.5 mg/l. There is a slight enrichment in nitrate and nitrite in the last three months of sampling, a similar trend to that observed at BW2.

Nitrates and Nitrites

The low concentrations of nitrates and nitrites implies that these anions interact very little with the weathering basalt in the aquifer system. Small enrichments in nitrate and nitrite composition, at BW2, SW1 and SW2, in the last three months of the sampling period may perhaps be due to some kind biological activity, possibly plant growth, in the late winter-early spring, near the entrance to the aquifer or at the aquifer mouth. This effect was not observed at BW1.
Figure 11.8
(1991/1992) Monthly nitrate/nitrite concentration (mg/L) for the sample localities BW1, BW2, SW1 and SW2, compared with maximum and minimum monthly air temperature (°C) and total monthly rainfall (mm).
11.4.4 Sulphate (SO$_4^{2-}$)

*Big Willow*

The concentration of sulphate at BW1 is very low, with most analyses less than 0.5 mg/l which is the sensitivity limit of the technique, however directly after the main rain events for the year there are small peaks in the SO$_4^{2-}$ concentrations, and at these times concentrations may be as great as 1 mg/l. At BW2 sulphate shows a consistently very low concentration throughout the sampling period (Figure 11.9).

*Sherwood*

At both SW1 and SW2 the sulphate concentrations in the spring waters are extremely low. There are no apparent enrichment or depletion trends (Figure 11.9).

*Sulphate*

The average concentration of sulphate in the local rainwaters is relatively high, in the order of 3.08 mg/l, compared with the measured groundwater concentrations (<1 mg/l). The weathering basalt within the aquifers appears to be a sink for sulphates. Although some buffering of the sulphate concentration is taking place, much of the rainwater entering the aquifers is already relatively dilute with respect to sulphate because the interaction of rainwater with vegetation at the land surface may result in the loss of sulphur. The greater fluctuation in sulphate concentration at BW1 may be attributed to the entry of rainwater with higher concentrations of sulphate into the borehole. Sulphate is present in such small proportions that it probably plays very little part in basalt weathering.
Figure 11.9
(1991/1992) Monthly sulphate concentration (mg/L) for the sample localities BW1, BW2, SW1 and SW2, compared with maximum and minimum monthly air temperature (°C) and total monthly rainfall (mm).
11.5 CATION ANALYSES

11.5.1 Calcium (Ca)

**Big Willow**

Calcium shows relatively high concentrations in the waters at both sites, with normal concentrations between 30 and 40 mg/l for BW1 and between 30 and 50 mg/l for BW2 (Figure 11.10). There is a large reduction in calcium concentration during the months of January, February and March at BW1 and February, March and April at BW2, with values dropping to a minimum of 4 mg/l and 17 mg/l respectively. Apart from this dilution event, calcium concentrations appear to be relatively constant.

**Sherwood**

Concentrations of calcium in the waters of the Sherwood aquifers lie in the range 30 to 40 mg/l throughout the year (Figure 11.10). Both sample sites show a notable drop in concentration for the months of February, March and April with minimum values of 30 mg/l at SW1 and 23 mg/l at SW2.

**Calcium**

Calcium concentration in local rainwater is in the order of 0.5 mg/l so the groundwaters analysed, with concentrations in the range 30 to 50 mg/l, are significantly enriched with respect to calcium. All three aquifer sites BW2, SW1, and SW2, show a clear reduction in concentration of calcium in the months of February to April, whereas at the borehole BW1 this drop commences one month earlier. Maximum rainfall for the year occurred in January, so it appears that BW1 was directly affected by an influx of rainwater through the small opening at the surface, while at the other localities a time lag of around one month occurred before similar dilution effects were observed. In addition, the minimum concentration of calcium in the waters at BW1 (4 mg/l) is much lower than that for all other sites (17 to 30 mg/l) suggesting that the waters in the aquifers are buffered somewhat and although they show dilution it is not to the same extent as is observed when the system is more open.
Chapter 11: Physicochemical Analysis of Basalt Groundwater 279

Figure 11.10
(1991/1992) Monthly calcium concentration (mg/L) for the sample localities BW1, BW2, SW1 and SW2, compared with maximum and minimum monthly air temperature (°C) and total monthly rainfall (mm).
11.5.2 Magnesium (Mg)

Big Willow

The measured concentrations of magnesium in the waters of BW1 borehole lie in the range 25 to 45 mg/l, and in the waters of the spring at BW2 lie between 30 and 40 mg/l (Figure 11.11). Much greater fluctuations in concentration are observed at BW1 than at BW2, and BW1 appears to show a decrease in concentration throughout the sampling period, broadly corresponding to changes in water temperature at this site. At both localities there is a large drop in concentration, to a minimum of 4 mg/l at BW1 and 17 mg/l at BW2, in late summer to spring. BW1 shows the reduction in magnesium concentration from January to March and at BW2 it occurs between February and April. In both cases there appears to be a slight enrichment in magnesium around May/June, directly after the period of low concentration.

Sherwood

The Sherwood springs show very constant magnesium concentrations for most of the year with values at SW1 lying between 30 and 35 mg/l, and at SW2 between 25 and 35 mg/l (Figure 11.11). Deviations from these normal concentrations include a drop in concentration from February to March to a minimum of 16 mg/l at both sites. Although not apparent in the analyses from SW1, there is a definite enrichment in magnesium concentration directly after the period of low concentration, at SW2, which is similar to the trends observed at Big Willow.

Magnesium

The concentration of magnesium in local rainwater is approximately 0.16 mg/l, so there is a notable enrichment in these groundwaters (25 to 45 mg/l) with respect to magnesium. As observed for calcium, there is approximately one month time difference between the magnesium concentration drop at BW1 and at the three aquifers BW2, SW1 and SW2. Again this can be attributed to the direct entry of rain into the borehole at BW1, and provides further evidence for a residence time for waters in the aquifers of 3 to 5 weeks.

The enrichment in magnesium observed directly after the period of rainwater flushing in these aquifers may relate to the late mobilisation of ions released during the flushing event but not physically removed from the aquifer at the time. This also follows a period of relatively low rainfall which implies that the recharge for the systems would be low, so even though there are still mobile ions present there is less water around and
Figure 11.11
(1991/1992) Monthly magnesium concentration (mg/L) for the sample localities BW1, BW2, SW1 and SW2, compared with maximum and minimum monthly air temperature (°C) and total monthly rainfall (mm).
consequently the concentration is higher. The fluctuations in values at BW1 are greater than all other sites because of direct interaction with the atmosphere.

11.5.3 Sodium (Na)

Big Willow

Sodium concentrations are considerably greater at BW1, 30 to 35 mg/l, than at BW2, 15 to 25 mg/l, indicating that there is some external influence on the sodium concentration at BW1 (Figure 11.12). As for calcium and magnesium, BW1 shows a sodium concentration decrease for the months January through March, but BW2 shows only a very small decrease in concentration and this commences in February. There is a slight increase in sodium concentration in December for BW2, but apart from this values are relatively constant.

Sherwood

The concentration of sodium in the waters of the Sherwood aquifers is extremely constant throughout the sampling period with only a slight decrease in values in the months February to April (Figure 11.12). All analyses lie in the range 12 to 20 mg/l sodium concentration.

Sodium

The aquifer waters at BW2, SW1 and SW2, have sodium concentrations within the range 12 to 25 mg/l, which, although they are considerably higher than local rainwater values (approximately 0.56 mg/l), are somewhat lower than the concentrations of calcium and magnesium, suggesting that the Na\(^{2+}\) cation is either not as readily mobilised from weathering basalt as the other cations, or there is less Na present in the weathering basalt to start with. BW1 sodium concentrations are higher, 30 to 35 mg/l, because of surficial Na enrichment. A reduction in sodium concentration commencing in January at BW1, is recognised commencing in February at the three other water sampling sites, BW2, SW1, SW2, and as for the other cations this is attributed to a dilution effect due to rainwater flushing through the aquifers after the heavy rains of January.
(1991/1992) Monthly sodium concentration (mg/L) for the sample localities BW1, BW2, SW1 and SW2, compared with maximum and minimum monthly air temperature (°C) and total monthly rainfall (mm).
Apart from BW1 which shows a large drop to minimum concentrations around 13 mg/l because this locality has been directly affected by rain, the concentration drops at the BW2, SW1 and SW2, are very small for sodium, especially when compared to the same effect for calcium and magnesium. Two features are illustrated here: firstly it shows the chemical buffering effect the aquifers have, whereby water is able to interact with the weathering rock to a greater or lesser degree depending on whether the throughflow is lower or higher respectively, which dampens the extreme fluctuations that would be observed if the system were more open, as in BW1. Secondly, it shows that because sodium does not normally have as high a concentration in aquifer waters it also does not show as great a dilution during rain flushing events. This may be because Na is largely combining with anions other than bicarbonate, most commonly chloride, and therefore does not show the depletion pattern observed for cations, like Mg and Ca, that are combining with bicarbonate. The small rise in concentration in December at BW2 appears to be a local fluctuation which may be related to surficial interaction with organic material at the spring mouth.

11.5.4 Potassium (K)

Big Willow

BW1 shows large fluctuations in potassium concentration, but there is still a significant decrease in concentration from February to March with a slight enrichment in K afterward (Figure 11.13). At BW2 there is no recognisable depletion in K concentration in late summer-early autumn, as observed at BW1. The maximum and minimum concentrations at BW1 are somewhat different to those at BW2, because BW1 shows much greater fluctuation, but the overall decrease in concentration from around 1.5 mg/l in November 1991 to around 0.8 mg/l in October 1992, is similar at both sites.

Sherwood

At the Sherwood springs the potassium concentrations were very low, 0.2 to 0.5 mg/l, which is not significantly different from the local rainwater concentrations of potassium, approximately 0.28 mg/l (Figure 11.13). Values were very constant throughout the sampling period at the Sherwood sites.

Potassium

The concentrations of potassium in the ground waters sampled, although higher than the concentration in local rainwater, 0.28 mg/l, are very low (<2.5 mg/l) reflecting the fact
Figure 11.13
(1991/1992) Monthly potassium concentration (mg/L) for the sample localities BW1, BW2, SW1 and SW2, compared with maximum and minimum monthly air temperature (°C) and total monthly rainfall (mm).
that not only are K-bearing phases present in extremely small amounts in basalt, but minerals such as K-feldspar are quite resistant to chemical weathering. At Sherwood it appears that there are almost no K-bearing phases actively weathering, either they are resistant to weathering or there are few present. It is likely that the K concentration is not greatly affected by the dilution event affecting other cations in the aquifers because potassium is present in such small amounts to start with. In addition, K is probably combining with anions other than bicarbonate, and therefore shows a dissimilar concentration/depletion pattern to bicarbonate.

11.5.5 Iron (Fe) and Manganese (Mn)

The first three months samples from both Big Willow and Sherwood were analysed for iron and manganese. However the concentrations of these cations was at or below the detection limit of the atomic absorption spectrophotometer (AAS) and thereafter their concentrations were not measured. These ions are oxidised as a result of weathering and so are mostly retained within the profile rather than being carried from the profile in the aquifer waters.

11.6 DUROV-ZAPOROZEC INTERPRETATION

The Durov-Zaporozec diagram (Zaporozec 1972) is a method of representing the chemistry of waters in order to evaluate their overall chemical signature. This facilitates the interpretation of the chemical behaviour of the water in the basalt weathering environment.

![Durov-Zaporozec diagram](image)
Big Willow

Waters from BW1 sampled in November and December of 1991 and after April of 1992, plot in the magnesium carbonate (MgCO₃) field (Figure 11.14). Calcium constitutes approximately 25 to 35% of the cation load for these samples, Mg accounts for 45 to 55%, and Na+K, 20 to 30%. Bicarbonate is abundant (50 to 60 % of the anion fraction), but the proportion of chloride ions is also relatively high (40-50%) with sulphate, nitrate and nitrite comprising less than 1%.

Three BW1 samples plot in the sodium potassium carbonate ((Na,K)CO₃) field showing that there is an excursion from the normal water chemistry in January, February and March of the sampling period. The April sample has a relatively high percentage of Na+K, which indicates that the processes influencing the change in chemical signature of the waters over the preceding months had a residual effect into April. Overall these samples are much less chloride rich (5 to 15%) compared with the samples for the rest of the year, with bicarbonate the more prevalent anion (85 to 95%).

The waters from BW2 plot wholly in the magnesium carbonate (MgCO₃) field and show very little compositional variation throughout the sampling period (Figure 11.15). Magnesium comprises approximately 45 to 60% of the cation fraction, with calcium making up around 25 to 40%, sodium 10 to 25% and potassium around 1%. The dominant anion is bicarbonate (70 to 85%), with chloride comprising most of the balance.
Chapter 11: Physicochemical Analysis of Basalt Groundwater

(10 to 25%), and sulphate, nitrate and nitrite present in extremely small proportions (<1%).

Sherwood

The aquifer waters sampled from SW1 cluster tightly in the magnesium carbonate (MgCO₃) field for most of the sampling period (Figure 11.16). Magnesium makes up 45 to 55% of the cation fraction, with calcium comprising 30 to 40% and sodium plus potassium 15 to 20% of the cations in SW1 waters. Bicarbonate forms 85% to 95% of the anion fraction, and chloride 5% to 15%. However, for the months February, March and April, the samples are more calcium rich (around 45%, magnesium approximately 40%) and hence show an excursion into the calcium carbonate (CaCO₃) field. These calcium rich samples contain a greater proportion of bicarbonate (>95%) compared with samples for other months.

![Figure 11.16](image)

**Figure 11.16**

Durov-Zaporozec diagram for 12 months water analyses (1991/1992) from sample site (SW1)

The SW2 waters all plot in the magnesium carbonate (MgCO₃) field, but the February and March samples plot very close to the boundary of the calcium carbonate (CaCO₃) field (Figure 11.17). In addition, the samples with the greatest proportion of bicarbonate in the sampling period, are those collected in February, March and April. The relative proportion of magnesium in the cation load is 40% to 55%, with calcium making up 30% to 40% and sodium and potassium combined accounting for 10% to 20%. Bicarbonate is the most prevalent anion (90% to 97%), with lesser proportions of chloride (3 to 10%) and sulphate, nitrate and nitrite barely detectable <1%. 
The dominant fluid type issuing from these aquifers are Mg-Ca bicarbonate fluids. Overall the water samples at each site are relatively tightly clustered and show very little compositional variation for most of the sampling period. Where there are changes in water chemistry, they coincide with the time interval in which the borehole and aquifers are affected by an influx of rainwater. The sample waters at this time are much more dilute than for the balance of the sampling period, which influences their ionic composition.

Despite a number of changes in the physical environment throughout the sample period, for example changes in rainfall, there is relatively little change in the overall composition of the waters at BW2, SW1 and SW2. In contrast, the water chemistry at BW1 is affected significantly by such fluctuations in physical environment. The most apparent explanation for this is that the system at BW1 is far more open than at the other three sites. However, the relatively stable aquifer water chemistry also implies that there is considerable chemical buffering taking place within the aquifers.
11.7 MINERAL STABILITY AND BASALT AQUIFER WATERS

The variations in the water chemistry of the spring waters reflects the water-rock interactions of the weathering process. Rainwaters with acid pH may be further acidified as a result of interaction with organic litter at the earth surface, and percolation through the soil zone, and have relatively low concentrations of calcium, magnesium, sodium and potassium. These waters interact with primary minerals in the basalt and form a suite of secondary minerals dominated by smectite clays with minor gibbsite, kaolin group clays and iron oxyhydroxides. The water compositions define a reaction path that trends towards equilibrium with the enclosing weathered basalt.

11.7.1 Activity-Activity Ratios of Major Cations

The activity - activity ratios of Monaro basalt aquifer water plotted on a log \((a \text{Mg}^{2+}/a \text{H}^+)^2\) versus log \((a \text{Ca}^{2+}/a \text{H}^+)^2\) (Figure 11.18a) describe a line with a 1:1 slope, and on a log \((a \text{Na}^+ /a \text{H}^+)^2\) versus log \((a \text{Ca}^{2+}/a \text{H}^+)^2\) (Figure 11.18b) they describe a line with 2:1 slope. Norton (1974) details almost identical results in his analysis of chemistry of waters draining andesitic lavas in Puerto Rico, attributing the scatter of points along the activity-activity line to increasingly variation in water discharge. In the Monaro data set the scatter of points can be attributed to greater and lesser flow of water through the aquifer (variation in dilution), which is directly related to local precipitation. The data points lie almost wholly in the smectite field, which is compatible with the observed secondary mineralogy of the weathered basalts (nontronite, beidellite and minor saponite, kaolinite/halloysite plus minor Fe-oxyhydroxides, mostly goethite).

A straight line vector can be drawn from the initial rain water composition through the issuing aquifer water compositions, indicating that the acid rain water is progressively modified as the primary basalt minerals are hydrolysed and cations (\(\text{Ca}^{2+}, \text{Mg}^{2+}, \text{Na}^+\) and minor \(\text{K}^+\)) are released into the aquifer solution at the expense of \(\text{H}^+\) ions. "The lines are coincident with the theoretical reaction path trend in solution composition expected for an acid solution, initially with low concentrations of calcium, magnesium and sodium, interacting with a rock that releases these cations to solution in equal molar concentrations (Helgeson 1969, 1970)."

Norton's (1974) and Helgeson's (1969, 1970) theoretical models are based on the assumption that the solution maintains chemical equilibrium with secondary phases. At times when Big Willow and Sherwood aquifer throughflow is reduced, there is greater fluid interface interaction and the aquifer water may reach equilibrium with the enclosing secondary minerals. Changes in local precipitation lead to fluctuating aquifer
Figure 11.18  
(a) Big Willow and Sherwood data plotted on activity diagrams for the system CaO-Na2O-Al2O3-SiO2-H2O at 25°C and assumed $a_{H_4SiO_4}=10^{-3.70}$ (after Norton 1974).
(b) Big Willow and Sherwood data plotted on activity diagrams for the system CaO-MgO-Al2O3-SiO2-H2O at 25°C and assumed $a_{H_4SiO_4}=10^{-3.70}$ (after Norton 1974).
throughflow, but the pH of the issuing aquifer waters are almost constantly in the range pH 6.5 - 8.5 (Figure 11.3). This indicates that the aquifer fluids approach equilibrium with the enclosing secondary minerals by the time they exit the aquifer, even when the aquifer water flow increases. Hence the assumption holds in the general sense. However, it is important to remember that many of the minerals in the secondary weathering suite, especially clays, are non-stoichiometric phases. The chemistry of the secondary products may change slightly, depending on the chemistry of the weathering fluids.

11.7.2 The Presence of Both Gibbsite and Smectite in the Secondary Mineral Suite

At Big Willow gibbsite was sampled near the surface in zones between basalt corestones where the smectitic suite of secondary products surrounding the corestones had been further weathered by near surface acidic fluids. This is a disequilibrium reaction if we look at the aquifer system as a whole. At this site gibbsite only forms where rain waters, further acidified after percolation through the soil zone, can interact with rubbly weathered basalt, usually only at top of profile in relatively open fractures. From the log ($a_{Mg}^{2+}/a_{H}^+$) versus log ($a_{Ca}^{2+}/a_{H}^+$) (Figure 11.18a) and log ($a_{Na}^{+}/a_{H}^+$) versus log ($a_{Ca}^{2+}/a_{H}^+$) (Figure 11.18b) diagrams kaolinite clays might be expected in the upper part of the profiles where more acid waters are interacting with enclosing phases. Kaolin group minerals were not observed at Big Willow. This implies that either kaolin group minerals had been wholly converted to gibbsite, or that the gibbsite was forming as an overprint on previously existing smectite dominant secondary weathering suite, and kaolin group minerals had not been formed as an intermediate phase.

Although activity data for silica is unavailable for this site, if the assumption that the aquifer waters exiting the springs are in equilibrium with the secondary mineral suite is made, as suggested by the consistent neutral to slightly alkaline pH of issuing fluids, these fluids would also be saturated with respect to amorphous silica. This enables graphical representation of the water data from Big Willow and Sherwood on the stability diagrams for silica versus calcium (Figure 11.19a), silica versus magnesium (Figure 11.19b) and silica versus sodium (Figure 11.19c).

According to the stability diagram for silica versus calcium (Figure 11.19a), natural juxtaposition of Ca-smectite and gibbsite without kaolinite forming can only occur if gibbsite formation occurs as an overprint. At Big Willow and Sherwood the rainwater entering the system is acid (pH = 5.13) and may be further acidified after passage through the soil zone and interaction with soil CO2. The rock along the open fractures is extremely weathered, supporting the field observations that gibbsite formation overprints an earlier formed suite of smectite bearing secondary minerals. It is clear that the gibbsite

(a) Big Willow and Sherwood data plotted on activity diagrams for the system MgO-Al₂O₃-SiO₂-H₂O at 25°C, stability fields from data in Helgeson (1969).

is not forming in equilibrium with the fluids issuing from the aquifer, instead it is in equilibrium with the acid water entering the aquifer system. When rainwater is plotted on the stability diagram (Figure 19a,b,c) it lies in the stability field for gibbsite.

11.8 GROUNDWATER AND THE WEATHERING OF BASALT

Monaro groundwater does interact with the fractured basalt through which it travels, as the ion concentration in the water issuing from the aquifers is significantly greater than the ion concentration in the local rainwater entering the aquifers. Magnesium and calcium are the dominant cations in the aquifer waters, and these cations are readily mobilised from basalt during weathering. Bicarbonate and chloride are the dominant anions, but waters are mostly bicarbonate rich. The dominance of bicarbonate and the equilibration of aquifer waters with respect to the secondary mineral assemblage explains why pH of the waters is consistently neutral to alkaline.

There is a definite relationship between large rain events and ion concentration in the aquifer waters. For the aquifers sampled there is a time lag of approximately 3-5 weeks between rain events and issue of water. This residence time has been evaluated by comparing the time that a large rainwater influx affected the borehole at BW1, which is a system open to the atmosphere, with the time that the dilution effects of the same rainy period were detected at the issue points of the aquifers. One month is probably a minimum residence time, and after dry periods the time waters remain within aquifers may be slightly longer.

There is a balance, during flushing events, between the increased weathering of minerals because of greater throughflow of water, and the shorter interval of rock interaction with a given volume of water. That is, the overall amount weathering may be greater but the concentration of mobilised ions in the water considerably less, because of dilution. In addition, ions mobilised during flushes may not be removed at that time, which leads to the concentration of ions in waters for a short time after flushing events, until the system stabilises again. However, for a large range of physical environmental conditions, the chemistry of the aquifer waters remains relatively constant, which reflects the chemical buffering that takes place within the aquifers.
CHAPTER 12

DISCUSSION

This discussion is divided into four sections:

PART (A) An overview of mineralogical changes during basalt weathering in eastern Australia;

PART (B) An overview of element mobility during basalt weathering in eastern Australia;

PART (C) Aqueous geochemistry of basalt weathering in the Monaro and implications for the weathering of basalt in eastern Australia; and,

PART (D) Paleoclimate, contemporary climate and basalt weathering in eastern Australia.

PART A: AN OVERVIEW OF MINERALOGICAL CHANGES DURING BASALT WEATHERING IN EASTERN AUSTRALIA

12(A).1 DISSOLUTION OF PRIMARY BASALT MINERALS

Petrographic, X-ray diffraction (XRD), scanning electron microscopic (SEM) and geochemical analysis has enabled observation of physical and mineralogical changes during basalt weathering. For eastern Australian basalts, phases commence weathering in the approximate order: basaltic glass, olivine, plagioclase, pyroxene and opaque oxides, but pyroxene weathers more rapidly than plagioclase, and is wholly weathered before plagioclase. This sequence is the same as that observed by Eggleton et al. (1987).

Basaltic Glass

Basaltic glass weathers, possibly through an amorphous intermediate (allophane), to smectite clays. Glass was not preserved in any of the basalts analysed in this study, which gives an indication of the susceptibility of glass to weathering. Smectite clays were often associated with goethitic material which imparted a yellow colouration. Some smectite formed after glass does not show fabric orientation, however, more common examples appear to have recrystallised, with increased weathering, and have an oriented fabric, sometimes showing concentric banding, which roughly preserves the original shape of the glassy area. One explanation for the transition in fabric type may be the formation of an early cell-textured protocristalline intermediate phase, as described for the weathering of feldspar, (Banfield & Eggleton 1990) which later recrystallises to form a more ordered fabric.
Olivine

Olivine weathers initially to smectite clays and Fe-oxyhydroxides, usually goethite, which form definite rims on phenocrysts. Mineralogy of these weathering rims on olivine, referred to as iddingsite rims, has been described by Eggleton (1984). Groundmass olivine is completely replaced very early in weathering. The first formed smectites are apparently dominated by trioctahedral phases, saponite and Fe-saponite, which subsequently break down to dioctahedral clays, usually nontronite and Fe-bearing beidellite, with increased removal of cations. Sometimes semi-amorphous intermediate phases, like hisingerite, are formed in this process. Porphyritic basalts with large olivine phenocrysts will have significant proportions of smectite present when they weather, until weathering proceeds to the point that smectites break down to form kaolin group clays. In the samples studied, halloysite was apparently more abundant than kaolinite in samples where smectite was breaking down to kaolin group clays.

Plagioclase Feldspar

Groundmass plagioclase are etched early in weathering but persist as relicts through into intensely weathered basalt. The etch pattern on small laths is difficult to observe, but chemical etching of plagioclase feldspar phenocrysts occurs at points of weakness in the plagioclase structure, along twin planes, cleavage planes, zone boundaries and around the edges of grains. Plagioclase can break down to smectite but may weather directly to kaolin group clays as well. The smectite formed on plagioclase is Al-rich and may be montmorillonite or beidellite. The kaolin group clay formed directly from plagioclase feldspar is most commonly kaolinite. Kaolinite formation occurs either in areas where there is high fluid flow through the profile, or under conditions where the weathering basalt has been relatively stable and well drained for an extended period of time (eg paleo-weathering profiles in the Monaro Volcanic Province).

Pyroxene

Pyroxene takes a long time to commence weathering, but once it does it weathers relatively rapidly as the cleavage planes of pyroxene allow weathering fluids to infiltrate the crystals relatively readily. Pyroxene generally weathers to smectite clays and Fe-oxyhydroxides, but a clear weathering sequence is difficult to observe. Orthopyroxene is less common than clinopyroxene in the basalts studied, but where present it may break down to vermiculite clay (eg Branxholme profile, north east Tasmania). Where pyroxene forms an ophitic texture with plagioclase feldspar laths, the feldspar is often partially weathered away before the pyroxene commences weathering. Weathered pyroxene
generally sits amidst a matrix of smectite clays, mostly nontronite and beidellite, with associated goethite.

\textit{Opaque Oxides}

These minerals form a number of populations. One population is the groundmass magnetite (titanomagnetite) and ilmenite opaque oxides which have angular morphology, sometimes elongate, that reflects the shape of the inter-plagioclase-lath space they originally formed in. In some samples there are larger microphenocrysts of euhedral pseudo-hexagonal magnetite, and the third population are those opaque oxides which are enclosed within the other primary minerals. The latter include small blocky grains of Cr-spinel, which are usually enclosed in olivine, and fine grains of chalcopyrite, if present, also enclosed within the ferromagnesian silicates.

All of these phases except chalcopyrite, are relatively resistant to weathering and so maintain their angular and euhedral shapes even in intensely weathered material. It is because of this resistance to chemical weathering that elements partitioned into these phases (e.g. Ti), are used as immobile elements for calculation of weathering indices. Physical concentration these minerals takes place in two principal ways: differential dissolution of minerals surrounding the resistant phases and associated compaction of unconsolidated material as the rock microstructure breaks down; and illuviation of material down profile and consequent concentration in cracks and void spaces. Where magnetite or ilmenite do show incipient dissolution, they form hematite. Chalcopyrite will generally oxidise in a free draining weathering environment to form a sulphate, which is soluble in percolating fluids.

\textbf{12(A).2 MASS LOSS DURING WEATHERING}

The dissolution of primary basalt phases and the formation of a secondary mineral assemblage dominated by clay minerals generally results in a mass decrease for the basalt, and consequently a density decrease, according to the relationship: density = mass/volume, given that volume does not increase. It follows that secondary precipitation of phases into a sample may cause an increase in weathered basalt density, as a result of the increase in mass, and there should be an associated increase in volume.

In localities where quartz veins cross-cut weathered profiles the protolith may be considerably weathered before the collapse of the microstructure disrupts the quartz vein. This observation has been used to provide some evidence for isovolumetric basalt weathering (Ollier 1984). However, the fact that saprolitic material may occupy a similar space to the parent material it developed from, does not mean that this weathered material
maintains the same mass, because the density of the material occupying the profile decreases. Hence, saprolitic material may appear isovolumetric in out-crop, in the early stages of weathering, but the mass loss indicated by the isocon technique remains a valid estimate of the degree to which the material has weathered. This concept is fundamental to the use of the net mass change $\Delta M$ (%) of a sample as a weathering index in this study.

12(A).3 FORMATION OF THE SECONDARY MINERAL ASSEMBLAGES

General trends in the formation of clay rich secondary mineral assemblages in weathered basalts studied from eastern Australia can be summarised by comparing characteristics such as cation exchange capacity (CEC) and Si:Al ratio of the clay separates, and clay content, with parameters indicative of the degree of weathering such as slope of the isocon ($m$) or net mass loss/gain $\Delta M$ (%). Further elaboration on the details of process can then be summarised from geochemical analyses, and petrographic, X-ray diffraction (XRD) and scanning electron microscope (SEM) observations.

12(A).3.1 Secondary Mineral Assemblage Dynamics for Weathered Basalts in Eastern Australia

![Cation Exchange Capacity (CEC) versus Silica:Aluminium Ratio](image)

*Figure 12.1*: Cation Exchange Capacity (CEC) versus Silica:Aluminium ratio for the eastern Australia basalt samples in this study. Note that there is a cluster at Si:Al ratio around 1:1 for CEC values <20, and a broader cluster at Si:Al ratio around 2:1 for CEC values >20. Samples with CEC values <20 and Si:Al ratios around 2:1 have some free silica in the clay separate.

The cation exchange capacity (CEC) of a weathered basalt sample is directly related to the amount and type of clay in the sample. Characteristically kaolin group clays have CEC
values less than 20 meq/100 g (kaolinite <10 meq/100 g) and smectitic clays have elevated CEC values with values for pure smectite in the range 80 meq/100 g to 150 meq/100 g (Drever 1982, p82).

A plot of cation exchange capacity versus Si:Al ratio of the clay separate for the eastern Australian basalt samples (Figure 12.1) displays two clear fields, samples with CEC values less than about 20 meq/100 g and Si:Al ratios around 1, and samples with CEC values greater than 20 meq/100 g and Si:Al values around 2. Hence, because kaolin group clays have a 1.1 ratio of Si:Al in their ideal lattice structure and smectite clays have a 2:1 ratio, the weathered basalt samples can be discriminated in a general way on the basis of whether the secondary mineral assemblage is dominated by kaolin group or smectite clays.

When the cation exchange capacity values for the eastern Australian basalts are compared with a corresponding weathering index, such as slope of the isocon ($m$) (Figure 12.2) or net mass change $\Delta M$ (%) (Figure 12.3) these two groupings (CEC<20 meq/100 g, CEC>20 meq/100 g) can still be distinguished. For least weathered samples smectites are the dominant clay type but more weathered samples have an increasing kaolin group clay content.

![Cation Exchange Capacity (CEC) versus Slope of Isocon (m)](image-url)

**Figure 12.2:** Cation Exchange Capacity (CEC) versus slope of the isocon ($m$) for the eastern Australia basalt samples in this study.

The removal of cations (Ca, Sr, Na, K, Rb, Mg) from primary minerals in the weathering basalt as a result of hydrolysis initially produces a secondary suite dominated by smectite clays. With continued removal of cations kaolin group clays are formed. Ultimately, almost all of the cations (including silica) are removed, leaving aluminium as the major residual cation, and gibbsite may form. This general sequence of mineral changes is characteristic of all the well drained basalt profiles analysed in this study,
however the rate of the changes in mineralogy varies greatly. In some cases kaolin group clays are formed without evidence of a smectite intermediate being preserved, and in one locality (Big Willow, Monaro) gibbsite was found in association with a smectite dominant secondary mineralogy with no kaolin group minerals preserved.

![Cation Exchange Capacity (CEC) versus Net Mass Loss (%)](image)

**Figure 12.3:** Cation Exchange Capacity (CEC) versus Net Mass Loss/Gain ΔM(%) for the eastern Australia basalt samples in this study.

In kaolin dominated profiles, because of the lesser capacity of kaolin to exchange cations with the percolating fluids (lower CEC), the fluid issuing from the profile may have a lower cation load than a fluid issuing from a smectite dominated weathering profile. Hence, the acid rainwater/meteoric fluids entering a kaolin dominated profile receive less cations from the enclosing minerals, and may not become as alkaline, with weathering, as equivalent fluids that have passed through a smectite dominated basalt weathering profile.

At Big Willow acid rainwater/meteoric fluids passing through a weathered basalt sequence with a smectite dominated secondary assemblage interact with the enclosing phases, and approach equilibrium with the enclosing mineralogy, ultimately issuing from the profile as neutral to alkaline fluids (Chapter 11). Measured soil pH is generally acid for profiles dominated by kaolin group clays compared with more alkaline pH for smectite dominated profiles (Figure 12.4).

<table>
<thead>
<tr>
<th>Dominant clay</th>
<th>Soil pH</th>
<th>CEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>kaolin group</td>
<td>low</td>
<td>low (&lt;20 meq/100 g)</td>
</tr>
<tr>
<td>smectite</td>
<td>high</td>
<td>high (&gt;20 meq/100 g)</td>
</tr>
</tbody>
</table>
Chapter 12: Discussion (A) Mineralogical Changes During Basalt Weathering

Figure 12.4: Cation Exchange Capacity (CEC) versus Soil pH for the eastern Australia basalt samples in this study. The horizontal dashed line is at pH 7.

Figure 12.5: Cation Exchange Capacity (CEC) versus Contemporary Annual Rainfall (mm) for the eastern Australia basalt samples in this study.

If contemporary rainfall is compared with cation exchange capacity for the eastern Australian basalt samples (Figure 12.5) there is a broad trend for areas with high rainfall to have lower cation exchange capacities. So in general, profiles with elevated fluid percolation are those with most cation depleted secondary phases, and those in more arid areas have smectite dominated secondary assemblages. However, prolonged percolation of fluids through weathering basalt would also eventually result in kaolin and gibbsite rich weathering profiles (e.g., paleo-weathering profiles Monaro Volcanic Province, Taylor et al. 1992). The broadness of the data spread implies that the contemporary climate environment, although influencing the most recently developed portion of the weathering profiles may be overprinting pre-existing paleo-weathering profiles which reflect...
paleoclimate environments different to those that prevail today. In areas where the contemporary rainfall is extremely high this overprint may completely erase evidence of earlier weathering. This concept is discussed further in the summary of paleoclimate, contemporary climate and basalt weathering in eastern Australia.

The actual capacity for clays to exchange cations depends on the proportion of clay minerals there is in a sample. When cation exchange capacity is compared with estimated clay mineral content (Figure 12.6), clay content is generally greater for samples with low CEC. As already discussed, more intensely weathered basalt samples are more kaolin rich, hence have lower CEC values. It follows that more intensely weathered samples would also have a higher clay content.

The estimated clay content values (based on the number of counts at the 4.5Å position on the bulk XRD traces) can be divided into four brackets:

- 0-100 counts <10% clay
- 100-200 counts 10-20% clay
- 200-300 counts 20-30% clay
- >300 counts >30% clay

Figure 12.6: Cation Exchange Capacity (CEC) versus Estimated Clay Content for the eastern Australia basalt samples in this study. The estimated clay content values are based on the number of counts at the 4.5 Å position on the bulk XRD traces.

These brackets are estimated on the basis of thin section evaluation of clay content and consideration of degree of net mass loss/gain ΔM(%), as the degree of weathering of a sample is proportional its clay mineral content. In addition those samples that register less than 100 counts are relatively fresh to incipiently weathered and are likely to have less than 10% clay content.
Average values of: net mass loss/gain ΔM(%) for basalt samples based on isocon interpretation; Si:Al ratio; dominant clay type; and, cation exchange capacity (CEC), for each clay content bracket, are summarised in Table 12.1.

Table 12.1

<table>
<thead>
<tr>
<th>ESTIMATED CLAY CONTENT</th>
<th>AVE. ΔM (%)</th>
<th>AVE. Si:Al</th>
<th>DOMINANT CLAY TYPE</th>
<th>AVE. CEC</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;10% clay</td>
<td>-9.75</td>
<td>2.39</td>
<td>Smectite (+Free Si)</td>
<td>30.56</td>
<td>(16)</td>
</tr>
<tr>
<td>10-20% clay</td>
<td>-17.17</td>
<td>2.19</td>
<td>Smectite</td>
<td>51.94</td>
<td>(31)</td>
</tr>
<tr>
<td>20-30% clay</td>
<td>-34.08</td>
<td>1.34</td>
<td>Kaolin (+Smectite)</td>
<td>28.54</td>
<td>(13)</td>
</tr>
<tr>
<td>&gt;30% clay</td>
<td>-46.75</td>
<td>1.01</td>
<td>Kaolin</td>
<td>9.75</td>
<td>(4 )</td>
</tr>
</tbody>
</table>

Samples with less than 10% clay content are generally the least weathered, hence the low average net mass loss/gain ΔM(%) for these samples. The Si:Al ratio is within the range for smectite clays but the silica value may be a little elevated if crushed primary silicate minerals from fresher samples are accidentally incorporated in the clay separate.

The average cation exchange capacity (CEC) is greater than 20 meq/100 g.

Samples with 10-20% clay content have an average net mass loss ΔM(%) of approximately -17%, higher than that for incipiently weathered basalts. This increase in clay content with degree of weathering is observed for all four brackets. The Si:Al ratio is very close to the 2:1 ratio expected for an ideal smectite lattice structure and the average cation exchange capacity (CEC) is highest for this clay content bracket indicating a high smectite content in the secondary mineral assemblage for most of these samples.

Samples with 20-30% clay content have an average net mass loss ΔM(%) of approximately -34% which implies that considerable weathering has taken place. This is reflected in a higher kaolin group clay content, and lower average Si:Al ratio (1.34) and CEC (28.54 meq/100 g) values.

Samples with greater than 30% clay content are generally the most weathered, hence the high average net mass loss ΔM(%) for these samples. The Si:Al ratio is very close to the 1:1 ratio expected for an ideal kaolin lattice structure and the average cation exchange capacity (CEC) is lowest for this clay content bracket indicating a high kaolin group clay content, and perhaps some gibbsite, in the secondary mineral assemblage for most of these samples.
12(A).3.2 Secondary Mineralogy - A Summary

Smectite Clays

Because the first weathering products derived from basaltic glass, olivine and pyroxene are smectite clays, and plagioclase may also weather to this phase, most of the weathering profiles studied had smectite in their clay fraction. As a general rule the smectite dominated profiles were either developed on younger basalts or were located in relatively arid areas, hence they had been subject to less fluid through-flow than those profiles that had kaolin group clays as their dominant secondary phase. Trioctahedral smectites (saponite, Fe-saponite) were abundant in incipiently weathered basalt, but as weathering proceeded dioctahedral phases (nontronite, beidellite and montmorillonite) became more abundant. Porphyritic basalts with ferromagnesian phenocrysts, were generally richer in smectite clays than more equigranular or fine grained basalts that did not have this phenocryst phase. This is simply because there was a greater proportion of primary olivine and pyroxene to weather to smectite. In addition, localities that had evidence of ponded fluids were dominated by smectite clays. Cations released into fluids during weathering may be concentrated in ponded fluids and therefore are available for re-incorporation into secondary phases, generally cation rich smectites. With time this ponded water may become silica saturated and establish equilibrium with the enclosing minerals.

Continued removal of cations from the smectite leads to the formation of kaolin group clays, and a number of profiles studied had both smectite and kaolin group clays present in the clay separate. Physically halloysite and kaolinite are associated with the more intensely weathered zones of the profiles. Hence, zones of preferred fluid flow, and rubbly weathered material adjacent to joints (onionskins) are more kaolin rich than the material immediately adjacent to weathering corestones. Kaolinite may form directly during the weathering of plagioclase feldspar, especially in onionskins and may also form as a result of the removal of cations from smectite clays. In the latter process, intermediate randomly interstratified kaolin-smectite clays may form.

Kaolin-Smectite Clays

Kaolin-smectite clays have been described from weathering profiles on volcanic ejecta and lava (Quantin et al. 1984, Wilson 1987, Delvaux 1988, 1989a, 1989b, Fontaine et al. 1989, Churchman & Lowe 1993) at a variety of latitudes and in a number of different climatic environments. It seems that they can form in any environment where smectite is breaking down to form kaolin group clays, that is, in profiles were the fluid
through-flow, especially adjacent to joints, is sufficiently great for kaolin group clays to form.

Interstratified kaolin-smectite clays can be detected using careful X-ray diffraction (XRD) on K⁺ saturated clay separates (Delvaux 1988, 1989b), or extremely fine clay separates (Churchman 1993), in conjunction with cation exchange capacity (CEC) information. Although the bulk XRD trace may resemble kaolinite or halloysite alone, an elevated CEC suggests that some interstratified 2:1 clays may be present. Conclusive identification can really only be achieved using transmission electron microscopy (TEM), which was beyond the scope of this study. However, the apparent presence of kaolin-smectite phases was noted at a few localities in this study.

Although these randomly interstratified clays are only positively identified at a few localities, the occurrence of kaolin-smectite clays is probably widespread. In theory, they should occur wherever smectite clays are weathered to kaolin group clays, and hence be present in almost all but the most arid and most humid environments. Ma & Eggleton (1995) describe 2:1 layers (possible smectite layers) that form on the surface of kaolinite particles during weathering. These layers may form as a result of excess free energy at the kaolinite surface. In Australia, kaolin-smectites have been recognised from Mount Gambier in South Australia, Sturgeon Volcanic Province in central north Queensland (pers. comm. Churchman 1992) and from this study in north Queensland (LMAC) on the western side of the Atherton Province and at Warrumbungles (WFT 4) in northern New South Wales. It is likely that kaolin smectite clays have been analysed in the past but not recognised as randomly interstratified phases, and hence have simply been recorded as kaolinite.

In secondary assemblages where smectite is the principal phase, and kaolin a minor phase, smectite-rich interstratified kaolin-smectites would be very difficult to detect using K⁺ saturation, XRD and CEC. Although the XRD trace might suggest the presence of kaolin-smectite phases the CEC and affinity for K⁺ would already be elevated because of the amount of smectite present (Moore 1993). Hence, the kaolin-smectites generally recognised from these sequences are the kaolin-rich end members of the continuum.

Kaolin Group Clays and Gibbsite

The kaolin group clays that develop in basalt weathering profiles may be halloysite or kaolinite. For the samples studied, halloysite tends to be more closely associated with smectitic material. Apparently halloysite is preferentially formed during the break down of smectite especially in environments where the cations released are not transported far. The interstratified kaolin-smectites in this case may be halloysite smectites, although this...
phase might form more readily in pyroclastic materials. In more freely draining areas of the profile, a kaolinite-smectite intermediate phase would predominate. In intensely weathered, well drained profiles where fluid through-flow is high, kaolin group clays are dominant, and kaolinite is generally more abundant than halloysite clays. Interstratified kaolin-smectites are no longer preserved. Ultimately, with the removal of silica, Al hydroxide (gibbsite) may form at the expense of kaolinite. There are clear trends in the most weathered profiles in this study (Millaa Millaa - QFT11, Innisfail - QFT8) which show the decrease in abundance of kaolinite with the increase in abundance of gibbsite up-profile. It is important to note that these end products can also be formed in areas with lower fluid through-flow provided the weathering basalt has been in a tectonically stable environment, and well drained, for an extended period of time.

**Vermiculite Clay**

Vermiculite was recognised from one locality (Branxholme, north east Tasmania) and is forming as a secondary product after orthopyroxene. In addition some chlorite, now completely replaced, may have been present in this basalt, formed due to deuteric alteration of the basalt shortly after its emplacement, and chlorite is a known precursor to vermiculite development in weathering (Evans 1992). Because Tasmania has always had a cool climate (Chapter 4) the rates of weathering reactions were probably relatively slow through time and this might enhance vermiculite development rather than more cation depleted phases.

**Iron Oxides and Oxyhydroxides**

Although hematite may form directly from the break down of primary minerals (Banfield *et al.* 1990) goethite appears to be the principal secondary Fe-bearing phase to form as primary minerals break down, especially in profiles with a limited fluid through-flow. In most of the profiles studied the concentration of goethite in the matrix of the rock was greater than the concentration of hematite. Clays formed from the breakdown of glass and groundmass phases were frequently found in association with goethite. Goethite and smectite clays (saponite, nontronite and Fe-beidellite) associated with the formation of rims around olivine early in weathering. However, hematite was concentrated around micro-fractures, near voids, adjacent to vesicles and in weathering rinds, i.e. proximal to exposed faces, where drying would affect the weathering products. In addition, the more pervasively weathered samples had greater concentrations of hematite throughout. The most evident exception to this pattern of Fe-oxyhydroxide distribution were the red coloured oxidised vesicular basalts (e.g. the lower basalt at Hellyer River, north west Tasmania). In these samples hematite dominated in the groundmass. This is not entirely an artefact of weathering, but rather a primary effect of oxidation of the basalt at the time.
of eruption. In deeply weathered profiles and in profiles where there has been considerable wetting and drying, hematite is the dominant secondary Fe-oxide. Clay vesicle linings, and late stage crack fills, however, are frequently goethite-rich as they have formed more recently as a result of passing fluids. With time, as the clays in the vesicles and cracks dry out, this goethite may dehydrate to hematite (Tardy et al. 1990).

These characteristics reflect the dehydration of goethite to hematite. In internal parts of the weathering basalt where secondary products are not subject to desiccation goethite tends to be preserved. However, near to exposed faces where the weathering basalt may experience drying, the goethite can dehydrate to hematite (Tardy et al. 1990). In deeply weathered profiles, the weathering basalt is much more open and goethite may be dehydrated readily in drier periods. As the weathering profiles mature, more goethite is able to dehydrate, hence the deeply weathered kaolin group clay rich profiles are generally red coloured because of the dominance of hematite in the weathered material. Despite the greater near surface desiccation in more arid areas, the weathering system is not so open because percolating fluids follow zones of preferred flow which generally pass through the most weathered material. In most cases there is a mixture of Fe-oxyhydroxide phases in weathered basalts.

Because the dominant clay mineral in profiles with low fluid through-flow is smectite, and goethite is more abundant in these materials, the soils developed under these conditions are usually yellow-brown in colour. Deeply weathered profiles which are generally kaolin rich, have a red colouration and hematite is the dominant Fe-oxide present. Hence a broad distinction can be made between soils of red or brown colour developed on basalts (Isbell et al. 1976, Isbell et al. 1977), and properties of these materials will differ from one another.

*Mn-Oxide Coatings*

These coatings were observed along fractures in some weathered basalt profiles, more commonly in the drier areas. Mn$^{2+}$ oxidises to Mn$^{4+}$ in the percolating fluids and the Mn coating is precipitated onto the wall of the fluid conduit. Hence a relatively resistant black coating may develop on crack walls between onionskins and rubbly weathered basalt, and along open joint faces.

*Anatase*

Anatase was not clearly identified by X-ray diffraction or petrographically in this study implying that if it is present it may be sub-microscopic in these samples. Clay chemistry
(Appendix 4) indicates that Ti maintains relatively high concentrations in many weathered materials, and titanaugite weathering is observed in thin section, so the presence of the secondary Ti-bearing phase anatase is likely.

**Carbonates and Zeolites**

Some zeolites form, in the natural pores of basalts, due to the flushing of the flow by fluids immediately after emplacement of the basalt. Depending on the geochemistry of the weathering fluids, zeolites can also be precipitated during weathering, for example chabazite (Ca-zeolite) present as a vesicle in the basalts of Hellyer profile, north west Tasmania. This is discussed further in the section on aqueous geochemistry of basalt weathering in the Monaro and implications for the weathering of basalt in eastern Australia. Calcite may be precipitated as a secondary phase during the weathering of basalt and may cause a secondary increase in mass for the weathered samples analysed, as observed for the Stock Route profile in Central Queensland.

**Phosphates**

Minor phases which occur within the secondary products, that may account for the anomalous enrichment of Ba, Pb, Ce, La and sometimes Sr and Y, are phosphates of the plumbogummite group. P mobilised from the dissolution of accessory apatite fix these elements in the secondary material in relatively insoluble phases. As other elements are continuously removed from the profile, the REE, Ba, Pb and Sr may be relatively enriched, and because these elements are present in small amounts, relative mass gains can be very large. The significance of the enrichment of these elements during weathering is discussed in the overview of observed element mobility during basalt weathering in eastern Australia.

**12(A).4 OTHER FACTORS AFFECTING FORMATION OF SECONDARY MINERALS**

**12(A).4.1 Drainage, Eh, Topography, pH and the Effects on Weathering**

The sampling technique for this study attempted to minimise the variation in weathering on the basis of Eh, drainage and topography. The crestal profiles are all relatively free draining, and therefore are dominantly oxic sequences. In addition the effect of aspect is minimised for crestal profiles. The relationship between the basalt weathering profiles and the pH and chemistry of infiltrating fluids is discussed in the section on aqueous geochemistry of basalt weathering in the Monaro and implications for the weathering of
basalt in eastern Australia. A review of basalt weathering in the differing climate environments of eastern Australia is discussed below in paleoclimate, contemporary climate and basalt weathering.

In order to minimise the effect of textural characteristics of the parent basalts on the secondary mineral assemblage, flow basalts were sampled rather than a mixture of flows and pyroclastics. However, textural variations in the parent flow basalts may have considerable affect on the nature of the weathering assemblage that develops.

12(A).4.2 Textural Variations in the Flow Basalts and the Effects on Weathering

Highly vesicular material is extremely porous and if vesicles are interlocking, the material is very permeable, and percolation of fluids through this basalt is enhanced. As a consequence, porous vesicular basalts may weather much more rapidly than massive basalts. Likewise jointing in the parent basalt will facilitate the percolation of weathering fluids and enhance chemical weathering. In areas with a dry climate, zones of preferred fluid flow may develop around joints, becoming the focus of the most intense weathering in the profile.

Porphyritic basalts may become porous if the phenocryst phase weathers rapidly to clays, as commonly occurs with olivine phenocrysts. Baked paleosols or buried clay-rich layers may act a laterally extensive impermeable barrier causing water to pond in the profile (eg. Hellyer profile, Tasmania). This creates perched aquifers, which are again zones of preferred fluid flow and a focus for weathering. Where waters are ponded cations may be concentrated and then re-incorporated into secondary products.

Rims of secondary weathering products develop around primary mineral grains, especially olivine, and once present may inhibit or slow further weathering of the primary phase. Within individual mineral grains weathering is concentrated along zones of weakness which correspond with cleavage planes, twin planes, zone boundaries, microfractures and the edges of grains. Hence etching of primary minerals occurs preferentially at these sites. Groundmass phases weather rapidly and this may be related, in part to the greater surface area of small grains open to attack. Secondary weathering products are more abundant adjacent to exposed faces in the basalt, for example, adjacent to cracks and vesicles and in weathering rinds. This occurs because the effects of diffusion are more intense closer to zones of fluid percolation.
PART B: AN OVERVIEW OF ELEMENT MOBILITY DURING BASALT WEATHERING IN EASTERN AUSTRALIA

Use of the graphical isocon technique (Chapter 1) has enabled the tracing of element mobility in weathering basalts. When the data are compiled for all localities in the study a general evaluation can be made about the behaviour of various elements during basalt weathering in eastern Australia.

It is significant to note that in many cases, similar observations of element mobility have been made in isolated, very focused studies of basalt weathering from localities around the world (for example: Craig & Loughnan 1964, Tardy and Nahon 1985, Eggleton et al. 1987, Delvaux et al. 1989, Herbillon 1989, Chittleborough 1991, Brimhall et al. 1992, Stanley 1995). This is the first comprehensive study, using uniform technique, of a large number of basalt weathering profiles, from a range of latitudes and hence a range of contemporary and paleoclimate environments. The significance of a study of this scale is that the observations put forward here, for well drained profiles in eastern Australia, are characteristic of a far greater range of weathering parameters and climate environments than those presented using a consistent methodology before. The use of a standard technique for all samples enables confident interpretation of the data set as a whole.

In addition, this enables some quantification of the mobility of elements with respect to degree of weathering of the parent basalt, most specifically the rate of loss of major elements, and similarly partitioning trace elements, with increase in basalt weathering. On plots of percentage mass loss/gain of a given element $\Delta M_e(\%)$ versus slope of the isocon ($m$) (degree of weathering) a regression line was calculated for the steepest part of the elemental mass loss curve. The slope of this line can be compared for the elements studied and a relative order of mobility put forward.

12(B).1 ELEMENTAL VARIATION DURING WEATHERING

The elements analysed in this study can be divided into two groups: those elements that behave according to the pattern previously documented for weathering of well drained, oxic, mafic volcanic and gabbro profiles, and those that may show unusual behaviour during weathering.

Processes observed for elements of the first grouping include: the rapid removal of the alkali and alkaline earth cations from the weathering profiles; progressive weathering of silica from the profile; the oxidation of iron during weathering resulting in the fixation of Fe, largely in secondary Fe-oxyhydroxides (goethite and hematite); similar oxidation of manganese to form coatings on weathered surfaces; the variable but limited mobility of
zinc and vanadium reflecting the original partitioning of these phases into relatively resistant primary minerals; the relatively high mobility of copper once Cu-sulphide is oxidised to sulphate; the limited element mobility of the actinides, thorium and uranium, given that these elements comprise a minimal trace in basaltic rocks in general; the residual concentration of chromium and nickel in weathering profiles. The observed mobility of each of these elements in the eastern Australian basalt weathering profiles studied, is documented briefly below.

Elements that fall into the second grouping include: the rare earth elements (REE) cerium and lanthanum, as well as yttrium, barium and lead, which may show anomalous enrichment in weathered materials, when generally they might be expected to be removed from the weathering profile in a similar fashion to the alkali and alkaline earth elements. This anomalous enrichment may be associated with secondary phosphate and sulphate minerals so the elements phosphorus and sulphur are considered together with REE, Y, Ba and Pb. Other elements that show unusual behaviour are those that are generally considered to be immobile during weathering, but are apparently mobile under certain weathering conditions. These include niobium, zircon, yttrium, aluminium and titaniam.

12(B).1.1 Alkali and Alkaline Earth Elements

Calcium and Strontium

Figure 12.7
Net Mass change (%) in Ca and Sr with increase in Slope of the Isocon (increase in degree of weathering)
Calcium (Ca) and strontium (Sr) partition very similarly in primary basalt minerals, hence are released at the same time during the weathering of basaltic glass, plagioclase feldspar, and to a lesser extent ferromagnesian silicate minerals. These cations are readily removed from the profile although Ca and Sr may be taken into secondary smectite clays and Sr may be adsorbed onto secondary products to a small extent causing slight fractionation. Generally the two elements show a similar strong depletion pattern early in weathering (Figure 12.7). Under alkaline conditions, if the percolating fluids are carbonate rich and saturated with respect to calcite, calcite may precipitate in voids in the weathering profile. Secondary enrichment of calcium as a result of precipitation of carbonate or perhaps zeolite minerals (e.g. chabazite) from percolating fluids is not always associated with secondary enrichment in Sr. At the Stock Route locality in the Peak Range, Central Queensland (EFT9), fractionation of Ca and Sr is observed. Relatively intense weathering of the basalt, initially depletes Ca and Sr, then when calcite precipitates, there is significant secondary enrichment of Ca, but only a small secondary enrichment in Sr. The regression line calculated for the steepest part of the elemental mass loss curve (Fig 12.7) for Ca has a slope of -186.06 and for Sr -195.14.

Potassium and Rubidium

![Net Mass Change versus Slope of Isocon](image.png)

**Figure 12.8**

Mass change (%) in K and Rb with increase in slope of the isocon (increase in degree of weathering)

Because K-bearing phases (alkali-feldspar, mica) are not common in basalt, the total concentration of potassium in fresh basalt is relatively low. Potassium (K) is released early in weathering during the devitrification of basaltic glass and the breakdown of plagioclase feldspar. Rubidium (Rb) has similar chemical properties to potassium and
shows similar behaviour during weathering. In general both elements are strongly depleted early in weathering (Figure 12.8). Some K and Rb may be taken up by smectite and retained in the secondary mineral assemblage, however more commonly K and Rb are taken up by plants or are lost from the weathering profile in solution. The regression line calculated for the steepest part of the elemental mass loss curve (Fig 12.8) for K has a slope of -183.52 and Rb -171.87.

**Magnesium**

Magnesium (Mg) is similar to the other alkali and alkaline earth elements in that it shows a strong depletion early in weathering (Figure 12.9). Magnesium is mobilised principally from weathering olivine and pyroxene and may be taken into secondary smectites once mobilised. The regression line calculated for the steepest part of the elemental mass loss curve (Fig 12.9) for Mg has a slope of -156.14.

![Net Mass Change versus Slope of Isocon](Mg)

**Sodium**

Sodium (Na) is mobile in the profiles studied and shows a strong depletion early in weathering (Figure 12.10) Sodium is released during dissolution of basaltic glass and plagioclase feldspar and is generally mobilised out of the system. Na may be present in secondary smectites and zeolites, but does not appear to be as readily incorporated in smectites as the other alkali and alkaline earth cations. The regression line calculated for
the steepest part of the elemental mass loss curve (Fig 12.10) for Na has a slope of -221.71.

\[\text{Net Mass Change versus Slope of Isocon} \]
\[\text{Na} \]

\[\begin{array}{c}
\text{Slope of Isocon} \\
0.00 & 1.00 & 2.00 & 3.00 & 4.00 \\
\end{array}\]

\[\begin{array}{c}
\text{Net Mass Change} \\
-100.00 & -80.00 & -60.00 & -40.00 & -20.00 & 0.00 & 20.00 & 40.00 \\
\end{array}\]

**Figure 12.10**
Mass change (%) in Na with increase in slope of the isocon (increase in degree of weathering)

12(B).1.2 Transition Elements and Semi-Metals

**Silica**

\[\text{Net Mass Change versus Slope of Isocon} \]
\[\text{Si} \]

\[\begin{array}{c}
\text{Slope of Isocon} \\
0.00 & 1.00 & 2.00 & 3.00 & 4.00 \\
\end{array}\]

\[\begin{array}{c}
\text{Net Mass Change} \\
-100.00 & -80.00 & -60.00 & -40.00 & -20.00 & 0.00 & 20.00 & 40.00 & 60.00 & 80.00 & 100.00 \\
\end{array}\]

**Figure 12.11**
Mass change (%) in Si with increase in slope of the isocon (increase in degree of weathering)
Silica (Si) is not as strongly transported from the profile as Ca, Sr, K, Rb, Mg and Na. Although silica is mobilised during the breakdown of basaltic glass and silicate minerals, this process progresses at a slower rate than the removal of the alkali and alkaline earth elements from the profiles studied. In addition, Si is incorporated into neoformed clay minerals as a fundamental part of their structure, which may be one explanation for the slower rate of loss of silica from the weathering profile (Figure 12.11). The regression line calculated for the steepest part of the elemental mass loss curve (Fig 12.11) for Si has a slope of -75.98.

**Figure 12.12**
Mass change (%) in Cu with increase in slope of the isocon (increase in degree of weathering)

**Copper**

Copper (Cu) may show a small relative enrichment during weathering but generally shows relatively strong depletion (Figure 12.12). Copper is present in basalts in very low concentrations. Minor amounts may be enclosed in ferromagnesian minerals but often copper is present in very fine grained disseminated Cu-sulphides (chalcopyrite) in basalts. Initially these minerals are enclosed in other phases and hence are not released, until the host mineral is disaggregated. Once the sulphides are released they are oxidised to sulphates and Cu is mobilised. Cu concentrations are low in waters issuing from basalts which in part is a reflection of the low concentration in basalts to start with, but also implies that the Cu mobilised during weathering is taken into secondary products. Cu appears to be strongly adsorbed onto Fe-oxyhydroxides and Mn-oxides in the weathered material and may be taken into the octahedral sheet of clays. In the samples
that show mass gain \((m < 1.00)\), Cu is relatively enriched. This trend parallels the concentration of secondary ferric oxides in the same samples, supporting the suggestion that Cu is closely associated with goethite and hematite in secondary products.

**Zinc and Vanadium**

Zinc (Zn) and vanadium (V) are largely enclosed within relatively resistant phases, such as magnetite. They may show relative enrichment due to illuviation of resistant phases from unconsolidated weathered basalt elsewhere in the profile leading to concentration in fractures and voids nearer the base of the unconsolidated material (Figure 12.13). Some vanadium may be enclosed in ferromagnesian silicate phases, especially pyroxene, where \(V^{3+}\) substitutes for \(Al^{3+}\) and/or \(Fe^{3+}\). Vanadium may be released during weathering of these silicates, and can be taken into dioctahedral smectites, or may substitute for ferric iron in hematite and goethite. Zinc substitutes for Fe and Mg in magnetite, other resistant mafic oxides, and ferromagnesian silicates. Zn associates with FeAl-oxyhydroxides and with clays in the weathering profile.

![Net Mass Change versus Slope of Isocon Zn and V](image)

**Figure 12.13**

Mass change (%) in Zn and V with increase in slope of the isocon (increase in degree of weathering)

**Chromium and Nickel**

Chromium (Cr) and nickel (Ni) are both released during the dissolution of olivine. Because the olivines in the parent basalts are mostly quite magnesian, a relatively high proportion of Ni may have partitioned into this phase because of the greater electronegativity of Ni compared with Mg. Chromium is predominantly enclosed within
the olivine in fine blocky grains of chrome spinel, while nickel is enclosed in the octahedral sites within the silicate, as well as occurring as a minor element in the spinel. Both show similar enrichment-depletion trends during weathering.

In unconsolidated material, Cr may be lost due to physical translocation of relatively resistant Cr-spinel. If the Cr-spinel is not mobilised from the weathering olivine, progressive enrichment of this phase takes place, in part because of the mass (and associated volume) loss during weathering. In addition, chromite may be concentrated as a result of eluviation of material from higher in the profile.

If chromium is released into solution it may exist as one of a number of cations depending on the Eh and pH of the solution. In general Cr solubility is very low at neutral pH, and higher in alkaline or acid solutions. There is some evidence that Cr\(^{3+}\) can be incorporated into dioctahedral smectites in the octahedral sites (Paquet et al. 1987) which may in part explain its residual nature in weathered basalt.

Ni\(^{2+}\) may be released from the weathering silicate into solution and subsequently incorporated into secondary FeMg-layer silicates, probably dioctahedral nontronite and trioctahedral saponite clays. Ni may also be taken into Fe-oxyhydroxides such as goethite and hematite. Hence, Cr and Ni are usually enriched in weathered material (Figure 12.14).

**Net Mass Change versus Slope of Isocon**

<table>
<thead>
<tr>
<th>Cr</th>
<th>Ni</th>
</tr>
</thead>
</table>

![Graph showing net mass change versus slope of isocon for Cr and Ni](image)

**Figure 12.14**

Mass change (%) in Cr and Ni with increase in slope of the isocon (increase in degree of weathering)
Manganese

Manganese (Mn) may be released from ferromagnesian silicates during weathering. In basalts most of the Mn is present in olivine which is a phase that weathers early. Manganese is progressively removed from the profile in the form Mn$^{2+}$, which is mobile (Figure 12.15). Mn$^{2+}$ may oxidise to Mn$^{4+}$ which is relatively insoluble and hence precipitate within the weathering material. This Mn precipitation frequently takes the form of a black Mn-rich coating on exposed surfaces, indicating that the Mn-oxide is precipitated from the weathering fluids. There is some evidence that Mn$^{2+}$ can be incorporated into the octahedral sheets of smectites (Paquet et al. 1987).

Figure 12.15
Mass change (%) in Mn with increase in slope of the isocon (increase in degree of weathering)

12(B).1.3 Actinides

Thorium and Uranium

Thorium (Th) and Uranium (U) are released from weathering of apatite and later in weathering may be released from metamict zircon. Th may show relatively strong enrichment in moderately weathered basalts, mostly as a result of adsorption onto secondary weathering products, clays in particular (Figure 12.16). U, in contrast does not show as strong enrichment and appears more readily removed than Th during weathering. The small enrichment in some relatively strongly weathered samples may be attributed to the presence of a resistant Th and U bearing phase, probably zircon.
12(B).2 RARE EARTH ELEMENTS (REE), BARIUM (Ba) AND LEAD (Pb)

The lanthanide elements generally have a $M^{3+}$ configuration in weathering profiles, they have large ionic radii, mostly bond ionically and during weathering they behave similarly to other lithophile elements of the alkali and alkaline earth groups (Ca, Sr, Na, K, Rb, Mg) and are readily removed from the profile once released from host minerals. However, the rare earth elements analysed (Y, Ce, La), and some trace elements (Ba, Sr, Pb) may show anomalous enrichments in incipiently to moderately weathered basalts.

Cerium

Cerium is released during the dissolution of apatite and, to a lesser extent from the break down of pyroxene, olivine and plagioclase feldspar. Because Cerium (Ce) may be fixed in the profile during weathering as a result of the oxidation of Ce$^{3+}$ to Ce$^{4+}$, it is believed to behave similarly to Mn, and is sometimes associated with Mn coatings in the weathered material. However, Ce enrichment/depletion patterns differ from those of Mn in two principal ways. Ce may show strong anomalous enrichment, sometimes exhibiting mass gains of up to 400% (Figure 12.17), whereas Mn does not show such large mass gains (Figure 12.15). In samples where Ce has elevated values, Mn does not show a similar enrichment. Secondly, Ce may show a moderate increase in concentration early in weathering followed by a progressive loss, whereas Mn is generally lost from the
weathering material, except in a few samples where secondary Mn-oxide coatings have precipitated. The oxidation of Ce during weathering may fractionate this element relative to the other rare earth elements (REE), which are generally readily removed from the profile.

**Figure 12.17**
Mass change (%) in Ce with increase in slope of the isocon (increase in degree of weathering)

**Lanthinum and Lead**

**Figure 12.18**
Mass change (%) in La and Pb with increase in slope of the isocon (increase in degree of weathering)
Cerium (Ce) apparently follows the enrichment trends for lanthanum (La), however values are more depressed for the former. Where La is anomalously enriched, Ce also shows large enrichment. Hence, either these elements are incorporated into a resistant phase and are being relatively enriched, or are being scavenged by secondary weathering products, or they are incorporated into a neoformed phase during weathering.

Lead (Pb) shows similar anomalous enrichment patterns to the rare earth elements, Ce and La, although it is not as strongly enriched as La (Figure 12.18). Because the Pb is largely derived from feldspar, and the lanthanides from apatite, these elements are not concentrated as a result of partitioning into a single resistant phase, and are therefore being enriched in secondary products. Ce, La and Pb can combine with phosphorus released from the weathering of apatite, to form the secondary, resistant phosphates of the plumbogummite group (Norrish 1957, Norrish 1968, Norrish & Rosser 1983, Banfield & Eggleton 1984, Banfield & Eggleton 1989, Price et al. 1991). Where samples do not show anomalous enrichment, La and Pb are relatively readily removed during weathering, although small amounts may be adsorbed onto secondary clays and Fe- or Mn-oxyhydroxides. Pb may also be fixed in the weathering products in secondary carbonates.

\[ \text{Phosphorus} \]

\[ \text{Net Mass Change versus Slope of Isocon} \]

\[ P \]

\[ \text{Figure 12.19} \]

Mass change (%) in P with increase in slope of the isocon (increase in degree of weathering)
Phosphorus (P) is principally derived from the dissolution of apatite and is present in very small quantities. In general, P is depleted relatively rapidly with weathering (Figure 12.19). There may be an enrichment period early in weathering associated with the concentration of P in apatite, until fine grained apatite crystals are released from their host minerals and are available for dissolution. Despite the presence of plumbogummite phases in some samples the P concentration is not enriched, implying that relatively small amounts of P are taken into these neoformed materials. In addition it reflects the localised nature of plumbogummite mineral neoformation, generally in the vicinity of dissolving apatite. Organisms are significant in the weathering of apatite, since they require phosphorous for their metabolism (Banfield & Eggleton 1989). Because the dissolution of apatite is more rapid in acid fluids, there is a correlation between kaolin rich deeply weathered profiles (acidic krasnozems) and strong depletion of phosphate.

**Barium and Sulphur**

Barium (Ba) shows anomalous enrichment in a number of samples (Figure 12.20), similar to the enrichments observed for Ce, La and Pb. Price (1991) describes secondary neoformation of extremely fine grained BaSO₄ in incipiently weathered basalt. For the samples from this study there is no apparent correlation between the Ba enrichment pattern and sulphur concentration. However, these neoformed phases are fine grained and form in localised areas, so the amount of S incorporated into secondary BaSO₄ is probably very small. Ba may also be fixed in the weathering products in secondary carbonates, in Mn coatings and by being adsorbed onto clays.

**Net Mass Change versus Slope of Isocon**

![Net Mass Change versus Slope of Isocon](image)

*Figure 12.20*

Mass change (%) in Ba and S with increase in slope of the isocon (increase in degree of weathering)
The enrichment pattern for sulphur (S) is strongly influenced by the presence or absence of sulphide minerals, which oxidise in the near surface environment, generally forming water soluble sulphates. In basalts the S concentration is extremely low so small changes in absolute concentration, may be observed as large mass changes (ΔM%). Hence, large enrichments are observed early in weathering when sulphide minerals are first exposed to percolating fluids (Figure 12.20) as the sulphur is released. However, once S is mobilised in an oxidising environment, strong depletion of S takes place relatively rapidly.

12(B).2.1 The Implications of Enrichment of Rare Earth Elements (REE), Barium (Ba) and Lead (Pb) During Basalt Weathering

Although Ce, La, Y, Ba, (Sr) and Ba are readily lost from the basalt profile with weathering, at times they show significant enrichment in incipient to moderately weathered basalt. Some elevation in concentration may be attributed to the partitioning of these elements into secondary carbonates or sulphates precipitated in the regolith profile, or as a result of incorporation of these cations in interlayer sites in clay minerals. Increases in Ba, Pb and Sr concentrations may show a significant correlation with carbonate precipitation in the weathering profiles. For example Pb is concentrated in the regolith profile at Stock Route locality, Central Queensland (EFT9) where secondary carbonates have precipitated, but there is not a corresponding enrichment in Ce, La, Y or Ba for these samples. Ce may show enrichment in the regolith when the other rare earth elements do not because of its capacity to oxidise from Ce$^{3+}$ to Ce$^{4+}$. However, for some samples in this study, the concentration of Ce, La, Y, Ba, (Sr) and Ba in the regolith was several orders of magnitude greater than the initial concentration in the basalt protolith (e.g. Dorrigo Plateau profile, Ebor Volcano, WFT10). It follows that there are neoformed phases that preferentially enhance the enrichment of Ce, La, Y and Pb and at times Ba and Sr follow a similar enrichment pattern.

The principal rare earth element bearing primary phase in basaltic rocks is apatite. There is some evidence that apatite may dissolve under acid weathering conditions, and organisms in the regolith profile may also break down apatite as they require phosphate for their metabolism (Banfield & Eggleton 1987). Scanning electron microscope images of a rod-like apatite crystal undergoing dissolution from the Nulla Volcanic Province, North Queensland (Plate 10.29) show hummocky shaped phosphate rich accumulations in the immediate vicinity of the dissolving apatite. These phases were not unequivocally identified but are thought to be phosphates of the plumbogummite group. Recognition of their presence provides an explanation for the significant increases in Ce, La, Y, Pb and
Ba in some weathered basalt samples. The localised nature of formation of these phosphate minerals around dissolving apatite suggests that phosphate-bearing species are only significant when phosphate concentrations are high. Otherwise phases such as carbonate would be more significant in fixing these elements in the weathering profile. In this study, the localised nature of the phosphate formation also explains why the concentration of Ce, La, Y, Pb and Ba is observed for some samples and not others, despite similar degrees of weathering.

Because incipiently weathered basalts may not appear weathered in hand specimen, or even in thin section, there is a danger that interpretation of trace element concentrations, with respect to magma evolution and history of formation of the volcanic rocks, may be flawed. Hence, the neoformation of resistant secondary phosphates of the plumbogummite group, which concentrate the elements Ce, La, Y, Pb and Ba during early weathering is important, as the concentrations of these elements may be interpreted as primary trace element concentrations in error. Price (1991) makes the point that "geochemical investigations of basalt petrogenesis are based on the assumption that analysed whole-rock samples are representative of original magma compositions." Where the trace element values have been elevated due to incipient weathering, but this weathering has not been recognised by petrographic assessment, the assumption that analysed whole-rock samples are representative of original magma compositions does not hold, and the analyses may be interpreted incorrectly.

12(B).3 ELEMENTS GENERALLY CONSIDERED IMMOBILE DURING WEATHERING

Niobium and Zirconium

Niobium (Nb) and zirconium (Zr) show very limited mass change (ΔM %) as these elements are relatively immobile during weathering (Figure 12.21). In general Nb and Zr are concentrated by weathering processes because of the stability of the main host mineral zircon. However, some samples show strong depletion early in weathering, and this is also recognised in those samples that show a mass gain (m <1.00). Nb and Zr are apparently mobile in alkaline fluids as those localities that have cross-cutting veining of carbonates and carbonate precipitation in voids in the weathered basalt, show depleted Nb and Zr totals. This is most clearly illustrated at the Stock Route locality, Peak Range (EFT9) where the profile has been flushed with carbonate fluids. This correlation of depletion in Nb and Zr with the presence of alkaline fluids may relate, in part, to enhanced dissolution of relatively resistant phases such as metamict zircon.
Chapter 12: Discussion (B) Element Mobility During Basalt Weathering

Net Mass Change versus Slope of Isocon

**Nb and Zr**

![Graph showing Nb and Zr](image)

**Figure 12.21**
Mass change (%) in Nb and Zr with increase in slope of the isocon (increase in degree of weathering)

_Yttrium_

Net Mass Change versus Slope of Isocon

**Y**

![Graph showing Y](image)

**Figure 12.22**
Mass change (%) in Y with increase in slope of the isocon (increase in degree of weathering)

Yttrium remains relatively immobile in most basalt weathering profiles, however, it partitions similarly to the lanthanides in secondary products and therefore may be
concentrated as a consequence of apatite dissolution and neoformation of secondary phosphates, as detailed above (Figure 12.22). In three samples from the Monpeelyata Canal profile, Central Tasmania, and two samples from the Sherwood profile, Monaro Volcanic Province, Y showed elevated values. However, the same samples had elevated values for Th and K, indicating that there was some mica present in the profiles. At Monpeelyata Canal there is some contribution of mica to the profile from lacustrine sequences upstream, and at Sherwood, only the samples below the intercalated lake sediment showed this effect. Hence, the principal mechanism for Y enrichment in weathering profiles is due to partitioning into secondary neoformed phases, but incorporation of micaceous material by aeolian or eluviation processes may cause anomalous concentration of this element.

The profiles where Y showed depletion were usually kaolin rich, acid weathering profiles in which Ce and La also showed a net loss in concentration. It appears that the immobility attributed to Y relates to its incorporation in the relatively resistant phase apatite, but as previously discussed apatite may be soluble in acid fluids.

**Aluminium**

The solubility of aluminium is largely controlled by pH, with greater mobility of Al at high and low pH values. In regolith profiles pH is around 6 to 8, the solubility of Al is very low, and hence this element is considered relatively immobile. If Al is mobilised during weathering it is generally incorporated into secondary phases leading to a relative concentration of Al during weathering (Figure 12.23).

Horizons where gibbsite has formed generally show an increase in Al content. Samples that showed a significant decrease in net concentration of Al were all from acid, kaolin rich, deep weathering profiles (WFT10, BW, TAS9), however, elsewhere in these profiles a concentration of gibbsite was sometimes present. Profiles that showed an increase in net Al concentration include those from the most arid contemporary climate environment (EFT22, EFT9) and some with relatively high contemporary rainfall (TFT6, TFT12, WFT10).
Titanium may show differential mobility depending on the primary mineral it is partitioned into. For example Ti partitioned into titanaugite is released earlier in the weathering process than Ti partitioned into ilmenite, because ilmenite is much more resistant to weathering. For example, at the Newell Highway profile, Warrumbungles Volcano, titanaugite is weathered before Ti-bearing opaque oxides. Titanium, if mobilised may be precipitated under weathering conditions as anatase. Generally Ti is considered relatively immobile because it is retained in resistant primary Ti-bearing oxides (ilmenite, titanomagnetite) or fixed as secondary anatase in the weathering profile, and for this reason it has been used as an index of weathering. However, Ti may be mobile during weathering, and may be released relatively early in weathering as a result of pyroxene weathering (Figure 12.24). In addition, ilmenite is not necessarily stable during weathering and can degrade to produce leucoxene, finely crystalline mixtures of rutile and pseudorutile; and other Ti-oxides as well as hematite or goethite.

When net mass change in titanium is plotted versus contemporary soil pH (Figure 12.25), for this study, there is a general trend which shows that as pH becomes more alkaline there is a greater net mass gain in Ti than when pH is acid. Samples that show limited net mass change in Ti for the entire pH range are thought to be those that have Ti mostly partitioned into relatively resistant primary phases. When the
contemporary soil pH is acid, there are a number of samples that show a net mass loss in Ti.

**Figure 12.24**
Mass change (%) in Ti with increase in slope of the isocon (increase in degree of weathering)

**Figure 12.25**
Soil pH versus Net Mass change (%) in Ti for the samples in this study.
Milnes & Fitzpatrick (1989) note that "acid, strongly leached soils derived from basic igneous rocks in the humid tropics and subtropics often contain substantial accumulations of Fe, Al and Ti oxides associated with a clay mineral suite characteristically dominated by 1:1 layer silicates". The observations for this example may be quite correct, however, when 17 profiles are compared from a range of latitudes in eastern Australia, it appears that there is significant Ti mobility, and enrichment, associated with alkaline weathering profiles, and notable transport of Ti out of many acid weathering profiles.

Iron

Total iron (Fe) concentration maintains a relatively constant value which plots close to the isocon at most localities and hence shows very little mass change, even with relatively intense weathering. If these data were interpreted independently, it would appear that iron may not be participating in the reactions of weathering. However, when mass changes for FeO (Fe$^{2+}$) and Fe$_2$O$_3$ (Fe$^{3+}$) are compared, FeO shows a strong early depletion and Fe$_2$O$_3$ a strong early enrichment (Figure 12.26). This reflects the oxidation of Fe$^{2+}$ to Fe$^{3+}$ during weathering, and the consequent fixing of Fe in the weathered material, generally as goethite or hematite after ferrihydrite. As other elements are progressively lost, Fe becomes relatively enriched and is one of the few elements preserved in deeply weathered profiles.

**Figure 12.26**

Mass change (%) in Fe with increase in slope of the isocon (increase in degree of weathering)
12(B).3.1 When are Relatively Immobile Elements Mobile?

Niobium and Zirconium

Niobium and zirconium seem to behave similarly for the weathering profiles studied. For most of the samples they are relatively immobile, and in general do not show significant enrichment, however, they may show considerable depletion during weathering. Two localities in particular, the Stock Route profile in the Peak Range volcanic province (EFT9) and the Hellyer River profile (TAS17) in north west Tasmania, are characterised by a strong depletion of Nb and Zr. In both cases there is some indication of flushing of the profiles by strongly alkaline fluids. The Stock Route profile has abundant secondary calcite in void spaces in the profile, and the Hellyer River profile has secondary chabazite, a calcic zeolite, precipitated in pore spaces. Profiles that show a moderate enrichment of Nb and Zr (EFT22, WFT4, WFT2, TAS27, SW) all have a smectite dominant secondary mineral assemblage and alkaline soil pH values. Hence, there is a strong indication that Nb and Zr may be mobile in alkaline fluids.

Zircon is commonly recorded as a residual mineral in soils and is widely regarded as a very stable mineral able to survive many cycles of weathering, sedimentary transport, diagenesis and metamorphism and antexis (Speer 1982, Milnes & Fitzpatrick 1989). Although there is some discussion in the literature of the corrosion of zircons, the correlation between zircon corrosion and alkaline fluids has only been made by Carroll (1953) who suggested that Ca- and Na-bicarbonate rich waters may be able to dissolve zircon. As shown by Durov-Zaporozec interpretation of aquifer waters at Big Willow, Monaro Volcanic province, Ca-Mg bicarbonate rich waters characterise the fluids issuing from a smectite rich weathered basalt profile. Hence, many of the profiles in this study are likely to have Ca-bicarbonate rich fluids and the dissolution of metamict zircon under these conditions may be enhanced. Metamict zircon, which has had its lattice array disturbed by enclosed radioactive elements, may be more susceptible to dissolution than normal zircon, because of the increased number of sites at which reaction may take place.

Yttrium

As described above Y enrichment in basalt regolith profiles is principally due to partitioning into secondary neoformed phases in a similar fashion to the lanthanides. However, the presence of micaceous material, introduced by aeolian or eluviation processes, may cause anomalous concentration of Y along with Th, K and Rb. Yttrium showed net mass loss in some profiles. All were kaolin rich, acid weathering profiles and Ce and La also showed depletion in these profiles. The immobility attributed to Y relates
to its incorporation in the relatively resistant phase apatite, however, apatite may be soluble in acid fluids.

**Aluminium**

The mobility of aluminium is difficult to characterise as Al is readily incorporated into secondary weathering products, however, for Al to be mobilised, high or low pH conditions must prevail. This might best be achieved by having relatively high fluid throughflow leading to localised acid pH conditions, or relatively low fluid throughflow, perhaps with some associated evaporation, leading to localised alkaline pH conditions. If the localised pH conditions are acid, gibbsite will be stable and may form, and Al may be taken into secondary clays, but if acid conditions persist some Al may be mobilised from the profile before it is incorporated into secondary phases. If the localised pH is alkaline, Al may be mobilised and concentrated in parts of the profile, but will generally not be removed, as there is insufficient fluid throughflow to transport Al from the profile before it is incorporated into secondary products.

**Titanium**

Apparently there is a subtle interplay between the mobility of Ti associated with silicate dissolution, the mobility of Ti associated with ilmenite dissolution, and the environments in which secondary Ti bearing phases are most likely to precipitate. Ti-bearing silicate (clinopyroxene) dissolution is most likely to be enhanced by percolation of an acid fluid which can contribute protons during hydrolysis. This is also likely to occur early in weathering. Hence Ti is mobilised into the percolating waters which, with increased hydrolysis, may evolve into bicarbonate fluids. Under these conditions secondary Ti-bearing phases (e.g. anatase) might precipitate. Meanwhile, ilmenite and other Ti-bearing oxides remain resistant during the early stages of weathering. The soil pH for a profile such as this will be alkaline as the secondary assemblage is usually dominated by smectite under these conditions. Anatase formation has been associated with wetting and drying in soil zones. Wetting and drying may optimise conditions for precipitation of anatase as Ti would be concentrated in the transporting fluids.

With continued weathering the secondary mineralogy of the profile will be dominated by kaolin group minerals, primary Ti-bearing silicates (clinopyroxene) will largely have been removed, and incipient dissolution of the primary Ti-bearing silicates may commence. The mechanism for ilmenite dissolution is not well understood, however, it seems there is a two-stage process of oxidation followed by hydrolysis (Grey & Reid 1975). Because hydrolysis is an integral part of this process, the presence of acid fluids would enhance ilmenite dissolution. Ti would become mobile in the acid fluids and may or may not
precipitate as a secondary phase, depending on the relative concentration of Ti in solution. The presence of organic acids may enhance Ti mobility (Correns 1978, Dumon & Vigneaux 1979). In addition, the percolation of acid fluids may remobilise the Ti partitioned into secondary anatase. A soil pH for a profile such as this would be acid, and there may be a relative increase or decrease in net mass of Ti depending on whether Ti is precipitated within the profile or mobilised out in the percolating solutions.

However, not all basalts have abundant titanaugute, so Ti may be largely partitioned into the primary Ti-bearing oxides. Under these conditions the net mass of Ti may not change throughout weathering until ilmenite dissolution commences. Overall, there will be a group of samples, over a range of soil pH values, where the net mass of Ti does not change because it is partitioned into resistant phases in these samples; there may be a greater net mass gain in Ti in more alkaline profiles because of enhanced conditions for precipitation, but there will be lesser Ti mobility because the percolating fluids will not remain acid; and there will be greater mobility of Ti in acid weathering profiles, to the point that some Ti may be lost from the profile under acid weathering conditions.

Iron

Approximately half of the samples in this study were analysed for the presence of FeO and Fe₂O₃. In all cases it was found that FeO (Fe²⁺) was strongly depleted in weathered basalts and Fe₂O₃ (Fe³⁺) was strongly enriched. As described above this is the expected redox behaviour for iron, the oxidation of Fe²⁺ to Fe³⁺ during weathering in an aerated profile. Although this chemical reaction usually takes place rapidly enough that most of the iron is preserved in the weathering profile, the known mobility of iron was sufficient to discount its reliable use as an immobile element for application of the isocon technique in this study. Hence, even for localities where total iron is expressed as Fe₂O₃, iron has not been considered an immobile element for application of the isocon technique. In most cases total iron plots on or near the isocon defined by other immobile elements and for these examples redox reactions have been efficient enough to preserve most of the iron within the profile.

12(B).4 CALCULATING THE RATE OF ELEMENTAL LOSS/GAIN

The slope of the elemental mass loss/gain curve allows the presentation of a quantified order of elemental loss/gain, for major elements and similarly partitioning trace elements, with increase in basalt weathering.

Na (-221.71) >Sr (-195.14) >Ca (-186.06) >K (-183.52)
>Rb (-171.87) >Mg (-156.14) >Al (-78.06) >Si (-75.98)
This order of elemental loss/gain compares with that of Eggleton & Keller (1984) but differs in that Mg is afforded a higher mobility in this study. While this observation is correct if elemental loss/gain alone is considered, Mg may also be enriched in weathered samples. Hence, although mobilised from primary phases relatively readily, Mg may be retained in the secondary weathering phases of the basalt and show a reduced rate of elemental loss/gain from a sample than is suggested here.

To interpret these diagrams in a more quantitative manner we use the standard equation \( y = mx + c \) where \( y \) is the percentage elemental mass loss/gain \( -\Delta M_e \text{ (%) } \), \( m \) is the slope of the elemental loss/gain curve presented above, \( x \) is the unit increment in the slope of the isocon from 1 (because the slope of the isocon for a fresh basalt is 1) and \( c (=0) \) is the \( y \)-intercept of the regression line.

For example for Ca: for every unit increment in the slope of the isocon from 1, estimated percentage elemental mass loss/gain \( -\Delta M_e \text{ (%) } \) of Ca is \(-186.06\%\), until 100\% elemental mass loss/gain is achieved. So, if the slope of the isocon is 1.5 (+0.5 of an increment from 1), the estimated percentage elemental mass loss/gain \( -\Delta M_e \text{ (%) } \) of Ca is \( y/m = -93.03\% \)

Net mass loss/gain \( -\Delta M \text{ (%) } \) for a basalt sample may also be used as a weathering index for that sample (Chapter 1) and can be calculated from the slope of the isocon using the relationship

\[-\Delta M \text{ (%) } = 100 \left( \left( \frac{1}{m} \right) -1 \right)\]

If the slope of the isocon is 1.5 then the net mass loss/gain \( -\Delta M \text{ (%) } \) for a basalt sample is \(-33.33\%\). For the same sample the estimated percentage elemental mass loss/gain \( -\Delta M_e \text{ (%) } \) of Ca is \(-93.03\%\).

So, for samples for eastern Australia, broad quantification of major element mass loss/gain is possible. It is important to remember that the regression line placed through the steepest part of the elemental loss/gain curve describes a field of data points for that element and while it is useful in providing a means of simplifying the information in that field, in nature it is important to recognise that the percentage elemental mass loss rate for a sample lies within a range described by the boundaries of that field, rather than forming a point on the regression line. From the eastern Australian basalt weathering data set more appropriate ranges in slope for each major element are detailed below (Table 12.2).
Table 12.2  RANGES IN SLOPE OF THE ELEMENTAL MASS LOSS CURVES FOR ELEMENTS AFFECTED BY BASALT WEATHERING

<table>
<thead>
<tr>
<th>Element</th>
<th>Slope of elemental mass loss curve</th>
<th>Measured range of slope values for eastern Australian basalts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>-221.71</td>
<td>-309.68 to -133.74</td>
</tr>
<tr>
<td>Sr</td>
<td>-195.14</td>
<td>-244.43 to -145.84</td>
</tr>
<tr>
<td>Ca</td>
<td>-186.06</td>
<td>-250.00 to -122.11</td>
</tr>
<tr>
<td>K</td>
<td>-183.52</td>
<td>-242.43 to -124.60</td>
</tr>
<tr>
<td>Rb</td>
<td>-171.87</td>
<td>-211.27 to -132.47</td>
</tr>
<tr>
<td>Mg</td>
<td>-156.14</td>
<td>-214.80 to -97.48</td>
</tr>
<tr>
<td>Al</td>
<td>-78.06</td>
<td>-138.52 to -17.64</td>
</tr>
<tr>
<td>Si</td>
<td>-75.98</td>
<td>-89.60 to -62.35</td>
</tr>
</tbody>
</table>

When these ranges are looked at more closely it is clear that there is considerable overlap for different elements and that the relative mobility order for some elements may change with changing weathering conditions. Eggleton *et al.* (1987) using a density contrast technique, observed a considerably different sequence than that described here (Ca>Mg>Na>K>P>Si>Mn>Al>Fe>Ti). Although the isocon technique is considered more precise, part of the explanation for such variation in observed element mobility sequence can be accounted for by overlap in the fields.

Another way of considering this information is to normalise the rates of cation loss with respect to the rate of loss of silica (Figure 12.27). Normalisation to silica is appropriate because it is a major component of the primary basaltic minerals in all of the samples; and, of the cations considered, silica is removed from the weathering basalt at the slowest rate. For example, Mg is lost at a rate approximately two times that of silica and Na is lost approximately three times faster than silica (Figure 12.27).

**Figure 12.27**

Rate at which major cations are lost during the weathering of basalt, with respect to silica
PART C: AQUEOUS GEOCHEMISTRY OF BASALT WEATHERING IN THE MONARO AND IMPLICATIONS FOR THE WEATHERING OF BASALT IN EASTERN AUSTRALIA.

12(C).1 GROUNDWATER AND THE WEATHERING OF BASALT IN THE MONARO VOLCANIC PROVINCE

The basalt groundwater study carried out at Big Willow and Sherwood localities in the Monaro volcanic province, confirms that groundwater actively interacts with the fractured basalt through which it travels. The ion concentration in the water issuing from the aquifers is significantly greater than the ion concentration in the local rainwater entering the aquifers, implying that the basalts through which the waters flow are the principal source for the ions. In addition there is a considerable pH change for the waters passing through the aquifers, from acid to neutral or slightly alkaline. These observations indicate that weathering profiles continue to be actively weathered under the contemporary climate regime, although the rates of weathering may differ from periods in the past.

12(C).1.1 Chemistry of the Weathering Fluids

Durov-Zaporozec interpretation of the chemistry of the issuing aquifer waters indicates that they are dominantly Mg-Ca bicarbonate fluids (Figures 11.14-11.17). If we consider that the rainwater entering the system is acid (pH=5.13), and may interact with CO\textsubscript{2} in the soil zone, the solution entering the system is a dilute carbonic acid (H\textsubscript{2}CO\textsubscript{3}) with a very low concentration of cations. As this acid interacts with primary minerals in the basalt, largely via the process of hydrolysis, a suite of secondary minerals is formed. At Big Willow and Sherwood this secondary mineral assemblage is dominated by the smectites nontronite, beidellite and minor saponite with subsidiary amounts of kaolinite, halloysite and gibbsite plus minor Fe-oxyhydroxides, mostly goethite.

Activity diagrams, (Figure 11.18a,b), and silica stability diagrams (Figure 11.19a,b,c), for the Big Willow and Sherwood systems, indicate that the the issuing fluids would be in equilibrium with a secondary mineralogy dominated by smectite clays. The water compositions, therefore, define a reaction path that trends towards equilibrium with the enclosing weathered basalt. Hence, the aquifer fluids approach equilibrium with the phases that surround them as they percolate through the weathering sequence. The vector drawn from the initial rain water composition through the issuing aquifer water compositions, on the activity diagrams indicate that the acid rain water is progressively modified as the primary basalt minerals are hydrolysed, and cations are released into the aquifer solution at the expense of H\textsuperscript{+} ions.
12(C)1.2 The Juxtaposition of Gibbsite and Smectite in the Big Willow Basalt Weathering Profile

At Big Willow, gibbsite was sampled near the surface in zones between basalt corestones where the smectitic suite of secondary products surrounding the corestones has been further weathered by near surface acidic fluids. When rainwater is plotted on the stability diagram for silica versus calcium (Figure 11.19a), it sits in the stability field for gibbsite. Hence, the gibbsite is not forming in equilibrium with the fluids issuing from the aquifer, instead it is in equilibrium with the acid water entering the aquifer system. This is recognised as a disequilibrium reaction if the aquifer system is considered as a whole.

It is most unusual to find smectite and gibbsite side by side in the same weathering profile unless the gibbsite is preserved from a paleoweathering profile. Smectite is often assumed to characterise incipiently to moderately weathered basalts or basalts that have been weathered under saturated conditions where cations are available in the ponded fluids for incorporation into secondary phases. At Big Willow the smectite dominated secondary assemblage is representative of incipient to moderate basalt weathering under cool, wet, oxic conditions.

Gibbsite formation, or bauxitic weathering, is frequently associated with deep weathering profiles in warm, wet, tropical environments (Bardossy 1974, McFarlane 1983, Ollier 1984, Nahon 1986, Frakes et al. 1987, Chamley 1989, Tardy et al. 1990, Bardossy and Aleva 1990). The recognition of the presence of gibbsite and smectite minerals together, and the simple mechanism for their contemporary formation, further emphasises problems with assumptions that weathering to the point of gibbsite formation is only associated with deep weathering profiles in warm, wet, tropical environments.

Activity diagrams (Figure 11.18a,b) and silica stability diagrams (Figure 11.19a,b,c) indicate that kaolinite clays might be expected as intermediate products of the weathering of smectite to gibbsite, however, kaolin group minerals were present in only minor proportions at Big Willow. The silica versus calcium stability diagram (Figure 11.19a) indicates that the natural juxtaposition of Ca-smectite and gibbsite with minor kaolinite forming can only occur if either, the pH of the system is extremely high, or if the gibbsite formation occurs as an overprint. Strongly alkaline fluids were not measured at Big Willow, either entering or exiting, the aquifer system so gibbsite formation as an overprint is more likely.

Many pre-basaltic and interbasaltic deep paleo-weathering profiles in the Monaro contain gibbsite and have been described as cool climate bauxites (Taylor et al. 1992), as paleoclimatic reconstructions for the Monaro Volcanic Province indicates that the climate
environment was cool throughout the Tertiary (Taylor et al. 1990). Contemporary gibbsite formation or bauxitisation during basalt weathering in the Monaro Volcanic Province provides support for the concept that gibbsite bearing weathering profiles can develop in cool climates provided the region is tectonically stable, the drainage good and sufficient time is allowed (Taylor et al. 1992).

12(C).1.3 Zeolite Formation During Basalt Weathering

The presence of zeolites in pore spaces in basalt flows are often attributed to a flushing of fluids through the lava, immediately after flow emplacement, while the basalt is still hot. However, there is evidence that some zeolite infilling of voids can be attributed to precipitation from percolating weathering fluids a considerable time after the cooling of the flow (e.g. Nashar & Davies 1960). In the stability diagrams for silica versus calcium for Big Willow and Sherwood localities (Figure 11.19a), the analysed issuing aquifer water lies within the stability field for Ca-smectite but also overlaps into the Ca-zeolite field. This implies that Ca-zeolite, for example chabazite, may be precipitated from weathering fluids, provided the fluid is sufficiently saturated with respect to chabazite. Several of the weathering profiles in this study had chabazite recognised as a vesicle fill product in void spaces. Although precipitation of zeolites and carbonates from weathering fluids would be enhanced in arid environments where evaporation may increasing their concentration in the fluid (e.g. calcite in weathered basalt at Stock Route profile, Central Queensland).

12(C).2 IMPLICATIONS FOR THE AQUEOUS GEOCHEMISTRY OF BASALT WEATHERING ELSEWHERE IN AUSTRALIA

Although rates of chemical reactions will vary depending on climate environment (i.e. due to variations in temperature and amount of fluid throughflow), some extrapolations can be made with respect to the characteristic aqueous geochemistry that might be expected for well drained, crestal profiles elsewhere in eastern Australia. Those weathering profiles that are incipiently to moderately weathered and have a smectite dominated secondary assemblage are likely to have similar aqueous geochemical processes taking place to those at Big Willow and Sherwood. That is, the percolating rainwater/meteoric fluid probably enters the system as a dilute acid and exits as a neutral to slightly alkaline fluid having contributed protons in place of cations during hydrolysis of the weathering basalt phases. The pH of the clay rich secondary assemblage is usually alkaline.

If this process is more advanced, and the profiles are dominated by a kaolin group clay rich secondary assemblage, dilute acid fluid entering the system may still hydrolyse
phases it encounters. However, a kaolin and gibbsite bearing suite has a much lower capacity to exchange cations, so the issuing fluid may be slightly acid to neutral. The pH of the clay rich secondary assemblage is usually acid.

Hence, for well drained basalt weathering profiles with moderate to high fluid through-flow, a combination of hydrolysis between water and solid phases, and residence time of water in the system, controls the composition of the aqueous phase. The two profile types described above might be considered end members of an acid trend of weathering (Chesworth 1992).

In arid environments the fluid percolation through well drained profiles is reduced and the secondary mineral assemblage may be dominated by a smectite rich secondary assemblage, as only limited transport of cations from the profile has taken place. In addition, the effects of evaporation may cause salts, carbonates and zeolites to be concentrated in the percolating fluids. Ultimately this may lead to the precipitation of these phases in the pore spaces in the weathering basalt, sometimes in specific horizons. This is described as the alkaline weathering trend by Chesworth (1992).

**12(C).3 CALCULATED RATES OF CONTEMPORARY CHEMICAL WEATHERING OF MONARO VOLCANIC PROVINCE BASALT**

Closer examination of the chemistry of the aquifer fluids, enables an evaluation of an average basalt dissolution rate for the Monaro Volcanic Province basalt as follows:

<table>
<thead>
<tr>
<th></th>
<th>BW1</th>
<th>BW2</th>
<th>RANGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>30-40</td>
<td>30-50</td>
<td>30-50</td>
</tr>
<tr>
<td>Mg</td>
<td>25-45</td>
<td>30-40</td>
<td>25-45</td>
</tr>
<tr>
<td>Na</td>
<td>(30-35)*</td>
<td>15-25</td>
<td>15-25</td>
</tr>
</tbody>
</table>

*elevated because borehole open to the surface

<table>
<thead>
<tr>
<th></th>
<th>SW1</th>
<th>SW2</th>
<th>RANGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>30-40</td>
<td>30-40</td>
<td>30-40</td>
</tr>
<tr>
<td>Mg</td>
<td>30-35</td>
<td>25-35</td>
<td>25-35</td>
</tr>
<tr>
<td>Na</td>
<td>12-20</td>
<td>12-20</td>
<td>12-20</td>
</tr>
</tbody>
</table>

Dissolution of approximately 400 mg/l basalt would released the following proportions of these major cations into solution, which are broadly equivalent to measured values.
Ca in issuing water 37.40 (mg/l)
Mg in issuing water 38.16 (mg/l)
Na in issuing water 10.76 (mg/l)

The estimated value for basalt dissolution rate (400 mg/l), taken together with the estimated average fluid flow in the aquifers (approximately 5-10 litre/minute flow rate) allows the calculation of the amount of basalt dissolution per year, approximately 2 tonnes/year. When this is averaged over the catchment area, e.g. for Big Willow approximately 1,000,000 m², a lowering rate due to basalt dissolution is approximately 0.7 mm/1000 years. This compares with the average chemical denudation rate for Australia which is approximately 0.8 mm/1000 years (Ollier 1991).

The rate of physical weathering can be calculated from the rate of stream incision with respect to the ages of the basalt the streams cut (57.5 Ma to 34 Ma, Wellman & McDougall 1974). The calculated value for lowering of the basalt due to physical weathering is in the order of :2-5 mm/1000 years (G. Taylor pers.comm.) and the average for Australia is approximately 5-50 cm/1000 years (Ollier 1991).

During the early Tertiary the climate in the Monaro was wetter (Taylor et al. 1990), hence the lowering of the basalts due to chemical weathering was greater than present. Although the rate of physical erosion in the past might have been enhanced by higher rainfall, the topography at that time was much more subdued as basalts had filled topographic depressions so the land surface relief was much less (Taylor et al. 1985, Veitch 1987, Brown et al. 1988). This implies that the rates of basalt stripping in the past, were similar or less than today, in the Monaro Volcanic Province.

12(C). 4 IMPLICATIONS FOR THE TECTONIC STABILITY OF THE MONARO VOLCANIC PROVINCE, EASTERN HIGHLANDS, SOUTH EAST AUSTRALIA, THROUGHOUT THE TERTIARY

Models for regional landscape evolution of the Eastern Highlands of south east Australia, which incorporates the Monaro Volcanic Province, are currently the topic of considerable debate. Recent research using Apatite Fission Track Analysis (AFTA) has led to the evolution of models that invoke stripping of a thick overburden of 1-2 km cover from large areas of the Eastern Highlands during the Mid-Cretaceous (90±10Ma) (Kohn & Gleadow 1984, O'Sullivan et al. 1995). This contrasts with landscape-based interpretations of general stability of the highlands with restricted denudation (e.g. Bird & Chivas 1993, Taylor et al. 1985, Taylor et al. 1990, Taylor et al. 1992).
Chapter 12: Discussion (C) Aqueous Geochemistry During Basalt Weathering 340

Because deep, pre-basaltic and intra-basaltic, paleo-weathering profiles are preserved in the Monaro (Craft 1933, Browne 1964, Taylor & Smith 1975, Brown et al. 1992, Taylor 1992), the chemical weathering rates must have been greater than the physical weathering rates in the past. It follows that there was only limited increase in local relative relief while these weathering profiles were developing, or the profiles would have been eroded. This observation has implications with respect to tectonic stability of the Monaro Volcanic Province through time, and suggests that the Monaro has been an area of relative tectonic quiescence throughout the Tertiary.

The calculated contemporary chemical dissolution rate from this study (~0.7 mm/1000 years) and the physical erosion rate (~2-5 mm/1000 years) for the Monaro Volcanic Province, are relatively low, reflecting the current tectonic stability. As detailed above, changes in tectonic stability need not be invoked to explain changes in physical and chemical weathering rates of basalt in the Monaro Volcanic Province, throughout the Tertiary. Hence, in the Monaro Volcanic Province, a progressively drier climate environment through the Tertiary, increased dissection of the basalt topography with the passage of time and tectonic stability from at least pre-Eocene times, best explains the present configuration of preserved deep pre-basaltic and intra-basaltic paleo-weathering profiles with contemporary weathering profiles developed on the overlying basalts.
PART D: PALEOCLIMATE, CONTEMPORARY CLIMATE AND BASALT WEATHERING IN EASTERN AUSTRALIA

Throughout the Cainozoic, Australian terrestrial climates have become cooler and the landmass increasingly arid. This transition has not been progressive and rather has been punctuated by cooler and warmer episodes (Chapter 4). Warm moist conditions enhance the processes of terrestrial weathering and regolith development, although these processes may take place in cooler environments over longer periods of time. For this reason, extended periods of warm humid climate identified in the:

(i) mid- to late-Paleocene,
(ii) the mid-late Eocene and
(iii) late Oligocene to early Miocene

might be expected to be periods when accelerated deep weathering occurred on the Australian landmass (Frakes et al. 1987). In addition, the Quaternary, with equable climates in the interglacials, may be another period when deep weathering might take place.

Weathering of basaltic rocks occurs from the time they solidify at the surface. If they are buried, but still near the land surface, they are subject to the percolation of subsurface fluids. Hence a basalt is not only subject to the weathering that takes place shortly after its emplacement, but is continuously weathered, at fluctuating rates, through time. There are periods during the Cainozoic when weathering is likely to have been more intense, so a basalt erupted prior to these periods will have experienced enhanced weathering at these times, provided it was within the zone of percolating weathering fluids.

Thus the weathering profile exposed near the land surface today is composite, reflecting the weathering history of the material at that site. The basalt may have been subjected to multiple deep weathering events or none, depending on the age of the material and the depth to which it has been buried, if buried at all. Weathering continues through time, although rates vary, so all profiles have a measure of contemporary overprint. In areas where the contemporary climate enhances weathering, for example coastal north Queensland where the rainfall and temperatures are high, the contemporary overprint may obliterate all evidence of former weathering.

In environments where contemporary weathering rates are low, for example in the Monaro Volcanic Province where the precipitation is relatively low, paleo-weathering profiles are well preserved. However, chemical weathering profiles will only be preserved if the local land surface degradation due to physical weathering (erosion) is limited. Some observations with respect to local tectonic stability can be implied on the basis of preservation of paleo-weathering profiles (Taylor et al. 1990). Buried or inter-
basaltic paleo-weathering profiles, some of which have been re-exposed at the surface, are documented in many east Australian basalt provinces (Crook 1956, Dudgeon 1982, Taylor et al. 1992, Brown et al. 1992), and frequently preserve evidence of past deep weathering events.

12(D).1 RELATIONSHIPS BETWEEN BASALT WEATHERING AND CLIMATE IN EASTERN AUSTRALIA

Tasmania

The basalt exposed in the Hellyer River Bridge profile, north west Tasmania is approximately 35 Ma to 36 Ma in age and has a clay mineral assemblage dominated by smectite. This locality currently has the highest rainfall of the three Tasmanian sites sampled, and in the early Eocene to Oligocene, the climate was sufficiently wet to sustain temperate rainforest (Hill 1984, Hill 1987b).

The profile on the central plateau at Monpeelyata, which is dated at 22 Ma to 24 Ma has a smectite rich clay assemblage. This locality is currently in an alpine area in a zone of rain-shadow. The presence of a rainforest with sub-alpine to alpine species represented in the late Oligocene to early Miocene, implies that the climate may have been moist but temperatures were cool to cold at this time.

The deeply weathered basalt at Branxholme in north east Tasmania, despite having an age of approximately 16 Ma, has principally altered to kaolin group clays, with some vermiculite. Moderate to high rainfall occurs in this area and temperatures are currently warm, however, temperate to sub-tropical rainforest was present in the Oligocene indicating a temperate to cool, wet climate.

The limited weathering and smectite dominant assemblage at Monpeelyata is characteristic of relatively arid environments. The deep weathering profile at Branxholme is dominated by kaolin group clays, indicative of considerably greater fluid throughflow than the other two profiles. This profile is in an area of relatively high rainfall, is well drained and warmer, both in the past and at present than the other two localities, hence a deep weathering profile has developed.

The basalt at Hellyer River Bridge, because it is an older basalt in an area that has had high rainfall in the past and continues to have high rainfall at present, might be expected to be the most intensely weathered of the three, but it is not. Possible explanations for this phenomenon are: that some of the weathering profile has been stripped away by erosion, or that there has been ponding of fluids at this locality resulting in the formation
of smectite clays in preference to kaolin group clays. A combination of both may have occurred as the basalt lies in an area where considerable dissection of the plains basalts has taken place, and there is a clay-rich impermeable layer between the two flows at this locality above which weathering fluids may have ponded.

**Southern New South Wales**

The basalts at Big Willow, which are between 36 Ma and 39 Ma old, have a dominantly smectite rich clay assemblage with minor kaolinite and some gibbsite. The Sherwood basalts, approximately 45 Ma to 49 Ma old, have a similar assemblage with abundant smectite, but gibbsite was not observed. The contemporary climate for both localities is cool and seasonal with large diurnal and seasonal temperature ranges. The Monaro Volcanic Province is currently in the rain shadow of the Snowy Mountains. The paleoclimate was cool to cold and was probably wetter in the early Tertiary, as cool temperate rainforest was supported at this time (Taylor et al. 1990).

Although deep weathering profiles have been observed in pre-basaltic and interflow positions in the Monaro Volcanic Province, the basalts weathering at the land surface generally do not show the pervasive weathering characteristic of these older sequences. The smectite dominant assemblages at both localities reflect the mineralogy of the corestone material which comprises the bulk of the basalt at each exposure. However, in zones of preferred fluid percolation at these localities, goethite and minor kaolinite, with some gibbsite (BW) form in between cores. In this setting it is not unusual to get sequences with almost no kaolinite preserved in the leached zone between cores, resulting in an assemblage comprised of smectite and gibbsite together, an unusual combination. Hence, relatively intense weathering is taking place but it is preferentially located along joint plains. This focussing of fluid flow is characteristic of basalt profiles weathering in environments with lower rainfall.

**Northern New South Wales**

The basalt flows on the Newell/Oxley Highway are between 13.5 Ma and 13.8 Ma in age and have a smectite-rich clay assemblage. At Chalk Mountain the lowermost sediments are likely to be older than the middle basalt (approximately 16.6 Ma) which in turn is older than the overlying relatively fresh hawaiite. The middle flow has a similar smectite clay assemblage to the Newell/Oxley Highway basalts, but the lowermost Chalk Mountain sediments are kaolin-rich, and are probably kaolin-smectite bearing.
The contemporary climate for these two localities is moderately wet, and warm and the paleoclimate in the Miocene was possibly wetter but still warm as sub-tropical rainforest was supported at that time (Kemp 1978, Holmes et al. 1983).

The deep weathering at the Dorrigo Plateau profile, Ebor Volcanic Centre (approximately 18 Ma to 19 Ma), has quite a different clay assemblage. It is dominated by kaolin group clays with some gibbsite present. The contemporary climate is cooler than the inland sites, with a higher rainfall, and the paleoclimate in the early Miocene was most likely wet and warmer than present (Stover & Patridge 1973, Martin 1973, Kemp 1978, Dudgeon 1982).

The more intense weathering, producing kaolin group clays, at the Dorrigo plateau locality may in part be associated with the warm period of the late Oligocene early Miocene, which is a period associated with deep weathering. The Newell/Oxley Highway locality, and the middle basalt at Chalk Mountain are slightly younger and would not have experienced the warm moist climates of this period, however, the lower sediments at Chalk Mountain may be of a similar age to the profile at Dorrigo. Dudgeon (1982) describes basalts overlying diatomites in the Main Range which are deeply weathered, and early Miocene in age. Hence this weathering profile is the same age as the deeply weathered Dorrigo basalts and possibly also the lower Chalk Mountain sediments.

The contemporary climate at the Dorrigo profile is such that continued weathering enhances the development of this deeply weathered profile. In addition, the weathered material has formed on an extremely porphyritic feldspar phyric basalt which was susceptible to intense alteration because of the porous nature of the rock once partially weathered.

**Northern New South Wales/Southern Queensland**

Both the Lismore locality and the Beechmont locality have kaolin rich weathered rock/soil assemblages with smectite-rich corestones preserved therein. The Lismore and Beechmont basalts are approximately 22 Ma in age and the contemporary climate is warm with a very high rainfall because of the proximity to the coast. Paleoclimate in this area around 22 Ma to 24 Ma was warm and humid (Dudgeon 1982, Holmes et al. 1983).

Both basalts sampled are sufficiently old to have experienced deep weathering in the early Miocene as per the lower Chalk Mountain sediments and the Dorrigo profile basalt in northern New South Wales. The presence of resistant corestones near surface implies that some of the weathering material may have been eroded from the land surface at both
Chapter 12: Discussion (D) Paleoclimate, Contemporary Climate and Weathering

Tweed localities. The contemporary climate has sufficiently high rainfall to considerably enhance the development of this kaolin rich profile.

Central Queensland

The contemporary climate at both West Springsure profile (EFT22) (~27.8 Ma) and Stock Route profile (EFT9) (~30 Ma) is relatively dry and warm. Grimes (1980) suggests that deep weathering profiles in this area relate to a late Oligocene-early Miocene deep weathering period, however, deep weathering profiles are preferentially preserved between flows in this area, and those exposed at the land surface are not deeply weathered. Hence it appears that the deep weathering profiles that Grimes (1980) recognised relate to an older period of deep weathering.

Because these localities are a considerable distance inland (200-300 km), it appears that this Central Queensland region was relatively dry and warm in the late Oligocene to early Miocene, that is, similar conditions to those that prevail currently. The clay mineral assemblage at both sample localities is dominated by smectite clays as the profiles have weathered in a semi-arid environment through time. Secondary calcite precipitated in veins cross-cutting these profiles is indicative of a period of significant fluid throughflow, however, the precipitation may have taken place in part because of supersaturation of fluids with respect to CaCO3 because of high evaporation rates.

Northern Queensland

The Fletcher Vale basalt profile (QFT1) (~1.2 Ma) in central northern Queensland has a warm contemporary climate with a wet season in the summer. The paleoclimate around 4 Ma to 4.5 Ma ago was possibly slightly more humid than present but still semi-arid as the region supported savannah woodland (Archer & Wade 1976). Smectite is the dominant clay mineral in the assemblage at this locality and reflects the weathering of this basalt in a relatively arid environment through time. The contemporary climate with summer rains may enhance weathering of basalt to smectite clays, and minor weathering to kaolin group clays might be expected in zones of preferred fluid flow through the basalt.

The Kennedy Highway profile exposes the relatively young (120,000 to 180,000 yr B.P.) Murronga Basalt, which forms an upstanding ridge on the older plains basalts. The clay mineral assemblage for this material is dominated by kaolin-group clays which is unusual when compared with the smectite-rich assemblages of the other sample sites from the contemporary semi-arid zone. Climate through the Quaternary has fluctuated with interglacials having conditions somewhat similar to contemporary climate. At this locality the climate is very seasonal with most of the rain occurring in the summer.
Because the lava sits atop the plains lavas it is free draining, and receives a large proportion of the incident precipitation, hence fluid throughflow in the rainy season would be optimised.

The localities in the Atherton volcanic province experience a tropical humid contemporary climate with high rainfall. At Innisfail on the coast and Millaa Millaa at the southern end of the Atherton Tableland, the contemporary rainfall is extremely high. Almost all weathering profiles in this vicinity are deep and are dominated by a kaolin group clay assemblage with gibbsite present high in the profile.

In this region of northern Queensland, contemporary climate is overprinting any paleo-weathering profiles to the point that paleo-weathering can no longer be recognised, and relatively mature weathering profiles dominated by a kaolin group clay assemblage, with Fe-oxyhydroxides and gibbsite, are common on the older basalts (1.6 Ma).

The Archer's Creek profile (approximately 1.2 Ma) is located on the western side of the province where the contemporary rainfall is less, and at this locality, smectite clays are associated with the least weathered basalt in the profile, but kaolin group clays dominate in the more intensely weathered material near the top of the profile.
CONCLUSIONS

A program of sampling of basalt regolith profiles on eastern Australian Cainozoic flow basalts has enabled an, case study style, interpretation of basalt weathering profile processes, from a range of contemporary climate environments. Sample sites cover a range of latitude (Millaa Millaa, Northern Queensland 17.31°S to Monpeelyata Canal, Central Tasmania 42.00°S), and a variety of contemporary climate and paleoclimate environments (summarised in Chapter 12(D)).

The Isocon Technique

The isocon technique has been used, for the first time on weathered rocks, for evaluation of geochemical analyses in association with field, mineralogical and optical observations. Use of this technique has enabled the characterisation of basalt regolith profiles in this study.

- The graphical isocon technique, is an appropriate technique to use in evaluating element enrichment and depletion, and mass change $\Delta M$ (%) as an indication of degree of weathering, in weathered rocks (Chapter 1). However, this must be carried out in close association with careful petrographic work and where possible X-ray diffraction also. The graphical isocon technique is superior to other weathering index techniques in that it uses comparison with at least two and up to five (or more) immobile elements rather than using comparison with a single element that is assumed immobile. Hence there is an internal check on the degree to which the immobile elements have remained so.

- Saprolitic material may appear isovolumetric, in outcrop, in the early stages of weathering, but the mass change indicated by the isocon technique provides an estimate of the degree to which the material has weathered. This concept is fundamental to the use of the net mass change $\Delta M$ (%) of a sample as a weathering index in this study.

Mineral Changes During Basalt Weathering

- For eastern Australian basalts, phases commence weathering in the approximate order: basaltic glass, olivine, plagioclase, pyroxene and opaque oxides, but pyroxene weathers more rapidly than plagioclase, and is wholly weathered before plagioclase. This sequence is the same as that observed by Eggleton et al (1987).
The general sequence of mineral changes characteristic of all the well drained basalt profiles analysed in this study involves the removal of cations (e.g. Ca, Sr, Na, K, Rb, Mg) from primary minerals in the weathering basalt as a result of hydrolysis which initially produces a secondary suite dominated by smectite clays. With continued removal of cations kaolin group clays are formed. Ultimately, almost all of the cations (including silica) are removed, leaving aluminium as the major residual cation, and gibbsite may form. However the rate of the changes in mineralogy varies greatly. In some cases kaolin group clays are formed without evidence of a smectite intermediate being preserved, and in one locality (Big Willow, Monaro) gibbsite was found in association with a smectite dominant secondary mineralogy with few kaolin group minerals preserved. Redox reactions lead to the concentration of the secondary Fe-oxides and hydroxides, hematite and goethite, in weathering products.

Element Mobility During Basalt Weathering

Element mobility patterns during basalt weathering show general similarities for profiles from differing contemporary climate environments within the eastern Australian Cainozoic basalts, however, the rates at which weathering proceeds is strongly influenced by the climate regime throughout weathering.

Processes affecting elements as previously documented for weathering of well drained, oxic, mafic volcanic and gabbro profiles include: the rapid removal of the alkali and alkaline earth cations from the weathering profiles; progressive weathering of silica from the profile; the oxidation of iron during weathering resulting in the fixation of Fe, largely in secondary Fe-oxides and oxyhydroxides (goethite and hematite); similar oxidation of manganese to form coatings on weathered surfaces; the variable but limited mobility of zinc and vanadium reflecting the original partitioning of these phases into relatively resistant primary minerals; the relatively high mobility of copper once Cu-sulphide is oxidised to sulphate; the limited element mobility of the actinides, thorium and uranium, given that these elements comprise a minimal trace in basaltic rocks in general; and, the residual concentration of chromium and nickel in weathering profiles.

Using the slope of the elemental mass loss curve, on plots of elemental net mass change versus slope of the isocon (degree of weathering), it is possible to quantify the order of preferred mobility of the major elements and some trace elements during weathering. The general order of element mobility for the eastern Australian basalts is:

\[
\begin{align*}
&\text{Na} \ (-221.71) > \text{Sr} \ (-195.14) > \text{Ca} \ (-186.06) > \text{K} \ (-183.52) \\
&\text{Rb} \ (-171.87) > \text{Mg} \ (-156.14) > \text{Al} \ (-78.06) > \text{Si} \ (-75.98)
\end{align*}
\]
where the values in brackets are the respective slopes of the mass loss curve for each element.

- Elements that have mobility patterns that differ from the processes previously described include: significant enrichment of the rare earth elements (REE) cerium and lanthanum, as well as yttrium, barium and lead, when generally they might be expected to be removed from the weathering profile in a similar fashion to the alkali and alkaline earth elements. This enrichment may be associated with secondary phosphate, carbonate and sulphate minerals. Secondary phosphates, most likely of the plumbogummite group, were observed in the immediate vicinity of dissolving apatite in weathered basalt from the Nulla Volcanic Province (QFT1), and this is thought to be the principal mechanism for the enrichment of Ce, La, Pb, Y and Ba, by several orders of magnitude, in incipiently to moderately weathered basalt. The significance of this observation is that trace element patterns from incipiently weathered basalts that, according to petrographic analysis appear relatively fresh, are interpreted in magma evolution studies, but may be anomalously enriched as a result of weathering, and errors in magma evolution evaluations may occur.

- Other elements that show unusual behaviour are those that are generally considered to be immobile during weathering, but are apparently mobile under certain weathering conditions. These include niobium, zirconium, yttrium, aluminium, titanium and iron. Niobium and zirconium appear to mobile in alkaline fluids. Ti shows a trend for the eastern Australian basalts that suggests that it is more readily concentrated in alkaline (smectite rich) profiles and is more depleted in acid (kaolin rich) profiles. This apparently contrasts with previous work that describes Ti enrichment in deeply weathered profiles. In general Ti is relatively enriched, however, opportunity for the precipitation of secondary Ti phases may be enhanced in alkaline weathering profiles. Niobium, Zr and Ti may all maintain a constant relative concentration if they are partitioned into resistant phases. Aluminium appears to vary with extremes of pH, both alkaline and acid, of the percolating aqueous solutions. This pH variation may occur in localised portions of the weathering profile, for example fluids entering the basalt weathering system may be quite acid. Iron is known to be mobile under weathering conditions as a result of redox reactions.

**Secondary Mineral Evolution**

A general sequence of secondary mineral evolution during flow basalt weathering can be defined, however, subtle chemical variations within weathering profiles allow the localised presence of unusual secondary products.
In general, basalts weather initially to smectite clays, in some cases through short range order phases which are X-ray amorphous. The smectite clay mineral suite is dominated by dioctahedral smectites (nontronite, beidellite, montmorillonite) with some trioctahedral smectite clays (Fe-saponite, saponite). Some primary minerals, in particular plagioclase feldspar, may be weathered directly to kaolin group clays, but smectite clays are more abundant overall, in the clay separate. As the trioctahedral/dioctahedral smectite rich secondary assemblage is weathered further, trioctahedral clays (Fe-saponite, saponite) break down to dioctahedral clays (nontronite, Fe-beidellite). With continued weathering, the smectite assemblage may commence break down to kaolin group clays (halloysite, kaolinite). Randomly interstratified kaolin-smectites may form as intermediate products in this break down. Halloysite appears to be the kaolin group clay preferentially formed as a result of the break down of smectite, but kaolinite is formed also. In more intensely leached profiles kaolinite is the dominant clay mineral. Further weathering, resulting in desilicification of kaolinite, leads to the formation of gibbsite.

If contemporary rainfall is compared with cation exchange capacity for the eastern Australian basalt samples, profiles with elevated fluid percolation are those with most cation depleted secondary phases, and those in more arid areas have smectite dominated secondary assemblages. However, prolonged percolation of fluids through weathering basalt would also eventually result in kaolin and gibbsite rich weathering profiles (eg paleo-weathering profiles Monaro Volcanic Province, Taylor et al. 1992).

The capacity for clays in the weathered basalts to exchange cations depends on how much clay there is in a sample and what kind of clay is present. The clay content in a weathered basalt sample is proportional to the degree of weathering. The percentage clay content in a weathered basalt sample approximates the percentage mass loss -ΔM (%) for the sample. There is a progressive decrease in the capacity for the secondary mineral assemblage to exchange cations as weathering proceeds. This corresponds with the decrease in smectite clay (high CEC) and increase in kaolin group clays (low CEC) in the weathered material.

Halloysite was more widespread in the products of basalt weathering than previously documented and appears to be the kaolin group clay preferentially formed during the break down of smectite clays, although kaolinite is also produced. Halloysite may even persist into extremely weathered material, although kaolinite is more dominant in this environment, for example at Dorrigo profile, northern New South Wales and Innisfail profile, northern Queensland. The lack of documentation of the presence of this clay in the past may have occurred because, in many cases the X-ray diffraction traces for halloysite are extremely similar to those for kaolinite unless the formamide test is carried out (Churchman et al. 1984).
Randomly interstratified kaolin-smectite clays, intermediate in the break down of smectite to kaolinite, are also widespread in the products of basalt weathering in eastern Australia, but are difficult to distinguish using cation saturation, X-ray diffraction and cation exchange capacity alone.

**Paleo-weathering Versus Contemporary Weathering**

The contemporary climatic environment influences the most recently developed portion of weathering profiles, which may overprint pre-existing paleo-weathering profiles. Paleo-weathering profiles provide a record of climate environments different to those that prevail today, however, they may be significantly modified. In areas where contemporary climatic conditions enhance deep weathering, paleo-weathering profiles near the land surface may be completely obliterated. In areas with limited contemporary fluid through-flow, deep paleo-weathering profiles, developed at times of accelerated weathering in the past, may be preserved. But, because regolith development is an ongoing process, preserved paleo-weathering profiles will have continued to weather through time, and hence, the secondary mineral assemblage will adjust in order to approach equilibrium with contemporary climate environments.

Once the clay mineralogy and element mobility for a number of profiles is compiled, some broad evaluations can be made in light of paleoclimate and contemporary climate. In this study it has been possible to relate the development of weathering profiles through time to the evolution of climate environment in eastern Australia (Chapter 12(D)).

**Aqueous Geochemistry and Basalt Weathering**

Close observation of aqueous geochemistry at two localities in the Monaro Volcanic Province has enabled interpretation of processes that take place in an actively weathering basalt profile. In addition it has: enabled an explanation of the unusual juxtaposition of smectite and gibbsite in one weathering profile in the Monaro, shown that zeolites may form in weathering profiles in equilibrium with the percolating fluids, and has allowed some evaluations with respect to tectonic stability of the Monaro Volcanic Province throughout the Tertiary.

The calculated contemporary chemical dissolution rate (~0.7 mm/1000 years) and the physical erosion rate (~2-5 mm/1000 years) for the Monaro Volcanic Province, are relatively low, reflecting the current tectonic stability. A progressively drier climate environment through the Tertiary, increased dissection of the basalt topography with the passage of time, and tectonic stability from at least pre-Eocene times, best explains the
present configuration of preserved deep pre-basaltic and intra-basaltic paleo-weathering profiles with contemporary weathering profiles developed on the overlying basalts. Hence, changes in tectonic stability need not be invoked to explain changes in physical and chemical weathering rates of basalt in the Monaro Volcanic Province, throughout the Tertiary. There is no indication that there has been stripping of overburden in the Monaro region, as suggested by Apatite Fission Track Analysis (AFTA) elsewhere on the Eastern Highlands (Kohn & Gleadow 1984, O'Sullivan 1995).

This study clarifies the processes of chemical weathering of basalt across a range of time and climate space, and integrates studies from carefully selected areas into a single extensive work, with a view to understanding the variations in processes and products of basalt weathering. In particular geochemical and mineralogical variations are characterised and an attempt to relate these to physicochemical variations in environment has been made.
APPENDIX 1

BASALT WEATHERING PROFILES

A.1.1 TERMINOLOGY

*Incipiently weathered basalt:* relatively fresh rock, with a thin rind and weak iron staining, corestones are not observed, jointed blocks are present. The rock is still indurated but the surface rind may crumble with a hammer blow. Earthy material is not yet present.

*Slightly weathered, degree of weathering:* has traces of alteration, including weak iron staining, and some earth material. Corestones, if present, are interlocked, there is slight decay of feldspars, and a few microfractures. Slightly weathered rock is easily broken with a hammer. A small amount of earthy material may be present between corestones and joint blocks.

*Moderately weathered basalt:* has strong iron staining and up to 50% earth material. Corestones, if present, are rounded within rubbly weathered basalt but the original interlocked, rectangular shape of the joint block can be recognised. Most feldspars have decayed, and there are microfractures throughout. Moderately weathered rock can be broken by a kick, but not by hand.

*Highly weathered basalt:* has strong iron staining, and more than 50% earth material. Corestones, if present, are free and rounded. Nearly all feldspars are decayed, and there are numerous microfractures. The material can be broken apart in the hands with difficulty.

*Very highly weathered basalt:* produced by the thorough decomposition of rock masses due to exposure to land surface processes. The material retains structures from the original basalt. It may be pallid it colour, and is composed completely of earth material. Corestones, if present, are rare and rounded. All feldspars have decayed. It can easily be broken by hand.

*Completely weathered basalt:* retains no structures from the original basalt. There are no corestones, but there may be mottling. It is composed completely of earth material.
A.1.2 TASMANIA

North West Tasmania Volcanic Province

On the remnant basalt plains in the north west of Tasmania, near the settlement of Guildford, a profile was sampled in a road cutting adjacent to the Hellyer River (41.26°S 145.41°E) at an elevation of 617 m (asl).

Hellyer River

The profile lies within the subdued topography of the plains basalts and the water table lies below the level of the lower flow. The lowermost vesicular basalt flow is more pervasively weathered than the overlying, more massive basalt. The contact between the basalts is irregular and there has been some injection of the overlying lava into depressions in the lower basalt. There is a very dense red brown oxidised layer at the contact, about 2-3 cm thick, which may be an incipient soil preserved between the two flows, and may have been baked.

Figure A.1
Local map for Hellyer River profile, north west Tasmania.
Appendix 1: Basalt Weathering Profiles A-3

Profile TAS 17 - Hellyer River, (ANU 54845) (Figure 3.2, Plate 3.1)

**Upper Basalt**
000 - 010 cm Skeletal soil
010 - 240 cm Olive (5Y 4/4) massive columnar jointed slightly weathered basalt (TAS 17/1), joint spacing 0.8-1.2 m.

**Lower Basalt**
240 - 243 cm Clay rich, dense red brown (oxidised) layer.
243 - 280 cm Greyish olive (5Y4/2) basalt corestones 10-15 cm in diameter (TAS 17/2) in rubbly weathered basalt material. A gold (10YR 6/8) coating was observed on some fracture surfaces.
280 - 310 cm Brown (2.5YR 4/6) highly weathered vesicular basalt (TAS 17/3). Vesicle fill material is white chabazite and yellowish brown (10YR 4/6) smectite clays.
310 - 400 cm Deep orange 5YR 5/8 moderately weathered vesicular basalt (TAS 17/5). Vesicle fill material is white chabazite (TAS 17/4) and yellowish brown (10YR 4/6) smectite clays.

**Central Tasmania Volcanic Province**

On the central Tasmanian highland plateau, the Monpeelyata canal drains Little Pine Lagoon (42.00°S 146.37°E). In the south wall of the canal, at an elevation of 1007 m (asl), a free draining basalt sequence 6 m thick is exposed.

**Monpeelyata Canal**

Two basalt flows crop out in this profile in the south wall of the Monpeelyata canal (Figure 3.1, Figure 3.6, Plate 3.4). In this area the basalt forms an area of subdued topography south and east of Little Pine Lagoon, and the canal is excavated through them to depth of about 6 m. In the lower lava there are some relatively sharp joint planes preserved but weathering has commenced wherever fluids have been able to percolate, forming rubbly onionskins surrounding smaller blocks and weathered material along the joint planes bounding larger blocks. The upper basalt is slightly vesicular, generally has smaller block development than the lowermost basalt, and stacks of corestones roughly preserve the original columnar jointing of this flow.
Appendix 1: Basalt Weathering Profiles A-4

Local map for Monpeelyata Canal profile, Central Tasmania.

Profile TAS 27 - Monpeelyata Canal, (ANU 54846) (Figure 3.1, Figure 3.6, Plate 3.4)

Upper Basalt

000 - 010 cm Gravelly, olive (5Y 5/4) skeletal soil.

010 - 210 cm Greyish olive (7.5Y 5/2) lightly vesicular, blocky weathered basalt (TAS27/3) with a dull yellow (5Y 7/6) smectite bearing surface coating and with greyish olive (7.5Y 4/3) corestones (TAS27/2) enclosed within olive (5Y 5/4) rubbly weathered basalt formed from exfoliating onionskins,(TAS27/1) with light yellowish brown (10YR 6/6) smectite bearing surface coatings.

Lower Basalt

210 - 380 cm Greyish olive (7.5Y 4/2) weathered, highly vesicular basalt (TAS27/4), possibly a flow top layer.

380 - 630 cm Greyish olive (7.5Y 5/2), incipiently to slightly weathered, sparsely vesicular basalt (TAS27/5) with a dark yellow (2.5YR 6/4) smectite bearing surface coating. This basalt is jointed forming large equant subangular blocks up to 1.2 m in dimension.
North East Tasmania Volcanic Province

Near the town of Branxholme in north west Tasmania (41.10°S 147.44°E), at an elevation of 176 m (asl), a deeply weathered basalt showing spectacular secondary iron staining, overlying a quartzose sediment, is exposed in a road cutting near the crest of a hill. Contemporary water table level lies below this exposure.

Branxholme

The contact between the sediment and the basalt is irregular and it appears the uppermost part of the sediment was soft and wet when the basalt flowed over it. Contact irregularities have formed due to variable load and fluid release at the time of emplacement of the basalt. The lower basalt is intensely weathered and is largely altered to clays, iron oxides and iron oxyhydroxides. In many places spheroidal weathering can only be recognised by colour changes. Very little of the original rock texture is preserved. The upper basalt is less weathered and has clearly defined, massive blocky corestones.

Figure A.3
Local map for Branxholme profile, north east Tasmania.
Appendix 1: Basalt Weathering Profiles A-6

Profile TAS 9 - Branxholme, (ANU 54847) (Figure 3.10, Plate 3.13)

Upper Basalt

0000 - 0020 cm  A skeletal to thin (red) brown (2.5YR 3/6) soil (TAS9/1) with incorporated corestone rubble.

0020 - 0350 cm  Greyish green (5BG 4/1) weathered basalt with clearly defined, massive blocky corestones (TAS9/3) up to 80 cm in diameter. Crumbly, (red) brown (5YR 4/6) soil-like weathered basalt (TAS9/2) has formed between the corestones, with a yellowish brown (10YR 5/6) coating on enclosed weathered basalt rubble.

Lower Basalt

0350 - 0950 cm  Intensely weathered basalt with spheroidal weathering recognised because concentric rings of alternating light yellowish brown (10YR 6/6) and yellowish brown (7.5YR 5/6) kaolin group clay materials (TAS9/4b) surround brown (2.5YR 4/6) extremely weathered remnant corestones (TAS9/4) with yellowish brown (7.5YR 4/6) "onion skins" (Plate 3.14).

0950 - 0980 cm  An irregular interval of dull orange yellow (2.5Y 8/6)(TAS9/5) and greyish olive (7.5Y5/3) (TAS9/6) kaolin group clay and smectite clay materials formed near the contact as a by-product of the interaction of the underlying water saturated sediment with hot basalt.

Sediment

0980 - 1200 cm  Dull orange yellow (2.5Y 8/6) quartzose sediment (TAS9/8) with a brownish olive (2.5Y 5/4) kaolin group clay rich layer (TAS9/7) near the top of the sediment which resembles a palaeosol.

A.1.3 SOUTHERN NEW SOUTH WALES

Monaro Volcanic Province

The Monaro Volcanic Province stretches from just north of Cooma south almost to Bombala on the Southern Highlands of New South Wales (Figure 4.1). Two localities were sampled in this province, one north of Cooma on the Big Willow property (36.06°S 149.05E) and one south west of Nimmitabel, on the Sherwood property (36.36° S 149.07°E). There are perched aquifers at both sites, but the regional water table lies below the level of the regolith profile exposures considered.
App

Appendix 1: Basalt Weathering Profiles A-7

Big Willow

The profile is partially obscured by depression filling swamp material which is associated with the fresh water spring at this site. The lower basalt crops out at the spring mouth, with a more intensely weathered basalt adjacent to a dam approximately 10 m above. The whole sequence is overlain by a transported black basaltic soil. Samples were taken from an upper mid-slope position.

![Local map for Big Willow profile, Monaro Volcanic Province.](image)

**Figure A.4**

Local map for Big Willow profile, Monaro Volcanic Province.

**Profile BW - Big Willow, (ANU 54848)** (Figure 4.2, Plate 4.1)

*Upper Basalt*

- 000 - 200 m Greyish olive (2.5Y 3/2) transported basaltic soil (BW0)
- 200 - 400 m Brownish olive (2.5Y 5/6) intensely weathered basalt corestones with concentric "onionskins" (BW-1, BW-2).

10 m interval Dark greyish brown (10YR 2/2) (BW5) organic swamp material associated with the fresh water spring at this site

*Lower Basalt*

- 000 - 080 cm Olive (7.5Y 4/4) weathered basalt (BW2).
- 080 - 150 cm Greyish olive (7.5Y 4/1) (BW4) to olive (5Y 3/2) (BW3) massive, moderately weathered, indurated basalt.
Appendix 1: Basalt Weathering Profiles A-8

Sherwood

This outcrop, lies in an upper mid-slope position on the side of a stream gulley. Two lavas are separated by a lacustrine deposit (SW2, SW4) which contains leaf fossils (Dansie 1993) at this site. Spheroidal weathering has led to the formation of well developed corestone formation in the basalt.

Figure A.5
Local map for Sherwood profile, Monaro Volcanic Province.

Profile SW - Sherwood, (ANU 54849) (Figure 4.6, Plate 4.10)

Upper Basalt
000 - 020 cm Transformed black basaltic soil and talus
020 - 200 cm Greyish olive (5Y 4/1) weathered basalt with corestones 15-20 cm in diameter (SW1), with rubbly weathered basalt between corestones

Sediments
200 - 250 cm Pale yellow green (7.5GY 8/1) to light grey (N 7/0) lacustrine deposit (SW2, SW4) with leaf fossils

Lower Basalt
250 - 420 cm Olive (5Y 4/4) weathered basalt with corestones up to 20 cm in diameter (SW6) lower in the flow and smaller greyish olive (5Y 4/2) corestones in the upper parts (SW5).
A.1.4 NORTHERN NEW SOUTH WALES

Warrumbungles Volcanic Province

The Warrumbungles Volcanic Province of northern New South Wales (Figure 5.1), is located approximately 500 km NW of Sydney, immediately west of the township of Coonabarabran. Profiles were sampled at two localities, one in a road cutting on the Newell/Oxley Highway (31.27°S 149.00°E) and another exposed in a small diatomite quarry on Chalk Mountain (31.07°S 149.04°E). Profiles at both sites lie above the regional water table level.

Newell/Oxley Highway

The sampled road cutting on the Newell/Oxley Highway is located at the crest of a rise and exposes a section through three basalt flows. A horizon of trachytic ash separates the upper two basaltic flows. The intensely weathered "onionskin" material from above and below the white trachytic ash is difficult to tell apart, and in places, where the ash layer pinches out or is obscured, the basalts appear continuous. In the middle basalt some large basalt blocks, in excess of 1 metre in diameter, are preserved between joint planes, with spheroidally weathered basalt between blocks.
Appendix 1: Basalt Weathering Profiles A-10

Profile WFT 4 - Newell/Oxley Highway, (ANU 54850) (Figure 5.2, Plate 5.1)

Upper Basalt

000 - 060 cm Dark yellowish brown (10YR 3/4) smectite rich basaltic soil (WFT4/10).

060 - 210 cm Weathered basalt with greyish olive (2.5Y 4/2) corestones 10 to 15 cm in diameter (WFT4/9) with greyish olive (2.5Y 4/3) onionskins. Smectite coatings on surfaces are yellowish brown (10YR 5/6).

Trachytic Ash

210 - 290 cm Greyish yellow (2.5Y 8/3), fine grained, feldspar rich trachytic ash (WFT4/8) with a deep orange (7.5YR 5/8) smectite bearing surface coating.

Middle Basalt

290 - 360 cm Sparsely vesicular, greyish olive (2.5Y 5/3) rubbly weathered basalt (WFT4/7) with deep orange (7.5YR 5/8) smectite bearing surface coatings and greyish yellow (2.5Y 8/3) vesicle fill material.

360 - 440 cm Greyish olive (2.5Y 4/3) rubbly weathered vesicular basalt (WFT4/6) with yellowish brown (7.5YR 5/6) smectite clay bearing surface coatings and light yellowish brown to gold (10YR 6/6 - 10YR 6/8) vesicle fill material.

440 - 550 cm Brownish olive (2.5Y 4/4) massive weathered basalt with brownish olive (2.5Y 4/6, 2.5Y 5/4) onionskins surrounding indurated corestones of various sizes (WFT4/4), mostly 15 to 20 cm in diameter, but some greyish olive (2.5Y 4/2) blocks up to 1 m (WFT4/5). Smectite rich surface coatings and vesicle fills are light yellowish brown (10YR 6/4, 10YR 6/6) and deep orange (7.5YR 5/8).

Lower Basalt

550 - 620 cm Brown (5YR 3/6) rubbly weathered scoriaceous basalt (WFT4/3), possibly a flow top breccia.

620 - 840 cm Greyish olive (2.5Y 5/3) moderately weathered highly vesicular basalt (WFT4/1) which is cross-cut by pale orange (7.5YR 8/4) chalky-textured veins and veinlets of calcium carbonate (WFT4/2). Vesicle fill materials are dull orange yellow (2.5Y 8/4) and deep orange (7.5YR 5/8).

Chalk Mountain

The basalt at this locality sits high in the topography, capping a thick diatomite deposit. Up to four basaltic layers are represented at this locality. The diatomite has been commercially exploited at this locality.
Profile WFT 2 - Chalk Mountain, (ANU 54851) (Figure 5.6, Plate 5.10)

Upper Basalt
000 - 600 cm Fresh greyish olive (10Y 5/1) hawaiite (WFT2 1/1)

Middle Basalt
600 - 810 cm Light greyish green (10BG 7/1) weathered basalt, with corestones (WFT2/8, WFT2/7) and greyish olive (5Y 4/2, 5Y 5/3) onionskins, that grade downward into greyish olive (2.5Y 4/1) vesicular basalt (WFT2/6) with pinkish beige (2.5YR 6/3) smectite bearing surface coating and greyish yellow to dull yellow (5Y 7/3, 5Y 7/4) vesicle fill material.

Lower Basalts
810 - 960 cm Greyish olive (2.5Y 4/1) intensely weathered basalt (WFT2/5) with white void filling chabazite.
960-1100 cm (Red) brown (2.5YR 4/6) intensely weathered basalt (WFT2/4).

Sediments
> 1100 cm Beige (10YR 6/3) to greyish yellow (2.5Y 6/3) quartzose sandy layer (WFT2/0) 30 cm thick, underlain by lacustrine sediments, largely composed of diatomite.
Ebor Volcanic Province

The Ebor Volcanic Province forms an arcuate highland, the Dorrigo plateau, in the New England region of northern New South Wales (Figure 5.1), and lies mid-way between the coastal township of Coffs Harbour and the large inland town of Armidale. The settlements of Dorrigo and Ebor sit atop Ebor Volcano. The sample site is west of Dorrigo (30.19°S 152.41°E).

Dorrigo Plateau

In an upper-slope position on a small hill on the Dorrigo plateau a very deep, red-brown weathering profile has developed on free draining weathered basalt.

Profile WFT 10 - Dorrigo Plateau, (ANU 54852) (Figure 5.10, Plate 5.19)

000 - 095 cm (Red) brown (2.5YR 3/6) kaolin group clay rich soil (WFT10/1), with a resinous dull yellow (5Y 8/4) kaolin clay and gibbsite bearing material (WFT10/4) locally infilling voids.

095 - 210 cm A lens of mottled pale gold coloured (7.5YR 6/8) kaolin clay rich sediment (WFT10/5) lies between upper saprolite layers at one side of the outcrop.
Appendix 1: Basalt Weathering Profiles A-13

095 - 260 cm  Dark yellowish brown (10YR 3/4) kaolin clay rich saprolitic weathered basalt (WFT10/6) with a resinous dull yellow (5Y 8/4) kaolin clay and gibbsite bearing material (WFT10/4) locally infilling voids.

260 - 370 cm  Brown (2.5YR 3/4) kaolin clay rich saprolitic weathered basalt (WFT10/7) with a resinous dull yellow (5Y 8/4) kaolin clay and gibbsite bearing material (WFT10/4) locally infilling voids.

370 - 500 cm  Grey clayey weathered material (WFT10/8) forms a prominent base to the deeply weathered profile.

> 500 cm  Greyish leaf (2.5YR 3/6) coloured weathered porphyritic basalt (WFT10/2), with white vesicle fill.

A.1.5 SOUTHERN QUEENSLAND/NORTHERN NEW SOUTH WALES

Tweed Volcanic Province

The Tweed Volcano straddles the border between north east New South Wales and south east Queensland, and lies immediately west of the town of Murwillumbah (Figure 6.1). Two profiles were sampled, one in the north at Beechmont (28.08°S 153.11°E) and another in the south at East Lismore (28.50°S 153.20°E). The Beechmont locality lies above the regional water table. Although the East Lismore profile does not appear to be effected by ponding of water associated with the regional water table, the pallid zones in this profile may have been enhanced by short term profile saturation in the past.

East Lismore

At this locality a single weathered basalt flow is exposed in a road excavation (Fig 6.1), in an upper slope position in the topography. There is significant vertical and lateral variation in the degree of weathering of this basalt, with a general increase in weathering away from corestones and, on a broader scale up-profile.
Figure A.9
Local map for East Lismore profile, Tweed Volcanic Province.

Profile TFT 6 - East Lismore, (ANU 54853) (Figure 6.2, Plate 6.1)

000 - 095 cm Deep orange (7.5YR 5/8) basaltic soil (TFT6/10).
095 - 200 cm Kaolin clay rich saprolite materials characterised by yellowish brown (10YR 5/6) through light brown to deep orange (5YR 5/6, 5YR 5/8) colouration (TFT6/5, TFT6/6, TFT 6/8) enclose pale coloured light yellowish brown (10YR 6/6) intensely weathered kaolin clay bearing zones (TFT6/7, TFT6/9). Coatings on joint surfaces within these leached zones range from gold (7.5YR 6/8) to deep orange (5YR 5/8) in colour, and void fill material is dull orange to dull orange yellow in colour (7.5YR 7/6, 10YR 8/4). These zones represent relict pathways of preferred fluid flow through the profile.
200 - 400 cm Greyish olive incipiently weathered corestones (TFT 6/1) and brownish olive to yellowish brown moderately weathered corestones (TFT6/3, TFT6/4) are relicts completely enclosed in yellowish brown (10YR 5/6) through light brown to deep orange (5YR 5/6, 5YR 5/8) coloured kaolin clay bearing saprolite. Pale gold coloured (10YR 6/8) kaolin clay bearing leached zones (TFT6/2) persist to depth.
Appendix 1: Basalt Weathering Profiles A-15

Beechmont

A single basalt flow, exhibiting well developed spheroidal weathering, is represented at this locality, on the elevated Beechmont plateau.

![Local map for Beechmont profile, Tweed Volcanic Province.](image)

Profile **TFT 12 - Beechmont, (ANU 54854)** (Figure 6.5, Plate 6.6)

000 - 070 cm  Deep orange (5YR 5/8) basaltic soil (**TFT12/1**) overlies and grades into rubbly brown (5YR 3/4) weathered basalt saprolite (**TFT12/2**).

070 - 400 cm  Brownish olive to deep orange coloured (2.5Y 4/6, 7.5YR 5/8) rubbly weathered basalt (**TFT12/3, TFT12/6**) is gradational into the weathered basalt saprolite above. This encloses dark greyish brown (2.5YR 3/3) corestones (**TFT12/4**), up to 15 cm in diameter, which appear to be more intensely weathered than the larger blocks lower in the profile. There are small areas of massive strong reddish orange (2.5YR 5/8) weathered basalt (**TFT12/5**) with primary jointing preserved. Larger brownish olive (2.5Y 5/6) corestones (**TFT12/7**), up to 30 cm in diameter, occur nearer the base of the flow, suggesting that this profile has principally been weathered from the top down.
Central Queensland

Springsure and Peak Range Volcanic Provinces

The Springsure and Peak Range volcanic provinces are located in the Emerald District, approximately 250 km from the coast in central Queensland (Figure 7.1). Two profiles were sampled, one west of Springsure township on the Dawson Developmental Road (24.07°S 147.59°E) and one east of Clermont township on the Stock Route Rd (22.47°S 147.47°E). Because these profiles both occur within plains basalts that have subdued topography, both may be affected by ponding waters associated with the regional water table. Such ponding events may be sporadic because of the semi-arid climate regime that prevails in this area, and the strongly seasonal precipitation.

Springsure

This basalt outcrops at the crest of a small rise in the basalt plains. The main flow represented at this locality shows well developed spheroidal weathering. Because of the semi-arid environment, the clay-bearing onionskin material dries and becomes a crumbly gravel which flakes away from the face and forms a rubble apron at the base of the profile. Incipiently weathered corestones persist to the land surface and it is not apparent that weathering occurred preferentially from the surface down. Corestone development in the vesicular flow top material is not as well developed as in the massive basalt elsewhere in the profile.

Figure A.11
Local map for Springsure profile, Springsure Volcanic Province.
Appendix 1: Basalt Weathering Profiles A-17

Profile EFT 22 - Springsure, (ANU 54855) (Figure 7.2, Plate 7.1)

000 - 010 cm Yellowish brown (10YR 4/4) dusty skeletal soil (EFT22/1) is composed of crumbly gravel material of disaggregated onionskins with some pebbles of less weathered basalt and in places corestone float.

010 - 200 cm Dark yellowish brown to dark greyish brown (7.5YR 3/4, 7.5YR 3/2) vesicular basalt (EFT22/5, EFT22/6) represents the flow top. Smectite bearing surface coatings are dark yellow through dull yellow to yellowish brown in colour (2.5Y 6/4, 5Y 7/4, 10YR 5/6) and resinous smectitic vesicle fill material brownish olive (2.5Y 5/6) in colour. White chalky calcium carbonate veins pass through the profile generally following the zones of more weathered material between corestones.

200 - 400 cm Greyish olive to greyish olive green (10Y 4/2, 5GY 4/1) basalt corestones (EFT22/3a EFT22/4) form resistant knobs in the face with the more weathered brown to brownish olive (2.5YR 4/4, 2.5Y 4/4, 2.5Y 4/6) corestones and rubbly weathered basalt (EFT22/2, EFT22/3) about them less prominent.

Peak Range

The weathered basalt profile is exposed in the wall of a small quarry in the plains basalts. There are two basalt flows represented at this locality. The lower basalt shows well developed spheroidal weathering and is cross-cut by chalky calcium carbonate veins. The red coloured vesicular flow top on the basalt is weathered in hand specimen but is indurated, and vesicles are lined with pale blue-grey smectite clays and calcite.

Profile EFT 9 - Peak Range, (ANU 54856) (Figure 7.5, Plate 7.6)

000 - 015 cm Dusty brownish olive (2.5Y 4/6) to dark yellowish brown (10YR 3/4) skeletal smectite bearing soil (EFT9/1) formed largely from rubbly weathered basalt material.

015 - 030 cm Light greyish green (5BG 6/1) smectite-rich clays (EFT9/2) have formed on the basalt, and nodular beige (10YR 6/3) carbonate material is recognised in the soil zone (EFT9/3).

Upper Basalt

030 - 320 cm Brownish olive (2.5Y 4/6) massive weathered basalt (EFT9/4) has well developed corestones enclosed in yellowish brown (10YR 5/6) onionskin material. Dark yellowish brown (10YR 3/4) weathered vesicular basalt (EFT9/5) at the base of the flow has dark yellow to light yellowish brown (2.5Y 6/4, 10YR 6/6) smectite clays and white secondary calcite, within
vesicles and voids. Concentrations of greyish yellow (10Y 8/2) clay minerals (EFT9/6) and white calcite (EFT9/7) occur in veins that cross-cut the basalt flow unit.

**Carbonate Layer**
320 - 350 cm Chalky textured white calcium carbonate material (EFT9/8).

**Lower Basalt**
350 - 590 cm Greyish brown (5YR 4/3) vesicular (EFT9/9) weathered basalt flow top grades downward into dark yellow (2.5Y 6/4) intensely weathered massive basalt (EFT9/10) forming the body of the flow. Brownish gold to dark yellow (10YR 5/8, 2.5Y 6/4) resinous smectite rich material and white chalky textured calcite fill vesicles throughout this basalt flow.

Figure A.12
Local map for Peak Range profile, Peak Range Volcanic Province.

A.1.7 NORTHERN QUEENSLAND

**Atherton Volcanic Province**

At the first sample site weathered basalt is exposed in a road cutting where the Kennedy Highway cuts Archers Creek (17.39°S 145.20°E), west south west of Ravenshoe. At the southern end of the Atherton Tableland, a profile was sampled just east of Millaa Millaa on the Palmerston Highway (17.31°S 145.38°E). The third profile was sampled inland of Innisfail (17.33°S 145.58°E) where a deep weathering profile has developed on basalt that
is being quarried for road aggregate. Although these profiles are elevated in the
topography, regional precipitation is sufficiently high to cause profile saturation for
extended periods (Chapter 8).

**Archers Creek**

This profile is in an upper slope position, is extremely thick and incorporates at least two
basalt flows.

![Local map for Archers Creek profile, Atherton Volcanic Province.](image)

**Profile LMAC - Archers Creek, (ANU 54857)** (Figure 8.2, Plate 8.1)

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<tr>
<th>Depth Range</th>
<th>Color/Description</th>
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<tr>
<td>000 - 100 cm</td>
<td>Gold (10YR 6/8) coloured goethitic soil (LMAC1)</td>
</tr>
<tr>
<td>100 - 200 cm</td>
<td>Deep orange (7.5YR 5/8) coloured goethitic soil (LMAC2)</td>
</tr>
<tr>
<td>200 - 210 cm</td>
<td>Deep brown (5YR 4/8) gravel to pebble sized, goethite coated, nodular material (LMAC3)</td>
</tr>
</tbody>
</table>

**Clay Rich Interval**

210 - 220 cm Strong orange (5YR 6/8) and dull orange (7.5YR 7/4) mottled clay (LMAC4).

**Upper Basalt**

220 - 290 cm Dark yellow to brownish olive (2.5Y 6/4, 2.5Y 5/4) weathered rubbly
clay-rich material (LMAC5, LMAC7) with gold (2.5YR 6/8, 7.5YR 6/8)
surface coatings, encloses vesicular, greyish olive (2.5Y 4/1, 7.5Y 4/1), intensely weathered corestones (LMAC6) with gold surface coatings (2.5Y 7/8).

290 - 540 cm Greyish olive (5Y 5/3, 2.5Y 5/3) basalt corestones (LMAC8, LMAC10) surrounded by brownish olive to yellowish brown (2.5Y 4/4, 10YR 4/4, 10YR 5/4) "onionskins" of more intensely weathered basalt (LMAC9). Surface coatings ranged in colour from deep orange (7.5YR 5/8) through brownish gold (10YR 5/8) to brownish olive (2.5Y 4/4).

540 - 655 cm Greyish olive (2.5Y 5/3) vesicular basalt at the base of the flow(LMAC12), higher in the sequence relict blocks of relatively fresh to incipiently weathered medium grey (N 5/0) basalt (LMAC22), with light yellowish brown (10YR 6/6) surface coatings, are exposed.

Clay Rich Interval
655 - 680 cm Greyish yellow (2.5Y 6/3) gleyed smectitic clay material (LMAC11, LMAC13, LMAC14).

680 - 695 cm A gold (10YR 6/8) coloured firm clay (LMAC15) with a dull orange yellow (2.5Y 7/6) surface coating.

Sediment Interval
695 - 890 cm Fining upward sequence of deep orange (5YR 5/8) weathered sediments (LMAC16, LMAC17, LMAC18, LMAC19). A well developed deep orange (5YR 5/8) zone with dull orange (7.5YR 7/6) or beige (10YR 7/3) mottles has formed as a result of the leaching of the sediment materials. Surface coatings range in colour from deep orange (5YR 5/8) through brown (5YR 3/6) to dark greyish brown (5YR 3/3).

Coarse (Fluvial) Sediment
910 - 920 cm Weathered gravelly gold (7.5YR 6/8) quartzose sediment (LMAC20) grades into the underlying conglomerate. Together they form a lens of fluviatile sediment that infills a small channel marginal to the lower basalt.

920 - 955 cm Unconsolidated conglomerate with rounded pebbles (LMAC21).

Lower Basalt
890 - 920 cm Greyish olive (2.5Y 3/2) weathered basalt (LMAC23) with light yellowish brown (10YR 6/6) surface coatings.

920 - 940 cm Greyish brown (10YR 5/3) weathered basalt (LMAC24) with light yellowish brown to dark greyish brown (10YR 6/4, 10YR 2/2) surface coatings.

940 - 995 cm Dark grey (N 3/0) massive, blocky basalt (LMAC25) with a white smectitic vesicle fill.
Millaa Millaa

This profile is located in a crest position in the topography, is deeply weathered and comprised of red coloured soil-like material with a relict spheroidal weathering texture preserved near the base of the outcrop. Generally the clay-rich materials do not preserve basaltic texture and indurated basalt was not encountered in this exposure. Samples were taken at approximately 70 cm intervals with QFT11/1 in the soil zone at the top and QFT11/7 at the base of the exposure.

---

Figure A.14

Local map for Millaa Millaa profile, Atherton Volcanic Province.

Profile QFT11 - Millaa Millaa, (ANU 54858) (Figure 8.7, Plate 8.10)

000 - 010 cm Gold (10YR 6/8) basaltic soil (QFT11/1)
010 - 020 cm Gold (10YR 7/8) basaltic soil (QFT11/2)
020 - 090 cm Gold (10YR 7/8) weathered basalt saprolite (QFT11/3)
090 - 160 cm Gold (10YR 7/8) weathered basalt saprolite (QFT11/4)
160 - 230 cm Dull orange yellow (10YR 7/6) weathered basalt saprolite (QFT11/5)
230 - 300 cm Dull orange yellow (10YR 7/6) weathered basalt saprolite (QFT11/6)
300 - 370 cm Dull orange yellow (2.5YR 7/6) weathered basalt saprolite (QFT11/7)
Palmerston Highway, Innisfail

This deeply weathered profile overlies incipiently weathered basalt exposed in a quarry face.

Figure A.15
Local map for Palmerston Highway profile, Innisfail, Atherton Volcanic Province.

Profile QFT8 - Palmerston Highway, Innisfail, (ANU 54859) (Figure 8.9, Plate 8.11)

000 - 040 cm Gold to strong reddish orange (7.5YR 6/8, 2.5YR 6/8) basaltic soil (QFT8/6, QFT8/7).

040 - 120 cm Dull orange to dull orange yellow (2.5YR 7/6, 5YR 7/6, 10YR 7/6) rubbly weathered basalt (QFT8/3, QFT8/4, QFT8/5).

120 - 430 cm Mottled dull orange yellow (10YR 7/6, 10YR 8/6) and dark bluish grey (5PB 4/1) kaolin group clay rich saprolite (QFT8/1, QFT8/2) Large darker grey coloured mottles are surrounded by more pallid clay.

Lower Basalt

>450 cm Incipiently weathered greyish yellow (2.5Y 8/1) basalt (QFT8/-1) exposed in a quarry face. Zones of greyish yellow (5Y 8/3) weathered basalt (QFT8/0) cross-cut the upper part of the lower basalt in a vein-like array. The contact between the relatively fresh indurated lower basalt and the overlying weathering profile is not exposed.
McBride Volcanic Province

The McBride Volcanic Province (Figure 8.1) lies approximately 150 km south west of Atherton and is bisected by the Kennedy Highway which truncates the Murronga Basalt approximately 12 km north of Conjuboy (18.35°S 144.44°E). A weathered profile on the Murronga Basalt was sampled in this road cutting. Although this basalt flow lies within a plains basalt field with subdued topography, local geomorphology suggests that this flow sits atop other flows and is relatively free draining. Ponding of waters within this flow was not apparent.

Kennedy Highway

![Local map for Kennedy Highway profile, McBride Volcanic Province.](image)

Profile QFT7 - Kennedy Highway, (ANU 54860) (Figure 8.11, Plate 8.13)

000 - 015 cm Light brown to yellowish brown (7.5YR 5/6, 5YR 5/4) dusty basaltic soil (QFT7/6, QFT7/7) with small pebbles of weathered basalt float throughout.

015 - 115 cm Dull yellow orange to deep orange (10YR 7/4, 7.5YR 5/8) rubbly weathered basalt (QFT7/4, QFT7/5).
Appendix 1: Basalt Weathering Profiles A-24

115 - 320 cm  Greyish yellow (2.5Y 8/2) massive basalt with blocky spheroidal weathering (QFT7/3) forming the body of the basalt flow.

320 - 400 cm  Pale beige to greyish yellow (10YR 8/1, 2.5Y 8/2) weathered basalt with poor corestone development (QFT7/1, QFT7/2) at the base of the flow unit.

Pebble sized fragments of weathered basalt fritters off the face and has formed a talus slope at the base of the exposure.

Nulla Volcanic Province

Approximately 150 km inland from Townsville, the Nulla Volcanic Province (Figure 8.1) lies to the south and south west of the Burdekin River. A profile was sampled in a small road aggregate quarry on the western side of Fletcher Vale Road (19.50°S 145.42E). Although this locality lies within a plains basalt field, ponding of waters within this flow was not apparent, and the profile appears to be free draining.

Fletcher Vale Road

![Local map for Fletcher Vale Road profile, Nulla Volcanic Province.](image)

Weathered basalt crops out in the wall of a small quarry from which it is extracted for road aggregate. A large scale, near vertical, rhombic, joint set forms jutting faces in the
excavated exposure. Most of the weathered basalt is blocky in nature but spheroidal weathering is well developed, especially lower in the profile. Central portions of larger blocks are only relatively fresh, hence this weathered basalt is useful road building material.

*Profile QFT 1 - Fletcher Vale Road, (ANU 54861)* (Figure 8.13, Plate 8.18)

000 - 010 cm  Dull orange yellow (2.5Y 7/3) skeletal basaltic soil.
010 - 100 cm  Greyish yellow to dull orange yellow (2.5Y7/3, 10YR 8/4, 2.5Y 8/4) weathered basalt (*QFT1/7, QFT1/8, QFT1/9*) formed flakes and veneers adjacent to joint planes.
200 - 300 cm  Greyish yellow (5Y 8/3, 7.5Y 8/2) incipiently weathered basalt (*QFT1/10, QFT1/6*) formed large joint bounded blocks.
300 - 400 cm  Dull orange yellow to dull yellow (2.5Y 7/6, 2.5Y 8/6, 5Y 8/4) weathered basalt, increasingly more weathered outward from corestones (*QFT1/2, QFT1/3, QFT1/4, QFT1/5*), is enclosed within rubbly dull orange yellow (2.5Y 7/4) weathered basalt (*QFT1/1*).
Table A.2.1 Chemical analyses for unweathered basalts as used for isocon interpretation of geochemical data

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Appendix 2: Least Weathered Equivalents A-28

Table A.1 Notes

* Total iron is expressed as Fe2O3 unless an analysis for FeO is shown

1 Nepheline-hawaiite from Northwest Tasmania
   (F. L. Sutherland unpublished data, sample DR1180)

2 Quartz-tholeiitic basalt from North Tasmania
   (F. L. Sutherland unpublished data, sample DR11808)

3 Alkali basalt from Northeast Tasmania
   (F. L. Sutherland unpublished data, sample DR11804)

4 Alkali basalt from Monaro Volcanic Province
   (Kesson 1972, sample K65 and Roach 1991, unpublished data, sample R3)

5 Hawaiite from Warrumbungle Volcanic Province
   (M. B. Duggan and B. W. Chappell, unpublished data, sample EAV30)

6 Quartz-tholeiitic basalt from Ebor Volcanic Centre
   (M. B. Duggan and B. W. Chappell, unpublished data, sample EAV214)

7 Olivine-tholeiitic basalt from Tweed Volcanic Province
   (Ewart et al, 1977, sample OR21, and Ewart 1982, sample 33037)

8 Hawaiite from Springsure Volcanic Province
   (Ewart, 1982, sample 38747 and A. Ewart, unpublished data, sample AK71)

9 Basanite from Peak Range Volcanic Province
   (J. Knutson and B. W. Chappell, unpublished data, sample EAV87)

10 Basanite from Atherton Volcanic Province
   (P. J. Stephenson and B. W. Chappell, unpublished data, sample EAV234)
APPENDIX 3

GEOCHEMICAL DATA
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Appendix 4: Clay Separate Chemistry and CEC A-54
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Appendix 4: Clay Separate Chemistry and CEC A-56
APPENDIX 5

BASALT GROUNDWATER SAMPLING AND ANALYTICAL METHODS

A.5.1 Water Sampling and Field Tests

Water Sampling for Anion-Cation Analysis

Two by 120 ml water samples were collected at each site, in sterile bottles that had been washed in the laboratory and were thoroughly rinsed in spring water prior to sampling. One 120 ml sample was acidified with a few drops of concentrated nitric acid (HNO₃) in order to keep any ions in solution that might otherwise precipitate out. Samples were kept on ice in a cooler for the return trip to Canberra and thereafter were stored at less than 4°C in the ANU Geology Department cool room until they were analysed. Analyses for cation and anion concentrations were run as soon as possible after sampling.

Turbidity, Colour, Odour

Turbidity and colour were assessed using visual comparison with nanopure water in glass and odour by "sniff test" comparison with odourless nanopure water.

Independent Water Temperature and pH

Independent water temperature was measured by immersing a standard laboratory mercury bulb thermometer into the issuing spring water, allowing the thermometer to stabilise, and reading it in the normal fashion. Water temperature was measured six times at each locality and the average temperature used as the final independent water temperature result. In all cases the HYDROLAB water temperature and independent water temperature measurements corresponded very well.

The measurement of pH was carried out using a Radiometer Copenhagen PHM 80 portable pH meter which was calibrated in the field and was adjusted for measured water temperature. pH was measured six times at each locality and the average pH used as the final independent pH measurement. In most cases the HYDROLAB pH measurements and the independent pH measurements corresponded well, and where there was a
discrepancy, additional pH measurements were taken in the field, and once again upon return to the laboratory.

HYDROLAB Tests

The HYDROLAB is a multi-probe device that is capable of measuring water temperature, water pH, dissolved oxygen concentration and electrical conductivity at the same time. The sample sites are at a similar altitude to Canberra, therefore it was appropriate to calibrate the HYDROLAB in the laboratory prior to, and after its use in the field. In addition there are automatic compensating electronics within the instrument.

At all localities it was not possible to immerse the HYDROLAB probes in spring water directly. Instead the probe cup provided was filled with sample water, the probes were immersed and the required values read off. This procedure was carried out six times for each sample and an average of these readings used as the final HYDROLAB information for each site each month.

Field Bicarbonate Test

Bicarbonate concentration was measured in the field as this concentration may change over a period of time if the waters are allowed to interact with atmospheric CO2. The technique used for the field bicarbonate test follows.

While stirring continuously, 0.02 N (N) sulphuric acid was titrated into a 200 ml (V1) sample of spring water, until the solution reached pH 4.7. The exact titrant volume (V2) and pH was recorded and then further acid was added to reduce the pH by exactly 0.3 units. The total titrant volume (V3) was recorded and then total alkalinity was calculated using the formula:

\[
\text{Total Alkalinity (mg/l CaCO}_3\text{)} = \frac{(2 \times V2) - V3 \times N \times 50,000}{V1}
\]
A.5.2 Laboratory Analysis

Atomic Absorption Spectrophotometry (AAS) Analysis of Cations

Concentrations of calcium, magnesium, sodium, potassium, iron and manganese were measured using standard techniques (Greenberg et al. 1992) on a Perkin Elmer 3100 Atomic Absorption Spectrophotometer (AAS) with Flow Injection Analysis System (FIAS) and automatic sampler, in the Applied Science Department, University of Canberra. Detection limits for the analyses are recorded in Table A.5.1.

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A.A.S. Atomic Absorption Spectrophotometry
F.I.A. Flow Injection Analysis

Table A.5.1
Detection limits for the analytical techniques employed for cation and anion analysis, Atomic Absorption Spectrophotometry (A.A.S.) and Flow Injection Analysis (F.I.A.) respectively.

Flow Injection Analysis (FIA) of Anions

Chloride concentration was measured using the Automated Ferricyanide method, sulphate concentration using the Automated Methyl Thymol Blue method, and nitrate and nitrite concentration using the Automated Cadmium Reduction method (Greenberg et al. 1992), on a TECATOR Flow Injection Analyser (FIA), in the Applied Science Department, University of Canberra.
A.5.3 Water Data Quality

Cation-Anion Balance

Water data quality was tested using a cation-anion balance where:

\[
\% \text{ imbalance} = \frac{(\text{anion concentration (meq/l)} - \text{cation concentration (meq/l)})}{(\text{anion concentration (meq/l)} + \text{cation concentration (meq/l)})}
\]

Any samples with % imbalance greater than 20% were discarded.

Total Dissolved Solids (TDS)

Because electrical conductivity is a measure of the concentration of salts in solution, if the total concentration of ions measured is divided by the measured conductivity a constant should be derived as expressed in the following relationship:

\[
\text{Calculated Total Dissolved Solids (mg/l)} = \frac{\text{Conductivity}}{0.55 \text{ to } 0.7}
\]

where the constant lies in the range 0.55 to 0.7 (Greenberg et al. 1992). In reality there may be a little more error in this constant than the range given suggests.

The samples from BW1 gave an average constant of 0.68, and for the three aquifers BW2, SW1 and SW2, the average constants for this relationship lay between 0.87 and 0.89. This implies that the conductivity measurements may have been slightly underestimated. However, the values for the three aquifers corresponded so closely that even if the data contained a small error, relative comparisons would still be valid.
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* Intercalated Sediments and Neoformed Clay Segregations
# APPENDIX 7

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