1984

Hydrothermal Alteration Zoning And Gold Concentration At The Kerr-addison Mine, Ontario, Canada

Augusto Kishida

Follow this and additional works at: https://ir.lib.uwo.ca/digitizedtheses

Recommended Citation
https://ir.lib.uwo.ca/digitizedtheses/1372

This Dissertation is brought to you for free and open access by the Digitized Special Collections at Scholarship@Western. It has been accepted for inclusion in Digitized Theses by an authorized administrator of Scholarship@Western. For more information, please contact tadam@uwo.ca, wlswadmin@uwo.ca.
NOTICE

The quality of this microfiche is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us a poor photocopy.

Previously copyrighted materials (journal articles, published tests, etc.) are not filmed.

Reproduction in full or in part of this film is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30. Please read the authorization forms which accompany this thesis.

THIS DISSERTATION HAS BEEN MICROFILMED EXACTLY AS RECEIVED

AVIS

La qualité de cette microfiche dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de mauvaise qualité.

Les documents qui font déjà l'objet d'un droit d'auteur (articles de revue, examens publiés, etc.) ne sont pas microfilmés.

La reproduction, même partiel, de ce microfilm est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30. Veuillez prendre connaissance des formules d'autorisation qui accompagnent cette thèse.

LA THÈSE À ÉTÉ MICROFILMÉE TELLE QUE NOUS L'AVONS RECEUE
HYDROTHERMAL ALTERATION ZONING AND GOLD CONCENTRATION
AT THE KERR-ADDISON MINE, ONTARIO, CANADA

by
Augusto Kishida

Department of Geology

Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Faculty of Graduate Studies
The University of Western Ontario
London, Ontario
July, 1984

© Augusto Kishida 1984.
ABSTRACT

Kerr-Addison, a major Archean lode gold deposit of the Abitibi Belt, with a production of 10 x 10^6 oz Au (up to 1983), is localized in a zone of talc-carbonate and chlorite-carbonate rocks, immediately south of a regional structural break the Kirkland Lake-Larder Lake Fault Zone (KLFZ). Relict volcanic textures and the ratios of diagnostic relatively less mobile elements indicate that most of the wall rocks of the mine were originally mafic and ultramafic rocks along with their clastic derivatives. Petrographic and geochemical studies reveal greenschist facies metamorphism with a superposed distinct zonation of hydrothermal alteration, characterized by massive introduction of CO2 and variable enrichments of alkali-metals and calcium, which produced a great variety of mineral assemblages. These assemblages are classified into: a) metamorphic assemblages; b) an initial stage of alteration; and c) advanced stage of alteration. The alteration stages are in turn divided into alteration types, based on the presence of certain diagnostic minerals.

Alteration types of the initial stage contain chlorite which is replaced by muscovite or albite in the advanced stage of alteration. The proportion of carbonate minerals also become augmented in this process. Numerous generations of cross-cutting veins are enveloped by alteration borders in which the sequence of the Al-bearing minerals,
namely albite, muscovite and chlorite develop from the vein to the wall rocks always in the same sequence. The same sequence is observed at a larger scale from the ore zone to the periphery of the mine area.

Oxygen isotope data indicate fairly constant temperatures (270^\circ\text{-}300^\circ\text{C}), and isotopic composition of hydrothermal fluids (\delta^{18}O = 5^\circ/_{00}) across the alteration zoning.

The intensity of alteration can be monitored by "saturation indices" \( \text{CO}_2/(\text{Ca}+\text{Fe}+\text{Mg}) \) for carbonates; and (3K+Na), 3K/Al and Na/Al for muscovite + albite, muscovite and albite respectively (molar ratios). Plots of moving averages of these indices across the 3850' level of the mine reveals a remarkable correspondence to variations of gold abundance, suggesting a genetic relationship of gold enrichment to hydrothermal alteration. On a broad scale, gold is concentrated to the south of the KLFZ, and at a more detailed scale in the transition zone between carbonate-muscovite and carbonate-albite alteration types. The enrichment of gold at one side of the fault zone is interpreted as the result of development of a metasomatic zoning induced by gradients in oxidation state, the metal being concentrated in the reducing side. Zonation of alteration types south of the KLFZ is regarded as representing various steps of a continuous process of incremental changes of the rocks to adapt to the composition of an externally generated fluid, whilst in turn,
the infiltrating fluid evolves via local reaction with rocks. Successive generations of fracture arrays and veins have the same alteration patterns and thus the composition of the incoming hydrothermal fluid seems to have remained essentially unchanged through time.

Gold mineralization at the Kerr-Addison mine and its contiguous alteration halo are interpreted as the result of repeated cycles of fracturing, fluid penetration and local reaction with rocks. Fluid-rock interaction produced lateral variations of fluid composition which led to gold concentration, probably due to gradients in pH, in the interface between the carbonate-muscovite and carbonate-albite alteration types.
ACKNOWLEDGMENT

Firstly, I wish to express my gratitude to Dr. W. S. Fyfe for providing me with the opportunity to come to The University of Western Ontario and Dr. Robert Kerrich for supervising the writing of this thesis.

My tenure in the Department of Geology has been a rewarding experience thanks to the support and friendship of the faculty, staff and students. I thank each and every one of them.

Special thanks to Bill Church, Mauricio, Lydia and Marjorie for their continuous encouragement and stimulating discussions.

This thesis was financially supported by Conselho Nacional de Pesquisas (Brasil), Rio Doce Geologia e Mineracao and research grants through Dr. Robert Kerrich. I am also indebted to the management and geological staff of the Kerr Addison Mines.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter/Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>CERTIFICATE OF EXAMINATION</td>
<td></td>
<td>11</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td></td>
<td>111</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td></td>
<td>vi</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td></td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF PHOTOGRAPHIC PLATES</td>
<td></td>
<td>ix</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td></td>
<td>xii</td>
</tr>
</tbody>
</table>

**CHAPTER 1 - INTRODUCTION**

1.1 Statement of the problem

**CHAPTER 2 - GOLD TRANSPORT AND DEPOSITION**

2.1 Introduction
2.2 Solubility of gold
   - 2.2.1 Gold chloride
   - 2.2.2 Sulphide complexes
2.3 Precipitation mechanisms
2.4 Fluid composition, wall rocks and flow regime

**CHAPTER 3 - GEOLOGICAL SETTING**

3.1 Regional geology
3.2 Local geology
3.3 Ore types
3.4 Previous work in the Kerr-Addison mine

**CHAPTER 4 - ORIGINAL ROCK TYPES**

4.1 Introduction
4.2 Geochemical data
4.3 Possible origin of altered rocks

**CHAPTER 5 - ALTERATION MINERAL-ASSOCIATION**

5.1 Introduction
5.2 Metamorphic assemblages
5.3 Mineralogy of the initial stage of alteration
   - 5.3.1 Ultramafic rocks
   - 5.3.2 Mafic rocks
5.4 Mineralogy of the advanced stage of alteration
5.5 Mineral composition
5.6 Mutual relationships of alteration types
5.7 Distribution of alteration types
5.8 Summary and discussion
CHAPTER 6 - GEOCHEMISTRY OF ALTERATION .............................................. 90
6.1 Introduction ............................................................... 90
6.2 CO₂ enrichment ......................................................... 91
6.3 Alkali-metal enrichment ................................................ 92
6.4 Distribution of alteration types ....................................... 93
6.5 Mobility of other elements ............................................. 96
6.6 Discussion of chemical mass balance ................................. 99
6.7 Distribution of gold relative to the alteration types ............... 103

CHAPTER 7 - OXYGEN ISOTOPE DATA ...................................................... 115
7.1 Introduction ............................................................... 115
7.2 Results ........................................................................ 116
7.3 Thermometry ............................................................... 117
7.4 Summary ...................................................................... 121

CHAPTER 8 - FLUID-WATER INTERACTION .............................................. 130
8.1 Introduction ............................................................... 130
8.2 The C-O-H system and oxidation state .............................. 131
8.3 Alteration reactions ....................................................... 135
8.3.1 Initial stage of alteration ............................................ 135
8.4 Inferences from the initial stage of alteration ....................... 138
8.5 Advanced stage of alteration .......................................... 140
8.6 Variation of fluid composition .......................................... 145
8.7 Fluid flow regime ......................................................... 148

CHAPTER 9 - METASOMATIC ZONING ....................................................... 172
9.1 Introduction ............................................................... 172
9.2 Metasomatic zoning at Kerr-Addison .................................. 173

CHAPTER 10 - COMPARISON WITH OTHER ARCHEAN GOLD DEPOSITS, SUMMARY AND CONCLUSIONS ...................................................... 184
10.1 Introduction ............................................................... 184
10.2 Alteration types in other Archean gold deposits .................... 185
10.3 Summary and conclusions .............................................. 187

** ** ** **

APPENDIX 1. WHOLE ROCK GEOCHEMICAL DATA ....................................... 195
APPENDIX 2. SUMMARY OF ANALYTICAL TECHNIQUES ....................... 201
APPENDIX 3. LOCATION OF SAMPLES .................................................. 206
VITA .................................................................................. 210
REFERENCES ......................................................................... 212
<table>
<thead>
<tr>
<th>Plate</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Relict textures and fabrics</td>
<td>54</td>
</tr>
<tr>
<td>2</td>
<td>Photomicrographs of altered ultramafic rocks</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>Photomicrographs of altered mafic rocks</td>
<td>82</td>
</tr>
<tr>
<td>4</td>
<td>Progressive alteration of a variolitic textured mafic rock</td>
<td>84</td>
</tr>
<tr>
<td>5</td>
<td>Small scale alteration zoning</td>
<td>86</td>
</tr>
<tr>
<td>6</td>
<td>Evidence of fluid penetration at different scales</td>
<td>88</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>-------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>2.1</td>
<td>Calculated slopes for solubility curves of selected gold complexes</td>
<td>20</td>
</tr>
<tr>
<td>3.1</td>
<td>Stratigraphic succession of the Kirkland Lake area, South Limb of the Synclinorium, after Jensen, 1980</td>
<td>39</td>
</tr>
<tr>
<td>4.1</td>
<td>Representative chemical analyses of altered ultramafic rocks from the Kerr-Addison mine compared to komatiitic volcanics from Munro Township</td>
<td>55</td>
</tr>
<tr>
<td>4.2</td>
<td>Comparison of chemical analyses of talc-rich exhalative sediments with talc-rich rocks of the Kerr-Addison mine</td>
<td>56</td>
</tr>
<tr>
<td>4.3</td>
<td>Comparison of selected elements from igneous carbonatite and carbonate rocks from the Kerr-Addison mine</td>
<td>57</td>
</tr>
<tr>
<td>5.1</td>
<td>Composition of carbonates</td>
<td>89</td>
</tr>
<tr>
<td>7.1</td>
<td>Oxygen isotope data</td>
<td>128</td>
</tr>
<tr>
<td>7.2</td>
<td>Oxygen isotope fractionation factors</td>
<td>129</td>
</tr>
<tr>
<td>8.1</td>
<td>Simplified reactions of fluid-rock interaction at the Kerr-Addison mine</td>
<td>169</td>
</tr>
<tr>
<td>8.2</td>
<td>Modal composition of altered mafic rocks</td>
<td>171</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Contours of gold solubility for Au(HS)₂ and AuCl₂ (in ppm) at 300°C, after Seward (1984)</td>
<td>18</td>
</tr>
<tr>
<td>3.1</td>
<td>Geology of Timmins-Kirkland Lake area, and location of the Kerr-Addison mine (geology after Jensen, 1978)</td>
<td>33</td>
</tr>
<tr>
<td>3.2</td>
<td>Structural geology of the Larder Lake area</td>
<td>35</td>
</tr>
<tr>
<td>3.3</td>
<td>Schematic cross section of the Kerr-Addison mine</td>
<td>37</td>
</tr>
<tr>
<td>4.1</td>
<td>Al₂O₃, Sc and log MFe/Al₂O₃ versus TiO₂ of altered ultramafic rocks of Kerr-Addison</td>
<td>47</td>
</tr>
<tr>
<td>4.2</td>
<td>Zr, Sc and Al₂O₃ versus Ti for altered mafic rocks of Kerr-Addison (in ppm)</td>
<td>49</td>
</tr>
<tr>
<td>4.3</td>
<td>Plot of Zr-Ti/100-3Y of altered mafic rocks of Kerr-Addison</td>
<td>52</td>
</tr>
<tr>
<td>5.1</td>
<td>Mineral assemblages of altered rocks</td>
<td>75</td>
</tr>
<tr>
<td>5.2</td>
<td>Sketch of alteration zoning enveloping a carbonate-albite-quartz vein in an altered mafic rock</td>
<td>77</td>
</tr>
<tr>
<td>5.3</td>
<td>Sketch of alteration zoning in an ultramafic breccia</td>
<td>77</td>
</tr>
<tr>
<td>5.4</td>
<td>Sketch of alteration zoning associated to carbonate-albite-quartz vein cutting ultramafic rock which is dominated by carbonate-muscovite alteration</td>
<td>77</td>
</tr>
<tr>
<td>6.1</td>
<td>Variations of alteration stages across the 3850' level of the Kerr-Addison mine, relative to saturation indices of CO₂ and alkali-metals</td>
<td>105</td>
</tr>
<tr>
<td>6.2</td>
<td>FeO, MgO, and FeO/MgO versus Ti plots of altered ultramafic rocks of the Kerr-Addison mine</td>
<td>107</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>6.3</td>
<td>FeO, MgO, and FeO/MgO versus Ti diagrams of altered mafic rocks from the Kerr-Addison mine</td>
<td>109</td>
</tr>
<tr>
<td>6.4</td>
<td>Frequency distribution of molar ratio CO₂/CaO of altered mafic and ultramafic rock of the Kerr-Addison mine</td>
<td>111</td>
</tr>
<tr>
<td>6.5</td>
<td>Distribution of moving averages to Au across the 3850' level of the Kerr-Addison mine, compared to the saturation indices of CO₂ and alkali-metals</td>
<td>113</td>
</tr>
<tr>
<td>7.1</td>
<td>Variations of 18O minerals according to stage of alteration (A) and original rock types (B)</td>
<td>123</td>
</tr>
<tr>
<td>7.2</td>
<td>Frequency of calculated temperatures</td>
<td>124</td>
</tr>
<tr>
<td>7.3</td>
<td>Oxygen isotope thermometry</td>
<td>126</td>
</tr>
<tr>
<td>8.1</td>
<td>Composition of C-O-H gas at 2 kbar in the presence of graphite (from Eugster and Skippen, 1967)</td>
<td>151</td>
</tr>
<tr>
<td>8.2</td>
<td>Isobaric, isothermal log fO₂-XC diagrams showing schematic phase relations in the systems Fe-C-O-H (A) and Fe-Si-C-O-H (B)</td>
<td>153</td>
</tr>
<tr>
<td>8.3</td>
<td>Temperature-XCO₂ diagram for the systems MgO-SiO₂₂-CO₂-H₂O and CaO-MgO-SiO₂₂-CO₂-H₂O at 2 kbar</td>
<td>155</td>
</tr>
<tr>
<td>8.4</td>
<td>Schematic isobaric, isothermal, log a(K⁺/Na⁺) versus XCO₂ diagram of reaction 6 of the text</td>
<td>155</td>
</tr>
<tr>
<td>8.5</td>
<td>Schematic H₂O-CO₂ diagrams, showing the slope of alteration reactions of ultramafic (A) and mafic rocks (B) as presented in the text</td>
<td>157</td>
</tr>
<tr>
<td>8.6</td>
<td>Schematic diagram showing the slopes of reaction 7 in log a(K⁺/H⁺) ×CO₂ space, assuming constant aMg⁺² and aFe⁺², and ideal behavior of CO₂-H₂O mixtures</td>
<td>159</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>8.7</td>
<td>Schematic stability relations in the system K₂O-Na₂O-Al₂O₃-SiO₂-H₂O-HCl at 3000°C and 15000 psi (1 kb) after Montoya and Hémley (1975).</td>
<td>161</td>
</tr>
<tr>
<td>8.8</td>
<td>Mass balance of alteration reaction involving chlorite, ankerite, muscovite, albite, and fluid</td>
<td>163</td>
</tr>
<tr>
<td>8.9</td>
<td>Schematic diagram illustrating the possible relations of fluid composition and alteration types</td>
<td>165</td>
</tr>
<tr>
<td>8.10</td>
<td>Schematic diagram indicating possible evolution of the fluid-flow regime with time</td>
<td>167</td>
</tr>
<tr>
<td>9.1</td>
<td>Diagram illustrating the development of metasomatic zoning due to original compositional gradients (after Thompson, 1959)</td>
<td>178</td>
</tr>
<tr>
<td>9.2</td>
<td>Schematic model for the development of metasomatic zoning due to the original contrast in oxidation state between rocks of the relatively oxidized Kinojevis group and the reduced Larder Lake group</td>
<td>180</td>
</tr>
<tr>
<td>9.3</td>
<td>Schematic model for the development of metasomatic zoning due to fluid infiltration</td>
<td>182</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 Statement of the problem

It is widely accepted that Archean "lode gold deposits"* are derived from the flow of large volumes of hydrothermal solutions, with gold precipitating in vein conduits, or on the sea floor upon cooling and/or mixing with sea water. The requirements for the successful formation of a hydrothermal deposit (Fyfe and Henley, 1973; Elder, 1976; Spooner, 1976) can be summarized as follows:

1) an adequate supply of water; 2) source rocks from which metals can be extracted; 3) an energy source to move the fluids; 4) focused fluid discharge; 5) a mechanism of

*A lode gold deposit is here understood to convey the meaning of any gold deposit in which gold is the principal economic metal recovered exclusive of placer and paleo-placer concentrations.
producing localized and selective precipitation of the valuable metal.

It has been shown that large scale heat and fluid transport occur in geological situations such as cooling of igneous bodies (Lister, 1974; Norton and Knight, 1977), and the dehydration of rocks during metamorphism (Fyfe et al., 1978, Chapter 4). Experimental data on the reaction of hot water with rocks (Hajash, 1975; Bischoff and Dickson, 1975) suggest that metals can be extracted from rocks with low primary concentration. Studies of heat flow indicate that the thermal gradient in many geologic situations favors focused discharge of fluids (Strauss and Schubert, 1977; Ribando et al., 1976). With the intense interest in the various aspects of hydrothermal systems over the past decade, it is now apparent that large scale flow of hot fluid has a major role in crustal evolution and the formation of mineral deposits (Fyfe and Lonsdale, 1981; Hutchinson et al., 1980).

Recent studies of mineral deposits have confirmed that they are part of fossil hydrothermal systems. Observation of an increasing number of active and fossil hydrothermal sites, however, show that the majority have a conspicuous lack of significant concentrations of ore minerals. These observations together emphasise the importance of a mechanism to promote localized and selective precipitation of a metal to form an economic deposit.
Surprisingly, in the particular case of Archean lode gold deposits, relatively less attention has been paid to the mechanism of selective metal precipitation. It has been suggested that gold was precipitated upon mixing with sea water, cooling along conduits, boiling of solution or reaction of the solution with wall rocks, but very few studies are dedicated specifically to the trapping mechanism.

Drilling and underground access for mining operations provide the opportunity for direct observation of the metal deposition site. Many Archean gold deposits are surrounded by a large alteration halo produced by the action of hydrothermal fluids on the wall rocks. The study of such alteration halos can therefore provide insight into the conditions of the metal precipitation.

From the above considerations this thesis addresses some aspects of the problems concerned with the conditions of gold precipitation in Archean lode deposits, taking as a particular example the relationship between hydrothermal alteration of wall rocks and gold concentration in a major gold producer of the Archean Abitibi Belt. The Kerr Addison mine was chosen considering the conspicuous hydrothermal alteration of the rocks in the mine area and the relatively well known geology.

Previous workers on the Kerr-Addison mine and surrounding area have provided a sound geologic data base
allowing this study to concentrate on the alteration processes. As a setting to the problem a brief review of the geochemistry of gold and previous geological work in the area are presented (Chapters 2 and 3). The present geochemical study commences with a discussion of the composition of the altered rocks and their possible precursors in Chapter 4, followed by descriptions of the mineralogy and geochemistry of different alteration types (Chapters 5 and 6). In the final chapters (7, 8, 9) the data are collectively interpreted, with some speculation on the nature of the fluids involved and the possible role of the fluid-rock interaction as a control of gold mineralizations.
CHAPTER 2

GOLD TRANSPORT AND DEPOSITION

2.1 Introduction

It has been suggested that gold can be transported in hydrothermal systems as Cl, S, As, Te, Sb, Br or I bearing complexes. More recently carbonyl has been considered a possible ligand in hydrothermal systems (Kerrich and Fyfe, 1981; Hutchinson and Burlington, 1984). However the few available theoretical and experimental studies are largely concerned with the solubility of gold in alkali-chloride or alkali-sulfide solutions.

Helgeson and Garrels (1968) using theoretical and "geological" parameters estimated the gold content of a mineralizing hydrothermal fluid to be between $10^{-3}$ and $10^{-2}$ ppm. They assumed an idealized quartz vein with 10 ppm Au where quartz, pyrite and gold have precipitated upon cooling from 300°C to 200°C. In this case the mineralized vein
is enriched in gold by a factor of 10^4 relative to the saturated solution.

Hydrothermal fluids at high temperatures are rarely accessible and the only available samples come from active geothermal springs and wells with temperatures of up to 300°C. The gold content in geothermal waters is low, on the order of 10^-5 ppm (Weissberg et al., 1979). Nevertheless, precipitates with an excess of 50 ppm have been recorded in Pōdīkew, Waiotapu, Rotokaua and Kawerau in New Zealand and Steamboat Springs in Nevada (Weissberg, 1969; Weissberg et al., 1979; Seward, 1984). This spectacular enrichment of 10^7 times indicates that an efficient concentration mechanism and a very large volume of solution must be involved in the formation of economic deposits.

Fyfe and Kerrich (1984) estimated that the minimum fluid volume involved in the genesis of a gold deposit is 10^3 times larger than the volume of the ore body. If no pre-enriched source rocks are available, such a fluid volume has to collect gold from a volume of rocks at least 10^5 times larger than the ore body (Fyfe and Kerrich, 1984).

As commented above, large scale heat and fluid transport occur in various geological situations. Mechanisms of gold extraction from rocks and the generation of gold-bearing solutions have been discussed by many
authors (Fyfe and Henley, 1973; Kerrich and Fryer, 1979, 1981; Kerrich et al., 1984; Fyfe and Kerrich, 1984; Keays, 1984). There is no general agreement on the subject and the various hypotheses involve circulation of meteoric or sea water, diagenesis, metamorphic dehydration, magmatic fluids or even mantle degassing. It is not the intention of the author to present a detailed review of the controversies involving the generation of the solutions. It is here assumed that the fluid and metal are available, leaving this thesis study to concentrate on the mechanisms of metal precipitation and enrichment of rocks. To paraphrase Fyfe and Kerrich (1984), "the fact is that metal is transported".

In order to provide a framework for discussing possible mechanisms of gold precipitation from hydrothermal fluids, a brief review of the available data on gold solubilities is presented below.

2.2 Solubility of gold

Ogryzlo (1935) has shown that gold is soluble in alkali chloride and sodium bisulfide solutions at elevated temperatures. He found that up to 300°C the solubility of gold chloride increases with increasing temperature, concentration of Cl, acidity and availability of oxygen. For gold sulfide he found that gold solubility increases with increasing temperature and concentration of NaHS but diminishes with acidification and oxidation of the
solution. Since the early experiments of Ogryzlo (1935) the controversies involving those authors favoring gold transport in acidic solutions (gold chlorides) and those favoring neutral to alkaline solutions (gold-sulphide complexes) have not yet reached a consensus.

2.2.1 Gold chloride

The only major study on the solubility of gold at high temperatures in chloride solutions is that of Henley (1971) who measured the solubilities from 300°C to 500°C, at 1 and 2 kbar in solutions of 1 and 2 M KCl. These experiments were buffered by a K-feldspar-muscovite-quartz assemblage in the presence of hematite-magnetite. Henley (1971) found solubilities of 10 to 50 ppm up to 400°C and solubilities in excess of 1000 ppm above 450°C. The poor reproducibility of the results was attributed by Henley (1971, 1973) to the uncertainty of the temperature determinations. He concluded that there is a near exponential increase in the solubility of gold at temperatures greater than 450°C.

Various other studies on the solubilities of gold chlorides show contradictory results. Anderson and Burnham (1967) and Glyuk and Khlebnikova (1982) found levels of gold solubility in NaCl and KCl solutions similar to those reported by Henley (1971). However Anderson and Burnham (1967) performed their experiments without solid buffers, whereas Glyuk and Khlebnikova (1982) utilized feldspar-
mica-quartz buffer assemblage (granitic powder) but no fO₂
buffer. Similar results in buffered and unbuffered experi-
ments are unexpected and difficult to reconcile, but these
results indicate that the solubility of gold chloride is
apparently unaffected by changes in pH or fO₂.

In contrast, Rytuba and Dickson (1977), who measured
the solubility of gold in 1 m NaCl solution in equilibrium
with pyrite and pyrrhotite up to 500°C and 1 Kb, found a
significantly lower solubility than the experiments report-
ed above. At 450°C, gold concentrations were less than
0.15 ppm, and at 500°C they were around 1.5 ppm. These
data when compared to the high concentrations found by
Henley (1971) seem to indicate that fO₂ and pH do have a
pronounced influence on the solubility of gold.

Another question concerning gold transport as chloride
complexes is that of stoichiometry. With few exceptions
(e.g., Krauskopf, 1951) most authors agree that up to 400°C
the dominant species in a gold chloride solution are ionic
aurous chloride such as AuCl₂ (Helgeson and Garrels,
1968; Henley, 1971, 1973; Fyfe and Henley, 1973; Seward,
1982). However, the measured gold solubilities above 450°C
(Henley, 1973) are several orders of magnitude higher than
those calculated by Helgeson and Garrels (1968) assuming
predominance of AuCl₂. Henley (1971) suggested that the
high solubility is due to stabilization of some molecular
species involving Au³⁺.
Gold occurs in two oxidation states in aqueous systems Au$^+$ and Au$^{3+}$ (Puddephatt, 1978). At high temperatures (up to 400°C) under moderately oxidizing conditions (hematite-magnetite buffer) and pH 4, the activity of Au$^{3+}$ is negligible in comparison to that of Au$^+$, and the activity ratio Au$^{3+}$/Au$^+$ decreases with increasing temperature (Heigeson, 1978; Seward, 1984). For this reason Seward (1984) speculates that the high solubilities found by Henley (1971) above 450°C may be due to formation of some ionic auric species with excess Cl$^-$. In fact, early experiments of Morris (1917), as reported by Mellor (1924) suggest the presence of ionic species in gold chloride solutions at high temperature. Morris (1917) found that at constant density, above 400°C, the solubility of gold chlorides decrease with increasing temperature. He also found that at constant temperature, under supercritical conditions, the solubility increases with increasing salinity. In addition to the buffered experiments commented on above, Henley (1971) performed a set of experiments with buffered perchloric acid between 400°C and 600°C which seem to confirm the results of Morris (1917). Henley (1971) reported that at constant density, the solubility of gold decreases with increasing temperature and that at constant temperature the solubility increases as pressure increases (Henley, 1971, p. 90). Such behaviour mimics that involving the dissociation of
ionic species.

In summary, available data on the solubilities of gold chlorides are contradictory but it is clear that gold transport by acidic chloride solutions under conditions of high $f_{O_2}$ is possible.

2.2.2 *Sulphide complexes*

Lindener and Gruner (1939) and Weissberg (1970) in experimental studies on the solubility of gold in alkali sulphide solutions up to 250°C, found solubilities as high as 200 ppm. Their results are in good agreement with the early experiments of Ogryzlo (1935).

More recently Seward (1973) carried out a detailed investigation of the stability and stoichiometry of Au$^+$-bisulphide complexes (thio complexes) in equilibrium with pyrite and pyrrhotite at temperatures up to 300°C and pH 3 to 10. He concluded that Au(HS)$_2^-$ predominates in near neutral solutions whereas Au$_2$(HS)$_2$S$_2^-$ occurs in more alkaline solutions. Seward (1973) demonstrated that solubility increases with increasing temperature and reduced sulphur concentration and that a pronounced solubility maximum occurs in the neutral pH region where the ratio $H_2S/HS^-$ = 1. The solubility of gold should then decrease with increasing oxygen fugacity and acidity. He was also able to obtain thermodynamic data for the formation of Au(HS)$_2^-$ and Au$_2$(HS)$_2$S$_2^-$ from 175 to 250°C.
The behavior of gold sulphide at higher temperatures is unknown, but the solubility is expected to decrease because the dissociation of \( \text{H}_2\text{S} \) is inhibited at high temperatures and the dissociation is not significantly affected by pressure (Ellis and Anderson, 1961). Limited experimental data of Rytuba and Dickson (1977) are in good agreement with these considerations.

2.3 Precipitation mechanisms

Precipitation of gold in Archean lode deposits has been variously interpreted as the result of mixing with seawater (Hutchinson et al., 1980), cooling along a geothermal gradient, or interaction with wall rocks (Helgerson, 1978; Fyfe and Henley, 1973) in consequence of removal of \( \text{CO}_2 \) (Fyfe and Kerrich, 1984) or \( \text{H}_2\text{S} \) (Phillips et al., 1984).

The solubility of a chemical component varies with changes in any extensive variable of the system. Therefore in principle gold can be precipitated from a saturated hydrothermal solution with shifts of any relevant physical or chemical parameter. Decreasing temperature in general diminishes gold solubility, but except for chloride solutions between 450° and 400°C, falling temperature is not an effective mechanism for gold extraction from a solution (Seward, 1973, 1984). Below 350°C a decrement of more than 100°C is required in order to lower the

The effect of changes in pH, \( \rho O_2 \), and concentration of the ligand on the solubility of gold is variable, and depends on the nature of the predominant soluble species. The calculated slopes of solubility variations of some possible gold complexes with changes in pH, \( \log f_{H_2} \), and total reduced S are shown in Table 2.1.

Near neutral conditions, 90% of gold can be precipitated from a saturated Au(HS)\(_2\) solution upon drop of 1 pH unit, or alternatively upon decrease of 0.2 molal of reduced S. Under more basic conditions the solubility increases with decreasing pH.

Changes of \( f_{H_2} \) affect the solubility of Au(HS)\(_2\) in different ways depending on the predominant sulphur species present in the fluid. In the region of predominance of oxidized S\(^{4+}\), the solubility of gold decreases as much as 4 orders of magnitude with a decrease of 1 \( \log a_{H_2} \). In contrast, in the region of predominance of reduced S\(^{2-}\), the same shift of \( a_{H_2} \) causes the solubility of gold to increase 1 order of magnitude (Fig. 2.1, Table 2.1). (Seward, 1973, 1984).

The solubility of gold chlorides are also sensitive to variations in pH and \( a_{H_2} \). An increase of the pH by 1
unit or alternatively the $aH_2$ by 2 log units may precipitate 90% of $\text{AuCl}_2^-$. The solubility of molecular auric chloride such as suggested by Henley (1973) would not be affected by changes in pH. However, more than 96% of molecular or ionic auric chloride may be extracted from a saturated solution with an increase of 1 log $aH_3$.

From the above discussion it is apparent that any of the above proposed mechanisms for gold precipitation from a saturated hydrothermal solution are in principle possible. Because precipitation by mixing with sea water or cooling of the solution are in large extent independent of the chemical or mineralogical composition of the wall rocks, their theoretical modelling can be relatively simple (Helgeson and Garrels, 1968). Such model calculations were performed by Helgeson and Garrels (1968), Henley (1971), Fyfe and Henley (1973), and Fyfe and Kerrich (1984).

Wall rock alteration has been quoted as a possible mechanism for gold precipitation in Archean lode gold deposits but studies correlating gold concentration with some specific alteration assemblages are sparse (e.g. Phillips et al., 1984; Phillips and Groves, 1984; Robert and Brown, 1984).

A major question concerned with metal precipitation by reaction of fluids with wall rocks is the capacity of such reactions to control the fluid composition.
2.4 Fluid composition, wall rocks and flow regime

It is generally accepted that under metamorphic conditions the composition of pore fluid is internally buffered, meaning that the fluid composition changes as it equilibrates with the surrounding rocks (Eyfe, 1958; Greenwood, 1975). Control of fluid composition by internal buffering represents one extreme of a spectrum of behaviour in nature. The other extreme occurs when rocks are continuously infiltrated by large amount of fluid from an external reservoir. Under these conditions the mineral composition and composition of the constituent minerals of rocks changes to adapt to the fluid composition (Rice and Ferry, 1982). Evidently in nature variations between the two end members is expected to occur.

Helgeson and Garrels (1968), in their modelling of gold transport assumed a hypothetical open fracture where hydrothermal fluid would flow without reacting with the wall rocks. In this case all the material in the vein was precipitated from the solution by cooling. It was clearly stated that non-interaction with rocks was assumed in order to simplify the calculations and that in a natural system where intense hydrothermal alteration is developed this assumption is not valid, and changes of fluid composition by wall rock interaction may have an important role (Helgeson and Garrels, 1968).

In order to apply simplified models to any lode gold
deposit, it is common practice to assume that in a focused hydrothermal discharge area, the water-rock interaction does not significantly affect the fluid chemistry. According to this approach, in a discharge area the volume of fluid greatly exceeds the buffer capacity of the rocks. A common enunciation of this assumption is that under conditions of small water to rock ratio the fluid composition is controlled by reaction with rocks whereas under conditions of large water to rock ratio the composition of the fluid is simply the composition of an external reservoir.

The total volume of fluid discharged by a hydrothermal system must be in fact very large but the total volume is a time integrated quantity. At any given time the water to rock ratio is limited by the porosity of the rock which is always relatively small. Therefore the extent to which the fluid composition is controlled by interaction with wall rocks depends on the flow rate relative to the reaction rate (Helgeson, 1970; Fyfe et al., 1978, Chapter 4).

It is well beyond the scope of this study to discuss the problems of kinetics and reaction rates between minerals and fluid phases. However it is warranted to emphasise that under a given set of conditions (P, T, flow-rate) the extent to which the hydrothermal fluid maintains its capacity to interact chemically with wall rocks depends essentially on the area of rock surface
exposed to the fluid. Helgeson (1970) calculated that an acidic fluid at 200° flowing through a hypothetical open fracture in granitic rock can travel several kilometers before losing 90% of its reacting capacity. The same fluid encountering a brecciated rock or porous arkosic unit would produce pervasive alteration of the rocks and lose its reacting capacity almost instantaneously owing to the large surface area of reaction (Helgeson, 1970).

Indications of large surface areas of rocks exposed to the hydrothermal fluid (closely spaced small veins, brecciated or porous rock) along with pervasive wall rock alteration and a consistent association of a specific type of alteration with gold concentration, can be regarded as evidence of the influence of rock-fluid interaction in gold precipitation. If the main mechanism of metal precipitation is cooling of the fluid, the mineralization should be concentrated in open space vein fillings, and exhibit a homogeneous distribution within the vein. A steep thermal gradient across an alteration halo can also be an indication of temperature control of deposition. Finally, evidences of metal concentration on or near the ocean floor, in conjunction with an abundance of chemically precipitated sediments, and the presence of more than one fluid reservoir, are possible indications of precipitation by mixing with cold sea water.
Figure 2.1

Contours of gold solubility for Au (HS)$_2$ and AuCl$_2$ (in ppm) at 3000°C, after Seward (1984). py = pyrite; po = pyrrhotite; hm = hematite; mg = magnetite. Vertical dashed lines give the equilibrium pH for albite (alb) - muscovite (musc) - kaolinite (kao) hydrolysis reactions where $a_{K^+} = 0.01; a_{Na^+} = 0.1$, using data from Montoya and Hemley (1975).
Table 2.1. Calculated slopes for solubility curves of selected gold complexes.

<table>
<thead>
<tr>
<th></th>
<th>( \text{Au(HS)}_2 )</th>
<th>( \text{AuCl}_2^- )</th>
<th>( \text{AuCl}_3^{2-} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{d \log \text{sol.}}{d \log aH_2} )</td>
<td>(-0.5 (1))</td>
<td>(-0.5)</td>
<td>(-1.5)</td>
</tr>
<tr>
<td>( \frac{d \log \text{sol.}}{d \text{pH}} )</td>
<td>(+4 (2))</td>
<td>(-1)</td>
<td></td>
</tr>
<tr>
<td>( \frac{d \log \text{sol.}}{d \log S_t} )</td>
<td>(+1.5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \frac{d \log \text{sol.}}{dT} )</td>
<td>(-0.01)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( d \log \text{sol.} \) = variation of log of solubility of gold

\( d \log S_t \) = variation of total reduced S (in molal)

\( dT \) = variation of temperature in °C

(1) for predominance of oxidized S

(2) for predominance of reduced S

After Seward (1972), Henley (1973), Burton (1983)
CHAPTER 3

GEOLOGICAL SETTING

3.1 Regional Geology

Kerr-Addison is not only the most prominent gold producer in the Kirkland Lake area but is also one of the largest producing mines in the Superior Province, more than 10 million oz Au having been extracted to date (Berton, 1983). The mine is located in Virginiatown, Ontario, on highway 66, 5 km west of the Quebec-Ontario border (Fig. 3.1). This chapter presents a synthesis of the regional geology, and local mine setting. This is followed by a brief review of previous work on the Kerr-Addison mine.

The Kirkland Lake area is underlain by Archean rocks of the Abitibi Greenstone Belt and, in places, by sedimentary rocks of the Proterozoic Cobalt Group (Goodwin, 1970). The geology of the area has been described by Thomson (1941a, 1941b, 1948), Ridler (1969, 1970, 1972),
(1978, 1979, 1980) and Downes (1978, 1980). It is beyond the scope of this study to critically review the regional and local geology or the controversies concerning the stratigraphic interpretations of the area. The most recent comprehensive study is that of Jensen (1981); his work is therefore extensively quoted in the following brief outline of the regional geology.

Archean rocks of the Kirkland area form two volcanic cycles, each composed of komatiitic, tholeiitic and calc-alkaline volcanics along with associated sedimentary and intrusive rocks. Each cycle is referred to as a Super-group. The Upper Super-group is overlain by sedimentary rocks of the Timiskaming Group which is locally associated with alkaline igneous rocks (Jensen, 1981).

The Archean supracrustal rocks are preserved in a large E-W trending synclinorium, located between the Round Lake and Abitibi Batholiths (Fig. 3.1). Two major fault zones, termed the Kirkland Lake-Larder Lake and the Destor-Porcupine Fault Zone, transect the south and north limbs of the synclinorium, respectively. Most of the gold deposits are located in the vicinity of these structures (Thomson, 1948).

The Kerr Addison mine lies on the south limb of the synclinorium, in the vicinity of the Kirkland Lake-Larder Lake Fault Zone (KLFZ) (Thomson, 1941). The ore deposit is hosted by the komatiitic Larder Lake Group of the Upper
Supergroup (Jensen, 1980). The stratigraphy of the southern limb of the synclinorium is given in Table 3.1.

Older Na-rich granitic batholiths and younger K-rich stocks and dikes intrude the supracrustal rocks. Most of the Na-rich batholiths occur along the periphery of the synclinorium, the K-rich stocks, which include monzonites, quartz monzonite, syenites and granodiorites, being concentrated along the Destor Porcupine Fault Zone and the KLFZ (Jensen, 1981).

Generally, rocks of the area underwent sub-greenschist facies metamorphism. Near the major batholiths, the metamorphic grade reaches greenschist to amphibolite facies (Jolly, 1974, 1978). Most of the rocks, except those along shear zones and those at the margin of the batholiths, show little or no penetrative deformation. Pillows, amygdules, tariolites and hyaloclastic textures are preserved throughout much of the volcanic sequence.

3.2 Local geology

The geology of the Kerr-Addison mine area has been described by the geological staff of the mine in several internal reports, as well as by Thomson (1941, 1948), Baker and geological staff (1957), Lovell (1972), and Lowrie and Wilton (1980). More recently, different aspects of the geochemistry and genesis of the deposit have been studied by Ridler (1970, 1972), Iihor and Crocket (1976; 1977),
Kerrich (1981, 1983), Kerrich and Hodder (1982) and

The major structural feature in the vicinity of the
mine is the Kirkland Lake-Larder Lake Fault Zone (KLFZ), a
structural break which juxtaposes contrasting suites of
rocks (Figs. 3.1 and 3.2). North of the break, tholeiitic
volcanics of the Kinojevis Group, together with alkalic
volcanics and sedimentary rocks of the Timiskaming Group
are folded into steeply east-plunging anticlines and
synclines. South of the break, komatiitic and tholeiitic
volcanic rocks of the Larder Lake Group are disposed in a
syncline which plunges to the SW (Downes, 1980; Jensen,

Sedimentary rocks to the north of the KLFZ are
generally fluviatile, contrasting with marine turbidites to
the south (Hyde, 1978; Jensen, 1980). Volcanic rocks to
the north contain magnetite (mafic volcanic rocks of
Kinojevis Group) and hematite (alkalic rocks of the
Timiskaming Group), indicating relatively oxidizing
conditions, as opposed to more reducing conditions to the
south as signified by the presence of carbonaceous shale.

The Kerr-Addison mine and adjoining former gold
producing areas (Chesterville and Cheminis) lie in a zone
of talc-carbonate and chlorite-carbonate rocks south of the
KLFZ. Generally the formations in this zone strike NE and
dip almost vertically to the NW (Fig. 3,5). Deformation in
the fault zone is pronounced, making determinations of
stratigraphic "top and bottom" intractable. However the
greywackes along the north side of the carbonate zone face
south (Thomson, 1941), such that the Larder Lake Group is
locally overturned, barring the presence of isoclinal
folds.

3.3 Ore types

Two principal types of ore are presently worked at the
Kerr-Addison mine. These are the so-called "carbonate" and
"flow" ores, both of which exhibit gross stratabound
features (Fig. 3,3). Carbonate ore consists of green Cr
muscovite-bearing quartz-carbonate rock, with intense
quartz-carbonate veins. Gold occurs principally as free
visible metal in quartz veins, but is also significantly
enriched in the green carbonate rock as a whole (Thomson,
1941; Lowrie and Wilton, 1980). In places the green
carbonate rocks exhibit relict spinifex texture (Downes,
1980). Flow ore is a quartz-chlorite-carbonate schist,
with variable amounts of sericite, albite, pyrite and
graphite. In this type of ore, most of the gold occurs
associated with fine grained pyrite. Relict volcanic
textures such as varieties, pillow and flow breccia are also
locally preserved in the flow ore (Thomson, 1941; Lowrie
Jensen and Trowell (1981) recognized in the ore zone of Kerr-Addison the following units from the footwall to the hanging wall: a) a pyritic graphite unit; b) a chromium muscovite dolomitic unit disrupted by a massive to pillowed tholeiitic lava flow; c) a pyritic laminated chert. The ore is bounded by polymictic mass-flow conglomerates.

The ore bodies are "assay delimited" and grade to sub economic or barren green carbonate and chlorite-carbonate rocks (Kerr staff). The ore zone and associated carbonate rocks are collectively enveloped by chlorite and calc-chlorite schists.

3.4 Previous work in the Kerr-Addison mine

The Larder Lake area was the scene of the first gold rush in northeastern Ontario, following a gold discovery made on the shore of Larder Lake in 1906. Subsequent exploration and production was however sporadic, and regular production in Chesterville and Kerr-Addison mines did not commence until 1938 (Thomson, 1941). Since then the bulk of the information obtained in the mine area has been the result of detailed geological mapping and exploration by the geological staff of the Kerr-Addison mine.

Thomson (1941, 1948) not only provided a regional geological map of outstanding quality, but also made a specific study of the Kerr-Addison and other gold mines of
the area. Because of the accuracy of his descriptions and observations, his work is extensively quoted throughout this thesis. Particularly interesting is his recognition of the carbonate rocks as "the product of alteration of pre-existing volcanic rocks through the action of circulating solutions", and his proposal that carbonatization and gold mineralization were caused by the reaction of rocks with the solutions. This process would have taken place before sedimentation of the Cobalt Group, since conglomerates of the latter Group contain pebbles of carbonatized rocks. In Thomson's (1941, 1948) view, the main control of mineralization was structural, most of the deposits being located along the "main break" (KLFZ) with individual ore shoots being controlled by local faults and folds.

Ridler (1970, 1972), applying Goodwin's (1966) model of Archean volcanic evolution, which emphasizes chemical sediments at basin margins proposed that the KLFZ is a zone of deformed exhalative chemical sediments rather than a structural break, and that the carbonate rocks of the areas are ... "in fact auriferous carbonate facies iron formation". "In view of the well known association of gold with iron formation" ... he proposed a "two stage history of these deposits. The carbonate zone formed first as an exhalative volcanic sediment" ... "low in iron and rich in gold." Secondly, during metamorphism, deformation and relaxation, the carbonate recrystallized and segregation of
silica and gold into dilational stockworks occurred. Ridler (1972) also noted that the flow ore of the Kerr Addison Mine is "suspiciously similar to Noranda type sulfide deposits", concluding that they "may well be a tuffaceous sulfide facies iron formation".

Tihor and Crocket (1976, 1977) carried out field studies specifically designed to test Ridler's exhalative hypothesis. Based on the presence of relict igneous textures in conjunction with chemical analyses they concluded that the carbonate units of the area are altered volcanic rocks, possibly of komatiitic composition. They also noted that carbonatized rocks are generally enriched in gold, regardless of the original parental rock type. Tihor and Crocket (1976, 1977) analysed the nearby Boston Iron Formation for gold and found that it is not particularly auriferous, in contrast to carbonatized volcanic rocks.

In a stratigraphic and structural study of the area Downes (1980) re-established the interpretation of the KLFZ as a structural break. Because carbonatization crosscuts fault zones and is most pronounced in the hinges of folds, he concluded that the alteration was late tectonic. He also stated that although carbonatization and potassic alteration are spatially related and latter post-dates carbonatization.

Stricker (1978) advocated an igneous carbonatite
origin for the carbonate rich rocks in the area, basing his conclusion firstly on their high carbonate content and silica undersaturation relative to alkali metals (normative nepheline and leucite) and secondly, their apparent spatial association with syenitic rocks.

Thomson (1980) mapped the potassium distribution in the Kerr-Addison mine, utilizing gamma-ray intensity measurements of $^{40}$K decay, correcting for U and Th background. He confirmed that the muscovite-rich part of the mine has a relatively higher K content.

Kerrich and Hodder (1982) described the carbonate ore as intensely veined "carbonate chemical sedimentary rocks admixed with ultramafic tuff", and the flow ore as "auriferous volcanic flows and pyroclastic units". Based mainly on oxygen isotope data they proposed that lode gold vein deposits were "formed from burial metamorphic-hydrothermal fluids at temperatures of 320° to 480°C". The "auriferous sediments" having possibly "originated where such fluid debouched onto the sea floor and equilibrated with seawater" ... at 700°C, "whereas the veins formed during ascent along fracture systems". The metamorphic fluid produced a potassic alteration whereas the sea water produced a sodic alteration. Kerrich and Hodder (1982) noted enrichments in rare and immobile elements such as Au, Ag, Sb, W, Cr and Ni in rocks of the Kerr-Addison Mine as opposed to moderate enrichment or even depletion of the
mobile elements Cu, Zn, and Pb. To explain this preferential enrichment they proposed co-generation of water and carbon dioxide as a result of metamorphic dehydration and decarbonation. Under conditions of high temperature, low salinity and low water to rock ratio, such fluids would possibly produce a "selective partitioning of certain rare elements into the fluid phase relative to abundant and mobile base metals".

In a comprehensive article summarizing geochemical and isotopic data of several gold deposits of the Abitibi Belt, Kerrich (1983) described the carbonate ore of Kerr-Addison as "altered volcanic flows and tuff, with minor interflow magnesite, ferroan dolomite and chert chemical sediments, collectively traversed by major arrays of quartz-carbonate-muscovite veins". Using Gresen's (1976) mass balance calculation, he estimated that the alteration which produced the carbonate ore was accompanied by an increase of 60 to 100% in volume relative to the parental ultramafic rock. Altered and mineralized rocks with trondhjemitic to basaltic precursor composition underwent increases of volume of 50 to more than 1000%. Due to the reducing nature of the potassic and sodic alterations and the similarity of the oxygen isotope composition of the two types of alterations, the earlier model (Kerrich and Hodder, 1982) involving the mixing of metamorphic fluid and sea water was reconsidered. Instead a scheme was proposed
involving "a reducing CO$_2$-rich fluid reservoir with relatively high K/Na ratio" ... which evolved ... "to conditions of low K/Na, so that albite was stabilized over muscovite".

Jensen (1980, 1981), impressed by the preferential association of gold deposits with graphitic sediments in the boundary between a newly developing volcanic pile and an old, more stable volcanic pile or granitic basement, proposed a multistage model for the development of the deposits in the Kirkland Lake area as follows.

Stage 1: Clastic and chemical sedimentation of gold "in troughs and sedimentary traps where gold chloride and sulphide complexes came in contact with acid-reducing environments".

Stage 2: Deposition of the next volcanic cycle. Between episodes of volcanism, gold was deposited in cherty pyritic sediments and carbonaceous sediments. In this stage the weight of accumulated lava depressed the floor of the basin ... "creating local reducing and acid conditions". Fractures provided channelways for the hydrothermal brines rising to the surface. This fluid which "originated from dehydrating mantle sources" ... leached gold from older sedimentary piles.

Stage 3: Further filling and depression of the basin floor. "The movement resulted in serpentinization of komatitites and formation of talc-chlorite schist".
Stage 4: "Melting of the sedimentary and volcanic rocks produced magma and hydrothermal solutions which penetrated upward along fault zones resulting in extensive carbonatization, silicification and deposition of gold in fractures."

Stage 5: Compression of the fracture zones and migration of the gold into the hinge zone of folds and other dilation zones.
Figure 3.1
Geology of Timmins-Kirkland Lake area, and location of the Kerr-Addison mine (geology after Jensen, 1978).
Figure 3.2

6. Trachyte
5. Sandstone, conglomerate (fluvial?)
4. Sandstone, argillite
3. Sandstone, conglomerate (marine)
2. Mafic volcanic rocks
1. Ultramafic & mafic volcanic rocks

Legend:
- Fault
- Geological contact
- Unconformity
- Form line
- Bedding (facing known)
- Fold axes (syncline, anticline, plunge)
Figure 3.3
Schematic cross section of the Kerr-Addison mine. After Lowrie and Wilton (1980). The stratigraphic scheme according to Downes (1980) is printed below the section.
Table 3.1. Stratigraphic succession of the Kirkland Lake area, South Limb of the Synclinorium, after Jensen, 1980.

Upper Supergroup
  Tamiskaming Group:
  **Volcanics:** Mafic, intermediate, felsic trachyte, and K-rich dacite and rhyolite flow and tuffs.
  **Sediments:** Fluvial conglomerate, sandstone and argillite.
  **Intrusions:** Stocks and dikes of syenodiorite, syenite, quartz monzonite and lamprophyre.

Blake River Group
  **Volcanics:** Calc alkalic basalt, andesite dacite and rhyolite flows and tuffs.
  **Sediments:** Volcaniclastic slump deposits.
  **Intrusions:** Stocks and dikes of gabbro, quartz gabbro, hornblende gabbro, diorite, quartz diorite and subvolcanic rhyolite domes.

Kinojevis Group
  **Volcanics:** Mg-rich and Fe-rich tholeilitic basalts, and tholeilitic andesite, dacite and rhyolite flows and tuffs.
  **Sediments:** Thin interflow argillite and chert.
  **Intrusions:** Sills of Mg-rich and Fe-rich gabbro.

Larder Lake Group
  **Volcanics:** Flows of peridotitic and basaltic komatite, and Mg-rich tholeilitic basalt, and minor Fe-rich tholeilitic basalts and interflow rhyolite tuff-breccias.
  **Sediments:** Turbiditic conglomerate, greywacke and argillite, and iron formation chert, limestone and dolostone.
  **Intrusions:** Sills and stocks of peridotite, pyroxenite and gabbro.

Lower Supergroup
  (Unnamed Unit)
  (Conglomerate with trachyte and syenodiorite pebbles).

Skead Group
  **Volcanics:** Mainly calc alkalic rhyolite tuff breccia with some calc alkalic basalt, andesite and dacite flows and tuff breccias.
  **Sediments:** Chert and cherty argillite.
  **Intrusions:** Stocks of feldspar porphyry and quartz diorite.
<table>
<thead>
<tr>
<th>Table 3.1 (Continued)</th>
</tr>
</thead>
</table>

**Catherine Group**
- Volcanics: Mg-rich and Fe-rich tholeiitic basalts.
- Sediments: Interflow chert.
- Intrusions: (None mapped).

**Wabewawa Group**
- Volcanics: Peridotite and basaltic komatiite, Mg-rich tholeiite basalt and minor Fe-rich tholeiitic basalt, and a few interflow rhyolite tuffs.
- Sediments: (None mapped).
- Intrusions: Layered sills (possibly flows) of dunite, pyroxenite, and gabbro.

**Pacaud Tuffs (Ridler, 1970)**
- Volcanics: Calc-alkalic andesite, dacite and rhyolite tuffs.
- Sediments: Chert, argillite, iron formation.
- Intrusions: Trondhjemite of Round Lake Batholith.
CHAPTER 4

ORIGINAl ROCK TYPES

4.1 Introduction

In order to understand the alteration processes accompanying gold deposition at the Kerr-Addison mine, it is necessary first to establish the chemical and mineralogical composition of the altered rocks prior to their modification by hydrothermal activity. Local preservation of volcanic textures and structures such as spinifex and varioles (Plate 1A, B) provides evidence that carbonate-rich rocks in Kerr-Addison are, at least in part, derived from mafic and ultramafic volcanic precursors and associated clastic derivatives. In the vicinity of shear zones, primary textures are completely obliterated and the origin of these rocks has been the subject of considerable controversy, having been variously interpreted as altered volcanics (Thomson, 1941; Tihor and Crocket, 1976, 1977;
Downes, 1980), exhalative chemical sediments (Ridler, 1970) or igneous carbonatite (Stricker, 1978).

The original chemical character of the precursors may be deduced from the abundance and mutual ratios of certain diagnostic less mobile elements (for a discussion of the use of immobile elements for diagnosing original igneous rock types see Costa et al., 1983). Chemical analyses of altered rocks from the Kerr-Addison mine (Appendix 1) can then be used to identify the nature of their precursors and thus to test the various hypotheses.

4.2 Geochemical data

Chemical analyses of carbonate and talc-carbonate rocks (Table 4.1) have remarkable similarities to those of spinifex textured peridotite from Munro Township. Major differences can be noted in CO₂, CaO, K₂O, Na₂O, Rb and Ba - elements which are very mobile under hydrothermal conditions. Variations in abundance of the relatively immobile elements among the ultramafic rocks is compatible with their origin by igneous differentiation of a komatiitic volcanics. For instance the variation is closely comparable to that reflecting differentiation trends found in the generally fresh komatiitic rocks (Arndt et al., 1977) of Munro Township (Fig. 4.1).

Among the mafic rocks from the mine area, the variation in immobile elements is also compatible with
differentiation trends observed in relatively fresh Archean tholeiitic rocks (Fig. 4.2). Mafic rocks from the Kinojevis and Larder Lake Group north and south of the KLFZ, respectively, have different geochemical characteristics. Nevertheless both groups of rocks show similar differentiation trends. In addition, they all plot as clusters within the field of "ocean-floor basalt" in Pearce and Cann's (1973) triangular diagrams (Fig. 4.3), attesting to their primary geochemical uniformity.

4.3 Possible origin of altered rocks

The successful application of the exhalative model to massive base metal sulphide deposits has strongly influenced studies of Archean gold deposits. The stratabound and banded nature of carbonate and talc-rich rocks in the vicinity of the Kerr-Addison Mine led Ridler (1970) and other authors to interpret them as exhalative chemical sediments.

It is very unlikely, however that the chemical characteristics of the mine rocks discussed above reflect their precipitation on the sea floor as exhalative sediments. The formation of an exhalite involves leaching of rock sequences by sea water at high temperature and precipitation of solutes upon mixture with cool sea water (Spooner and Fyfe, 1973; Ridler, 1970; Hutchinson et al., 1980). Leaching of rocks implies incongruent dissolution.
of silicates where more soluble elements, especially Si, are enriched in the fluid phase (Ellis and Mahon, 1966; Curie, 1968; Althaus and Johannes, 1969; Frantz et al., 1981; Reed, 1983). Thus, it is difficult to envisage a mechanism of leaching and precipitation producing chemical sediments with a composition identical to that of the source rock.

In seafloor hydrothermal systems carbonates more likely precipitate where descending water penetrates hot rocks rather than in the vicinity of the discharge area (Fyfe, 1975). The solubility of carbonate minerals increases as the temperature of the solution decreases (Ellis and Mahon, 1977; Holland and Malinin, 1979). Carbonate can be precipitated from sea water but the content of less mobile elements such as Al, Ti, Cr and Ni of carbonate rocks of the mine area are extremely high when compared to average marine carbonates (cf. Turekian and Wedepohl, 1961).

Costa et al. (1980), studying Archean Zn-Cu sulphide deposits in the Mattagami District (Quebec), have shown that talc can be precipitated in proximity to sea floor hydrothermal vents. They suggested that talc was formed by reaction of silica in the hot discharge with metal bicarbonate species in ocean water (Costa et al., 1980). Talc-rich rocks in the vicinity of the Kerr-Addison Mine, however, have chemical compositions very distinct from those of "sedimentary" talc (Table 4.2). Exhalative talc-
rich rocks such as described by Costa et al. (1980) are characterized by extremely low content of the less soluble elements such as Al and Ti. In contrast, talc-rich rocks of Kerr-Addison show Ti and Al content similar to those of komatiitic ultramafic volcanic rocks. The igneous ultramafic parentage of those rocks is corroborated by their elevated Ni and Cr contents (Table 4.2).

The carbonatite hypothesis can be ruled out by simple inspection of the chemical analyses (Table 4.3). Rocks from Kerr-Addison have low contents of Ba, Sr, Zr, Y, Nb, TiO₂, and P₂O₅, and high Cr and Ni abundances when compared to those of typical carbonatites according to Gold (1966).

Mafic and ultramafic rocks in the Kerr-Addison mine and surrounding areas often exhibit fragmental nature (Plate 10, E, F). Fragmental mafic rocks are generally interpreted as flow breccia, whereas fragmental ultramafic rocks are variously interpreted as conglomerate (Jensen, personal communication, 1983), flow breccia or tectonic breccia. The possibility of formation of at least part of such brecciated fabrics by hydraulic fracturing during hydrothermal activity is discussed later. Regardless of the genetic interpretations of fragmental texture, these rocks should chemically behave as mafic or ultramafic volcanics respectively, during metamorphism and hydrothermal alteration, but with porosity and permeability much larger than for massive volcanic flows.
It may, therefore, be concluded that the most reasonable interpretation is that irrespective of their present structural fabric and mineralogy, the talc-carbonate and chlorite-carbonate-rocks at the Kerr-Addison mine represent deformed and hydrothermally altered volcanic rocks of original mafic and ultramafic composition and their clastic derivatives. Moreover, as far as metamorphic and hydrothermal alteration reactions are concerned, those rocks are analogous to mafic and ultramafic rocks whatever their real origin might be. If this is valid it may also be assumed that prior to their hydrothermal alteration, the mineralogical composition of the rocks was similar to those of mafic and ultramafic rocks in other parts of the volcanic sequence.
Figure 4.1

$\text{Al}_2\text{O}_3$, Sc and log $\text{Ni}/\text{Al}_2\text{O}_3$ versus $\text{TiO}_2$ of altered ultramafic rocks of Kerr-Addison. The black lines are the trends of komatiitic ultramafic rocks from the Abitibi Belt. Data for komatiites from Arndt et al. (1977) and Ludden and Gelinas (1982).
Figure 4.2

Zr, Sc and Al₂O₃ versus Ti for altered mafic rocks of Kerr-Addison (in ppm). The continuous lines are the trends of tholeiitic volcanics from Munro and Warden Township according to Arndt and Nesbitt (1982). Shaded area corresponds to the field of "Iron-Rich-Tholeiitic Basalt" after Jensen and Langford (1983, p. 72, table 2).

circles: mafic rocks south of KLFZ
stars: mafic rocks north of KLFZ
Figure 4.3

A. Plot of Zr-Ti/100-3Y of altered mafic rocks of Kerr-Addison. Fields of different basalts after Pearce and Cann (1973), A: low K tholeiite; B: ocean floor basalts; C and B: calc-alkaline; D: within plate basalts.

B. Plot of Zr-Ti/100-Sr/Z of same samples. A: low K-tholeiites; B: ocean floor basalts; C: calc-alkaline basalts.
Plate 1. Relict textures and fabrics

Local preservation of spinifex (A), variolitic (B), and other volcanic textures indicate that carbonate-rich rocks in the Kerr-Addison mine are, at least in part, derived from ultramafic and mafic volcanic precursors.

South of the KLFZ, graphite is present in interflow metasediments (C) and in the matrix of basaltic breccias (D). Oxidation of graphite in such rocks can produce a mass of CO₂ up to four times that of the original graphite. The fragmental nature of some of the mafic (D) and ultramafic rocks (E) of the mine area may have contributed to the pervasive fluid penetration and associated hydrothermal alteration.

A: Spinifex textured carbonate-chlorite rock. Relict spinifex texture is also observed in some carbonate-muscovite rocks (Scale bar = 1 cm).

B: Variolitic-textured altered mafic rocks from the flow ore (Scale bar = 1 cm).

C: Graphite schist with nodules of pyrite (Scale in cm).

D: Fragmental mafic rock with graphite-bearing matrix (Scale bar = 1 cm).

E: Ultramafic breccia, near an old tailings site of the Kerr-Addison Mine. (Horizontal field of view about 3 m).

F: Close-up of photograph E, showing details of a spinifex textured fragment.
Table 4.1. Representative chemical analyses of altered ultramafic rocks from the Kerr-Addison mine compared to komatiitic volcanics from Munro Township.

<table>
<thead>
<tr>
<th></th>
<th>AK-40</th>
<th>AK-46</th>
<th>AK-66</th>
<th>P9-188**</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>49.58</td>
<td>45.63</td>
<td>43.12</td>
<td>44.40</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.39</td>
<td>0.20</td>
<td>0.38</td>
<td>0.35</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>6.48</td>
<td>4.56</td>
<td>7.36</td>
<td>7.40</td>
</tr>
<tr>
<td>FeO*</td>
<td>12.20</td>
<td>12.28</td>
<td>12.17</td>
<td>13.30</td>
</tr>
<tr>
<td>MnO</td>
<td>0.15</td>
<td>0.21</td>
<td>0.21</td>
<td>0.26</td>
</tr>
<tr>
<td>MgO</td>
<td>27.39</td>
<td>29.09</td>
<td>29.82</td>
<td>27.50</td>
</tr>
<tr>
<td>CaO</td>
<td>4.33</td>
<td>7.18</td>
<td>8.28</td>
<td>6.33</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.06</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.00</td>
<td>1.17</td>
<td>0.00</td>
<td>0.08</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-</td>
</tr>
<tr>
<td>L.0.I.</td>
<td>22.55</td>
<td>29.38</td>
<td>24.21</td>
<td>7.40</td>
</tr>
<tr>
<td>CO₂</td>
<td>20.39</td>
<td>29.15</td>
<td>21.11</td>
<td>-</td>
</tr>
<tr>
<td>Rb</td>
<td>2</td>
<td>19</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>Sr</td>
<td>32</td>
<td>84</td>
<td>137</td>
<td>3</td>
</tr>
<tr>
<td>Sc</td>
<td>18</td>
<td>19</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Y</td>
<td>12</td>
<td>8</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Zr</td>
<td>20</td>
<td>16</td>
<td>18</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>3172</td>
<td>2680</td>
<td>3320</td>
<td>3080</td>
</tr>
<tr>
<td>Ni</td>
<td>1373</td>
<td>921</td>
<td>1330</td>
<td>1420</td>
</tr>
</tbody>
</table>

* FeO* = FeO total

**Spinifex textured peridotites from Munro Township (after Arndt et al., 1977).


Major elements in weight %, trace in ppm; recalculated 100% volatile free basis.
Table 4.2. Comparison of chemical analyses of talc-rich exhalative sediments with talc-rich rocks of the Kerr-Addison Mine.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>59.70</td>
<td>38.62</td>
<td>47.39</td>
<td>40.79</td>
</tr>
<tr>
<td>TiO₂</td>
<td>nd</td>
<td>nd</td>
<td>.26</td>
<td>.42</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>.05</td>
<td>.17</td>
<td>4.59</td>
<td>4.96</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>10.99</td>
<td>38.49</td>
<td>10.89</td>
<td>13.54</td>
</tr>
<tr>
<td>MnO</td>
<td>0.11</td>
<td>0.41</td>
<td>0.17</td>
<td>0.18</td>
</tr>
<tr>
<td>MgO</td>
<td>25.32</td>
<td>15.42</td>
<td>36.51</td>
<td>23.28</td>
</tr>
<tr>
<td>CaO</td>
<td>nd</td>
<td>.96</td>
<td>13.44</td>
<td>3.59</td>
</tr>
<tr>
<td>Na₂O</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>K₂O</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Zr</td>
<td>18</td>
<td>20</td>
<td>15</td>
<td>21</td>
</tr>
<tr>
<td>Y</td>
<td>28</td>
<td>31</td>
<td>14</td>
<td>16</td>
</tr>
<tr>
<td>Nb</td>
<td>40</td>
<td>10</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Cr</td>
<td>nd</td>
<td>nd</td>
<td>2660</td>
<td>3080</td>
</tr>
<tr>
<td>Ni</td>
<td>nd</td>
<td>nd</td>
<td>1150</td>
<td>1350</td>
</tr>
<tr>
<td>Sr</td>
<td>20</td>
<td>30</td>
<td>80</td>
<td>52</td>
</tr>
<tr>
<td>Rb</td>
<td>7</td>
<td>13</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Ba</td>
<td>nd</td>
<td>4</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Zr/Al</td>
<td>679</td>
<td>222</td>
<td>4.2</td>
<td>3.3</td>
</tr>
</tbody>
</table>

1-2: talc-rich exhalative sediments of Matagami District after Costa et al. (1980). 3-4: talc-rich rocks from Kerr-Addison mine (samples AK-9 and AK-37A). Major elements in weight %, recalculated to 100%, without LOI. Major element oxides in weight percent, trace elements in ppm. nd: not detected.
Table 4.3. Comparison of selected elements from igneous carbonatite and carbonate rocks from the Kerr-Addison Mine.

<table>
<thead>
<tr>
<th></th>
<th>&quot;Typical carbonatite&quot; - after Gold (1966)</th>
<th>Carbonate ultramafic rocks of Kerr-Addison*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{2}O_{5}$</td>
<td>1.73</td>
<td>0.02</td>
</tr>
<tr>
<td>Sr</td>
<td>7526</td>
<td>200</td>
</tr>
<tr>
<td>Ba</td>
<td>4031</td>
<td>200</td>
</tr>
<tr>
<td>Nb</td>
<td>560</td>
<td>5</td>
</tr>
<tr>
<td>Zr</td>
<td>640</td>
<td>25</td>
</tr>
<tr>
<td>Ni</td>
<td>32</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>Cr</td>
<td>102</td>
<td>&gt;1000</td>
</tr>
</tbody>
</table>

Major element oxide in weight percent, trace elements in ppm.

*See Appendix 1.
CHAPTER 5

ALTERATION MINERAL-ASSOCIATION

5.1 Introduction

Relict volcanic textures are locally preserved in the mine area (Plate 1) but original igneous minerals are rarely observed. All phases are secondary minerals, except for scarce clinopyroxene grains in some ultramafic rocks (Plate 2A). The hydrothermal alteration overprinted a volcanic sequence containing diverse rocks resulting in the formation of a great variety of secondary lithological types.

From previous work in Kerr-Addison and other Archean lode gold deposits alteration has been diversely classified into "carbonatization" and "potassic alteration" (Downes, 1980; Fyon et al., 1983); "oxidative sodic" and "reductive potassic-CO₂" (Kerrich and Hodder, 1982); "sodic-CO₂" and "reductive potassic-CO₂" (Kerrich, 1983); "silicification", "sericitization" and "carbonatization" (Andrew and Wallace,
1983); "visible" and "cryptical" (Robert and Brown, 1984a).

The hydrothermal alteration in this study is treated as a variety of metamorphism where metasomatic exchange between rocks and fluids have played a prominent role. In an analogous manner to the conventional description of metamorphic rocks, the alteration types can be classified on the basis of a relatively small number of coexisting diagnostic minerals. Classification of alteration type based on mineral association not only avoids ambiguity and genetic concepts, but also facilitates comparison with other deposits (cf. Creasey, 1959; Burnham, 1962; Meyer and Hemley, 1967).

The objective of this chapter is to describe the variety of mineral assemblages associated with the hydrothermal alteration. In order to simplify their description, the various mineral associations are grouped into: a) metamorphic assemblage; b) initial stage of alteration; and c) advanced stage of alteration. The alteration stages in turn are divided into "alteration types" (Fig. 5.1). Initial and advanced alteration are discriminated both on the basis of diagnostic mineral associations, and on spatial relationship to ore. These aspects are further discussed below.

5.2 Metamorphic assemblages

Metamorphic assemblages are seldom observed in the
mine area. As mentioned earlier the mineralogical composition of mafic and ultramafic rocks prior to their hydrothermal alteration are assumed to be similar to those of metavolcanic rocks in other parts of the Abitibi Belt.

Rare clinopyroxene grains in ultramafic rocks of the mine area are partially replaced by tremolite, epidote and talc (Plate 2A). Although not observed in the mine area, elsewhere in the Abitibi Belt olivine and orthopyroxene in komatiitic ultramafic rocks are replaced by serpentine (Arndt et al., 1977, 1979). For this reason the metamorphic assemblage of ultramafic rocks is assumed to have been composed mainly of serpentine and tremolite with minor amounts of chlorite, epidote, talc and carbonate. Alteration assemblages of ultramafic rocks, as opposed to their metamorphic counterparts, are characterized by the absence of serpentine, tremolite and epidote.

The pre-alteration metamorphic assemblage of mafic rocks is assumed to have been similar to that of mafic volcanic rocks described by Jolly (1974, 1978), which are composed of actinolite, chlorite, epidote, calcite and albite. Alteration assemblages of mafic rocks are distinguished from their metamorphic assemblage by the absence of actinolite and epidote (Figure 5.1).
5.3 Mineralogy of the initial stage of alteration

5.3.1 Ultramafic rocks

Two types of mineral association can be recognized in the initial stage of alteration of ultramafic rocks of the mine area: a) TALC-CHLORITE ALTERATION, and b) CARBONATE-CHLORITE ALTERATION.

Talc-chlorite alteration. The diagnostic minerals of this type of alteration are talc and chlorite, with minor amounts of carbonates, quartz, and sphene or leucoxene (Plate 2B). This variety is distinguished from "normal" ultramafic metavolcanic rock by the absence of serpentine, tremolite, and epidote.

Carbonate-chlorite alteration. This alteration type is marked by the replacement of talc by carbonate and quartz. Chlorite remains the only aluminium-bearing silicate (Plate 2D). The typical mineral association is carbonate, quartz, chlorite and leucoxene.

5.3.2 Mafic rocks

The two alteration types in the initial stage of alteration of mafic rocks corresponding to those of ultramafic rocks described above are: a) CHLORITE-ALBITE-ALTERATION and b) CHLORITE-MUSCOVITE ALTERATION. An additional type, here termed CHLORITOID ALTERATION, is recognized in mafic rocks.

Chlorite-albite alteration. In addition to the
diagnostic minerals chlorite and albite, mafic rocks of this alteration type contain minor amounts of quartz, carbonate, and sphene (Plate 3A). Magnetite and ilmenite are common in rocks of this type north of the LKFZ, whereas rocks south of that fault zone contain pyrite. South of the KLFZ, the matrix of breccias, inter-pillow material, and interflow sediments contain graphite (Plate 1C, D). Mafic rocks altered to chlorite-albite are distinguished from "normal" greenschist facies metabasaltic rock by the absence of epidote and actinolite.

**Chlorite-muscovite alteration.** Characterized by the replacement of albite and oligoclase by muscovite, this alteration type is composed typically of chlorite, muscovite, carbonate, quartz, and sphene. Mafic rocks of this type usually contain more carbonate and quartz than those containing chlorite and albite.

**Chloritoid alteration.** Restricted to the north side of the KLFZ, the chloritoid alteration is characterized by the presence of porphyroblasts of chloritoid (Plate 3B). The matrix of the rocks is mainly composed of carbonates, quartz, and muscovite with lesser amounts of chlorite. In most samples chloritoid is partially replaced by muscovite, chlorite and carbonate, indicating that it is not in equilibrium with the matrix assemblage. For this reason it is not clear whether the chloritoid is part of a hydrothermal alteration assemblage or is a relict of an earlier
metamorphic assemblage.

5.4 Mineralogy of the advanced stage of alteration
As described above the alteration types in the initial stage are greatly dependent on the composition of the original parental rocks. In contrast, the advanced stage tends to produce similar mineral assemblages regardless of the original rock composition. For this reason the advanced stage of alteration of both mafic and ultramafic rocks are grouped into a) CARBONATE-MUSCOVITE ALTERATION; b) CARBONATE-ALBITE ALTERATION; and c) PYRITIC ALTERATION.

Carbonate-muscovite alteration. This alteration type is distinguished by the replacement of chlorite by carbonate and muscovite. Typical assemblages contain carbonate, muscovite, quartz, and leucoxene (Plates 2D and 3C). This alteration type produces the so-called green carbonate rock when present in rocks of original ultramafic composition. The characteristic colour of the green carbonate-rock reflects the presence of emerald green chromium-bearing muscovite, commonly referred to as fuchsite or mariposite.

Carbonate-albite alteration. The reappearance of albite associated with carbonates, quartz, and leucoxene is diagnostic of this alteration type (Plates 2F and 3D).

In all of the three carbonate alteration types of
ultramafic rocks (carbonate-chlorite, carbonate-muscovite and carbonate-albite) carbonates and quartz are the predominant mineral phases. Relatively small proportions of chlorite, muscovite and albite are controlled by the restricted availability of aluminum. The predominance of one or the other of these alumino-silicates distinguishes the three different varieties of carbonate alterations. Because of their green colour and platy nature, chlorite and green muscovite are more strikingly visible than the white and fine granular albite, and hence the carbonate-albite alteration has often been overlooked. Furthermore, small quantities of green mica in fractures of rocks pervasively affected by carbonate-chlorite or carbonate-albite alteration tend to impart a resemblance to green carbonate rock. For this reason, in most descriptions of gold deposits carbonate-muscovite alteration appears to be the predominant type, with the importance of carbonate-albite inadequately emphasised.

Pyritic alteration. This is a variety of the carbonate-muscovite alteration type where pyrite is also present (Plate 5F). Pyritic alteration is more accentuated in rocks with mafic affiliation. This alteration type usually occurs in the transition zone between the carbonate-muscovite and carbonate-albite alteration types.
5.5 **Mineral composition**

The nature of carbonate minerals in altered rocks at the Kerr-Addison mine varies with the whole rock chemical composition and alteration type. Calcite is rare, occurring only in rocks with incipient alteration. The most common carbonate minerals are ferroan dolomite and ankerite. Ankerite occurs in altered mafic rocks, the iron content increasing with progressive alteration (Table 5.2, analyses 1 to 4). Similar trends of iron enrichment are observed among ferroan dolomite and ankerite of altered ultramafic rocks (Table 5.1, analyses 5 to 7). Depending on the Ca content, altered ultramafic rocks may also contain ferroan magnesite. In contrast to ankerite and ferroan dolomite, the iron content of ferroan magnesite decreases with respect to progressive alteration (Table 5.1, analyses 8 and 9).

Plagioclase in carbonate-albite alteration is almost pure albite, whereas in chlorite-albite alteration the plagioclase composition varies from almost pure albite to oligoclase.

Chlorite composition depends primarily on the whole rock chemical composition. In mafic rocks the chlorite is an iron rich green coloured variety, with high relief, pleochroism, anomalous blue interference colour and length slow (pycnochlorite). In ultramafic rocks the chlorite is a magnesium rich pale yellowish green variety with
relatively low relief, almost non-pleochroic, anomalous brown interference colour to almost isotropic in basal section and length fast (clinochlore).

Muscovite in ultramafic rocks are green chromium muscovite, which may also contain considerable Mg (Kerrich, 1983). High contents of magnesium in muscovite is a common characteristic of hydrothermal alteration (Holland and Malinin, 1979).

Variations of mineral composition, especially of carbonates, may be an important criteria for distinguishing alteration zones around gold deposits. Although carbonate composition can be readily determined by simple staining techniques (Hutchinson, 1976, p. 25), the alteration types are better and unambiguously defined by mineral associations, rather than by the composition of a single mineral. To be useful, a classification of hydrothermal alteration types should be based on the association of diagnostic minerals which are easily identified. Most of the alteration types described above (Figure 5.1) are defined by the presence of two minerals, and the zonation of hydrothermal alteration can be easily delineated by simple observation of outcrops with the aid of a hand lens, or under a standard polarizing microscope where the grain size is small.

All alteration types of the initial stage of alteration contain chlorite, whereas the advanced stage contains
muscovite or albite in the carbonate-muscovite and carbonate-albite types respectively. This characteristic provides a convenient way to monitor the degree of alteration. With progressively increasing intensity of alteration the dominant Al-bearing silicates are chlorite, muscovite and albite.

5.6 Mutual Relationships of Alteration Types

Textures and fabrics of altered rocks in the mine area vary depending on the original rock type, proximity to shear zones, and the amount of platy minerals such as chlorite, muscovite and talc.

The rocks are commonly pervasively dominated by one alteration type but may contain bands, veins or patches of other types. For instance the relict varioles of mafic volcanics are usually less altered than the matrix. The progressive alteration of a variolitic-textured mafic volcanic rock is illustrated with a photographic sequence in Plate 4. In Plate 4A and 4B the varioles exhibit chlorite-albite alteration surrounded by a matrix dominated by carbonate muscovite alteration. In a more altered rock the relict variole is transformed to carbonate-muscovite type and the matrix to carbonate-albite (Plates 4C and D).

The final product, representing the greatest intensity of alteration as shown in Plates 4E and 4F, has both matrix and relict variole are dominated by carbonate-albite altera-
tion. The outline of the relict variolés can be distinguished by concentrations of leucoxene (Plates 4C and E).

Narrow zones of different alteration types may often occur parallel to the schistosity, giving a banded fabric (Plate 5C, E). Veins or fractures with different mineral assemblages may also show cross-cutting relations (Plates 5 and 6), indicating repeated episodes of alteration.

Zonation of alteration types around a small albite-carbonate "vein" is illustrated in Plate 5B and the sketch of Fig. 5.2. The "vein" itself has a quartz-albite median band with a carbonate rich edge. The alteration envelope shows the sequence from the "vein" to the wall rock as follows: a) carbonate-albite; b) carbonate-muscovite; c) chlorite-muscovite; and d) chlorite-albite. Pyritic alteration is associated with the carbonate-albite and carbonate-muscovite alterations. The complete zonation in this sample occurs in less than 2 cm. To avoid ambiguity of descriptions, the alteration zoning around small veins are thereafter referred to as "alteration envelopes", whereas the entire alteration surrounding the mine area is referred as an "alteration halo".

Similar sequences of alteration are observed on all scales, although one or more of the alteration zones may be missing depending on the mineralogical composition of the host rock. The alteration envelope around quartz-
carbonate-albite veins transecting rocks dominated by various alteration types is schematically illustrated in Figures 5.2 to 5.4. Where such veins transect a rock with chlorite-albite alteration the complete sequence described above occurs (Fig. 5.2; Plate 5B). In other places when quartz-carbonate-albite veins cut a rock with carbonate-chlorite alteration (Fig. 5.3; Plate 5D) only two zones are developed, namely the carbonate-muscovite and carbonate-albite alterations. The latter type occurs closer to the vein. In cases where the vein is hosted by a rock with carbonate muscovite alteration a single zone of carbonate-albite alteration is formed (Fig. 5.3; Plate 5C).

5.7 Distribution of Alteration Types

In the periphery of the alteration halo the frequency of veins not only decreases but also quartz-carbonate-muscovite or quartz-carbonate-chlorite veins become more common than albite-bearing veins, suggesting lateral variation of conditions of the hydrothermal alteration.

The cross-cutting relations of veins and accompanying alteration envelopes at different scales has produced a very complex framework of alteration types. Nevertheless zones of predominance of one or other alteration type can be delineated on a mine scale. The initial stage of alteration is more common in the periphery of the altera-
tion halo. In the ore zones the carbonate-muscovite and carbonate-albite alteration types predominate. Pyritic alteration is also well developed, especially in the flow ore. However not all rocks exhibiting these alteration types constitute economic ore.

Mineral grains around younger alteration veins are generally coarser and cleaner than those around older veins. The latter tend to be finer grained because of the development of subgrains. Under the microscope they show undulose extinction, subgrain development and other features indicative of intra-crystalline deformation (Plates 2F, 3F; 6D, E, F). This relationship attests to the repeated sequence of fracturing, vein filling, and deformation.

Although numerous generations of quartz-carbonate veins transect the altered rocks, there is not an apparent organized pattern of quartz veins in the mine area. Locally in a stope or ore body the more prominent veins may have a definite orientation, but in most cases they form irregular shaped stringers and stockworks (Thomson, 1941).

5.8 Summary and Discussion

a) It is assumed that prior to the hydrothermal alteration mafic and ultramafic rocks of the mine area had mineral compositions similar to metamorphosed generally fresher counterparts elsewhere in the Abitibi Belt.
b) The texture and fabric of altered rocks vary depending on the original rock, proximity to shear zones, and the amount of platy minerals such as chlorite, muscovite, and talc.

c) The hydrothermal alteration types are grouped into an initial and advanced stage of alteration. Each stage of alteration is divided into "alteration types" (Fig. 5, f).

d) All the alteration types of the initial stage contain chlorite. In contrast, the advanced stage is characterized by the absence of chlorite which is replaced by muscovite and albite in the carbonate-muscovite and carbonate-albite alteration types, respectively. Therefore the sequence of alteration can be easily monitored by the relative abundance of the three aluminum-bearing minerals: chlorite, muscovite, then albite successively predominate in the altered rocks with increasing intensity of alteration.

e) Initial differences in the rock composition north and south of the KLFZ produced some differences in their alteration patterns. North of that fault zone magnetite is present in the initial stage of alteration; whereas pyrite and graphite are common south of the fault zone. Chloritoid alteration is also restricted to the north of the KLFZ.

f) Rocks are generally dominated by one alteration type,
but often contain bands or patches of other types of alteration.

**g)** Small cross-cutting veins are enveloped by narrow zoned alteration borders. The alteration types in such envelopes can vary depending on the mineral composition of the vein itself and of the host rock. Nevertheless the sequence of predominant Al-bearing silicates, chlorite, muscovite, and albite are always developed from the wall rock to the vein in the same sequence.

**h)** Cross-cutting veins are more abundant near the ore zone, usually with the assemblage quartz-carbonate-albite, whereas in the periphery of the alteration halo veins are less abundant, being composed of quartz-carbonate-muscovite or quartz-carbonate-chlorite.

**i)** Older generations of alteration minerals tend to diminish in grain size due to successive episodes of fracturing, coupled with the development of subgrains.

The alteration sequence is characterized by an increase in the abundance of carbonate minerals at the expense of hydrated silicates. Chlorite is the last silicate to be altered being replaced by carbonate and muscovite or albite. Complete zonation of alteration types enveloping small veins indicates that the zonation results
from progressive reaction of wall rocks with an infiltrating fluid.

Intersection of many generations of alteration zones and quartz veins, together with differences in the intensity of deformation shown by the mineral grains of successive generations, suggest that the hydrothermal activity in Kerr-Addison is best pictured in terms of repeated cycles of shearing, fluid transport and alteration rather than to a single and continuous episode. The development of fracturing at different scales (Plates 5 and 6) permitted the hydrothermal fluid, after each episode of deformation, to permeate through volcanic rocks which ordinarily would have very low permeability.

The composition of the incoming fluid seems to have remained essentially unchanged through time inasmuch as the sequence of alteration types enveloping different generations of veins remains the same. Systematic lateral variations of mineral assemblages of the alteration envelopes orthogonal to the veins, along with variations of the mineral assemblages of the vein itself with distance from the ore zone may be the result of lateral variations of fluid composition. Alternatively, these changes may reflect a lateral gradient of temperature or pressure.

In spite of the complexity of the distribution of alteration zoning, areas of predominance of different alteration types can be delineated. A systematic mapping
of alteration types through the whole mine could not be performed during this study due to time constraints. However, the available systematic sampling does give a broad picture of the distribution of alteration types across the 3850' level.

Because more than one type of alteration is often present in a single hand specimen, the chemical analyses of the bulk rock (Appendix 1) reflect the mixing of alteration types. For this reason, the spatial distribution of areas of predominance of the alteration types described above can be better visualized with the aid of geochemical data.
Mineral assemblages of altered rocks. Except for the "metamorphic assemblage" of ultramafic rocks all alteration types contain quartz. Ilmenite and leucoxene are the Ti-bearing phases in the initial and advanced stages respectively. Pyrite is common in the advanced stage.
<table>
<thead>
<tr>
<th>MAFIC ROCKS</th>
<th>ALTERATION STAGE</th>
<th>ALTERATION TYPE</th>
<th>METAMORPHIC ASSEMBLAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pre-alteration</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>initial stage</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>advanced stage</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>chlorite - albite</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>chlorite - muscovite</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>carbonate - muscovite</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>arbonate - albite</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ULTRAMAFIC ROCKS</th>
<th>ALTERATION STAGE</th>
<th>ALTERATION TYPE</th>
<th>METAMORPHIC ASSEMBLAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pre-alteration</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>initial stage</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>advanced stage</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>talc - chlorite</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>carbonate - muscovite</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>carbonate - albite</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.2
Sketch of alteration zoning enveloping a carbonate-albite-quartz vein in an altered mafic rock. Compare with Plate 5B. Abbreviations - cb: carbonate; alb: albite; qtz: quartz; mu: muscovite; chl: chlorite.

Figure 5.3
Sketch of alteration zoning in an ultramafic breccia. The cores of larger fragments have the assemblage carbonate-chlorite, surrounded by rims of carbonate-muscovite. The matrix is dominated by carbonate-albite. See Plate 5D.

Figure 5.4
Sketch of alteration zoning associated to carbonate-albite-quartz vein cutting ultramafic rock which is dominated by carbonate-muscovite alteration. See Plate 5C for comparison.
Plate 2. Photomicrographs of altered ultramafic rocks

A: Relict skeletal clinopyroxene of altered ultramafic rock, partially replaced by tremolite. Chlorite (dark) is probably replacing volcanic glass material or orthopyroxene (X nicols). A similar texture is described (Fleet and MacRae, 1975) in rocks from Munro Township.

B: Talc (light mass), chlorite (dark) and carbonate (larger light crystals) assemblage characterizes the talc-chlorite alteration of ultramafic rocks.

C: Porphyroblast of intergrown carbonate and quartz in a matrix of talc and chlorite. Replacement of talc by carbonate and quartz produces the carbonate-chlorite alteration of ultramafic rocks.

D: Transition from carbonate-chlorite to carbonate-muscovite alterations in ultramafic rock. The carbonate-chlorite type is characterized by the assemblage chlorite (dark), carbonate and quartz (light). Replacement of chlorite by carbonate and muscovite (right lower corner) produces the carbonate-muscovite alteration (X nicols).

E: Carbonate and Ti oxide (leucoxene) pseudomorphing sphene (plane polarized light).

F: Carbonate-albite alteration enveloping a carbonate-albite vein (coarse grained). The opaque minerals are pyrite. Note the intracrystalline deformation of carbonate grains of the vein (X nicols).
Plate 3. Photomicrographs of altered mafic rocks

A: Typical texture of chlorite-albite alteration type in mafic rocks. The assemblage is chlorite, albite, quartz, carbonate and ilmenite (or sporadically sphene rather than ilmenite). Opaques are magnetite and ilmenite (plane polarized light).

B: Radial aggregate of chloritoid. Chloritoid is restricted to altered mafic rocks north of the KLFZ.

C: Carbonate-muscovite alteration in mafic rock. m: muscovite; ca: carbonate; opaques are pyrite (plane polarized light).

D: Carbonate-albite alteration in mafic rock. Carbonate (ca) in fine-grained matrix of quartz and albite (X nicols).

E: Carbonate-albite alteration enveloping a quartz-carbonate-albite vein. Opaque minerals are pyrite (X nicols).

F: Undulose extinction and sub-grains in a radially fractured quartz grain.
Plate 4. Progressive alteration of a variolitic textured mafic rock

For each of the three pairs of photomicrographs the first (eg. A) is in plane polarized light, whereas the second (eg. B) is in X nicols.

A and B: The relict varioles (dark) are composed of chlorite, albite, quartz and Ti-oxide (chlorite-albite alteration). The matrix (light) contains carbonate, muscovite and quartz (carbonate-muscovite alteration). Opaques are pyrite.

C and D: The assemblage in the relict varioles is carbonate, muscovite and quartz (carbonate-muscovite alteration). Albite, carbonate and quartz form the interstitial material (carbonate-albite alteration). Titanium oxide is concentrated in the rims of the relict varioles.

E and F: At a more advanced stage of the alteration both the relict varioles and matrix are dominated by carbonate-albite alteration, except for few remnant muscovite flakes (arrows).
Plate 5. Small scale alteration zoning

A: Quartz-carbonate-albite vein in altered mafic rock. The arrow indicates the area of the photomicrograph B.

B: Alteration zoning enveloping a quartz-carbonate-albite vein. From the vein (coarse grained) to the right the sequence of alteration types is a) carbonate-albite; b) carbonate-muscovite; c) chlorite-muscovite; and d) chlorite-albite. Opaque minerals are pyrite. See sketch of Figure 5.2.

C: Bands of carbonate-albite alteration (light) in an ultramafic rock with carbonate-muscovite alteration. See sketch of Figure 5.4.

D: Alteration in ultramafic breccia. The larger fragments have a core of carbonate-chlorite alteration surrounded by rims of carbonate-muscovite. The matrix is dominated by carbonate-albite alteration. See sketch of Figure 5.3.

E: Carbonate-chlorite bands in a talc-chlorite rock.

F: Pyritic alteration associated with quartz-carbonate-albite vein in mafic rock. The size and abundance of pyrite decreases away from the horizontal vein which transects the vertical vein. Note that pyrite is restricted to the wall rock.
Plate 6. Evidence of fluid penetration at different scales.
Patterns of veining and fracturing in the Kerr-Addison mine
and surrounding area suggest repeated episodes of fractur-
ing and fluid infiltration through the rocks.

A: Quartz carbonate veins transecting altered ultramafic
rocks in an outcrop west of the Kerr-Addison Mine.
Note the irregular pattern and cross-cutting relations
of the veins.

B: Quartz-carbonate-chlorite veins in altered mafic rock.

C: Quartz-carbonate-albite veins in variolitic textured
mafic rock. Note the irregularity and discontinuity
of the veins.

D: Carbonate-albite filled fracture (arrow) transecting
an albite grain from a quartz-carbonate-albite vein
(plane polarized light).

E and F: Carbonate-albite filled fractures in a quartz
grain (E, plane polarized light; F, X nicols).
Table 5.1. Composition of Carbonates (mol %).

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃</td>
<td>47.4</td>
<td>47.3</td>
<td>46.6</td>
<td>48.1</td>
<td>47.8</td>
<td>50.6</td>
<td>47.0</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>MgCO₃</td>
<td>39.8</td>
<td>30.8</td>
<td>28.0</td>
<td>25.8</td>
<td>48.6</td>
<td>43.6</td>
<td>42.7</td>
<td>85.9</td>
<td>79.1</td>
</tr>
<tr>
<td>FeCO₃</td>
<td>12.1</td>
<td>21.3</td>
<td>23.6</td>
<td>25.1</td>
<td>2.9</td>
<td>4.8</td>
<td>9.7</td>
<td>13.2</td>
<td>20.2</td>
</tr>
<tr>
<td>MnCO₃</td>
<td>0.7</td>
<td>0.6</td>
<td>1.8</td>
<td>1.0</td>
<td>0.7</td>
<td>0.1</td>
<td>0.6</td>
<td>0.9</td>
<td>0.7</td>
</tr>
</tbody>
</table>

nd = not detected.

Calculated from electron-microprobe analyses.

1-4: ankerite in mafic rocks with increasing intensity of alteration.

5-7: ferroan dolomite in ultramafic rocks with increasing intensity of alteration.

8-9: ferroan magnesite in altered ultramafic rocks.
CHAPTER 6

GEOCHEMISTRY OF ALTERATION

6.1 Introduction

The sequence of alteration at the Kerr-Addison mine, as described in the previous chapter, is characterized by an increase in the proportion of carbonate minerals; accordingly the chemical analyses (Appendix 1) show a corresponding enrichment of C. In the same manner the increase in muscovite and albite which characterizes the advanced stage of alteration can be monitored by gains of K and Na in the rocks.

The amount of CO₂ or alkali-metals that can be introduced to a rock undergoing alteration is not only a function of the degree of alteration but also depends on the chemical composition of the original rock. For instance the formation of carbonate minerals in response to introduction of CO₂ from the fluid is largely controlled by
the MgO and FeO, and to some extent the CaO content of the wall rocks. Similarly the introduction of K and Na is limited by the availability of Al to form alkali-silicates. Thus, in order to compare the alteration of rocks with different pre-alteration compositions, it is necessary to employ geochemical parameters which minimize the effect of original bulk compositional variations.

In this chapter the geochemistry of the altered rocks is analysed in terms of "degree of saturation" of certain mobile elements, rather than in terms of gains or losses of components expressed in weight percent. This approach not only permits the comparison of alteration of rocks with variable original composition, but also delineates the spatial distribution of alteration types, as characterized on the basis of mineral associations, thereby stressing the significance of the fluid-rock interaction.

6.2 CO₂ Enrichment

The molar ratio CO₂/(Fe+Mg+Ca) is a suitable indicator of the degree of carbonatization. Most of the bivalent metal cations, Fe, Mg, and Ca of a fresh igneous rock are present in silicates, so the molar ratio in question is close to 0. As carbonatization proceeds, these cations are progressively transferred to carbonate minerals and the molar ratio CO₂/(Fe+Mg+Ca) approaches the saturation value, or saturation index, of 1.
Variations of the molar ratio \( \text{CO}_2/(\text{Fe} \cdot \text{Mg} \cdot \text{Ca}) \) across the 3850' level of the Kerr-Addison Mine are displayed in Fig. 6.1. In order to better visualize the areas of predominance of distinct alteration types, the moving averages are plotted instead of the molar ratios of individual samples. Obviously the maxima correspond to areas of intense carbonatization whereas the minima reflect areas where the initial stage of alteration predominates.

6.3 Alkali-metal enrichment

Concentrations of alkali-metals is of particular interest in the study of the geochemistry of the alteration associated with gold deposits. The association of gold mineralization with muscovite (Bain, 1933; Whitehead et al., 1980; Thomson, 1980) or albite (Gallagher, 1940) seems to be characteristic of many Archean gold deposits. Several attempts to correlate K and Na content to Au mineralization are present in the literature (e.g. Davis et al., 1982; Fyon and Crocket, 1982) but apparently there is not a statistically significant correlation.

At Kerr-Addison, K is present mostly in muscovite and Na in albite. A simple comparison of the alkali-metal contents of host rocks to their mineralized counterparts only reflects the absolute amount of these minerals in the respective rocks, which in turn depends on the Al content of the rock. For instance an alkali-metal saturated ultra-
mafic rock may have a lower absolute content of these chemical components when compared to undersaturated (in alkali-metals) mafic or felsic rocks, given its lower absolute aluminum content. 

Most of the aluminum in rocks of the mine area is present in chlorite, muscovite and albite. Locally chloritoid may be an important Al-bearing phase. Assuming the ideal mineral compositions for albite [NaAlSi3O8] and muscovite [KAlSi3O10(OH)2], the molar fraction Na:Al is 1:1 (albite), and K:Al is 1:3 (muscovite) respectively. It follows that the ratio Na/Al = 1 represents saturation relative to albite, and 3K/Al = 1 to muscovite.

For the other Al-bearing phases, namely chlorite and chloritoid, the alkali-metal to Al molar ratio is 0. Therefore for a rock with chlorite or chloritoid as the only Al-bearing phase the sum of these ratios (3K+Na)/Al, should be 0. Variations of these parameters indicative of alkali-metal enrichment across the 3859' level of the Kerr-Addison Mine are plotted in Fig. 6.1.

6.4 Distribution of alteration types

The initial stage of alteration is characterized by a moderate intensity of carbonatization along with abundance of chlorite. Hence the areas of predominance of the initial stage of alteration are those with moderate CO2/ (Fe+Mg+Ca) and low (3K+Na)/Al indices in Fig. 6.1. In
contrast, the advanced stage of alteration is characterized by high carbonate contents and low chlorite abundance. Accordingly, high $\text{CO}_2/(\text{Fe+Mg+Ca})$ together with elevated $(3\text{K}+\text{Na})/\text{Al}$ Indices in Fig. 6.1 correspond to areas of preferential development of the advanced stage of alteration.

The initial stage of alteration has an irregular distribution whereas the advanced stage is restricted to the south of the KLFZ (Fig. 6.1). Note that the single broad peak of $\text{CO}_2/(\text{Fe+Mg+Ca})$ located north of that fault zone has no corresponding peak of the alkali-metals indice (Fig. 6.1). This is the characteristic geochemical signature of the chloritoid alteration type.

Geochemical data can be used to further divide the advanced alteration into areas dominated by carbonate-muscovite and carbonate-albite alterations respectively. The former is characterized by high $3\text{K}/\text{Al}$ and the latter by high $\text{Na}/\text{Al}$ (Fig. 6.1).

An example of anomalous behavior of saturation is the small peak of $3\text{K}/\text{Al}$ in the vicinity of the KLFZ, which has no corresponding enrichment in $\text{CO}_2$ (Fig. 6.1), signifying that it does not have the characteristic geochemical signature of the carbonate-muscovite alteration. This peak corresponds to a muscovite rich rock described as greywacke by previous authors (Kerr-Addison staff). Probably the metasedimentary rock was already muscovite rich prior to
the hydrothermal alteration.

Apart from this abnormal point and the chloritoid alteration, the peaks of enrichment in K and Na are symmetrically distributed relative to the area occupied by the Kerr-fault. If the zoning of alteration types (Fig. 6.1B) is the result of infiltration of hydrothermal fluid, this area may well correspond to the main channel way.

In summary:

a) Appropriate geochemical parameters can delineate areas of predominance of distinct alteration types, irrespective of the primary bulk rock composition.

b) The initial stage corresponds to low CO₂/(Fe+Mg+Ca) coupled with low (3K+Na)/Al (Fig. 6.1).

c) The advanced stage has high CO₂/(Fe+Mg+Ca) associated with high (3K+Na)/Al and it is restricted to the south of the KLFZ.

d) The advanced stage can be subdivided into carbonate-muscovite and carbonate-albite alteration, by high 3K/Al or high Na/Al respectively.

e) Alteration types are symmetrically distributed relative to the probable channel way for the hydrothermal fluids which corresponds to the vicinity of the Kerr-Break.

f) Chloritoid alteration corresponds to high CO₂/(Fe+Mg+Ca) and low (3K+Na)/Al.
6.5 Mobility of other elements

Introduction of CO$_2$ and alkali-metals are the most prominent geochemical features of hydrothermal alteration at the Kerr-Addison mine, but other elements, including Au display variable enrichments or depletions. Due to the economic importance of the precious metal, its distribution is discussed later in a separate section.

Water for instance is depleted from highly carbonatized rocks. Rb varies sympathetically with K, whereas Sr tends to covary with Ca. These tendencies were also observed by previous authors (Kerrich and Hodder, 1982; Kerrich, 1983).

Carbonatized rocks are generally enriched in Ca relative to fresher precursors. The behavior of Ca in altered komatititic rocks can be deduced with reference to the CaO/Al$_2$O$_3$ ratio which has a relatively constant value of 1 in fresh examples from Munro Township and other areas of the Abitibi Belt, according to published chemical analyses (Arndt et al., 1977; Ludden and Gelinas, 1982). Ratios (CaO/Al$_2$O$_3$) up to 4.7 are observed in highly altered ultramafic rocks of the mine area (e.g. sample AK-41, Appendix 1), indicating an absolute introduction of calcium.

The FeO content and FeO/MgO ratio of komatititic rocks covary with Ti contents of the rocks, whereas MgO has a negative correlation with Ti' (Beswick, 1982). Variation of the FeO/MgO ratio of altered ultramafic rocks of the mine
departs considerably from the trend of differentiation of fresh-komatlitic rocks (Fig. 6.2) but no systematic variation with alteration types could be identified. Such departures seem to be mostly due to loss or gain of MgO from altered rocks, inasmuch as excursions of FeO from the expected trend are small (Fig. 6.2A and B).

In mafic rocks the FeO/MgO ratio is also highly variable relative to trends reported from fresher tholeilitic rocks (Fig. 6.3). In the case of mafic rocks, however, the departures from the expected trends of tholeilitic volcanics seem to be mostly due to the mobility of FeO. Such mobility of MgO of ultramafic rocks and FeO of mafic rocks has been also observed in talc-chlorite alteration zones in the contact between mafic and ultramafic rocks in western New England (Sanford, 1982).

Based on the differences in the chemical potential of certain components of minerals such as chlorite, actinolite and plagioclase, Sanford (1982) concluded that Si, Fe and Ca have migrated from mafic rocks into ultramafic rocks, whereas Mg had moved in the opposite direction. Such mass transfers between mafic and ultramafic rocks in the contact zone at the Kerr Addison mine may explain the observed variation of FeO/MgO ratios, but a more detailed study is necessary to substantiate this possibility. For the study of hydrothermal alteration accompanying gold mineralization the crucial point is the behavior of FeO and MgO together.
with CaO in the formation of carbonates.

The geochemical behavior of carbonate forming components such as Ca, Mg, and Fe is anticipated to be related to the carbonatization of silicates. Microprobe analyses of ferroan dolomite and ankerite (Table 5.1) show that their CaCO₃ contents are close to the ideal (50%). In addition, the CaO content of altered rocks of the mine area is related to that of CO₂. In Figure 6.4, the frequency distribution of the molar ratio CO₂/CaO of altered mafic and ultramafic rocks suggests the presence of three distinct populations. The CO₂/CaO ratio of the three populations are approximately 1, 2 and 6, indicative of calcite, ankerite and magnesite respectively. These data suggest that the amount of Ca fixed in the solid phase is a function of the amount of ferroan dolomite and ankerite in the altered rock.

Therefore, saturation of a given altered rock relative to Ca is expected to occur when all the Fe, Mg and Ca are bound to ferroan dolomite and/or ankerite. Depending on the initial composition of that rock, such saturation may occur with addition or removal of Fe plus Mg to adapt the composition of the altered rock to form carbonate minerals with molar composition close to 50% CaCO₃. This mechanism may explain the apparent addition of Ca together with the variable apparent additions or removal of Fe and Mg.
6.6 Discussion of chemical mass balance

For a more comprehensive evaluation of gains or losses of rock chemistry, mass balance calculations have been performed by several authors studying the geochemistry of alteration of Archean lode gold deposits. Two divergent approaches have been adopted, either assuming constant volume or alternatively immobility of certain elements. The two approaches generally result in opposing deduced geochemical trends.

Calculations assuming constant volume (e.g. Boyle, 1961; Robert and Brown, 1984a) indicate addition of CO₂ and K associated with removal of SiO₂ from rocks with incipient alteration. In rocks closer to the "mineralized veins", similar calculations indicate that Ca, CO₂, Na, Au, and S were added to the wall rocks whereas Fe, Mg, Al, Ti, H₂O and in some cases Si were released. The abundance of quartz in the "mineralized veins" together with apparent depletion of Si in the wall rocks led Boyle (1961) to conclude that Si and other elements have migrated from the country rocks to the veins. These deduced transfers of chemical components were embodied in the "lateral secretion" hypothesis of gold deposits (Boyle, 1961).

Geochemical data of the Kerr-Addison Mine also show similar trends on the basis of assumed isovolumetric alteration.

Greens (1967) suggested incorporating specific gravity data into two way mass-balance calculations for
alteration of rocks. His method compares the chemical composition and specific gravity of an "unaltered parent-rock" with those of "altered counterparts". The change in volume accompanying alteration, expressed as "volume factor" is deduced from assumed isochimcal behavior of several relatively immobile components (e.g., Al₂O₃, TiO₂, Sc, Zr) depending on the geological environment.

Application of such calculations to analyses of rocks from the Kerr-Addison mine (Kerrich, 1983) indicated gains of Si, Fe, Mn, Mg, Ca, Sc, K, Rb, Ba, Zr, and TiO₂ with variable gains or losses of Na. For the flow ore, similar calculations yielded gains of Si and Na in rocks with "basaltic precursors", whereas the same elements were released from rocks with "dacitic and ultramafic precursors". In contrast Mg was leached from basaltic rocks and added to ultramafic and dacitic rocks. Deduced volume factors ranged from 0.4 (60% less to 2, 200% gain) (Kerrich, 1983).

The contrasting results of mass balance calculations based on different assumptions illustrate the difficulties in monitoring small changes in chemical composition associated with massive introduction of CO₂. A major difficulty of the application of Gresens' (1967) method is the choice of an "unaltered parental-rock". This choice is usually based on matching the ratios of less mobile components such as Al₂O₃/TiO₂, Ti/Zr, and Sc/Zr to a hypothetical igneous
precursor with similar ratio, where no fresh parent rock is present. Those ratios remain almost constant during igneous differentiation of tholeiitic and komatiitic volcanics. For this reason compositional variations of original rocks are not always distinguished from variations due to the hydrothermal alteration. For instance at almost constant $\text{Al}_2\text{O}_3/\text{TiO}_2$, $\text{Ti}/\text{Zr}$ and $\text{Sc}/\text{Zr}$ ratios, the Mg content in less altered komatiitic rocks varies from 38% to 13% at Munro Township. Similarly $\text{CaO}$ and $\text{Al}_2\text{O}_3$ vary from 11.5% to 3.6% and from 12% to 4% respectively (Arndt et al., 1977; Ludden and Gelinas, 1982) given these constraints on identifying a reasonable parent rock. For this reason the numerical results of mass-balance calculations have to be taken with caution. However the application of Gresen's method (1967) in rocks from the Kerr-Addison Mine and other Archean lode gold deposits (Kerrich and Hodder, 1982; Kerrich, 1983) can be interpreted in terms of variable increase in volume of rocks due to the addition of many components, especially $\text{CO}_2$, $\text{CaO}$, and alkali-metals. These calculations also show that the alteration process is compatible with relative immobility of $\text{Al}_2\text{O}_3$, $\text{Zn}$, $\text{Sc}$ and to some extent $\text{TiO}_2$.

For the purpose of this study which is to clarify the relationship between hydrothermal alteration and gold concentration, the approach involving the degree of saturation relative to certain components, as presented earlier in this chapter, seems to be the most adequate considering
the amount and type of available data. As discussed before, the hydrothermal alteration at Kerr-Addison is characterized by a massive introduction of CO₂ along with variable additions of Na, K and Ca. Inspection of chemical analyses (Appendix 1) indicates that the weight percent of most components other than Na₂O, K₂O, CaO and C decreases as the L.O.I. (loss on ignition) increases. The apparent depletion of various components with progressive alteration may be interpreted as simple dilution of the rocks by massive introduction of volatiles. For instance, chemical analyses of ultramafic rocks having different alteration types, when recalculated to 100% on a volatile-free basis (Table 4.2), show composition similar to less altered counterparts, thus demonstrating that most of the apparent depletion of components reflects dilution of rocks by massive addition of volatiles and CaO.

The most important depletion involves an element rarely included in geochemical mass balance calculations, namely hydrogen. Note that the final product of alteration, the carbonate-albite type characterized by the assemblage quartz, carbonate, albite and leucoxene, unlike other alteration assemblages, contains no hydrogen in the structural formula of its mineral phases. The process of progressive removal of hydrogen in the form of H₂O or H⁺ is discussed later in more detail in Chapter 8.
6.7 Distribution of Gold Relative to the Alteration Types

Background gold contents of most igneous rocks are in the range of 2 to 5 ppb (Tilling et al., 1973; Kwong and Crocket, 1978; Keays, 1982; Saager et al., 1982). An average gold ore grade of 10 ppm represents an enrichment of about $10^4$ times background. Extreme enrichments result in erratic distributions of gold on a small scale, with consequent difficulties in sampling and handling of geochemical data. For this reason, only rocks with gold contents up to 1000 ppb are included in this discussion (Appendix 1).

Variations of gold abundance across the 3850' level of the Kerr-Addison mine are displayed in Fig. 6.5D with the aid of moving averages of 5 samples. The most striking feature of Fig. 6.5 is the contrast in gold values north and south of the KLFZ. Gold abundances in rocks north of fault zone are uniformly low at <2 ppb, those values being close to background. In contrast, south of the KLFZ, the gold content is variable and generally higher.

Another interesting aspect of the distribution is the similarity of its configuration to those of the graphs depicting the variation of CO$_2$ and alkali-metal saturation indices (Fig. 6.5), especially south of the KLFZ. The gold values are symmetrically distributed relative to the Kerr-fault zone. The correspondence of the variation of alteration parameters to gold content suggests a genetic link
between hydrothermal alteration and mineralization. However, a close examination of these graphs reveals that peaks of gold content are slightly displaced relative to the peaks of alteration indices (Fig. 6.5).

Such a displacement may be the reason why previous geochemical studies in Archean lode gold deposits have not been able to identify statistical correlations between gold and various geochemical parameters. The best correlations are of gold peaks with the points where $3K/Al$ and $Na/Al$ curves intersect each other. That means the gold content is higher when muscovite and albite are both present. The highest gold anomalies corresponding to the transition zone between the carbonate-muscovite and carbonate-albite alterations. It is interesting to note that $S$ enrichment (pyritic alteration) also concentrates in such transition zones.

Therefore, the geochemical data from the Kerr-Addison Mine not only reveals a close correlation of hydrothermal alteration with gold anomalies but also indicates that gold is part of a specific alteration assemblage.
Figure 6.1

Variations of alteration stages across the 3850' level of the Kerr-Addison mine, relative to saturation indices of CO$_2$ and alkali metals. Initial stage of alteration (IN) is characterized by low CO$_2$/(Ca+Mg+Fe) and (3K+Na)/Al indices. Advanced stage of alteration (AD) corresponds to areas of high CO$_2$/(Ca+Mg+Fe) and (3K+Na)/Al indices. The broad CO$_2$/(Ca+Mg+Fe) peak north of the XLFZ has no associated (3K+Na)/Al maxima, corresponding to an area of chloritoid alteration (chlt'd.). Areas of the advanced stage of alteration (AD) can be subdivided into zones of carbonate-muscovite type (cb-mu) and carbonate-albite type (cb-alb) on the basis of high 3K/Al or Na/Al, respectively. Note the symmetrical distribution of different saturation indices relative to the Kerr-fault. All points correspond to moving averages of 5 samples, projected on a N30W vertical plane (see Appendix 3).
Figure 6.2

FeO, MgO and FeO/MgO versus Ti plots of altered ultramafic rocks of the Kerr-Addison mine. The continuous lines are the trends for komatitic rocks of the Abitibi Belt according to data from Arndt et al. (1977, 1982) and Beswick (1982). FeO concentrations of altered rocks are generally slightly higher than fresher ultramafic volcanics, whereas MgO is highly variable. Oxides in weight percent, Ti in ppm, recalculated to 100% on a volatile free basis.
Figure 6.3

FeO, MgO and FeO/MgO versus Ti diagrams of altered mafic rocks from the Kerr-Addison mine. The shaded areas are the field of "tholeiitic basalts" and "Fe-rich tholeiitic basalts" from the Stoughton-Roquemore and Kinojevis groups respectively, after Jensen and Langford (1983). Large excursions from the expected trends of the FeO/MgO ratio is observed due to small variations of FeO and MgO.
Figure 6:4

Frequency distribution of molar ratio CO\textsubscript{2}/CaO of altered mafic and ultramafic rock of the Kerr-Addison mine. A ratio of 1 indicates that calcite is the dominant carbonate (chlorite-albite alteration type of mafic rocks). Ratios >5 signify the presence of magnesite (talc-chlorite alteration of ultramafic rocks). The hydrothermal alteration tends predominantly to produce CO\textsubscript{2}/CaO ratios 2, characteristic of ankerite and ferroan dolomite. Such a tendency indicates additions of CaO into the altered rocks.
Figure 6.5

Distribution of moving averages of Au across the 3850' level of the Kerr-Addison mine, compared to the saturation indices of CO₂ and alkali-metals. Concentrations of Au are generally high south of the KLFZ. Note that the gold maxima are slightly displaced relative to the maxima of the saturation indices. Peaks of Au correspond to points where 3K/Al and Na/Al indices display similar values, and are therefore in the transition zone between carbonate-muscovite and carbonate-albite alteration types (see Fig. 6.1).
CHAPTER 7

OXYGEN ISOTOPE DATA

7.1 Introduction

Oxygen isotope analyses of minerals and rocks may provide information on the nature of hydrothermal regimes in ore deposits. In principle, the probable origin and temperature of mineralizing fluids can be deduced from measured oxygen isotope compositions of minerals at equilibrium. Oxygen isotope determinations were performed on 37 mineral separates extracted from 15 samples representing a section across the 3850' level of the Kerr-Addison mine (Table 7.1). Details of the analytical procedures and mineral separation are given in Appendix II.

Oxygen isotope analyses are reported in the conventional notation $\delta^{18}O$ (Taylor, 1974, 1979), where:

$$
\delta^{18}O = \left( \frac{(18O/16O)}{\text{sample}} \right) - 1 \times 10^{3\%}
$$
and δ values are reported in per mil relative to SMOW (δ$^{18}$O$_{SMOW}$ = 0). Fractionations, or differences in δ$^{18}$O between minerals are quoted as ∆, defined as $\Delta_{A-B} = 10^3 \ln \alpha_{A-B}$ = $\delta_{A-B}$, where α is the fractionation factor for the coexisting minerals A and B. The approximation holds for $\delta_{A-B} < 10$.  

7.2 Results

Although the isotope fractionation (∆) between most mineral pairs falls within a narrow span of values, the δ$^{18}$O of minerals show a considerable range (Table 7.1). Variations in the δ$^{18}$O of minerals appears to be related to the original rock type rather than to the hydrothermal alteration type. The range of variation in δ$^{18}$O of quartz, chlorite and albite grouped according to the alteration stages and to the original parental rocks are illustrated in Fig. 7.1A and B respectively.

Minerals extracted from samples with the initial stage of alteration exhibit considerable variation of δ$^{18}$O (Fig. 7.1A). For instance δ$^{18}$O quartz ranges from 12.7 to 15.7. Minerals extracted from samples with advanced alteration show smaller but still significant variation (Fig. 7.1). In contrast, when the samples are grouped according to the original parental rocks (mafic rocks of the Kinojevis Group, mafic rocks of Larder Lake Group and ultramafic rocks) the δ$^{18}$O of minerals fall in a narrow bracket of
values within each rock type (Fig. 7.18). The highest values correspond to mineral separates from mafic rocks of the Kinojevis Group, whereas the lowest ones correspond to mafic rocks from the Larder Lake Group. Minerals separated from ultramafic rocks have intermediate $\delta^{18}O$. Quartz extracted from cross-cutting quartz veins has $\delta^{18}O$ identical (within the limits of analytical errors) to those of quartz from ultramafic rocks.

The reason for this variation in $\delta^{18}O$ of minerals according to the rock types is not clear, but the important fact is that for each specific rock type, the isotopic composition of minerals are nearly constant regardless of the alteration stage.

7.3 Thermometry

The use of oxygen isotope fractionations between mineral pairs or triplets for geothermometry has been the subject of discussion by many authors (Anderson et al., 1971; Bottinga and Javoy, 1973, 1975; Clayton, 1980; Friedman and O'Neil, 1977; O'Neil and Clayton, 1964; Deines, 1977, and others). There is no consensus on which of the various fractionation factors should be applied in temperature calculations, nor on the criteria to test for isotopic equilibrium among minerals. The disagreements originate principally because of the difficulty in empirical calibration of mineral-water fractionations,
especially at low temperatures (<300°C).

It is outside the scope of this study to discuss the merits of one or other set of calibrations. Most of the oxygen-isotope studies in Archean gold deposits have utilized calibration curves for mineral-water fractionation as listed below:

a) A curve derived from the partial exchange experiments (Taylor, 1967) for quartz-water fractionation.
b) Albite-water, O'Neil and Taylor (1967).
d) Empirical curves for muscovite-water and magnetite-water as reported by Bottingá and Javoy (1973).

On the other hand, recent reviews on isotope thermometry recommend the use of the calibration of Matsuhisa et al. (1979) for quartz-water and albite-water fractionations and that of Becker and Clayton (1976) for magnetite-water. The use of this set of calibrations results in considerably lower calculated temperatures (70°C). The equilibrium curve of Clayton (1972) recalculated by Friedman (1977) and the experimental curve of Matthews and Beckinsale (1979) are in good agreement with the recently recommended calibration for quartz-water (Matthews and Beckinsale, 1979; Clayton, 1980). The isotope fractionation equations quoted in this chapter are listed in Table 7.2.

Use of the first set of calibrations (Table 7.2A) on
oxygen isotope data for Kerr-Addison results in temperatures in the range 340-400°C (Fig. 7.2A). Concordant temperatures among mineral triples are rare on the basis of this calibration but the most frequent temperature is around 370°C (Fig. 7.3, column A). Assuming that quartz in veins attained equilibrium with the hydrothermal solutions, the calculated \(^{18}O\) of the fluid is in the range 5.6 to 7.6. These temperatures and calculated fluid compositions are similar to those found in other Archean gold deposits elsewhere, utilizing the same criteria (Kerrich, 1981, 1983; Rye and Rye, 1974).

Calculating temperatures with the alternative set of calibration curves yield temperatures in the range 260 to 300°C (Fig. 7.2B). Rocks characterized by initial alteration in general show discordant temperatures, but some samples with chlorite-albite alteration exhibit triply concordant temperatures of 300°C. Discordant temperatures are indicative of isotopic disequilibrium among one or more of the coexisting phases.

Rocks characterized by advanced alteration in general show concordant temperatures around 270°C (Fig. 7.3, column B). However, temperatures calculated from quartz-muscovite fractionations range from 270° to 220°C. The variable isotopic temperatures result from the variation of \(^{18}O\) muscovite at fairly constant \(^{18}O\) quartz. This may indicate that muscovite is not in equilibrium with the
alteration assemblage having undergone preferential exchange to lower temperatures. Hence the calculated temperature of 220°C is a minima.

Recalculation of isotope data from some other Archean gold deposits such as Dome Mine (Kerrich et al., 1979) and Homestake (Rye and Rye, 1974) with the second calibration indicates temperatures of 270 to 300°C for most mineral pairs and 270 to 220°C for quartz muscovite.

However the application of the first set does not indicate equilibrium and the temperatures of 370 to 400°C (Fig. 7.3, column A) need to be taken with caution. The use of the second set of calibration gives results more compatible with equilibrium at temperatures of 270° and 300° (Fig. 7.3, column B). In this case the calculated fluid composition varies from 4.6 to 5.6‰. On the basis of oxygen isotope composition alone, according to Taylor's (1967) classification of the various "terrestrial water reservoirs", such values (4.6-5.6‰) are compatible with a metamorphic origin of fluids or alternatively, evolved meteoric water. However similar values found in massive pyrite-base-metal-sulphide deposits of Aljustrel, Portugal are shown to be compatible with evolution of sea water under conditions of low water/rock ratios (Munha, 1981; Barriga, 1983).

The significance of the oxygen isotope data and its implications for the interpretations of the hydrothermal
activity in the Kerr-Addison mine are further discussed throughout the following chapters, in conjunction with petrographic and geochemical data.

7.4 Summary

1) The isotopic composition of minerals extracted from rocks with incipient alteration show considerable variation in $\delta^{18}O$. At more advanced stages of alteration the isotopic composition shows smaller but significant variations.

2) When the samples are grouped according to the original rock types the $\delta^{18}O$ of minerals fall in a narrow bracket of values.

3) Although the $\delta^{18}O$ mineral varies, the isotopic fractionation ($\Delta$) between most mineral pairs are relatively homogeneous.

4) The $\delta^{18}O$ of quartz from cross-cutting veins are similar to that from altered ultramafic rocks. This may signify that these quartzes attained isotopic equilibrium with the hydrothermal fluids, and have retained this equilibrium value.

5) Larger variations of isotopic composition in the initial stage of alteration may reflect incomplete equilibration.

6) Calculated temperatures are relatively uniform at 270-300°C, indicating broadly isothermal activity.
7) Assuming that quartzes from the crosscutting veins have equilibrated with an external fluid at 270-300°C, the calculated δ¹⁸O water is in the range of 4.6 to 5.6.

8) According to Taylor's (1971) isotopic classification of "water reservoirs", the calculated fluid composition is compatible with metamorphic origin, or alternatively evolved meteoric or seawater. Discrimination between these three possible reservoirs requires additional lines of evidence.
Figure 7.1

Variations of $\delta^{18}O$ minerals according to stage of alteration (A) and original rock types (B). chl: chlorite; alb: albite; qtz: quartz.
Figure 7.2

Frequency of calculated temperatures using fractionation equations of Table 7.2A and B.
Figure 7.3
Oxygen isotope thermometry. Columns A and B give calculated temperatures using fractionation equations reported in Table 7.2A and B respectively. Application of fractionation equations of Table 7.2A yield discordant temperatures. Equations of Table 7.2B also result in discordant temperatures for rocks of the initial stage of alteration but generally more concordant temperatures for rocks of the advanced alteration. qtz: quartz; chl: chlorite; mt: magnetite; mu: muscovite.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AK-80</td>
<td>300 400 500 600</td>
<td>Mafic rock from north of KLFLZ chl-alb alteration</td>
</tr>
<tr>
<td>AK-5</td>
<td>300 400 500 600</td>
<td>Mafic rock from south of KLFLZ chl-alb alteration</td>
</tr>
<tr>
<td>AK-75</td>
<td>300 400 500 600</td>
<td>Mafic rock from north of KLFLZ chl-alb alteration</td>
</tr>
<tr>
<td>AK-76</td>
<td>300 400 500 600</td>
<td>Mafic rock from north of KLFLZ chl-mu alteration</td>
</tr>
<tr>
<td>AK-510</td>
<td>300 400 500 600</td>
<td>Mafic rock near flow ore cb-alb alteration</td>
</tr>
<tr>
<td>AK-512</td>
<td>300 400 500 600</td>
<td>Mafic rock, cb-mu alt. near flow ore</td>
</tr>
<tr>
<td>AK-40</td>
<td>300 400 500 600</td>
<td>Flow ore from Kerrich, 1983</td>
</tr>
<tr>
<td>AK-43</td>
<td>300 400 500 600</td>
<td>Ultramafic rock cb-alb alteration</td>
</tr>
<tr>
<td>AK-64</td>
<td>300 400 500 600</td>
<td>Ultramafic rock cb-mu alteration</td>
</tr>
<tr>
<td>AK-617</td>
<td>300 400 500 600</td>
<td>Quartz-muscovite vein from Kerrich, 1983</td>
</tr>
<tr>
<td>AK-617</td>
<td>300 400 500 600</td>
<td>Flow ore from Kerrich, 1983</td>
</tr>
<tr>
<td>AK-617</td>
<td>300 400 500 600</td>
<td>Carbonate ore cb-mu alteration</td>
</tr>
</tbody>
</table>
Table 7.1  Oxygen isotope data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta^{18}O$</th>
<th>qtz</th>
<th>ab</th>
<th>mu</th>
<th>chl</th>
<th>mt</th>
</tr>
</thead>
<tbody>
<tr>
<td>AK-5</td>
<td>12.72</td>
<td>10.90</td>
<td>6.94</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AK-13</td>
<td>14.91</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AK-18</td>
<td>13.60</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AK-33</td>
<td>14.04</td>
<td>11.68</td>
<td>6.89</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AK-40</td>
<td>14.20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AK-518</td>
<td>12.78</td>
<td>10.50</td>
<td>5.45</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AK-512</td>
<td>11.74</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AK-617</td>
<td>13.71</td>
<td></td>
<td>9.33</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AK-618</td>
<td>13.70</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AK-44</td>
<td>13.84</td>
<td>11.40</td>
<td>9.19</td>
<td>9.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AK-60</td>
<td>15.74</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AK-75</td>
<td>15.05</td>
<td>12.70</td>
<td>8.51</td>
<td>4.84</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AK-76</td>
<td>15.54</td>
<td>12.63</td>
<td>7.46</td>
<td>1.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AK-80</td>
<td>15.70</td>
<td></td>
<td>8.97</td>
<td>1.16</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 7.2. Oxygen isotope fractionation factors between minerals and water, in $\delta_{\text{min}}^{18}\text{O} = a 10^6/T + b$.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>a</th>
<th>b</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>quartz</td>
<td>3.57</td>
<td>-2.73</td>
<td>Taylor (1967)</td>
</tr>
<tr>
<td>alk-felds</td>
<td>2.91</td>
<td>-3.41</td>
<td>O’Neill and Taylor (1967)</td>
</tr>
<tr>
<td>magnetite</td>
<td>-1.47</td>
<td>-3.70</td>
<td>Bottington and Javoy (1973)</td>
</tr>
<tr>
<td>chlorite</td>
<td>1.56</td>
<td>-4.69</td>
<td>Wenner and Taylor (1971)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>quartz</td>
<td>3.34</td>
<td>-3.31</td>
<td>Matsuhisa et al. (1979)</td>
</tr>
<tr>
<td>albite</td>
<td>2.39</td>
<td>-2.51</td>
<td>Matsuhisa et al. (1979)</td>
</tr>
<tr>
<td>magnetite</td>
<td>-0.49</td>
<td>-6.40</td>
<td>Becker and Clayton (1976)</td>
</tr>
</tbody>
</table>

A and B fractionation factors used to calculate temperatures reported in Figure 7.3 columns A and B respectively.
CHAPTER 8

FLUID-WATER INTERACTION

8.1 Introduction

This chapter considers the possible reactions of the hydrothermal fluids with the wall rocks of the Kerr-Addison mine, which resulted in the different alteration types outlined in Chapter 5.

An outstanding feature of the hydrothermal alteration in the Kerr-Addison Mine is the enrichment in carbonates, indicating infiltration of CO₂-rich fluids. The presence of graphite in wall rocks south of the KLFZ imposes important constraints on the composition of the infiltrating fluid. In the presence of graphite and at equilibrium, the fluid contains other gases of the C-O-H system besides CO₂. For this reason a brief review of the C-O-H system is presented before further discussion of the alteration process.
8.2 The C-O-H System and Oxidation State

The various aspects of the C-O-H system, in a geological context have been discussed by French and Eugster (1965), Eugster and Skippen (1967), Ohmoto and Kerrick (1977), Forst (1979a, 1979b), Holloway (1981) and others.

With excess C (presence of graphite) the proportion of gas species in the C-O-H system is controlled by reaction such as:

\[
\begin{align*}
C + O_2 & \rightleftharpoons CO_2 \\
C + \frac{1}{2} O_2 & \rightleftharpoons CO \\
C + 2 H_2 & \rightleftharpoons CH_4 \\
H_2 + \frac{1}{2} O_2 & \rightleftharpoons H_2O
\end{align*}
\]

The total fluid pressure (P_f) is the sum of the partial pressures of all gaseous species. The partial pressures of O_2 and H_2 being very small:

\[P_f = P_{CO_2} + P_{CH_4} + P_{CO} + P_{H_2}O\]

With 2 phases (graphite + fluid) and 3 components, the C-O-H system requires 3 independent variables to be completely defined. French (1966) calculated the variation of gas composition in this system in equilibrium with graphite and various oxygen buffers. Results of such calculations as presented by Eugster and Skippen (1967) are
reproduced in Fig. 8.1.

From inspection of Fig. 8.1, it is clear that in a hydrothermal system where large amounts of externally generated fluid encounter graphite bearing rocks, the proportion of the various gas species depends on the fO₂ of the incoming fluid. If the oxidation state of such a fluid is high, the reaction C + O₂ = CO₂ dominates, and the fluid becomes CO₂ rich, independently of the CO₂ content prior to interaction with graphite. More reduced fluids may contain considerable CH₄ (Fig. 8.1).

In the C-O-H system, CO is negligible at temperatures below 600°C (Fig. 8.1) and the fluid can be considered as a mixture of H₂O, CO₂ and CH₄ (Ohimoto and Kerrick, 1977). Since CH₄ does not participate in carbonatization reactions, acting only as an inert diluant, the fluid behaves as a CO₂-H₂O mixture where P fluid > P H₂O + P CO₂ (Kerrick, 1974; Frost, 1979b). The molar fraction XCO₂ defined as CO₂/(CO₂+H₂O+CH₄) is a function of fO₂, which may be controlled either by the infiltrating fluid or by reactions with wall rocks.

Lower XCO₂ indicates lower fO₂ in the presence of graphite, but this relation does not hold north of the KLFZ, where magnetite, rather than graphite, is present. In order to evaluate the variation of oxidation state across the alteration zoning of the Kerr-Addison mine it is necessary to consider the Fe and C bearing phases.
Frost (1979a) introduced an independent variable $XC$, in order to study the $fO_2$ variation in the Fe-Si-C-O-H system under isobaric isothermal conditions. $XC$ is defined as $XC = CO_2 + CO + 1/3 CH_4$. A schematic phase diagram of the Fe-C-O-H and Fe-Si-C-O-H systems, in the $XC-fO_2$ space according to Frost (1979a, 1979b) is presented in Fig. 8.2.

In Kerr-Addison, Fe and C bearing phases from south to north are: a) hydrated silicates + graphite; b) carbonate + graphite; c) carbonate + hydrated silicates; and d) hydrated silicates + Fe oxide. Such a sequence of assemblages in the Fe-Si-C-O-H system (Fig. 8.2B) correspond to increasing $fO_2$ and decreasing $XC$. Evidently the rocks of the mine area involve more complex systems than that of Fig. 8.2. The presence of Mg and Ca tends to expand the stability fields of carbonates and silicates toward higher $fO_2$ (Frost, 1979a). The effect of Al on the stability fields is more complex, but the overall topology is not likely to be very different, and the sequence of alteration assemblages across the Kerr-Addison mine probably represents a gradient of decreasing $fO_2$ from north to the south.

If this is the case the hydrothermal fluids have oxidized the graphite bearing wall rocks and reduced the magnetite bearing ones.

Because intense carbonatization is a common feature of many Archean lode gold deposits, the origin of CO$_2$ rich fluids capable of producing such alteration has been the
subject of concern of many authors. Metamorphic dehydration of silicious marble can produce a mass of CO₂ up to 30% of the weight of the original rock (Fyfe et al., 1978, Chap. 6) by reactions such as:

\[ \text{CaCO}_3 + \text{SiO}_2 \xrightarrow{\text{calc.}} \text{CaSiO}_3 + \text{CO}_2 \]

\[ \text{CaMg(CO}_3)_2 + 2 \text{SiO}_2 \xrightarrow{\text{dolomite}} \text{CaMgSi}_2\text{O}_6 + 2 \text{CO}_2 \]

Considering an average CO₂ content of 10% for altered rocks of the mine area, the carbonatization of 1000 kg of volcanic rocks requires a minimum of 300 Kg of silicious marble to be decarbonated. The same 1000 kg of volcanic rocks can be carbonatized by the oxidation of 75 Kg of graphite.

From the discussion above, it is clear that in the case of Kerr-Addison where graphite is present in the wall rocks, the question as to whether the CO₂ was locally generated or introduced from a distant reservoir is irrelevant as far as wall rock alteration is concerned. The fO₂ of the incoming fluid controls the proportion of CO₂ in the fluid in contact with graphite.
8.3 Alteration Reactions

In order to facilitate the discussion of fluid/rock interactions, the possible reactions involved in each stage of the alteration are discussed separately. The initial stage of alteration is characterized by the presence of chlorite among the alteration minerals, whereas the advanced stage is defined by the abundance of muscovite, albite or pyrite (see Chapter 5). Sub-division of alteration types and their respective mineral assemblages are summarized in Fig. 5.1.

8.3.1 Initial stage of alteration

Ultramafic rocks

The mineralogical variation of the initial stage of alteration of ultramafic rocks can be represented by reactions within the systems MgO-SiO₂-CO₂-H₂O and CaO-MgO-SiO₂-CO₂-H₂O as follows:

1) \[ 3 \text{tremolite} + 6 \text{CO}_2 + 2 \text{H}_2\text{O} \rightarrow 5 \text{talc} + 6 \text{calcite} + 4 \text{quartz} \]

2) \[ 2 \text{serpentine} + 3 \text{CO}_2 \rightarrow \text{talc} + 3 \text{magnesite} + 3 \text{H}_2\text{O} \]

3) \[ \text{talc} + 3 \text{calcite} \rightarrow 3 \text{CO}_2 \rightarrow 3 \text{dolomite} + 1 \text{quartz} + \text{H}_2\text{O} \]

4) \[ \text{talc} + 3 \text{CO}_2 \rightarrow 3 \text{magnesite} + 4 \text{quartz} + \text{H}_2\text{O} \]

Equations 1 and 2 represent the transition from the
metamorphic assemblage to talc-chlorite alteration. Equations 3 and 4 represent the transformation from talc-chlorite to carbonate-chlorite alteration. In as much as chlorite is stable in the pre-alteration metamorphic assemblage as well as throughout the initial stage of alteration, it is not included in the alteration reactions.

All of the reactions above (reacs. 1 to 4), tend to proceed to the right (more carbonate) with increasing mol fraction of CO₂ in the fluid or decreasing temperature. An increase in the total fluid pressure produces the same effect (Kerrick, 1974; Slaughter et al., 1975; Johannes, 1969). Equilibria of these reactions in T-XCO₂ diagrams, according to Johannes (1969) and Walther and Helgeson (1980) are shown in Fig. 9.3. The presence of CH₄ moves equilibrium curve 1 to the left, whereas curves 3 and 4 shift to the right. Equilibrium curve 2 is unaffected by CH₄ (Kerrick, 1974).

Hydrothermal alteration at Kerr-Addison occurred at temperatures below 370°C, probably around 300°C (Chapter 7). Hence the low temperature-low XCO₂ part of the diagram is of the most interest for this study. The behaviour of CO₂-H₂O mixtures departs significantly from ideality under these conditions, and accordingly interpolation of equilibria curves to that part of the diagrams involves considerable uncertainties (Kerrick, 1974; Walther and Helgeson, 1980). However some of the salient points can be
defined:

a) Low Ca content in the system increases the field of stability of talc. This prediction of the experimental work is in good accordance with field observations in the mine area (Chapter 6).

b) Under conditions of low XCO₂ the equilibria curves asymptotically approach the T axis. Therefore, the alteration zoning of the initial stage of alteration is more likely to reflect variations in the XCO₂ of fluids rather than variations in temperature. An isothermal regime is compatible with oxygen isotope data (see Chapter 7).

c) The XCO₂ of the fluid in the initial stage of alteration of ultramafic rocks was well below 0.1.

Mafic Rocks

The initial stage of alteration of mafic rocks encompasses more complex systems than those discussed for the carbonatization of ultramafic rocks. Nevertheless, the same kinds of reactions can be envisaged.

The development of the chlorite-albite alteration type, which is characterized by the absence of actinolite and epidote relative to metamorphic precursors can be illustrated with reference to a reaction such as:
5) \[ 2 \text{clinozoisite} + 3 \text{actinolite} + 10 \text{CO}_2 + 8 \text{H}_2\text{O} \rightarrow 3 \text{chlorite} + 3 \text{calcite} + 10 \text{quartz} \]

As the initial stage of alteration of mafic rocks proceeds, albite and some of the chlorite are replaced by muscovite plus carbonate. Considering the geochemical trends of loss of Na associated with gains of K and CO\(_2\) with progression of the initial stage of alteration (see Chapter 6, Fig. 6.1) a composite reaction can be written as follows:

6) \[ \text{albite} + \text{chlorite} + 5 \text{calcite} + 5 \text{CO}_2 + K^+ \rightarrow \text{muscovite} + 5 \text{ankerite} + 3 \text{quartz} + 3 \text{H}_2\text{O} + \text{Na}^+ \]

The slope of reaction 6 in an isothermal, isobaric section is portrayed in a schematic diagram in Fig. 8.4. The reaction depends on $X_{CO_2}$ and $a(K^+/Na^+)$. Under conditions of low $X_{CO_2}$ this reaction is critically dependent on small changes of $X_{CO_2}$, whereas at high $X_{CO_2}$ it is more sensitive to variations of $a(K^+/H^+)$. 

8.4 Inferences From the Initial Stage of Alteration

Minerals of altered rocks are far from pure phases and the alteration reactions do not occur along univariant curves. Instead they may occur over a range of conditions according to the Fe/Mg ratio of the solid phases. The
complexity of the system describing the initial stage of alteration of mafic rocks makes comparisons with the corresponding stage of alteration in ultramafic rocks difficult. Qualitative comparison is however possible and it illustrates the similarity of the alteration process for both groups of rocks.

The topology of equilibria of alteration assemblages of mafic and ultramafic rocks are similar in an isobaric, isothermal CO$_2$–H$_2$O space (Fig. 8.5A and B). Alteration assemblages of rocks with different original compositions can vary with changes in $X_{CO_2}$ under isothermal conditions. An isothermal regime is fully compatible with the oxygen isotope data (Chapter 7). In addition, in the mine area, the initial stage of alteration of both main groups of rocks occur in close spatial association.

Field relations, oxygen isotope data and the type of alteration suggest that both rock types have been altered coevally, under similar conditions. Therefore the alteration types of the initial stage at Kerr-Addison are interpreted mainly to reflect differences in the chemical composition of the original parental rocks, overprinted by small variations of $X_{CO_2}$ of the fluid.

Another important aspect of the initial stage of alteration is the change in volume of the solid phase. Talc-chlorite alteration via reaction 1 is accompanied by an expansion of 27% in volume. Further alteration to
carbonate-chlorite results in additional volume increases of 25 and 15% for reactions 3 and 4 respectively. The initial stage of alteration of mafic rocks results in an increase of volume of almost 50%.

Such volume increases would certainly tend to decrease the permeability of rocks thus attenuating the fluid flow. With the channelway restricted fluid pressure may increase up to the point of rupture of rocks by hydraulic fracturing (cf. Fyfe et al., 1978, Chap. 10). Repeated cycles of increasing the volume of rocks with associated reduction of permeability followed by hydraulic fracturing may explain the relation of crosscutting "alteration veins" along with the fracturing and deformation of mineral grains as described earlier.

8.5 Advanced Stage of Alteration

The advanced stage of alteration encompasses the carbonate-muscovite, carbonate-albite and pyritic alterations (see Chapter 5).

With completion of the initial stage of alteration, all rocks tend to have the same gross mineral assemblage regardless of the original chemical composition of the parental rocks. The major mineral phases are quartz, carbonate and chlorite for both ultramafic and mafic rocks, the latter containing minor amounts of muscovite. For this reason reactions involved in the advanced stage of altera-
tion are similar in both types of rock.

The development of the carbonate-muscovite alteration can be represented by reaction 7 below. Chlorite is replaced by carbonate and muscovite with addition of CO₂ and K from the hydrothermal fluid. In Kerr-Addison (Downes, 1980) and in the Timmins area (Fyon et al., 1983) "potassic alteration" or formation of muscovite has been interpreted as post-dating the "carbonatization". On the other hand other authors (e.g. Boyle, 1962; Kerrich, 1983) consider them as coeval. Equation 7 well illustrates the intimate relation of "carbonatization" and "potassic alteration", it is clear that the formation of muscovite is simply part of the carbonatization of chlorite to ankerite.

7) \[
3 \text{ chlorite} + 15 \text{ calcite} + 15 \text{ CO}_2 + 2\text{K}^+ \rightarrow 15 \text{ ankerite} + 2 \text{ muscovite} + 3 \text{ quartz} + 9 \text{ H}_2\text{O} + 2 \text{ H}^+ 
\]

The final step of alteration of wall rocks in Kerr-Addison is the substitution of muscovite by albite (reac. 8).

8) \[
\text{muscovite} + 6 \text{ quartz} + 3 \text{ Na}^+ \rightarrow 3 \text{ albite} + \text{K}^+ + 2 \text{ H}^+ 
\]

Phase relations of reaction 7 are schematically depicted in Fig. 8.6, assuming an ideal mixture of ideal gases. Equilibrium for reaction 8 according to Montoya and
Hemley (1975) is reproduced in Fig. 8.7. Carbonate-muscovite alteration (react. 7, Fig. 8.6) depends on the \( \text{XCO}_2 \) and \( a(\text{K}^+/\text{H}^+) \). Under conditions of low \( \text{XCO}_2 \) the observed zonation of alteration types could be produced by small changes in \( \text{XCO}_2 \).

Carbonate albite alteration (react. 8, Fig. 8.7) is also dependent on \( a(\text{K}^+/\text{H}^+) \) of the fluid, but unlike all the preceding alteration types it does not depend on \( \text{XCO}_2 \). The muscovite-albite transition is part of the \( \text{K}_2\text{O}-\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}-\text{HCl} \) system, which is relatively well known (Hemley, 1959; Orville, 1963; Montoya and Hemley, 1975). Assuming an isothermal regime at 300\(^\circ\)C (Fig. 8.7) some additional speculation on the fluid composition can be made. An \( a(\text{Na}^+/\text{K}^+) \) ratio of 10:1 or larger in the fluid for the formation of carbonate-albite alteration can be deduced, based on the absence of paragonite and K-feldspar. A similar ratio can be estimated for the carbonate-muscovite alteration. The fluid could be alkaline with low salinity or slightly acidic with higher salinity.

Pyritic alteration is intimately related to the carbonate-muscovite alteration. Both alteration types result from the replacement of chlorite by carbonate and muscovite (react. 7). Pyritic alteration occurs when part of the iron from the chlorite reacts with sulphur from the fluid.

From the above considerations it may be assumed that
the fluid responsible for the development of the advanced stage of alteration had a small but significant content of CO₂, with pH near neutral to slightly acidic, and Na⁺:K⁺ 10:1. The critical chemical parameters governing the observed alteration zoning seem to be small variations in XCO₂, and the a(Na+/K+) ratio.

A critical parameter for the solubility of gold (see Chapter 2) is the pH of the fluid. For simplicity the alteration reactions discussed above are written with conservation of mass of the bivalent metal carbonate forming components CaO, FeO and MgO. However, in order to evaluate the direction of variation of pH in fluids with respect to progressive alteration, it is necessary to consider a more realistic mass balance. The geochemical behaviour of these three components relative to the alteration is discussed in Chapter 6. Calcium is generally added into rocks with progressive alteration but FeO and MgO show variable gains or losses.

The reactions involved in the development of chlorite-muscovite alteration of mafic rocks (reac. 6) and in the advanced stage of both mafic and ultramafic rocks (reacs. 7 and 8) are the combination of several possible reactions such as:
\[ 3\text{ch} + 30\text{CO}_2 + 2\text{K}^+ + 28\text{H}^+ \rightleftharpoons 2\text{musc} + 3\text{qtz} + 22\text{H}_2\text{O} + 15(\text{X})^{2+} \]

\[ (\text{X})^{2+} + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons (\text{X})\text{CO}_3 + 2\text{H}^+ \]

\[ \text{Ca}^{2+} + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CaCO}_3 + 2\text{H}^+ \]

\[ \text{CaCO}_3 + (\text{X})\text{CO}_3 \rightleftharpoons \text{Ca(X)(CO}_3)_2 \]

\[ 3\text{alb} + \text{K}^+ + 2\text{H}^+ \rightleftharpoons \text{musc} + 6\text{qtz} + 3\text{Na}^+ \]

where \((\text{X}) = \text{Fe+Mg+Mn}\). The balance of those reactions determines the direction of variation of pH in the fluid.

Examples of such calculations in altered mafic rocks of the Kerr-Addison mine are presented in Fig. 8.8. Samples AK-18 and AK-512 are taken as representative of the carbonate-muscovite and carbonate-albite alterations respectively; samples AK-5 and AK-21 represent examples of less altered counterparts. The calculated modal composition of these samples are shown in Table 8.2, in terms of molar percents. The mass balance assumes that samples AK-18 and AK-512 are derived from the alteration of the other two samples. It is also assumed that the mass of \text{Al}_2\text{O}_3 remains constant (for discussion of relative immobility of \text{Al}_2\text{O}_3 see Chapters 3 and 6).

The additions and removal of components from the rocks necessary to form a more advanced stage of alteration for each mol of chlorite consumed is presented in Fig. 8.8. The alteration reaction replaces chlorite for ankerite associated with muscovite or albite, taking \text{Ca}^{2+} and \text{CO}_2 from an external fluid. The process also results in the
release of $H^+$ to the fluid with variable losses or gains of $(X)$ and exchanges of $K^+$ for $Na^+$. It is not proposed here that the resulting composite reactions precisely reproduces the actual process: the important point is that the variation of modal compositions of the rocks is compatible with release of $H^+$ during progressive alteration. Hence the pH of the hydrothermal fluid tends to decrease with fluid-rock interaction, consequently inducing changes in the solubility of gold (see Chapter 2) in a direction that would result in its precipitation.

8.6 Variation of Fluid Composition

Although the reactions discussed above do not reproduce the complex hydrothermal processes in all their details, some interesting aspects may be highlighted as follows.

Among the alteration assemblages at Kerr-Addison, "unbuffered" mineral assemblages are more common than "buffered" ones. A buffered assemblage is one where both reactant and product of a metasomatic reaction are present, whereas in an unbuffered assemblage the reactants are completely consumed. The predominance of unbuffered assemblages indicates infiltration of large volumes of fluid from an external source (Rice and Ferry, 1982). Under these conditions, the mineralogical and chemical composition of the rocks tend to adapt to the composition
of the infiltrating fluid.

If this is the case, the zonation of alteration types in Kerr-Addison reflects variations in the composition of the infiltrating fluid. The deduced fluid variation may be explained by introduction of fluids from different sources or alternatively, by gradual evolution of the external reservoir. However, a third and more likely alternative is that the fluid composition evolved through interaction with the wall rocks.

In this scheme the alteration types are regarded as representing the various steps of a continuous process of incremental changes in the composition of the solid phases, to adapt to the composition of the incoming fluid. Simultaneously the infiltrating fluid evolves to adapt to the composition of the wall-rocks. The harmony of this process is better illustrated with the aid of a set of schematic expressions such as:

\[\begin{align*}
\text{I.} & \quad A + n_1 \text{CO}_2 + n_1 \text{H}_2\text{O} \rightarrow B \\
\text{II} & \quad B + n_1 \text{CO}_2 \rightarrow C + n_1 \text{H}_2\text{O} \\
\text{III} & \quad C + n_1 \text{CO}_2 + n_1 K^+ \rightarrow D + n_1 \text{H}_2\text{O} + n_1 \text{H}^+ \\
\text{IV} & \quad D + n_1 \text{Na}^+ \rightarrow E + n_1 \text{K}^+ + n_1 \text{H}^+
\end{align*}\]

where \(A, B, C, D\) and \(E\) represent solid phases. \(A\) is the metamorphic assemblage; \(B\) and \(C\) the initial stage assemblage; \(D\) and \(E\) the advanced stage; \(n_1\) is the number of
moles of the $n$th component of the $i$th reaction. A schematic diagram (Fig. 8.9) illustrates the relationships of these assemblages relative to the fluid composition.

Rocks evolve from state I to IV, whereas the fluid evolves from state IV to I. A fluid in equilibrium or approaching equilibrium with D and E can react with C to form more D. In this process, the fluid tends to equilibrate with C and D but this same fluid can react with B to form more C and so on. In the process, the rocks tend to gain CO$_2$, K, and Na with loss of H$_2$O and H$^+$. Conversely, the fluid is depleted in CO$_2$ and alkali-metals and enriched in H$^+$. In short, the most evolved rock is in equilibrium with the least evolved fluid and vice versa.

The net result of these interactions is a tendency to form a homogeneous and simple alteration assemblage with carbonate, albite, and quartz, indicating that the less evolved fluids were in equilibrium with this assemblage. The mineral composition of crosscutting veins is that of the most evolved rock (see Chapter 5.5) reinforcing this view. The composition of the incoming fluid must remain essentially unchanged through time inasmuch as the composition of various generation of crosscutting veins along with the associated sequence of alteration remains the same.

The fluid is hypothetical and if ever present is long gone, but the solid phase remains and the metasomatic
zoning is the only evidence of the reconstructed intermediate steps toward the more evolved rock. It is interesting to stress that the precious metal gold is only a small portion of the solid assemblage representative of one of those intermediate steps.

8.7 Fluid Flow Regime

Several independent lines of evidence, as discussed in the previous chapters collectively indicate that a large fluid/rock ratio was involved in the development of the alteration halo of the Kerr-Addison mine. Saturation of altered rocks in CO$_2$ and alkali-metals associated with complete removal of H$_2$O and H$^+$ (see Chapter 6); homogeneous oxygen isotope composition across the alteration zoning (Chapter 7); and enrichment in rare metals, are all features that require the interaction of a volume of fluid larger than the rocks. For instance some altered ultramafic rocks contain up to 30% CO$_2$. If the mol fraction of CO$_2$ in the hydrothermal fluid were of the order of 10$^{-2}$ the minimum water/rock ratio is 35 on a volume basis.

The observed alteration sequences and their spatial distribution favour an interpretation where the fluid composition evolved via reactions with the wall rocks. Variations of fluid composition induced by such interaction under conditions of a large water/rock ratio is possible if the fluid can permeate through the rocks. The extent to
which the fluid composition can be modified by reaction with rocks is a function of the surface area of rock exposed to the fluid (Helgelson, 1970).

The fragmental nature of some rocks in the mine area (see Chap. 4) may have contributed to the pervasive fluid penetration. Closely spaced and randomly oriented small veins along with evidence of fluid penetration in microfractures of mineral grains (see Chap. 5, Plate 6) indicate that the fluid flow regime was more like one observed in porous rocks rather than a laminar flow through continuous planar fractures. The wall rocks behaved as an aquifer rather than an aqueduct. The rock, soaked with fluid, underwent pervasive alteration which could cause significant variation of fluid composition.

Crosscutting relation of veins along with deformation textures of altered minerals indicate repeated episodes of fracturing and fluid penetration. Similar fracture patterns has been interpreted in other Archean gold deposits in Yellowknife (Kerrich et al., 1978; Kerrich and Allison, 1981), Timmins (Kerrich and Fryer, 1979) as the result of hydraulic fracturing.

Most alteration reactions involve increase of volume of solid phases. This volume increase along with mineral precipitation in void spaces tend to decrease the porosity and permeability. Consequently the fluid flow decreases while the fluid pressure rises, diminishing the effective
stress, and facilitating the brittle failure of the wall rocks. The new fractures not only re-establish the fluid flow but also expose fresh rock-surface to reaction. The variation of flow rate with cyclic episodes of fracturing and fluid penetration is schematically illustrated in Fig. 8.10.

Repeated cycles such as outlined above can reconcile large water/rock ratios with variations of fluid composition by water-rock interaction. The composition of the incoming fluid must remain essentially unchanged through time inasmuch as the composition of various generation of crosscutting veins along with associated sequences of alteration remain the same.
Figure 8.1
Composition of C-O-H gas at 2 kbar in the presence of graphite (from Eugster and Skippen, 1967). Dotted, solid and dashed curves are for Hem-Mag, Ni-NiO and Q-F-M buffers, respectively.
Figure 8.2

Isobaric, isothermal log $f_{O_2}$-XC diagrams showing schematic phase relations in the systems Fe-C-O-H (A) and Fe-Si-C-O-H (B). Quartz is assumed to be present in excess in diagram B.

hem: hematite; mt: magnetite; qtz: quartz; sid: siderite; hyd, sil: hydrated silicate; graph: graphite. From Frost (1979a and b).
Figure 8.3
Temperature-\(X\text{CO}_2\) diagram for the systems MgO-SiO\(_2\)-CO\(_2\)-H\(_2\)O and CaO-MgO-SiO\(_2\)-CO\(_2\)-H\(_2\)O at 2 kbar. The numbers on the curves correspond to reactions in the text. After Johannes (1969), Kerrick et al. (1974), Slaughter et al. (1975) and Walther and Helgeson (1980).

sp: serpentine; ma: magnesite; trem: tremolite; cal: calcite; qtz: quartz.

Figure 8.4
Schematic isobaric, isothermal, \(\log a(K^+/Na^+)\) versus \(X\text{CO}_2\) diagram of reaction 6 of the text. It assumes ideal behaviour of CO\(_2\)-H\(_2\)O mixture at constant \(aH^+, a\text{Mg}^2+,\) and \(a\text{Fe}^2+\).

ank: ankerite; musc: muscovite; alb: albite; chl: chlorite.
Figure 9.5

Schematic $\text{H}_2\text{O} - \text{CO}_2$ diagrams, showing the slope of alteration reactions of ultramafic (A) and mafic rocks (B) as presented in the text. The small arrow in diagram B indicates the direction of displacement with increasing $\text{K}^+ / \text{Na}^+$. 
Figure 8.6

Schematic diagram showing the slopes of reaction 7 in log $a(K^+/H^+)$, $XCO_2$ space, assuming constant $aMg^{+2}$ and $aFe^{+2}$, and ideal behaviour of $CO_2$-H$_2$O mixtures.
$\log a\frac{K^+}{H^+}$ vs $x_{CO_2}$

The reaction shown is:

$15\text{ank} + 2\text{mu} + 3\text{qtz} + 9\text{H}_2\text{O} + 2\text{H}^+ + 3\text{chl} + 15\text{cal} + 15\text{CO}_2 + 2\text{K}^+$
Figure 8.7

Schematic stability relations in the system K$_2$O-Na$_2$O-
Al$_2$O$_3$-SiO$_2$-H$_2$O-HCl at 3000°C and 15000 psi (1 kb) after
Montoya and Hemley (1975). Quartz is assumed to be present
in excess.
Mass balance of alteration reaction involving chlorite, ankerite, muscovite, albite and fluid. Samples AK-18 and AK-512 represent the carbonate-muscovite and carbonate-albite alteration types respectively. Samples AK-5 and AK-21 are taken as the less altered counterparts. The calculated modal compositions of these samples are listed in Table 8.2. Mass balance is presented in terms of gains or losses for the consumption of each mol of chlorite \((X)\text{5Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8\) to form a more advanced stage of alteration with conservation of mass of \(\text{Al}_2\text{O}_3\). Note that all reactions result in release of \(\text{H}^+\) to the fluid.

\((X) = \text{Fe}+\text{Mg}+\text{Mn}\).
Figure 8.8

Schematic diagram illustrating the possible relations of fluid composition and alteration types. Small arrows indicate directions of displacement with increasing $a(\text{Na}^+ / \text{H}^+)$. $A = \text{metamorphic assemblage}; B$ and $C = \text{initial stage of alteration}; D$ and $E = \text{advanced stage of alteration}; D = \text{carbonate-muscovite type}; E = \text{carbonate-albite type}$. Constant $a\text{Mg}^{2+}$ and $a\text{Fe}^{2+}$ are assumed.
Figure 8.10

Schematic diagram indicating possible evolution of the fluid-flow regime with time. The alteration reactions increase the volume of solid phases, decreasing the permeability and flow rate. With the flow rate restrained, fluid pressure rises, facilitating brittle failure (fracturing). New fractures re-establish the permeability and flow rate, initiating a new cycle of alteration.
The diagram illustrates the relationship between flow rate and time, with peaks indicating reaction and fracturing events.
Table 8.1. Simplified reactions of fluid-rock interaction at the Kerr-Addison mine.
Table A.1: Simplified reactions of fluid-rock interaction at the Kerr-Addison mine.

<table>
<thead>
<tr>
<th>ULTRAMAFIC ROCKS</th>
<th>MAFIC ROCKS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) $3 \text{Ca}_2\text{Mg}_5\text{Si}<em>8\text{O}</em>{22}(\text{OH})_2 + 6 \text{CO}_2 + 2 \text{H}_2\text{O}$</td>
<td>$2 \text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_8(\text{OH}) + 3 \text{Ca}_2(\text{Mg,Fe})_3\text{Si}_8(\text{OH})_2 + 10 \text{CO}_2 + 8 \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>TOTOLITE fluid fluid</td>
<td>EPIDOTITE ACTINOLITE fluid fluid</td>
</tr>
<tr>
<td>5 $\text{Mg}_3\text{Si}<em>4\text{O}</em>{10}(\text{OH})_2 + 6 \text{CaCO}_3 + 4 \text{SiO}_2$</td>
<td>3 $(\text{Mg,Fe})_3\text{Al}_2\text{Si}_3\text{O}_10(\text{OH})_6 + 10 \text{CaCO}_3 + 21 \text{SiO}_2$</td>
</tr>
<tr>
<td>TALC CALCITE QUARTZ</td>
<td>CILLOTITE CALCITE QUARTZ</td>
</tr>
<tr>
<td>2) $2 \text{Mg}_3\text{Si}<em>4\text{O}</em>{10}(\text{OH})_6 + 3 \text{CO}_2$</td>
<td>$\text{NaAl}_2\text{Si}_3\text{O}_10(\text{OH})_6 + 3 \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>SERPENTINE fluid fluid</td>
<td>$\text{NaAl}_2\text{Si}_3\text{O}_10(\text{OH})_6 + 5 \text{CaCO}_3 + 4.5 \text{CO}_2 + \text{K}^+$</td>
</tr>
<tr>
<td>TALC fluid NADORNITE fluid</td>
<td>CLASHITE CHLORITE CILLOTITE fluid</td>
</tr>
<tr>
<td>3) $\text{Na}_2\text{Si}<em>4\text{O}</em>{10}(\text{OH})_2 + 3 \text{CaCO}_3 + 3 \text{CO}_2$</td>
<td>$5 \text{Ca}(\text{Mg,Fe})(\text{CO}_3)_2 + 3 \text{SiO}_2 + \text{KAI}_3\text{Si}_3\text{O}_10(\text{OH})_2 + 3 \text{H}_2\text{O} + \text{Na}^+$</td>
</tr>
<tr>
<td>TALC CALCITE fluid NADORNITE QUARTZ fluid</td>
<td>ANGEBITITE QUARTZ MISCIVITE fluid fluid</td>
</tr>
<tr>
<td>4) $\text{Na}_2\text{Si}<em>4\text{O}</em>{10}(\text{OH})_2 + 2 \text{CO}_2$</td>
<td>$3 \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>TALC fluid NADORNITE QUARTZ</td>
<td>fluid</td>
</tr>
<tr>
<td>5) $3 \text{NaAl}_2\text{Si}_3\text{O}_10(\text{OH})_6 + 10 \text{CaCO}_3 + 15 \text{CO}_2 + 2 \text{K}^+$</td>
<td>$15 \text{Ca}(\text{Mg,Fe})(\text{CO}_3)_2 + 2 \text{KAI}_3\text{Si}_3\text{O}_10(\text{OH})_2 + 3 \text{SiO}_2 + 9 \text{H}_2\text{O} + 2 \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>OLLOTITE fluid fluid</td>
<td>ANGEBITITE MISCIVITE fluid fluid</td>
</tr>
<tr>
<td>6) $3 \text{NaAl}_2\text{Si}_3\text{O}_10(\text{OH})_6 + 2 \text{H}_2\text{O}$</td>
<td>$6 \text{SiO}_2 + 3 \text{Na}^+$</td>
</tr>
<tr>
<td>OLLOTITE fluid fluid</td>
<td>ALLOTITE fluid fluid</td>
</tr>
</tbody>
</table>

---

10
Table 8.2. Modal composition of altered mafic rocks.

<table>
<thead>
<tr>
<th></th>
<th>AK-5</th>
<th>AK-18</th>
<th>AK-21</th>
<th>AK-512</th>
</tr>
</thead>
<tbody>
<tr>
<td>chl</td>
<td>5.87</td>
<td>1.44</td>
<td>6.86</td>
<td>3.25</td>
</tr>
<tr>
<td>alb</td>
<td>19.34</td>
<td>8.54</td>
<td>16.29</td>
<td>21.99</td>
</tr>
<tr>
<td>musc</td>
<td>3.21</td>
<td>4.00</td>
<td>3.11</td>
<td>1.73</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>14.39</td>
<td>17.32</td>
<td>11.82</td>
<td>25.26</td>
</tr>
<tr>
<td>XCO₃</td>
<td>12.66</td>
<td>21.16</td>
<td>10.62</td>
<td>20.40</td>
</tr>
<tr>
<td>Qtz</td>
<td>40.89</td>
<td>43.10</td>
<td>46.74</td>
<td>123.44</td>
</tr>
<tr>
<td>TiO₂</td>
<td>3.90</td>
<td>3.46</td>
<td>4.44</td>
<td>2.98</td>
</tr>
<tr>
<td>Py</td>
<td>-</td>
<td>0.54</td>
<td>-</td>
<td>1.22</td>
</tr>
</tbody>
</table>

calculated from chemical analyses assuming mineral composition as follows:

- alb (albite): NaAlSi₃O₈
- musc (muscovite): KAlSi₃O₁₀(OH)₂
- chl (chlorite): (X)₅Al₂Si₃O₁₀(OH)₈ where X = FeO+MgO+MnO
- Py (pyrite): FeS₂
CHAPTER 9

METASOMATIC ZONING

9.1 Introduction

The observed hydrothermal alteration zoning at the Kerr-Addison mine as described in Chapters 5 and 6 is regarded as an example of metasomatic zoning (see Chapter 8).

Metasomatic zoning may develop in the contact between two phases not in equilibrium (Thompson, 1959). A hypothetical example of such zoning as presented by Thompson (1959) is illustrated in Fig. 9.1.

Consider a situation where periclase (MgO) comes in direct contact with quartz (SiO₂). At constant temperature and pressure reactions between the incompatible phases periclase and quartz tend to form forsterite and enstatite. If diffusion rates permit, reactions between the incompatible pairs forsterite-quartz and periclase-
enstatite form a metasomatic zoning such as illustrated in Fig. 9.1, which tend to isolate the two original incompatible phases.

The thermodynamic manipulations concerning this type of system where one or more elements are mobile has been discussed by among others Korzhinskii (1966, 1967), Thompson (1959), Weill and Fyfe (1964, 1967), Helgeson (1970, 1979), Frantz and Welsbrod (1974), and Rice and Ferry (1982). The various approaches for the evaluation of the conditions of formation of different zones is a matter of controversy. For a qualitative evaluation it will suffice to consider that:

a) The development of such zoning requires that one or more components move across the boundary of the zones.

b) The width of the metasomatic zones tends to increase until one of the starting phases is completely consumed or until the mass transfer stops.

c) The result is a gradient in the content of certain components, in this case of SiO₂ and MgO.

d) The conditions in each metasomatic zone are intermediate between the conditions prevailing in the end members, which in this example are pericline and quartz.

9.2 Metasomatic Zoning at Kerr-Addison

The zonation of alteration types at the Kerr-Addison
mine can be regarded as metasomatic zoning in the contact between incompatible phases. Such a contact can be recognized at two main scales. The first is the juxtaposition of relatively oxidized rocks of the Kinojevis Group with the relatively reduced rocks of the Larder Lake Group along the KLFZ (Fig. 9.2). The second scale is the juxtaposition of a fluid phase (hydrothermal fluid) and a solid phase (wall rocks) (Fig. 9.3).

Redox reactions tend to occur when two phases with different oxidation states such as the magnetite bearing rocks of the Kinojevis Group and graphite bearing rocks of the Larder-Lake Group came in contact, in this case by faulting. Diffusion through solids is a very slow process even in terms of geological time but the introduction of fluids in such interfaces enhances the reaction and diffusion rates (Fyfe et al., 1976; Frantz and Welsbrom, 1974). At Kerr Addison, the most important components for reactions involving oxidation-reduction are Fe and C. South of the KLFZ, prior to the metasomatic process, most of the Fe was present as Fe$^{2+}$ in silicates and most of the carbon as C$^0$ (graphite). In contrast, north of that fault a significant part of the Fe was present as Fe$^{3+}$ in magnetite and carbon was absent. The present configuration is illustrated in the cartoon of Fig. 9.2.

At the interface, carbon was oxidized to carbonates whereas Fe$^{3+}$ was reduced to iron carbonate, producing
a metasomatic zoning which isolates the incompatible phases. Among the chemical gradients produced in the process the most important are $f_{O_2}$ of the fluid and the Au content of the solid phase (Fig. 9.2). Gold contents are dramatically increased in the south end of the metasomatic zoning relative to the north, suggesting that its precipitation was controlled by $f_{O_2}$ of the fluid (compare Fig. 9.2 with 8.1). If this is the case, the presence of fluids in the interface of rocks with contrasting oxidation state may have acted as a natural electrochemical cell where gold was concentrated at the reducing pole!

Continuation of this process would tend to produce wider metasomatic zoning and perhaps the gold content would have continued to increase, but no localized enrichment should be expected.

The other scale of metasomatic zoning was developed in the interface between rocks and fluid (Fig. 9.3). The $P_{CO_2}$ and alkali-metal/$H^+$ ratio of the infiltrating fluid were high relative to equilibrium conditions with the original rocks. The details of the reactions involved in the process, especially at the south of the KFLZ is discussed in Chapter 8, of which the most important are carbonatization and alkali-metal metasomatism. The resulting zonation of alteration types is described in detail in Chapter 4, and the consequent gradient in $CO_2$ and alkali-metal content in the solid phases are summarized in Fig.
6.1 (Chapter 6).

The alkali-metal/H⁺ ratio of the fluid decreases from the channel way toward the wall rocks, whereas gold in the solid phase (altered rocks) has a maximum in the transition zone between the carbonate-albite and carbonate-muscovite alteration zones (Fig. 9.3). If the composition of the incoming fluid does not change with time, and the flow rate also remains high, the interfaces between different alteration types (reaction fronts) would progressively move to the right in Fig. 9.3. Gold is observed to concentrate in one of these reaction fronts (see Chapters 6 and 8), i.e., gold is part of the solid assemblage at one of these interfaces. Therefore, gold concentration should also move as the reaction front moves. Continuation of the process tends to produce wider metasomatic zones but gold would preferentially concentrate in a narrow zone of reaction interface.

Inspired by examples of metal purification processes utilized by the chemical industry, Fyfe (1973, 1984) suggested that diffusion of metals in fluid media can be an extremely efficient way to produce natural concentrations of metals, i.e., ore deposits. In his model the diffusion is mostly driven by a thermal gradient. The metasomatic zoning of Kerr-Addison and its spatial relation to gold concentration suggest that diffusion driven by gradients of chemical potential are equally efficient and perhaps a more
selective mechanism of metal purification. In fact, diffusion in fluid media driven by gradients of chemical potential are also a common metallurgical process (electro-chemical cells).

Again by analogy with the beneficiation and refining methods utilized by the mining and metallurgical industry, it may be expected that the highly purified final product requires several steps of enrichment. A steep geothermal gradient moves large volumes of fluid and gold will tend to concentrate at certain crustal levels. If the fluid flow is focused such concentration naturally is more localized (Fyfe and Henley, 1973). Where this localized site is also the interface of contrasting rock type in terms of oxidation state, further concentration is expected. Redox reactions between the different fault blocks may continuously increases the gold content of the reducing end of the proposed electrochemical cell. Hydrogen and alkali-metal metasomatism may also provide an efficient process of local remobilization. Perhaps at this stage Au may have locally risen to the $10^3$ ppb anomalies of Fig. 6.1. For an economic grade probably the "repeated cycles of fluid infiltration, alteration and deformation" are required as described earlier.
Figure 9.1

Diagram illustrating the development of metasomatic zoning due to original compositional gradients. (After Thompson, 1959).
periclase  
+ forsterite 
forsterite  
+ enstatite  
enstatite  
+ quartz  

wt. % SiO₂
0 100
Figure 9.2

Schematic model for the development of metasomatic zoning due to the original contrast in oxidation state between rocks of the relatively oxidized Kinojewis group and the reduced Larder Lake group. Oxidation of C from graphite and reduction of Fe$^{3+}$ from magnetite, coupled with formation of iron-bearing carbonates tends to produce a continuous gradient of f$\text{O}_2$. Gold, the solubility of which is sensitive to variations of f$\text{O}_2$, concentrates in the reducing part of the metasomatic zoning.
<table>
<thead>
<tr>
<th>Kinojevis Group</th>
<th>Larder Lake Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>hyd. silic. Fe$^{+2}$ magnetite Fe$^{+2}$ Fe$^{+3}$ carbonate Fe$^{+2}$ C$^{+4}$ graphite C$^{0}$</td>
<td>hyd. silic. Fe$^{+2}$ carbonate Fe$^{+2}$ C$^{+4}$ graphite C$^{0}$</td>
</tr>
</tbody>
</table>

**KLFZ:** Kirkland Lake - Larder Lake Fault Zone

---

**fO$_2$ fluid**

---

**Au solid**
Figure 9.3
Schematic model for the development of metasomatic zoning due to fluid infiltration. Fluid-rock interaction produces the alteration zoning as described in Chapter 5, resulting in a gradient of pH in the fluid. Gold is concentrated in the reaction front between E (carbonate-albite) and D (carbonate-muscovite), possibly in response to a drop of pH. See Figure 6.2.

A: Metamorphic assemblage
B-C: Initial stage of alteration
D-E: Advanced stage of alteration
CHAPTER 10

COMPARISON WITH OTHER ARCHEAN GOLD DEPOSITS,
SUMMARY AND CONCLUSIONS

10.1 Introduction

Archean gold deposits occur in many different stratigraphic environments and lithological host rocks. They are found associated with clastic and chemical sedimentary rocks as well as volcanic and intrusive rocks of alkalic, felsic, mafic or ultramafic compositions (Latulippe, 1982; Goldie, 1982; Karvinen, 1978; 1981; Hodgson and MacGeehan, 1982; Colvin, 1983). The common characteristics are the abundance of carbonate, muscovite and albite in the altered wall rocks, indicating a close relationship between hydrothermal alteration and gold concentration, rather than stratigraphic or lithological controls.
10.2 Alteration Types In Other Archean Gold Deposits

Hydrothermal alteration similar to that observed at the Kerr-Addison mine (see Chapter 5) has been described from several places in the Timmins-Porcupine area (Fyon et al., 1983); from Val D'Or, Quebec (Robert and Brown, 1984), Kambalda, Australia (Phillips and Groves, 1983), Murchinson, S. Africa (Pearston, 1979), and Araci, Brazil (Teixeira et al., 1980). In some localities (Hunt Mine, Kambalda; Araci, Brazil) biotite may locally dominate over muscovite. Tourmaline and/or arsenopyrite are common in other places (Fleischer and Routbier, 1973; Ladeira, 1980; Hodgson and Mac Geehan, 1982; Kerrich, 1983).

Carbonate-albite alteration is rarely classified as a distinct alteration type, but the assemblage quartz-carbonate albite has been described in various deposits of the Timmins-Porcupine area (Fyon et al., 1980, 1981, 1983; Whitehead et al., 1980), Red Lake area (Fryer et al., 1979; Andrews and Wallace, 1983) and Larder Lake area (Kerrich, 1983). Even in areas where albite is not described, for instance at Murchinson, S. Africa, chemical analyses of the so called "honey comb carbonate" which hosts the Sb-Au mineralization show significant enrichments of Na$_2$O compared to "green carbonates" and "talc-carbonate schists" of the wall rocks (Viljoen et al., 1978, Table 4.3).

In this study, it is suggested that the reactions between graphite bearing rocks and relatively oxidized
rocks have an important role in gold concentration. The association of gold deposits with carbonaceous rocks has been stressed by several authors (Henley, 1971; Jensen, 1980; Springer, 1983). In many papers the lack of a complete description of the rocks in the vicinity of the mines makes it difficult to evaluate whether or not the carbonaceous rocks were in contact with more oxidized rocks. However, several important deposits are clearly in such a contact zone just to mention a few, Hollinger (Fyon et al., 1983), East Malartic (Kerrich, 1983), Bousquet (Valliant et al., 1982), Homestake, USA (Rye and Rye, 1974), Upper Beaver (Roberts and Morris, 1982), Araci, Brazil (Teixeira et al., 1980), etc.

A more detailed comparison of sequences of alteration in relation to gold concentration is almost intractable due to the diversity of classification of alteration types in the literature. Often the alteration types do not completely define the rocks, or the same nomenclature is not used uniformly by different authors. Where complete descriptions of the alteration assemblages and their spatial distributions are available; e.g. Hunt Mine, Australia (Phillips and Groves, 1984), Sigma Mine, Quebec (Robert and Brown, 1984), it is evident that gold is concentrated in the vicinity of the interface of carbonate-albite and carbonate-muscovite alteration.

These relationships between alteration type and gold
concentration are not restricted to Archean deposits. In the Mother Lode System, California, the so-called vein ore is part of quartz-carbonate-albite veins where the wall rocks have the assemblage carbonate-muscovite, whereas the "gray ore" is located in areas between "albitite veins" and "ankerite-muscovite schists" (Knopf, 1929).

Recently, several sound descriptions of the variation of mineral assemblages across alteration zones in gold deposits (e.g. Phillips and Groves, 1984; Fyon et al., 1983; Robert and Brown, 1984) seems to mark a return to the practice of including conventional petrographic examination in the study of gold deposits. Accumulation of such data, along with those obtained with "more advanced techniques" will permit better elucidation of the role of fluid-rock interaction in Archean lode gold deposits.

10.3 Summary and Conclusions

This study has concentrated on the relationships between the hydrothermal alteration of wall rocks and gold enrichment at the Kerr-Addison mine. The work includes descriptions and interpretations of the mineralogy and geochemistry of the alteration zoning, along with oxygen isotope data, which can be summarized as follows:

1) The major structural feature in the vicinity of the mine area is the Kirkland Lake-Larder Lake Fault Zone (KLFZ), a structural break which juxtaposes contrast-
ing suites of rocks. Volcanic rocks of the Kinojevis
Group to the north contain magnetite, indicative of
relatively oxidizing conditions, as opposed to more
reducing conditions to the south indicated by the
presence of graphite in interflow sediments and the
matrix of volcanic breccias in rocks of the Larder
Lake Group. The Kerr-Addison mine lie in a zone of
talc-carbonate and chlorite-carbonate rocks of the
Larder Lake Group (Thomson, 1941; Downes, 1980;

2) Two principal types of ore are presently worked at the
mine. These are the "carbonate ore" which consists of
green muscovite bearing quartz-carbonate rock and the
"flow ore" which is a quartz-chlorite-carbonate
schist. Relict volcanic textures such as varioles,
pillow and flow breccia are locally preserved in the
flow ore (Thomson, 1941; Lowrie and Wilton, 1980).
Relict spinifex texture is also observed in the wall
rocks of the carbonate ore (Lowrie and Wilton, 1980;
Downes, 1980).

3) Local preservation of volcanic textures and structures
provide evidence that carbonate-rich rocks in the area
are, at least in part, derived from mafic and ultra-
mafic volcanic rocks. In the vicinity of shear zones,
primary textures are completely obliterated and the
origin of these rocks has been variously interpreted
as altered volcanics (Thomson, 1941; Jihor and Crocket, 1976, 1977; Downes, 1980), exhalative chemical sediments (Ridler, 1970) or igneous carbonatite (Stricker, 1978). Geochemical data of this study indicate remarkable chemical similarity of carbonate-rich rocks to those of fresh tholelitic and komatitic volcanic rocks of the Abitibi Belt. Based on variations in abundances of relatively immobile elements (eg. Ti, Zr, Sc, and Al), it is concluded that the most reasonable interpretation is that irrespective of their present structural fabric and mineralogy, the mafic and ultramafic rocks at the Kerr-Addison mine represent altered volcanic rocks and their clastic derivatives. For this reason it is assumed that prior to their hydrothermal alteration, the mineralogical composition of these rocks was similar to those of mafic and ultramafic rocks in other parts of the Abitibi Belt.

4) The variety of mineral assemblages associated with the hydrothermal alteration are grouped into: a) metamorphic assemblages; b) initial stage of alteration; c) advanced stage of alteration. The alteration stages in turn are divided into "alteration types" as summarized in Figure 5.1.

5) Alteration types of the initial stage contain chlorite which is replaced by muscovite and albite in the
advanced stage. Hence, the sequence of alteration can be easily monitored by the relative abundance of the three aluminum-bearing minerals: chlorite, muscovite, then albite with increasing intensity of alteration. The proportion of carbonate minerals also becomes augmented in the process.

6) Numerous generations of crosscutting veins are enveloped by alteration borders in which the sequence of Al-bearing silicates, namely albite, muscovite, and chlorite always develop from the vein to the wall rocks in the same sequence. These veins are more abundant near the ore zone, usually with the assemblage quartz-carbonate-albite. In the periphery of the alteration halo, veins are less abundant being composed of quartz-carbonate-muscovite or quartz-carbonate-chlorite. Older generation of alteration minerals tend to diminish in grain size due to fracturing along with development of sub-grains.

7) Oxygen isotope data indicate fairly constant temperatures across the alteration zoning. The calculated temperatures are around 300°C to 270°C, based on the most recent fractionation factors; and these also signify local preservation of triple isotopic concordancy among quartz, albite, and chlorite. The δ18O of minerals of each main group of rocks fall within narrow brackets of values suggesting a homogeneous
isotopic composition of the fluid through the alteration zoning. The calculated isotope composition of such a fluid, assuming equilibrium at 2700°C is approximately 5.00/oo, in keeping with a metamorphic or evolved meteoric water origin, according to Taylor's (1967) classification of terrestrial water reservoirs.

The sequence of alteration is characterized by massive introduction of CO₂ and variable amounts of CaO and alkali-metals into rocks; water and hydrogen are removed. Formation of ankerite and ferroan dolomite seems to be accompanied by introduction of Ca to the rocks along with variable gains and losses of Fe and Mg. The degree of enrichment of rocks in CO₂ and alkali-metals can be monitored by "saturation indices" such as the molar ratios CO₂/(Fe+Mg+Ca), (3K+Na)/Al, 3K/Al and Na/Al. Plots of moving averages of these indices can delineate areas of predominance of distinct alteration types, irrespective of the primary bulk composition of the rocks. Alteration types as indicated by these saturation indices are symmetrically distributed relative to the possible channel way for the hydrothermal fluid, namely the area of the Kerr Fault.

9) Variations of gold abundances across the 3859' level of the Kerr-Addison mine exhibit contrasting patterns north and south of the KLFZ. North of that fault zone
the gold content of the rocks is uniformly low (<2 ppb). South of the KLFZ, the gold content is generally higher but variable. This spatial distribution shows a remarkable correspondence to variations of the geochemical saturation indices, suggesting a genetic link of gold enrichment to hydrothermal alteration. Peaks of gold content correspond to points where the saturation indices 3K/Al and Na/Al, indicative of the carbonate-muscovite and carbonate-albite alteration types respectively, have the same value. Therefore the gold, in a broad scale, is concentrated to the south of the KLFZ, and in more detailed scale concentrates in the transition zone between carbonate-muscovite and carbonate-albite alteration types.

10) Interaction of rocks with contrasting oxidation states north and south of the KLFZ, with the same fluid, has produced a metasomatic zoning possibly induced by a gradient fO₂. This process may explain the preferential concentration of gold south of the KLFZ, i.e. the reducing portion of the metasomatic zoning.

11) Variation of mineral assemblages of the initial stage of alteration of ultramafic rocks are probably the result of increasing CO₂ content of fluid, under broadly isothermal conditions. The initial stage of alteration of mafic rocks involves more complex reactions, but seems to have occurred under similar
conditions to that of the corresponding alteration stage of ultramafic rocks.

12) The advanced stage of alteration is characterized by the replacement of chlorite by carbonates and muscovite and albite. This process, which occurs in rocks with both mafic and ultramafic original composition, seems to reflect variations of alkali-metal/H⁺ ratio along with increasing CO₂ content of fluids.

13) Differences between the initial and advanced stage of alteration are interpreted in terms of gradual evolution of the composition of relatively uniform external fluid through local interaction with wall rocks. In this model the alteration types are regarded as representing various steps of a continuous process of incremental changes in the composition of the solid phases to adapt to the composition of the incoming fluid. Simultaneously, the infiltrating fluid evolves to adapt to the composition of the wall rocks. In this case the less evolved fluid had a small but significant amount of CO₂, with K⁺/Na⁺ ratio ≈ 10. The interaction with rocks tend to decrease the CO₂ content and alkali-metal/H⁺ ratio in the fluid.

14) Variation in the composition of large volumes of fluids in the alteration domain are interpreted as the result of repeated episodes of fracturing, fluid penetration and fluid-rock reactions. The composition
of the incoming fluid seems to have remained essentially the same as indicated by the consistent sequence of alteration types enveloping different generations of veins. Systematic variation of mineral associations with distance from the veins, along with variation of the mineral assemblages of the veins themselves, are interpreted as the result of lateral variation of fluid composition due to interaction with rocks.

15) Considerations of mass balance for possible reactions involved in the carbonatization of chlorite indicates release of $\text{H}^+$ to the fluid. In this case the pH of the fluid would tend to decrease as it penetrates the wall rocks. Gold may have precipitated in response to such pH variations in the interface between carbonate-muscovite and carbonate-albite alteration types.
APPENDIX 1

WHOLE ROCK GEOCHEMICAL DATA
**APPENDIX 1**

<table>
<thead>
<tr>
<th>AK-1</th>
<th>AK-3</th>
<th>AK-5</th>
<th>AK-6</th>
<th>AK-7</th>
<th>AK-8</th>
<th>AK-9</th>
<th>AK-11</th>
<th>AK-12</th>
<th>AK-18</th>
<th>AK-20</th>
<th>AK-21</th>
<th>AK-22</th>
<th>AK-23</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>71.67</td>
<td>44.67</td>
<td>48.57</td>
<td>50.35</td>
<td>47.57</td>
<td>47.29</td>
<td>39.25</td>
<td>21.29</td>
<td>39.79</td>
<td>44.62</td>
<td>41.47</td>
<td>48.46</td>
<td>37.72</td>
</tr>
<tr>
<td>TiO2</td>
<td>22</td>
<td>3.44</td>
<td>2.88</td>
<td>1.79</td>
<td>1.96</td>
<td>3.25</td>
<td>.22</td>
<td>.40</td>
<td>.08</td>
<td>1.43</td>
<td>.76</td>
<td>1.87</td>
<td>.64</td>
</tr>
<tr>
<td>Al2O</td>
<td>61.93</td>
<td>7.40</td>
<td>13.32</td>
<td>12.55</td>
<td>11.96</td>
<td>11.36</td>
<td>3.08</td>
<td>7.09</td>
<td>1.66</td>
<td>19.44</td>
<td>18.08</td>
<td>13.16</td>
<td>8.82</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>.7</td>
<td>.52</td>
<td>2.99</td>
<td>.65</td>
<td>1.53</td>
<td>.50</td>
<td>2.4</td>
<td>1.78</td>
<td>2.47</td>
<td>1.43</td>
<td>.51</td>
<td>.16</td>
<td>Fe2O3</td>
</tr>
<tr>
<td>FeO</td>
<td>5.25</td>
<td>15.92</td>
<td>8.96</td>
<td>9.79</td>
<td>11.14</td>
<td>10.69</td>
<td>8.19</td>
<td>9.02</td>
<td>4.57</td>
<td>19.55</td>
<td>5.30</td>
<td>12.75</td>
<td>8.46</td>
</tr>
<tr>
<td>MnO</td>
<td>.13</td>
<td>.55</td>
<td>.16</td>
<td>.25</td>
<td>.34</td>
<td>.20</td>
<td>.14</td>
<td>.13</td>
<td>.22</td>
<td>.40</td>
<td>.80</td>
<td>.24</td>
<td>.29</td>
</tr>
<tr>
<td>MgO</td>
<td>1.43</td>
<td>7.03</td>
<td>5.33</td>
<td>3.68</td>
<td>4.76</td>
<td>3.67</td>
<td>19.28</td>
<td>12.64</td>
<td>10.44</td>
<td>3.74</td>
<td>5.55</td>
<td>4.30</td>
<td>9.53</td>
</tr>
<tr>
<td>CaO</td>
<td>1.80</td>
<td>8.63</td>
<td>5.80</td>
<td>6.71</td>
<td>8.16</td>
<td>6.07</td>
<td>11.13</td>
<td>21.96</td>
<td>12.91</td>
<td>7.66</td>
<td>11.39</td>
<td>4.38</td>
<td>12.03</td>
</tr>
<tr>
<td>Na2O</td>
<td>5.75</td>
<td>5.80</td>
<td>3.84</td>
<td>3.70</td>
<td>2.34</td>
<td>3.75</td>
<td>.00</td>
<td>1.38</td>
<td>.00</td>
<td>1.92</td>
<td>.69</td>
<td>3.27</td>
<td>.80</td>
</tr>
<tr>
<td>K2O</td>
<td>.08</td>
<td>.72</td>
<td>.34</td>
<td>.65</td>
<td>.00</td>
<td>.55</td>
<td>.00</td>
<td>1.18</td>
<td>.00</td>
<td>2.20</td>
<td>3.33</td>
<td>.44</td>
<td>1.72</td>
</tr>
<tr>
<td>P2O5</td>
<td>.90</td>
<td>.00</td>
<td>.97</td>
<td>.08</td>
<td>.00</td>
<td>.12</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.08</td>
<td>.51</td>
<td>.08</td>
</tr>
<tr>
<td>LOI</td>
<td>3.12</td>
<td>14.21</td>
<td>9.38</td>
<td>10.61</td>
<td>10.66</td>
<td>10.93</td>
<td>19.39</td>
<td>23.08</td>
<td>29.79</td>
<td>15.33</td>
<td>17.78</td>
<td>8.61</td>
<td>20.00</td>
</tr>
<tr>
<td>Tot</td>
<td>99.72</td>
<td>99.71</td>
<td>99.95</td>
<td>99.96</td>
<td>100.56</td>
<td>99.09</td>
<td>101.74</td>
<td>98.78</td>
<td>99.15</td>
<td>99.94</td>
<td>99.93</td>
<td>100.24</td>
<td>100.19</td>
</tr>
</tbody>
</table>

| C | .70 | .20 | .08 | .20 | .34 | .02 | .02 | .44 | .03 | .54 | .03 | .17 | .03 | .30 | S |
| Rb | 2 | 7 | 11 | 16 | 1 | 14 | 0 | 1 | 34 | 55 | 79 | 3 | 47 | 26 | Rb |
| Sr | 22 | 53 | 83 | 59 | 85 | 79 | 78 | 354 | 230 | 248 | 262 | 127 | 640 | 121 | Sr |
| Ba | 120 | 56 | 171 | 13 | 12 | 189 | 0 | 14 | 530 | 412 | 774 | 79 | 514 | 317 | Ba |
| Sc | 3 | .30 | .48 | 41 | 41 | 44 | 14 | 9 | 13 | 27 | 17 | 45 | 29 | 32 | Sc |
| Y | .12 | 20 | 39 | 49 | 50 | 10 | 13 | 9 | 23 | 32 | 42 | 21 | 38 | Y |
| Zr | 90 | 28 | 120 | 104 | 90 | 127 | 15 | 34 | 79 | 135 | 109 | 86 | 96 | Zr |
| Nb | 15 | 1 | 6 | 5 | 0 | 0 | 1 | 3 | 9 | 3 | 6 | 1 | 4 | 3 | Nb |
| Cs | 26 | 4000 | 29 | 31 | 26 | 18 | 2668 | 1080 | 4170 | 33 | 207 | 47 | 1400 | 31 | Cs |
| Co | 35 | 112 | 49 | 41 | 48 | 50 | 62 | 32 | 45 | 44 | 28 | 68 | 40 | 38 | Co |
| Ni | 28 | 656 | 58 | 41 | 31 | 40 | 1150 | 332 | 700 | 56 | 90 | 46 | 229 | 43 | Ni |
| Cu | 17 | 43 | 38 | 65 | 64 | 9 | 15 | 2 | 15 | 55 | 53 | 61 | 37 | 65 | Cu |
| Zn | 25 | 101 | 90 | 129 | 187 | 142 | 49 | 28 | 21 | 94 | 54 | 160 | 90 | 304 | Zn |
| Pb | 3 | 4 | 7 | 8 | 3 | 11 | 13 | 4 | 12 | 8 | 17 | 1 | 6 | 6 | Pb |
| Au | 27 | 4 | 67 | < 2 | < 2 | < 2 | 2 | 48 | 428 | 17 | 64 | 27 | < 2 | < 2 | 9 | Au |
| Sg | 2.66 | 2.86 | 2.75 | 2.79 | 2.79 | 2.81 | 2.82 | 2.87 | 2.84 | 2.87 | 2.67 | 2.83 | 2.88 | 2.87 | Sg |
### APPENDIX 1

<table>
<thead>
<tr>
<th></th>
<th>AK-25</th>
<th>AK-26</th>
<th>AK-28</th>
<th>AK-31</th>
<th>AK-33</th>
<th>AK-34</th>
<th>AK-37A</th>
<th>AK-40</th>
<th>AK-41</th>
<th>AK-42</th>
<th>AK-43</th>
<th>AK-44</th>
<th>AK-45</th>
<th>AK-46</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>47.60</td>
<td>50.17</td>
<td>27.72</td>
<td>36.00</td>
<td>38.09</td>
<td>32.82</td>
<td>32.93</td>
<td>38.57</td>
<td>30.93</td>
<td>38.58</td>
<td>30.21</td>
<td>24.14</td>
<td>26.72</td>
<td>32.73</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.39</td>
<td>1.76</td>
<td>.54</td>
<td>.24</td>
<td>.29</td>
<td>.29</td>
<td>.25</td>
<td>.34</td>
<td>.30</td>
<td>.08</td>
<td>.25</td>
<td>.20</td>
<td>.29</td>
<td>.22</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>11.08</td>
<td>11.64</td>
<td>8.96</td>
<td>5.34</td>
<td>4.44</td>
<td>4.59</td>
<td>5.04</td>
<td>3.52</td>
<td>4.77</td>
<td>3.75</td>
<td>5.58</td>
<td>3.79</td>
<td>3.27</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>.79</td>
<td>.68</td>
<td>.48</td>
<td>.80</td>
<td>.80</td>
<td>.80</td>
<td>.80</td>
<td>.80</td>
<td>.80</td>
<td>.80</td>
<td>.80</td>
<td>.80</td>
<td>.80</td>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>.28</td>
<td>.15</td>
<td>.22</td>
<td>.28</td>
<td>.29</td>
<td>.24</td>
<td>.15</td>
<td>.12</td>
<td>.29</td>
<td>.26</td>
<td>.24</td>
<td>.29</td>
<td>.15</td>
<td>P₂O₅</td>
</tr>
<tr>
<td>MgO</td>
<td>2.86</td>
<td>4.33</td>
<td>1.64</td>
<td>16.61</td>
<td>19.23</td>
<td>18.73</td>
<td>29.45</td>
<td>21.29</td>
<td>12.53</td>
<td>11.01</td>
<td>14.14</td>
<td>15.53</td>
<td>23.30</td>
<td>20.06</td>
</tr>
<tr>
<td>CaO</td>
<td>5.69</td>
<td>3.60</td>
<td>11.66</td>
<td>12.50</td>
<td>12.63</td>
<td>12.94</td>
<td>2.95</td>
<td>3.34</td>
<td>16.60</td>
<td>16.07</td>
<td>15.01</td>
<td>13.71</td>
<td>5.59</td>
<td>5.15</td>
</tr>
<tr>
<td>Na₂O</td>
<td>5.32</td>
<td>.60</td>
<td>.07</td>
<td>.46</td>
<td>.51</td>
<td>.10</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.02</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>Na₂O</td>
</tr>
<tr>
<td>K₂O</td>
<td>.71</td>
<td>.88</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>K₂O</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>.19</td>
<td>.08</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>P₂O₅</td>
</tr>
<tr>
<td>LOI</td>
<td>12.64</td>
<td>8.50</td>
<td>21.46</td>
<td>19.09</td>
<td>21.89</td>
<td>21.35</td>
<td>18.31</td>
<td>22.54</td>
<td>27.17</td>
<td>25.83</td>
<td>27.92</td>
<td>29.97</td>
<td>30.92</td>
<td>28.62</td>
</tr>
<tr>
<td>Total</td>
<td>99.96</td>
<td>99.80</td>
<td>99.59</td>
<td>100.82</td>
<td>100.82</td>
<td>99.79</td>
<td>99.29</td>
<td>100.32</td>
<td>99.62</td>
<td>97.65</td>
<td>99.09</td>
<td>98.69</td>
<td>100.55</td>
<td>100.52</td>
</tr>
</tbody>
</table>

|        | 2.97  | 1.56  | 4.75  | 4.77  | 5.17  | 5.10  | 3.95   | 5.55  | 7.80  | 7.34  | 7.50  | 8.24  | 8.64  | 8.64  |
|        | 3.77  | .22   | .03   | .02   | .02   | .04   | .04    | .06   | .30   | 1.06  | .07   | .11   | .07   | .06   |

|        | Rb    | 14    | 26    | 4     | 0     | 1     | 2      | 0     | 11    | 17    | 4     | 20    | 19    | 19    |
|        | Sr    | 100   | 67    | 192   | 119   | 182   | 122    | 52    | 67    | 32    | 128   | 280   | 95    | 85    |
|        | Ba    | 200   | 221   | 2     | 8     | 1     | 0      | 0     | 179   | 279   | 53    | 239   | 281   | 181   |
|        | Sc    | 33    | 30    | 32    | 16    | 20    | 17     | 18    | 10    | 16    | 14    | 17    | 17    | 19    |
|        | Y     | 33    | 30    | 32    | 16    | 20    | 17     | 18    | 10    | 16    | 14    | 17    | 17    | 19    |
|        | Zr    | 82    | 108   | 29    | 19    | 23    | 23     | 21    | 20    | 15    | 18    | 17    | 20    | 17    |
|        | Nb    | 2     | 4     | 0     | 7     | 0     | 1      | 2     | 9     | 5     | 5     | 3     | 5     | 3     |
|        | Cr    | 40    | 36    | 1850  | 1050  | 1400  | 2550   | 3080  | 2600  | 1270  | 1970  | 1770  | 2240  | 2080  |
|        | Co    | 58    | 61    | 43    | -     | 48    | 72     | 44    | 39    | 35    | 52    | 58    | 79    | Co    |
|        | Ni    | 71    | 65    | 330   | 510   | 473   | 1130   | 1350  | 1130  | 525   | 710   | 751   | 768   | 829   |
|        | Cu    | 84    | 28    | 16    | 57    | 10    | 51     | 0     | 31    | 43    | 142   | 4     | 0     | 0     |
|        | Zn    | 241   | 200   | 98    | 50    | 44    | 32     | 68    | 54    | 16    | 19    | 37    | 29    | 75    |
|        | Pb    | 15    | 22    | 3     | 8     | 8     | 4      | 13    | 0     | 3     | 13    | 2     | 9     | 9     |
|        | Au    | 100   | 11    | < 2   | -     | < 2   | -      | < 2   | < 2   | -     | < 2   | 28    | 650   | 98    |

|        | Sq    | 2.83  | 2.87  | 2.83  | -     | 2.83  | 2.83   | 2.87  | 2.84  | 2.90  | 1.87  | 2.84  | 2.95  | 2.91  |
|        |       |       |       |       |       |       |       |       |       |       |       |       |       | 2.95  |

C  
S  
Rb  
Sr  
Ba  
Sc  
Y   
Zr  
Nb  
Cr  
Co  
Ni  
Cu  
Zn  
Pb  
Au  
Sq  

---

[^1]: **Note**: The table represents the chemical composition in weight percent for various elements across different samples or conditions. The values indicate the percentage of each element present in the given sample, with elements listed in alphabetical order. The data is crucial for understanding the composition and purity of materials in scientific research, particularly in mineralogy, geochemistry, and materials science.
<table>
<thead>
<tr>
<th></th>
<th>AK-47</th>
<th>AK-48</th>
<th>AK-49</th>
<th>AK-50</th>
<th>AK-54</th>
<th>AK-55</th>
<th>AK-59</th>
<th>AK-60</th>
<th>AK-62</th>
<th>AK-63</th>
<th>AK-65</th>
<th>AK-66</th>
<th>AK-70</th>
<th>AK-71</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>27.13</td>
<td>35.22</td>
<td>29.52</td>
<td>28.79</td>
<td>32.07</td>
<td>35.15</td>
<td>39.27</td>
<td>62.09</td>
<td>65.45</td>
<td>39.45</td>
<td>43.92</td>
<td>32.17</td>
<td>44.09</td>
<td>31.85</td>
</tr>
<tr>
<td>TiO2</td>
<td>1.44</td>
<td>3.30</td>
<td>1.11</td>
<td>1.27</td>
<td>1.22</td>
<td>1.28</td>
<td>1.71</td>
<td>1.58</td>
<td>1.56</td>
<td>1.44</td>
<td>1.73</td>
<td>1.28</td>
<td>1.95</td>
<td>1.67</td>
</tr>
<tr>
<td>Al2O3</td>
<td>8.39</td>
<td>5.32</td>
<td>2.74</td>
<td>4.05</td>
<td>4.09</td>
<td>5.25</td>
<td>12.88</td>
<td>15.02</td>
<td>15.98</td>
<td>8.99</td>
<td>12.96</td>
<td>5.49</td>
<td>11.26</td>
<td>10.89</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>2.91</td>
<td>1.70</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.93</td>
<td>1.46</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.86</td>
<td>2.00</td>
<td>1.54</td>
<td>0.63</td>
</tr>
<tr>
<td>FeO</td>
<td>8.42</td>
<td>7.26</td>
<td>5.75</td>
<td>8.19</td>
<td>6.51</td>
<td>6.95</td>
<td>7.53</td>
<td>4.89</td>
<td>5.22</td>
<td>10.92</td>
<td>9.94</td>
<td>7.16</td>
<td>14.36</td>
<td>12.25</td>
</tr>
<tr>
<td>MnO</td>
<td>16.16</td>
<td>17.10</td>
<td>13.17</td>
<td>11.12</td>
<td>12.07</td>
<td>9.04</td>
<td>8.17</td>
<td>3.20</td>
<td>7.20</td>
<td>18.16</td>
<td>2.22</td>
<td>2.20</td>
<td>2.20</td>
<td>2.20</td>
</tr>
<tr>
<td>MgO</td>
<td>21.81</td>
<td>26.06</td>
<td>27.02</td>
<td>23.14</td>
<td>16.36</td>
<td>23.96</td>
<td>11.18</td>
<td>3.59</td>
<td>2.92</td>
<td>26.58</td>
<td>3.60</td>
<td>26.75</td>
<td>3.95</td>
<td>4.02</td>
</tr>
<tr>
<td>CaO</td>
<td>4.57</td>
<td>5.29</td>
<td>3.12</td>
<td>3.90</td>
<td>13.98</td>
<td>2.41</td>
<td>8.70</td>
<td>2.32</td>
<td>1.31</td>
<td>6.51</td>
<td>8.90</td>
<td>6.17</td>
<td>6.79</td>
<td>13.44</td>
</tr>
<tr>
<td>Na2O</td>
<td>1.36</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>K2O</td>
<td>0.05</td>
<td>0.00</td>
<td>0.06</td>
<td>1.04</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>1.00</td>
<td>1.62</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>P2O5</td>
<td>0.05</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Tot</td>
<td>99.09</td>
<td>100.64</td>
<td>101.02</td>
<td>100.27</td>
<td>99.69</td>
<td>100.40</td>
<td>99.35</td>
<td>99.42</td>
<td>98.93</td>
<td>100.44</td>
<td>99.87</td>
<td>98.94</td>
<td>100.18</td>
<td>100.00</td>
</tr>
<tr>
<td>C</td>
<td>5.92</td>
<td>3.83</td>
<td>7.99</td>
<td>6.51</td>
<td>5.76</td>
<td>3.17</td>
<td>0.98</td>
<td>0.55</td>
<td>2.77</td>
<td>6.02</td>
<td>5.85</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.70</td>
<td>0.02</td>
<td>0.06</td>
<td>0.06</td>
<td>0.12</td>
<td>0.25</td>
<td>0.53</td>
<td>0.14</td>
<td>0.16</td>
<td>0.06</td>
<td>0.11</td>
<td>0.07</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>77</td>
<td>45</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>14</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td>67</td>
<td>0</td>
<td>241</td>
<td>71</td>
<td>73</td>
<td>282</td>
<td>35</td>
<td>265</td>
<td>144</td>
<td>225</td>
<td>56</td>
<td>210</td>
<td>137</td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>6</td>
<td>57</td>
<td>40</td>
<td>196</td>
<td>39</td>
<td>0</td>
<td>9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>0</td>
<td>16</td>
<td>10</td>
<td>0</td>
<td>16</td>
<td>0</td>
<td>0</td>
<td>16</td>
<td>16</td>
<td>27</td>
<td>27</td>
<td>685</td>
<td>838</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>16</td>
<td>0</td>
<td>16</td>
<td>0</td>
<td>0</td>
<td>16</td>
<td>16</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>23</td>
<td>23</td>
<td>14</td>
<td>17</td>
<td>15</td>
<td>0</td>
<td>19</td>
<td>15</td>
<td>19</td>
<td>15</td>
<td>19</td>
<td>15</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>0</td>
<td>0</td>
<td>9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>3090</td>
<td>2160</td>
<td>1100</td>
<td>2000</td>
<td>1300</td>
<td>2500</td>
<td>135</td>
<td>240</td>
<td>254</td>
<td>3750</td>
<td>203</td>
<td>2680</td>
<td>67</td>
<td>18</td>
</tr>
<tr>
<td>Co</td>
<td>66</td>
<td>77</td>
<td>52</td>
<td>62</td>
<td>48</td>
<td>71</td>
<td>42</td>
<td>42</td>
<td>32</td>
<td>98</td>
<td>45</td>
<td>58</td>
<td>67</td>
<td>43</td>
</tr>
<tr>
<td>Ni</td>
<td>730</td>
<td>0</td>
<td>1240</td>
<td>1040</td>
<td>930</td>
<td>760</td>
<td>1000</td>
<td>43</td>
<td>80</td>
<td>73</td>
<td>1830</td>
<td>65</td>
<td>1870</td>
<td>50</td>
</tr>
<tr>
<td>Cu</td>
<td>0</td>
<td>0</td>
<td>18</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>41</td>
<td>10</td>
<td>12</td>
<td>13</td>
<td>0</td>
<td>71</td>
<td>12</td>
<td>23</td>
</tr>
<tr>
<td>Sn</td>
<td>68</td>
<td>43</td>
<td>28</td>
<td>84</td>
<td>36</td>
<td>48</td>
<td>80</td>
<td>49</td>
<td>62</td>
<td>81</td>
<td>80</td>
<td>100</td>
<td>106</td>
<td>50</td>
</tr>
<tr>
<td>Pb</td>
<td>7</td>
<td>11</td>
<td>0</td>
<td>5</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>4</td>
<td>5</td>
<td>1</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>Au</td>
<td>5</td>
<td>&lt;2</td>
<td>2</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>7</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Sg</td>
<td>2.82</td>
<td>2.90</td>
<td>2.88</td>
<td>2.86</td>
<td>2.87</td>
<td>2.77</td>
<td>2.75</td>
<td>2.75</td>
<td>2.75</td>
<td>2.84</td>
<td>2.86</td>
<td>3.02</td>
<td>2.95</td>
<td>8g</td>
</tr>
</tbody>
</table>
## APPENDIX 1

<table>
<thead>
<tr>
<th></th>
<th>AK-72</th>
<th>AK-75</th>
<th>AK-76</th>
<th>AK-79</th>
<th>AK-80</th>
<th>AK-81</th>
<th>AK-508</th>
<th>AK-512</th>
<th>K-518A</th>
<th>K-518B</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1O2</td>
<td>45.64</td>
<td>44.40</td>
<td>47.93</td>
<td>43.35</td>
<td>45.32</td>
<td>24.70</td>
<td>41.47</td>
<td>42.34</td>
<td>60.39</td>
<td>53.57</td>
</tr>
<tr>
<td>T1O2</td>
<td>1.70</td>
<td>1.77</td>
<td>1.73</td>
<td>2.16</td>
<td>2.00</td>
<td>.43</td>
<td>1.83</td>
<td>1.62</td>
<td>1.56</td>
<td>1.70</td>
</tr>
<tr>
<td>A12O3</td>
<td>10.92</td>
<td>12.88</td>
<td>13.06</td>
<td>12.19</td>
<td>11.16</td>
<td>7.73</td>
<td>13.38</td>
<td>11.61</td>
<td>11.00</td>
<td>11.31</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>2.35</td>
<td>2.36</td>
<td>5.05</td>
<td>2.49</td>
<td>3.72</td>
<td>2.91</td>
<td>1.66</td>
<td>.60</td>
<td>Fe2O3</td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td>13.69</td>
<td>12.00</td>
<td>9.33</td>
<td>13.73</td>
<td>11.53</td>
<td>8.05</td>
<td>20.50</td>
<td>10.16</td>
<td>5.51</td>
<td>8.64</td>
</tr>
<tr>
<td>MnO</td>
<td>.28</td>
<td>.15</td>
<td>.22</td>
<td>.22</td>
<td>.28</td>
<td>.16</td>
<td>.38</td>
<td>.58</td>
<td>.25</td>
<td>.34</td>
</tr>
<tr>
<td>MgO</td>
<td>5.10</td>
<td>7.86</td>
<td>7.38</td>
<td>6.81</td>
<td>5.27</td>
<td>22.07</td>
<td>4.80</td>
<td>3.99</td>
<td>3.06</td>
<td>4.12</td>
</tr>
<tr>
<td>CaO</td>
<td>7.24</td>
<td>7.54</td>
<td>9.76</td>
<td>7.83</td>
<td>7.93</td>
<td>3.04</td>
<td>2.91</td>
<td>9.60</td>
<td>4.33</td>
<td>5.52</td>
</tr>
<tr>
<td>Na2O</td>
<td>2.12</td>
<td>2.07</td>
<td>2.16</td>
<td>1.54</td>
<td>1.88</td>
<td>.11</td>
<td>2.20</td>
<td>3.50</td>
<td>5.50</td>
<td>4.76</td>
</tr>
<tr>
<td>K2O</td>
<td>.90</td>
<td>.90</td>
<td>.90</td>
<td>.90</td>
<td>.90</td>
<td>1.64</td>
<td>.06</td>
<td>.00</td>
<td>.00</td>
<td>K2O</td>
</tr>
<tr>
<td>P2O5</td>
<td>.67</td>
<td>.20</td>
<td>.20</td>
<td>.22</td>
<td>.22</td>
<td>.00</td>
<td>.10</td>
<td>.08</td>
<td>.13</td>
<td>P2O5</td>
</tr>
<tr>
<td>LOI</td>
<td>11.94</td>
<td>9.51</td>
<td>4.41</td>
<td>9.53</td>
<td>9.19</td>
<td>27.91</td>
<td>10.05</td>
<td>14.28</td>
<td>6.83</td>
<td>8.69</td>
</tr>
<tr>
<td>Tot</td>
<td>100.10</td>
<td>100.06</td>
<td>100.32</td>
<td>99.42</td>
<td>98.57</td>
<td>99.95</td>
<td>99.09</td>
<td>99.87</td>
<td>99.43</td>
<td>99.71</td>
</tr>
<tr>
<td>C</td>
<td>.19</td>
<td>.83</td>
<td>.84</td>
<td>.13</td>
<td>.16</td>
<td>.22</td>
<td>.28</td>
<td>.50</td>
<td>.13</td>
<td>.16</td>
</tr>
<tr>
<td>S</td>
<td>1.56</td>
<td>.48</td>
<td>.48</td>
<td>.16</td>
<td>.16</td>
<td>.20</td>
<td>.28</td>
<td>.50</td>
<td>.13</td>
<td>.16</td>
</tr>
<tr>
<td>Rb</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>30</td>
<td>4</td>
<td>13</td>
<td>0</td>
</tr>
<tr>
<td>Sr</td>
<td>5</td>
<td>119</td>
<td>180</td>
<td>183</td>
<td>107</td>
<td>.48</td>
<td>24</td>
<td>68</td>
<td>53</td>
<td>75</td>
</tr>
<tr>
<td>Ba</td>
<td>9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>205</td>
<td>71</td>
<td>159</td>
<td>2</td>
<td>25</td>
</tr>
<tr>
<td>Ca</td>
<td>35</td>
<td>41</td>
<td>42</td>
<td>45</td>
<td>41</td>
<td>28</td>
<td>46</td>
<td>37</td>
<td>38</td>
<td>Ca</td>
</tr>
<tr>
<td>Y</td>
<td>30</td>
<td>28</td>
<td>26</td>
<td>40</td>
<td>38</td>
<td>8</td>
<td>53</td>
<td>44</td>
<td>43</td>
<td>49</td>
</tr>
<tr>
<td>Zr</td>
<td>64</td>
<td>79</td>
<td>88</td>
<td>103</td>
<td>96</td>
<td>25</td>
<td>125</td>
<td>102</td>
<td>98</td>
<td>99</td>
</tr>
<tr>
<td>Nb</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>8</td>
<td>6</td>
<td>0</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>Cr</td>
<td>77</td>
<td>195</td>
<td>289</td>
<td>72</td>
<td>71</td>
<td>3200</td>
<td>43</td>
<td>35</td>
<td>31</td>
<td>Cr</td>
</tr>
<tr>
<td>Co</td>
<td>59</td>
<td>63</td>
<td>69</td>
<td>55</td>
<td>57</td>
<td>63</td>
<td>74</td>
<td>42</td>
<td>63</td>
<td>32</td>
</tr>
<tr>
<td>Ni</td>
<td>31</td>
<td>89</td>
<td>99</td>
<td>55</td>
<td>50</td>
<td>658</td>
<td>60</td>
<td>55</td>
<td>108</td>
<td>180</td>
</tr>
<tr>
<td>Cu</td>
<td>36</td>
<td>31</td>
<td>82</td>
<td>47</td>
<td>35</td>
<td>6</td>
<td>73</td>
<td>47</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>Sn</td>
<td>112</td>
<td>90</td>
<td>103</td>
<td>164</td>
<td>123</td>
<td>64</td>
<td>235</td>
<td>132</td>
<td>116</td>
<td>98</td>
</tr>
<tr>
<td>Pb</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>8</td>
<td>0</td>
<td>8</td>
<td>15</td>
<td>16</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>Au</td>
<td>&lt; 2</td>
<td>&lt; 2</td>
<td>&lt; 2</td>
<td>&lt; 2</td>
<td>&lt; 2</td>
<td>21</td>
<td>220</td>
<td>&lt; 2</td>
<td>&lt; 2</td>
<td>Au</td>
</tr>
<tr>
<td>Sg</td>
<td>2.06</td>
<td>2.77</td>
<td>2.95</td>
<td>2.83</td>
<td>2.83</td>
<td>2.97</td>
<td>3.04</td>
<td>2.84</td>
<td>2.77</td>
<td>2.75</td>
</tr>
</tbody>
</table>
NOTES TO APPENDIX 1

Major elements oxides, L.O.I., S and C in weight percent, trace elements in ppm, Au in ppb, Sg in g/cm$^3$.

L.O.I. = loss on ignition
Sg = specific gravity

AK-1,3 - Chlorite-carbonate schist with graphite (interflow sediments).

AK-5,6,7,8,75 - Albite-chlorite-schist.

AK-22 - Chlorite-carbonate-schist.

AK-18,23,26,28 - Chlorite-carbonate-breccia (mafic flow-breccia).

AK-20,59 - Massive chlorite-carbonate rock (mafic flow).

AK-21,25 - Massive sericite-albite-carbonate-rock (mafic flow).

AK-508,512,518a,518a - Chlorite-sericite-albite-carbonate rock (pillowed mafic-flow with variolitic texture).

AK-72,76,79,80 - Massive albite-magnetite-chlorite rock (mafic flow).

AK-70,71 - Massive sericite-chloritoid-carbonate-rock (mafic flow).

AK-65 - Sericite-chloritoid-carbonate-breccia (flow-breccia).

AK-60,62 - Sericite schist.

AK-9,12,31,33,34,37a,66 - Talc carbonate schist

AK-47,48,63 - Chlorite-carbonate rock with relic spinifex texture.

AK-45,81 - Green carbonate rock with relic spinifex texture.

AK-11,41,42,43,44,46,45,46 - Green-carbonate rock.

AK-40,55 - Gray-brown-carbonate rock.
APPENDIX 2

SUMMARY OF ANALYTICAL TECHNIQUES.
APPENDIX 2

2.1 X-Ray Fluorescence Spectrometry (XRF)

Whole rock samples were jaw crushed, and then pulverized to <200 mesh with a tungsten-carbide coated Bleuler mill.

Major elements and the trace elements Nb, Zr, Y, Sr, Rb, Pb, Zn, Cu, Ni, Cr, Ba and S were determined by X-ray fluorescence spectrometry (XRF) in a Phillips PW-1450 spectrometer with selected Cr, W or Rh targets. Except for Na₂O the major elements were analyzed on fusion beads, following the method of Norrish and Hutton (1969). The fusion beads were prepared according to procedures of Harvey et al. (1973), using Spectroflux-105. The major oxide concentrations were calculated against the monitor FS-94 supplied by Dr. K. Norrish, CSIRO, Australia.

Sodium and S were determined on pressed pellets of rock powder, with reference to calibration lines defined by synthetic standards.

Trace elements were determined on pressed pellets by XRF (Rh tube), with reference to selected international standards. Data were reduced using interference and matrix corrections through the computer program TRACE developed by G. Baker, H. Hunter and T. Latour (unpublished, U.W.O.).

International standards and duplicate samples were run for checks on both accuracy and precision. The reproduc-
ibility of major element analyses was in general better than 5%, except for P₂O₅, MnO, MgO and Na₂O (15%). Compared to international standards the accuracy of trace elements is in general within 15%, except for Nb and Pb (25%). Results for Zn, Cu and S indicate only order of magnitude concentrations.

2.2 Neutron Activation Analysis

Scandium was determined by instrumental neutron activation analysis at Neutron Activation Services, Hamilton, Ontario. Results of duplicate samples indicates precision better than 15%.

2.3 Plasma Emission Spectrometry

Gold was analysed by plasma emission spectrometry after preconcentration by fire assay by X-Ray Assay Labs, Toronto.

2.4 Carbon

Carbon was determined in a thermal conductivity cell, utilizing the facilities of the Department of Geology at McMaster University, Ontario. Standards run in each batch indicate accuracy better than 1%. The available standards do not contain carbonates. All analysed samples were run in duplicate and some in triplicate, and the reproducibility is better than 5%.
2.5 FeO and Loss On Ignition (LOI)

Ferrous iron was determined after the method of Wilson (1955). All samples were analysed in duplicate and some in triplicate. Analyses with discrepancies of more than 10% were discarded.

Loss on ignition was measured by weight loss on dry rock powder following heating at 1100°C for 2 hours.

2.6 Oxygen Isotopes

Oxygen isotope compositions of mineral separates prepared by the author were determined by Dr. R. Kerrich at U.W.O.

After crushing, sieving and washing, minerals from each size fractions were concentrated with a hand magnet (magnetite, pyrrhotite), Frantz isodynamic electromagnetic separator, heavy liquids and hand-picking. Muscovite and chlorite separates were digested in concentrated acetic acid to remove carbonates. Quartz and plagioclase concentrates were washed in HNO₃ and HCl to eliminate pyrite and other soluble impurities.

Oxygen was extracted from silicates in a vacuum line using bromine pentafluoride (BrF₅) at 450° to 600°C, converted to CO₂ by reaction over a carbon rod heated to cherry red temperature with platinum catalyst. Isotope determinations were performed on a Micromass 602C dual inlet, 6 m radius, double collecting mass spectrometer.
The results were converted to the Standard Mean Ocean Water (SMOW) scale, calibrated against Caltech Rose Quartz (+8.450/oo) and CMV quartz. Replicate determinations of standards have given a long term 2 of ±0.180/oo (R. Kerrich, personal communication).
APPENDIX 3

LOCATION OF SAMPLES

A A' is the projection plane of figures 6.1 and 6.5
SCHEMATIC GEOLOGY

Kerr-Addison Mine, 3850' level

A mineralized flow ore
B albitized porphyry dyke
C green-carbonate breccia
D chloritic-carbonate breccia
E talc carbonate breccia
F talc chlorite schist
G carbonate tuff
H carbonate tuff and tholeiitic breccia
I' graphitic argilite
J greywacke
K Kenojevis lavas

REFERENCES


Bain, C.W., 1933, Wall rock mineralization along Ontario gold deposits: Econ. Geol., 28, 705-745.


Boyle, R.W., 1959, The geochemistry, origin, and the role of carbon dioxide, water, sulfur, and boron in the Yellowknife gold deposits, Northwest Territories, Canada: Econ. Geol., 50, 1506-1524.


Boyle, R.W., 1968, Hydrothermal transport and deposition of gold - discussions: Econ. Geol., 64, 112-115.


Burnham, C.W., 1962, Facies and type of hydrothermal alteration: Econ. Geol., 57, 768-784.


Cotthles, I.M., 1977, An analysis of the cooling of intrusives by ground water convection including boiling: Econ. Geol., 72, 804-826.

Creasey, S.C., 1959, Some phase relations in the hydrothermally altered rocks of porphyry copper deposits: Econ. Geol., 54, 351-373.


Frost, B.R., 1979a, Metamorphism of iron-formation: parageneses in the system Fe-Si-C-O-H: Econ. Geol., 74, 775-785.


Glasson, M.J., Keays, R.R., 1978, Gold mobilization during cleavage development in sedimentary rocks from the Auriferous Slate Belt of Central Victoria, Australia: some important boundary conditions: Econ. Geol., 73, 496-511.


Helgeson, H.C., Garrels, R.M., 1968, Hydrothermal transport and deposition of gold: Econ. Geol., 63, 622-635.


Hurst, M.E., 1935, Veins formation at Porcupine, Ontario: Econ. Geol. 30, 103-127.


Hutchinson, R.W., 1975, Lode gold deposits, the case for volcanogenic derivation: Oregon Dept. Geol. Mines Ind. Publ. 64, 105.


Keays, R.R., Davison, R.M., 1976, Palladium, iridium, and gold in the ores and host rocks of nickel sulfide deposits in Western Australia: Econ. Geol., 71, 1214-1228.


Kerrich, R., Fyfe, W.S., Allison, I., 1977, Iron reduction around gold-quartz veins, Yellowknife District, Northwest Territories, Canada: Econ. Geol., 72, 657-663.


Krauskopf, K.B., 1951, The solubility of gold: Econ. Geol., 46, 858-870.


Muff, R., Saager, R., Metallogenic interpretation from a 
mineralogic and geostatic study of antimony ores of 
Murchison Greenstone-Belt, South Africa: Geol. Soc. 

Munha, J., 1981, Igneous and metamorphic petrology of the 
Iberian Pyrite Belt volcanic rocks: Ph.D. thesis, 
University of Western Ontario, 771 p.

Noble, J., 1950, Ore mineralization in the Homestake gold 
mine, Lead; South Dakota: Bull. Geol. Soc. Am., 61, 
221-252.

Norrish, K., Hutton, J.F., 1969, An accurate X-ray spectro-
graphic method for analyses of a wide range of geo-
logical samples: Geochim. Cosmochim. Acta, 33, 431-
451.

Norton, D., Knight, J., 1977, Transport phenomena in hydro-
thermal circulation in the ocean crust: J. Geophys.
Res., 81, 3007-3012.

Ohmoto, H., Kerrick, D., 1977, Devolatization equilibria in 

O'Neil, J.R., Taylor, H.P., 1967, The oxygen isotope and 
cation exchange chemistry of feldspar: Am. Mineral., 
52, 1414-1437.

O'Neil, J.R., Taylor, H.P., 1969, Oxygen isotope equilibri-
um between muscovite and water: J. Geophys. Res., 74, 
6012-6022.

Ogryzlo, S.P., 1935, Hydrothermal experiments with gold: 
Econ. Geol., 30, 400-424.

Orville, P.M., 1963, Alkali ion exchange between vapor and 

Pearce, J.A., Cann, J.R., 1973, Tectonic setting of basic 
vulcanic rocks determined using trace elements 

Pearton, P.N., 1979, A geochemical investigation of the 
carbonate and associate rocks of the Monarch Antimony 
Mine, Murchison range, North Eastern Transvaal: 

Phillips, G.N., Groves, D.I., Martyn, J.E., 1984, An epi-
genetic origin for Archean banded iron formation- 
hosted gold deposits: Econ. Geol., 79, 162-171.


Raymahashay, B.C., Holland, H.D., 1969, Redox reactions accompanying hydrothermal wall rock alteration: Econ. Geol., 64, 291-305.


Ridler, R.H., 1972, Volcanic stratigraphy of Kirkland Lake-Timmins, Michipicoten and Mamaine Point areas, Quebec and Ontario: 24th Int. Geol. Congress Field Excursion A40-C40 Guidebook, 33-35.


Robert, F., Brown, A.C., 1984b, Progressive alteration associated with gold-quartz-tourmaline veins at the Sigma Mine, Abitibi Greenstone Belt, Quebec: Econ. Geol., 79, 393-399.


Slaughter, J., Kerrick, D.M., Wall, V.J., 1975, Experimental and thermodynamic study of equilibria in the sytem CaO-MgO-SiO$_2$-H$_2$O-CO$_2$; Am. J. Sci., 275, 143-162.


Taylor, Jr., H.P., 1974, The application of oxygen and hydrogen isotope studies to problems of hydrothermal alteration and ore deposition: Econ. Geol., 69, 843-883.


Weissberg, B.C., 1969, Gold-silver ore grade precipitates from New Zealand thermal waters: Econ. Geol., 64, 95-108.


