Aqueous sulfide oxidation and feldspar dissolution (geochemical reaction modeling using CHILLER).

Christopher Kenneth. Lauzon

University of Windsor

Follow this and additional works at: https://scholar.uwindsor.ca/etd

Recommended Citation
https://scholar.uwindsor.ca/etd/1208

This online database contains the full-text of PhD dissertations and Masters' theses of University of Windsor students from 1954 forward. These documents are made available for personal study and research purposes only, in accordance with the Canadian Copyright Act and the Creative Commons license—CC BY-NC-ND (Attribution, Non-Commercial, No Derivative Works). Under this license, works must always be attributed to the copyright holder (original author), cannot be used for any commercial purposes, and may not be altered. Any other use would require the permission of the copyright holder. Students may inquire about withdrawing their dissertation and/or thesis from this database. For additional inquiries, please contact the repository administrator via email (scholarship@uwindsor.ca) or by telephone at 519-253-3000 ext. 3208.
INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.
Aqueous Sulfide Oxidation and Feldspar Dissolution
(Geochemical Reaction Modeling Using CHILLER)

by
Christopher Kenneth Lauzon

A Thesis
Submitted to the College of Graduate Studies and Research
Through the Department of Earth Sciences
in Partial Fulfillment
of the Requirements for the Degree of
Master of Science
at the University of Windsor

Windsor, Ontario, Canada
1999

© 1999 Christopher Kenneth Lauzon
The author has granted a non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of this thesis in microform, paper or electronic formats.

The author retains ownership of the copyright in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author’s permission.

L’auteur a accordé une licence non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de cette thèse sous la forme de microfiche/film, de reproduction sur papier ou sur format électronique.

L’auteur conserve la propriété du droit d’auteur qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

0-612-52594-5
ABSTRACT

The oxidation of sulfides (primarily pyrite and pyrrhotite) exposed in mine waste accumulations may produce acid mine drainage (AMD), which is characterized by a low pH, a high sulfate content, and the presence of dissolved metals. In this study, CHILLER (a FORTRAN computer modeling program that models geochemical reactions) was used to study how various feldspars (albite, anorthite and microcline) neutralize/buffer the acid generated from pyrite oxidation. Pyrite:feldspar ratios of 1:4, 1:1 and 4:1 were modeled to determine the effects of changing the pyrite:feldspar ratio. The results from the 1:1 pyrite:feldspar reaction models were explored in detail.

For each reaction model, a different series of mineral pH-buffering assemblages formed from the products of the feldspar dissolution reactions, buffering the acidity to different values. The 1:1 pyrite:microcline reaction model produced: goethite, diaspore, kaolinite, quartz, clinochlore, daphnite, stilbite and muscovite. The following minerals formed from the 1:1 pyrite:albite reaction model: goethite, diaspore, kaolinite, quartz, clinochlore, daphnite, stilbite, celadonite and paragonite. The 1:1 pyrite:anorthite reaction model yielded the following minerals: goethite, diaspore, kaolinite, clinochlore, daphnite, stilbite, laumontite, calcite and margarite. The 1:1 pyrite:microcline reaction model reached equilibrium first with a final equilibrated pH of approximately 8.3. The 1:1 pyrite:anorthite reaction model was the last model to reach equilibrium with a final equilibrated pH of approximately 13.5.

Altering the pyrite:feldspar ratio (1:4, 1:1 and 4:1) had no affect on the sequence of alteration minerals formed, so the resultant buffering reactions, buffered pH values and
final equilibrated pH were the same for each group of modeled reactions. Increasing/decreasing the pyrite:feldspar ratio only affected the point at which the final equilibrated pH was reached. In all three groups of models the final equilibrated pH was reached first by the 1:4 (pyrite:feldspar) reaction models while the 4:1 (pyrite:feldspar) reaction models were the last to reach final equilibration.
He knows not his own strength that hath not met adversity.
—Ben Jonson
ACKNOWLEDGEMENTS

I would like to sincerely thank my advisors, Dr. Peter Hudec and Dr. Iain Samson, for all of their support and guidance, but most of all for their patience and understanding. Without their help this study would not have been completed and for that I am greatly indebted to them.

The author also wishes to thank Ingrid Churchill for all of her assistance and guidance within the Geochemistry Lab. Always a source of information and never to busy to offer a helping hand, her generosity was never taken for granted.

I would also like to acknowledge Mrs. Usha Jacob, Ms. Wendy Dupuis, Chris Allen, Dr. M. Franklin and Dr. M. A. Holder-Franklin from the Biology department, as they were all instrumental in my crash course in Microbiology.

James L. Palandri (a Ph.D. candidate studying geochemistry with Professor Mark Reed’s research group) and Mark H. Reed (co-author of program CHILLER) are also owed thanks. Correspondence with them regarding CHILLER and SOLVEQ helped me through many frustrating nights.

Special thanks are extended to my loving parents, for being there when I most needed them and never questioning my abilities.

Finally, the following individuals are also owed recognition for their advice, assistance and time: Dr. Ihsan Al-Aasm, Ian Kerr, Maria Cioppa, and Cyrus Ghamari.
# TABLE OF CONTENTS

**ABSTRACT** ......................................................................................................................... iii  
**ACKNOWLEDGEMENTS** ....................................................................................................... vi  
**LIST OF TABLES** ................................................................................................................ ixi  
**LIST OF FIGURES** ............................................................................................................... xi  
**LIST OF APPENDICES** ......................................................................................................... xii  
**LIST OF ABBREVIATIONS** ................................................................................................... xiii  

## I  INTRODUCTION ........................................................................................................... 1  

## II  OBJECTIVES and SCOPE ............................................................................................ 8  

## III  THEORETICAL CONSIDERATIONS ............................................................................. 10  
(A)  *Geochemical Modeling* ........................................................................................................ 10  
(i)  *Titration Models* ................................................................................................................ 10  
(ii)  *Fixed-Fugacity Models* ........................................................................................................ 11  
(iii)  *Buffering* .......................................................................................................................... 12  
(B)  *Graphic Presentation of Data* ............................................................................................. 14  
(C)  *Geochemical Reaction Modeling with SOLVEQ and CHILLER* .......................................... 19  
(i)  *SOLVEQ* ............................................................................................................................. 19  
(ii)  *SOLRUN, GEOCAL and SOLOUT* ..................................................................................... 19  
(iii)  *CHILLER* .......................................................................................................................... 20  
(iv)  *CHILLRUN and CHILLOUT* ............................................................................................ 21  
(v)  *SOLThERM and MINOX* .................................................................................................... 22  
(vi)  *Newton-Raphson Iteration and Convergence* .................................................................. 23  
(D)  *Sulfide Oxidation* .................................................................................................................. 25  
(i)  *Pyrite Oxidation* .................................................................................................................. 26  
(ii)  *Pyrrhotite Oxidation* ............................................................................................................. 31  
(E)  *Thiobacillus Ferrooxidans* ..................................................................................................... 33  
(F)  *Gangue Dissolution* ............................................................................................................. 34  
(i)  *Feldspar (Aluminosilicate) Dissolution* ............................................................................. 36  
(ii)  *Carbonate Dissolution* ........................................................................................................ 39  

## IV  EXPERIMENTAL PROCEDURES .................................................................................... 40  

## V  MODELING and RESULTS .............................................................................................. 42  
(A)  *CHILLRUN Setup Essentials* ............................................................................................ 42  
(i)  *Fluid Chemistry for the Water-Rock Titrations* ................................................................. 42  
(ii)  *Mineral Chemistry for the Water-Rock Titrations* ............................................................ 43  
(iii)  *SINC and SLIM* .................................................................................................................. 44  
(B)  *Sulfide Oxidation and Feldspar Dissolution Reactions* ...................................................... 45  
(i)  *100 % Pyrite* ....................................................................................................................... 45  
(ii)  *100 % Pyrrhotite* .................................................................................................................. 49
(iii) Pyrite and Feldspar Reactions ............................................. 53
   (a) 50 % Pyrite + 50 % Microcline ........................................ 55
   (b) 50 % Pyrite + 50 % Albite ............................................... 63
   (c) 50 % Pyrite + 50 % Anorthite ......................................... 71

VI DISCUSSION ........................................................................... 81
   (A) 100 % Pyrite and 100 % Pyrrhotite ...................................... 81
   (B) 1:1 Pyrite + Albite, Pyrite + Anorthite, Pyrite + Microcline .... 85
   (C) 1:4, 1:1 and 4:1 Pyrite + Feldspar Ratios .......................... 93

VII CONCLUSIONS ..................................................................... 96

VIII RECOMMENDATIONS ............................................................ 98

REFERENCES ............................................................................ 100
APPENDICES ............................................................................ 107
VITA AUCTORIS ......................................................................... 166
LIST OF TABLES

Table 1. Characteristics of Acid Rock Drainage (Ritchie, 1994a)..........................6

Table 2. Median precipitation values of seven sites worldwide (hundreds of analyses) (Freeze and Cherry, 1979). pH = 5.5 @ 25 °C and 1 bar. ..........................................................43

Table 3. A summary of the main features/results of the 1:1 Pyrite:Microcline reaction model illustrating the minerals present, produced and consumed, pH and buffering reactions (with buffered pH values where applicable) for the points and intervals of Figure 6..........................................................62

Table 4. A summary of the main features/results of the 1:1 Pyrite:Albite reaction model illustrating the minerals present, produced and consumed, pH and buffering reactions (with buffered pH values where applicable) for the points and intervals of Figure 7......................70

Table 5. A summary of the main features/results of the 1:1 Pyrite:Anorthite reaction model illustrating the minerals present, produced and consumed, pH and buffering reactions (with buffered pH values where applicable) for the points and intervals of Figure 8..........................................................79
LIST OF FIGURES

Figure 1. A simple cartoon illustration of a titration model. Reactants are incrementally added to the aqueous system with time (Bethke, 1996). .......................................................... 11

Figure 2. An illustration of a single pH-buffered and multiple-step pH-buffered model. ................................................. 13

Figure 3A. An example of a stacked reaction path modeling diagram. .................. 17

Figure 3B. An example of the same stacked reaction path modeling diagram presented in Figure 3A (except not in log form). .................... 18

Figure 4. Reaction of 100 % pyrite (Appendix A, Figure 1) with water (Table 2) at 25 °C and no atmospheric contact. ......................... 46

Figure 5. Reaction of 100 % pyrrhotite (Appendix A, Figure 11) with water (Table 2) at 25 °C and no atmospheric contact. .................... 50

Figure 6. Reaction of 50 % pyrite and 50 % microcline (Appendix A, Figure 4) with water (Table 2) at 25 °C and no atmospheric contact. ............................................. 57

Figure 7. Reaction of 50 % pyrite and 50 % albite (Appendix A, Figure 2) with water (Table 2) at 25 °C and no atmospheric contact. .............. 65

Figure 8. Reaction of 50 % pyrite and 50 % anorthite (Appendix A, Figure 3) with water (Table 2) at 25 °C and no atmospheric contact. ............ 74

Figure 9. The activity curves for H⁺ from the 100 % Pyrite and 100 % Pyrrhotite reactions modeled with CHILLER (Figures 4 and 5 respectively). .................................................................. 83

Figure 10. The activity curves for Fe²⁺ from the 100 % Pyrite and 100 % Pyrrhotite reactions modeled with CHILLER (Figures 4 and 5 respectively). .................................................................. 83

Figure 11. The activity curves for SO₄²⁻ from the 100 % Pyrite and 100 % Pyrrhotite reactions modeled with CHILLER (Figures 4 and 5 respectively). .................................................................. 84

Figure 12. The activity curves for H⁺ from the 50 % Pyrite and 50 % Feldspar (microcline, albite and anorthite) reactions modeled with CHILLER (Figures 6, 7 and 8 respectively). ........................................... 88
Figure 13. The activity curves for $O_2^0$ from the 50 % Pyrite and 50 % Feldspar (microcline, albite and anorthite) reactions modeled with CHILLER (Figures 6, 7 and 8 respectively)......................88

Figure 14. The activity curves for $Fe^{2+}$ from the 50 % Pyrite and 50 % Feldspar (microcline, albite and anorthite) reactions modeled with CHILLER (Figures 6, 7 and 8 respectively)......................89

Figure 15. The activity curves for $SO_4^{2-}$ from the 50 % Pyrite and 50 % Feldspar (microcline, albite and anorthite) reactions modeled with CHILLER (Figures 6, 7 and 8 respectively)......................89

Figure 16. The activity curves for $Al^{3+}$ from the 50 % Pyrite and 50 % Feldspar (microcline, albite and anorthite) reactions modeled with CHILLER (Figures 6, 7 and 8 respectively)......................91

Figure 17. The activity curves for $AlO(OH)^0$ from the 50 % Pyrite and 50 % Feldspar (microcline, albite and anorthite) reactions modeled with CHILLER (Figures 6, 7 and 8 respectively)......................91

Figure 18. The activity curves for $H^+$ from the 1:4, 1:1 and 4:1 Pyrite:Microcline reactions modeled with CHILLER......................95
LIST OF APPENDICES

APPENDIX A: CHILLRUN files used to run CHILLER...........................................108

APPENDIX B: SINC and SLIM values for the CHILLRUN files in Appendix A ...121

APPENDIX C: 1:4 and 4:1 (Pyrite:Feldspar (Ab, An, and Mc)) Graphs .................134

APPENDIX D: Key Components of SOLRUN ......................................................148

APPENDIX E: Key Components of CHILLRUN .................................................152

APPENDIX F: List of Reactions ........................................................................158
LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abb</th>
<th>Abbreviation</th>
<th>Abb</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ab</td>
<td>albite</td>
<td>An</td>
<td>anorthite</td>
</tr>
<tr>
<td>Cal</td>
<td>calcite</td>
<td>Cdn</td>
<td>celadonite</td>
</tr>
<tr>
<td>Clcl</td>
<td>clinohlore</td>
<td>Dph</td>
<td>daphnite</td>
</tr>
<tr>
<td>Dsp</td>
<td>diaspore</td>
<td>Gt</td>
<td>goethite</td>
</tr>
<tr>
<td>Kln</td>
<td>kaolinite</td>
<td>Lmt</td>
<td>laumontite</td>
</tr>
<tr>
<td>Mag</td>
<td>magnetite</td>
<td>Mc</td>
<td>microcline</td>
</tr>
<tr>
<td>Mrg</td>
<td>margarite</td>
<td>Ms</td>
<td>muscovite</td>
</tr>
<tr>
<td>Pg</td>
<td>paragonite</td>
<td>Po</td>
<td>pyrrhotite</td>
</tr>
<tr>
<td>Py</td>
<td>pyrite</td>
<td>Qtz</td>
<td>quartz</td>
</tr>
<tr>
<td>Stb</td>
<td>stilbite</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Figure 1.* Abbreviations for rock-forming minerals (Kretz, 1983).

<table>
<thead>
<tr>
<th>Abb</th>
<th>Formula</th>
<th>Abb</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ab</td>
<td>NaAlSi₃O₈</td>
<td>An</td>
<td>Na₂O - feldspar</td>
</tr>
<tr>
<td>An</td>
<td>CaAl₂Si₂O₈</td>
<td>Cal</td>
<td>CaCO₃ (carbonate)</td>
</tr>
<tr>
<td>Cal</td>
<td></td>
<td>Cdn</td>
<td>K(Mg,Fe²⁺)(Fe³⁺,Al)Si₄O₁₀(OH)₂ (Fe - mica)</td>
</tr>
<tr>
<td>Clcl</td>
<td>(Mg)₃Al₂Si₃O₁₀(OH)₈ (Mg - chlorite)</td>
<td>Dph</td>
<td>(Fe)₃Al₂Si₃O₁₀(OH)₈ (Fe - chlorite)</td>
</tr>
<tr>
<td>Dsp</td>
<td>Al₂O(OH)</td>
<td>Gt</td>
<td>FeO(OH) (Fe - hydroxide)</td>
</tr>
<tr>
<td></td>
<td>(Al - hydroxide)</td>
<td>Kln</td>
<td>Al₂Si₂O₅(OH)₄ (clay mineral)</td>
</tr>
<tr>
<td>Lmt</td>
<td>CaAl₂Si₄O₁₂·4H₂O (Ca - zeolite)</td>
<td>Mag</td>
<td>Fe₃O₄ (Fe - oxide)</td>
</tr>
<tr>
<td>Mag</td>
<td></td>
<td>Mc</td>
<td>KAlSi₃O₈ (K - feldspar)</td>
</tr>
<tr>
<td>Mrg</td>
<td>CaAl₂(Al₂Si₂O₁₀)(OH)₂ (Ca - mica)</td>
<td>Ms</td>
<td>KAl₂Si₃O₁₀(OH)₂ (K - mica)</td>
</tr>
<tr>
<td>Ms</td>
<td></td>
<td>Pg</td>
<td>NaAl₂(Al₂Si₃O₁₀)(OH)₂ (Na - mica)</td>
</tr>
<tr>
<td>Pg</td>
<td></td>
<td>Po</td>
<td>Fe₁₄S (Fe - sulfide)</td>
</tr>
<tr>
<td>Po</td>
<td></td>
<td>Py</td>
<td>FeS₂ (Fe - sulfide)</td>
</tr>
<tr>
<td>Qtz</td>
<td>SiO₂ (silicate)</td>
<td>Stb</td>
<td>NaCa₂(Al₂Si₃O₃₆)·14H₂O (Na,Ca - zeolite)</td>
</tr>
</tbody>
</table>

*Figure 2.* Mineral formulae.
I INTRODUCTION

The accumulation of mine wastes such as tailings and waste-rock that contain sulfide minerals (i.e. pyrite and pyrrhotite) are often potential locations for acid generation. As a result, Acid Mine Drainage or AMD has become a serious environmental issue and concern for the agencies that regulate the mining industry and the companies that run the mining operations (Ritchie, 1994a; Scharer et al., 1994; Eger et al., 1994). The oxidation of the sulfide minerals exposed in waste-rock piles and tailings impoundments may produce acid mine drainage, which is characterized by (Gould et al., 1994; Alpers et al., 1994; Blowes and Ptacek, 1994; Eriksson and Destouni, 1994; Dietz et al., 1994):

- a low pH,
- a high sulfate content, and
- the presence of dissolved metals (i.e. Fe, Mg, Ni).

According to Jambor (1994) and Robertson (1994) tailings represent the accumulation of mill processed gangue (sand-silt size), separated during the ore processing procedure. Waste-rock on the other hand, represents the rock that must be removed from an orebody in order to expose and excavate the ore, and ranges from gravel to boulder size debris (Bates and Jackson, 1984). Tailings and waste-rock are two forms of mine waste (gangue) that are primarily composed of the non-economic rocks or minerals present in an orebody (Bates and Jackson, 1984). The ore in base-metal and precious-metal mining operations can contain more than 90 % gangue, therefore, large volumes of tailings are generated and disposed of near the sites of these operations.
(Robertson, 1994). Although the separation and concentration process removes the economically desirable component of an ore, the recovery of valuable minerals is never 100% efficient. As a result, tailings will contain small amounts of the economic ore minerals not removed through processing (Jambor, 1994). Waste-rock may also contain small amounts of the economic ore minerals, but at much lower grades than the main orebody itself.

The generation of mining waste, as mentioned above, also represents a spatial problem for mining companies regardless of whether or not AMD is produced as the waste accumulates. Mine engineers, consultants and planners must consider the size of the disposal sites required for the waste-rock and tailings accumulations as this affects the overall extent of the minesite and costs of operation (Jambor, 1994). For example, a mine that mills at 6,000 tpd (tonnes per day) (with an ore grade of about 6%) requires a disposal site capable of handling approximately 2,000,000 tonnes of tailings annually. Let us consider the Valley Copper Mines in British Columbia, a porphyry copper deposit that mills at 135,000 tpd with an ore grade of only about 0.5% Cu (Jambor, 1994). The bulk of the processed ore in this example is accumulated as tailings at a rate of approximately 45,000,000 tonnes per year. The Canadian base-metal mining industry has produced over 12,000 ha of tailings and roughly 350,000,000 tonnes of waste-rock within the last four or five decades that has been identified as acid-generating material (Itzkovitch and Feasby, 1993). According to Aachib et al. (1994) the preliminary estimate for remediation costs for this mine waste with present technology amounts to more than 5 billion dollars (Canadian). As these illustrations have shown, the disposal
sites required for waste-rock and tailings accumulations are extremely large, the potential for acid generation within these site is infinite, and the cost of cleanup immense.

To compound the spatial arrangement and mine waste accumulation problems, the conventional method used for treating AMD involves chemical neutralization and precipitation using lime. Liming (the addition of lime to the mine waste) produces a high volume sludge that is composed of unstable metal hydroxides and gypsum (Gould et al., 1994; Rowley et al., 1994; Rao et al., 1994; Murdock et al., 1994). As some mine waste accumulations have the potential to generate acid for longer periods of time then others, excessive amounts of this high volume sludge will be produced at these sites through this remediation method. As a result, liming affects the spatial arrangement of these sites and increases the size of the impoundment required for the accumulation of the mining waste. Metals (i.e. Fe, Ni and Cu) may also be lost with this method of remediation, which, if recovered, could provide revenue that would offset part of the treatment and disposal costs while decreasing the sludge volume (Rao et al., 1994; Hubbard et al., 1994; Schultz et al., 1994). In addition, the lime sludge may be considered a hazardous waste if toxic metals (i.e. Hg) are present in sufficient quantities, further increasing the cost of disposal (Rowley et al., 1994; Hubbard et al., 1994; Schultz et al., 1994). According to Murdock et al. (1994) there are advantages when lime is used as a treatment method in the control of AMD. Lime is an inexpensive product that is widely available, easily handled, and the reactions involved are controllable and predictable. According to Gould et al. (1994) and Rowley et al. (1994) however, continuous liming is not a tolerable long-term remediation method for the control of AMD and more stringent and strict guidelines
are needed for the new advances in the area of AMD neutralization. The onsite treatment of acid mine drainage by chemical means is an expensive, long-term commitment, considering that drainage problems can persist for over a hundred years (Eger et al., 1994; Gould et al., 1994).

Many ore deposits (that contain sulfides) also have acid-consuming minerals associated with the mineralization or in nearby host and country rocks (Day, 1994). According to Jambor (1994) tailings and waste-rock accumulations are not necessarily acid generators, the potential for acid production will depend upon the mineral composition of the mine waste. Acid-neutralization reactions according to Blowes et al. (1994) are essential for controlling the byproducts of sulfide oxidation in mine waste accumulations and reducing the impact they have on the environment. The pH within these environments is a balance between the acid-producing sulfide oxidation reactions and the acid-consuming mineral dissolution reactions. If there are more acid-producing minerals in the mine waste accumulation, the resulting pH will be acidic. If the acid-consuming minerals dominate the mine waste pile, the pH will be near neutral to basic. The presence of acid-consuming minerals also affects the release of dissolved metals (i.e. Fe, Ni, Pb) into the mine wastes pore water (Blowes et al., 1994). The higher the rate of sulfide oxidation the greater the metal concentration found in the pore water. Therefore, in all waste-rock and tailings accumulations there are some minerals that oxidize to produce acid and release harmful elements, and other minerals that react with the acids to neutralize them. Stable precipitates can form as a result of the acid-neutralization process and harmful elements may be incorporated into their structure (Jambor, 1994). Mixing
mine wastes (containing sulfides) with acid-consuming minerals may be a conceivable low cost alternative, under certain conditions, for the control or prevention of AMD. If properly constructed, this in situ alternate waste management technique (mixing) may provide adequate protection against AMD without the continued maintenance or long term obligations required with other remediation methods (Day, 1994).

According to Jambor (1994) the bulk of tailings produced from sulfide-bearing ore deposits will generally consist of quartz, various silicates, carbonates, and iron sulfides. Pyrite and pyrrhotite are the most abundant sulfide minerals present in mine waste accumulations according to Alpers et al. (1994). Therefore, it can be generalized that acid mine drainage (in mine waste accumulations) results from the oxidation of pyrite (FeS$_2$) and/or pyrrhotite (Fe$_{1-x}$S), (where $x$ may vary from 0 to 0.125 (Nicholson, 1994)) (Jambor, 1994; Yanful et al., 1994)). Jambor (1994) notes that the presence of other (low abundance) sulfides and sulfosalts such as, arsenopyrite (FeAsS), chalcopyrite (CuFeS$_2$), galena (PbS), sphalerite [(Zn,Fe)S], and tetrahedrite-tennantite [(Cu,Fe)$_{12}$Sb$_4$S$_{13}$-(Cu,Fe)$_{12}$As$_4$S$_{13}$] can also present problems. The oxidation of these low abundant minerals is usually responsible for the most deleterious elements produced in mine waste effluents. Table 1 gives some of the typical characteristics observed and measured (under natural surficial conditions) as a result of Acid Rock Drainage (ARD) (Ritchie, 1994a). According to Lin (1996) AMD can be referred to in the general sense as acid rock drainage. The acidity of a later-phase ARD effluent typically falls within a pH range of 2 to 4 and results in the mobilization of metal ions. The concentration of the metal ions typically ranges from 1 to 3000 mg/L and have a significant impact on the environment as
well as reducing the quality of potable groundwater supplies. The presence of dissolved salts (Ca, Mg, Al, and sulfate) further magnify these impacts on the environment. Ferrous and ferric ions, ferric oxides, hydroxides and jarosites produce the common yellowish-orange to reddish-brown discoloration and reduce visibility in the receiving waters.

<table>
<thead>
<tr>
<th>Property</th>
<th>Typical associated chemical species</th>
<th>Concentration Range</th>
<th>Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidity</td>
<td>Sulfuric acid</td>
<td>pH 2 to 4</td>
<td>- mobilization of metal ions</td>
</tr>
<tr>
<td>Iron</td>
<td>Ferrous and ferric ion; Ferric oxides, hydroxides; Jarosites</td>
<td>100 to 3000 mg/L</td>
<td>- discoloration and turbidity in receiving waters as pH increases and ferric salts precipitate</td>
</tr>
<tr>
<td>Heavy metals</td>
<td>Copper, magnesium, zinc, cadmium, mercury, lead, arsenic, radium</td>
<td>1 to 200 mg/L</td>
<td>- reduction in aquatic flora and fauna; - bioaccumulation; - reduction in quality of potable groundwater supplies</td>
</tr>
<tr>
<td>Total dissolved salts</td>
<td>Calcium, magnesium, aluminum, sulfate</td>
<td>100 to 30,000 mg/L</td>
<td>- reduction in quality of potable groundwater supplies - reduction in quality of water supplies for stock</td>
</tr>
</tbody>
</table>

Sulfide oxidation is dependent upon a number of factors which define the environment within the waste-rock or tailings pile (Ritchie, 1994a). Some of these factors include temperature, pH, oxygen concentration of the pore fluid, rainfall
frequency (flushing rate), chemical composition of the pore fluid, mineralogy of the mine waste, and the microbial population. Certain microbes increase the rate of sulfide oxidation and the subsequent generation of sulfuric acid and metal ions within the mine waste environment. The oxidation rate of sulfides can be catalyzed by the presence of iron-consuming bacterium (i.e. *Thiobacillus Ferroxidans*) (Rich and Hutchinson, 1994; Feasby et al., 1994). The optimal growth conditions for *T. ferroxidans* are around a pH of 2 to 3, but they can survive within near-neutral pH environments (Nordstrom, 1982).
II OBJECTIVES and SCOPE

The objective of this study was to investigate the effect that feldspar dissolution has on sulfide oxidation.

- the initial intent was to experimentally examine how different feldspars neutralize the acid generated from aqueous sulfide oxidation:
  - the results from the experimental reactions could not be used for the purpose of this study
  - these results were inconclusive and did not bear any logic when compared to similar work

Thus, it was decided to simulate the reactions using computer models. The FORTRAN computer modeling program CHILLER was selected to model these geochemical reactions.

- CHILLER computes the chemical equilibria of complex systems consisting of solids, gases, and an aqueous phase (Reed, 1982)

- CHILLER models a variety of situations that include:
  - fluid-fluid mixing, gas or rock titrations, boiling, condensation, and evaporation (Reed and Spycher, 1998)

The geochemical models were constructed to examine how feldspar dissolution (albite, anorthite, and microcline) and the resultant mineral assemblages buffer sulfide oxidation.

- sulfide:feldspar ratios of 1:4, 1:1 and 4:1 were modeled with CHILLER to determine what affect the ratios would have on the results

8
three models were constructed for each feldspar:

- microcline, albite and anorthite were each modeled with CHILLER at ratios of 1:4, 1:1 and 4:1 (sulfide to feldspar)

The results from CHILLER for each of the model/simulations are presented in stacked reaction path modeling diagrams.

- these diagrams allow for an organized and orderly presentation of the stability relations among alteration minerals and between minerals and the aqueous phase (Reed, 1997)

- the details from these diagrams illustrate how the specified modeling reaction proceeded through a series of alteration mineral assemblages

- Figure 3A is an example of a stacked reaction path modeling diagram produced with CHILLER (by reacting pyrite and water)
III  THEORETICAL CONSIDERATIONS

(A)  Geochemical Modeling

A properly designed geochemical model can be used to represent simplified versions of reactions that take place in nature or the laboratory. These models must not be overly simplified to the point of being impractical nor so elaborate that they cannot be applied to realistic problems (Bethke, 1996). For a model to be complete there must be a balance between its practicality and the realism it is trying to portray. The important features of a successfully created geochemical model should be portrayed without attempting to show every chemical or mineralogical detail or change (Bethke, 1996).

(i)  Titration Models

Titration models involve reactions between an initial fluid of known composition and reactants which, if they are minerals, are undersaturated with respect to the initial fluid (Bethke, 1996). The reactants are incrementally added (titrated) into the system and over the course of the reaction path they dissolve until equilibrium is reached and the reaction stops (Figure 1). This process may cause minerals to precipitate as they become saturated within the aqueous phase or force pre-existing minerals within the system (either original components or previously precipitated) to dissolve. The system continues to evolve until the fluid is saturated with each titrated reactant or the reactants are exhausted (Bethke, 1996). If the reactants are exhausted, the modeler can increase the amount of the reactants that are incrementally added to the aqueous phase and continue
Figure 1. A simple cartoon illustration of a titration model. Reactants are incrementally added to the aqueous system with time (Bethke, 1996).

to do so until equilibrium is reached. Once equilibrium is reached, any and all reactants titrated into the system will continue to accumulate without any further interactions.

(ii) Fixed-Fugacity Models

Models that buffer the fugacities of one or more gases, either through atmospheric contact or some other source, are known as fixed-fugacity path models (Bethke, 1996). The earth’s atmosphere acts as a buffer for the chemistry of many geochemical processes that occur at or near its surface. The chemistry of an aqueous phase will reach equilibrium with a buffer (i.e. the atmosphere) if the reaction is slow enough to maintain equilibrium. Gases from the atmosphere will either dissolve out of the atmosphere or exsolve into it during this process (Bethke, 1996).
A fixed-fugacity path model, according to Bethke (1996), can produce results that are different from the results obtained in a simple titration model that is closed to the atmosphere. As an example, consider the following reaction in which the reactant pyrite is oxidized and goethite is produced:

\[
\text{FeS}_2 + \frac{5}{2}\text{H}_2\text{O} + \frac{15}{4}\text{O}_2^0 \rightleftharpoons \text{FeOOH} + 4\text{H}^+ + 2\text{SO}_4^{2-}
\]

\(\text{pyrite}\quad \text{goethite}\) \hfill (1)

In a simple titration model that is closed to the atmosphere, the dissolved oxygen within the aqueous phase controls the reaction rate. As pyrite is converted to goethite in reaction 1 the dissolved oxygen is consumed and pyrite oxidation ceases with time. Water that is fully saturated with air at 1 atmosphere and 20 °C contains about 9 ppm O\(_2\)\(^0\) (Brown et al, 1991). Therefore, only a small amount of pyrite is consumed in reaction 1 due to the lack of an O\(_2\) buffer. In a fixed-fugacity path model, however, the activity of O\(_2\)\(^0\) (reaction 1) is buffered by the atmosphere and remains in equilibrium with the atmosphere. The atmospheric buffering of O\(_2\)\(^0\) allows reaction 1 to proceed until all of the pyrite is consumed (Bethke, 1996).

(iii) Buffering

The term buffering refers to the ability to resist change. When some variable of a chemical system fixes the value of a specific component, this component is buffered by that variable. For example, if the pH of an aqueous solution is held constant by the mineral composition of the system, the pH of that system is said to be buffered by the mineral composition and this buffer is referred to as a mineral pH buffer. In the previous
case of O$_2^0$ being buffered by the atmosphere, this buffer is referred to as an atmospheric O$_2$ buffer.

Figure 2 illustrates the difference between a single pH-buffered and multiple-step pH-buffered model (for the purpose of this illustration the axes are not that important, but the water/rock ratio (w/r) will be discussed in the following section). Curve B represents a multiple-step pH-buffered model, the flat stair stepping shape is indicative of a series of good mineral pH buffers. Sufficient amounts of H$^+$ are produced, offsetting the amount of H$^+$ consumed (where the curve flattens out) and each step depicts a separate pH-buffering reaction that begins and ends when a balancing ion is depleted or the buffering mineral assemblage changes (Reed, 1997). Curve A represents a single pH-buffered model, pH is not buffered until the reaction reaches final equilibration, and the resulting curve changes very little in shape compared to curve B.

![Figure 2](image)

**Figure 2.** An illustration of a single pH-buffered and multiple-step pH-buffered model. A – single pH-buffered model, B - multiple-step pH-buffered model.
(B) **Graphic Presentation of Data**

Stacked reaction path modeling diagrams allow the presentation of the stability relations among alteration minerals and between minerals and the aqueous phase in an organized and concise manner (Reed, 1997). Figures 3A and 3B are examples of stacked reaction path modeling diagrams produced with CHILLER (by reacting pyrite and water). These figures are used here to illustrate why the data was presented in log form; the specifics about the data displayed in these diagrams is not important at this point. Each of these figures presents the same results; the only difference between them is that the data displayed in Figure 3A is in log form. As can be seen in Figure 3B, the specifics of the reaction cannot be discerned from the data displayed. By presenting the same data in log form (Figure 3A) however, details about such things as how the pH is buffered by the formation of buffering minerals can be seen. Consequently, all of the diagrams used to describe the reactions modeled with CHILLER are displayed in log form.

The x-axis for these diagrams represents a measure of composition for the system in terms of the water/rock ratio (w/r) (Figure 3A). The w/r is calculated by dividing the mass of water in the initial aqueous phase by the mass of rock titrated into the system (Reed, 1997). As more rock is titrated into the system, the resulting w/r ratio decreases and proceeds from a large to small value as the graph is read from left to right. The composition of the fluid within these diagrams changes continuously with the changing w/r (Reed, 1997). At any point along the x-axis, the w/r defines an equilibrium state that is unique to that specific composition of rock and initial fluid.
The diagrams displayed in this study apply to closed-system rock titrations (no material leaves the geochemical system after it has been added). The titrated minerals react with the aqueous phase to produce new minerals that precipitate from solution. These newly formed minerals then either remain stable with the aqueous phase or, they become unstable and are incorporated into the aqueous phase with the possibility of other stable mineral precipitates forming. This process continues until the geochemical system reaches equilibrium. The models and corresponding diagrams described within this text represent how the chemistry of a repository (containing 1 kg of rainwater) would evolve as rock is incrementally titrated into the system, and allowed to equilibrate before the next incremental addition of rock. This process continues as more and more rock is incrementally titrated into the repository (refer to Figure 1), until final equilibration is reached. As a result, when the graphs are read from left to right, the w/r ratio decreases as more rock is titrated into the system.

The w/r can be thought of as a measure of porosity within a system or as a measure of reaction progress within that system. As porosity is a measure of the volume of void space within a pile of unconsolidated sediments, it follows that, if these sediments are fully saturated, the porosity is a measure of the w/r for the sediments. Therefore, as any of the reaction models progress and more and more rock is titrated into the system, the porosity of the system decreases due to compaction within the repository. Eventually a point is reached in which the titrated sediments are completely compacted and an equilibrium state is reached in which the components of the system are static. Only the titrated components within the system continue to change (increase) as they are added to
the system. Alternately, the w/r could be thought of as a measure of reaction progress within that system. As minerals are titrated into the system the w/r decreases and reactions occur between the solid and aqueous phases. This process continues until the system approaches equilibrium, after which, only the titrated minerals accumulate within the system because there are not enough components left in the system to drive the reactions. As previously discussed, the composition of the fluid within the system changes continuously with the changing w/r and each w/r defines an equilibrium state that is unique to that specific composition of rock and initial fluid.

The geochemical models used to produce the diagrams hereinafter were constructed to show how the availability of oxygen and the buffering ability of feldspars (albite, anorthite, and microcline) affect sulfide oxidation. Utilization of the closed-system w/r to models like these, according to Reed (1997), can only be valid where an equilibrium state exists within the aqueous phase. While this slightly limits the interpretability of the spatial and temporal relations as they apply to natural settings, it is applicable to a broader range of situations. Modeling with the w/r represents a balance between the equilibrium relationships of pure models (like those presented hereinafter) and a complete treatment (including infiltration, diffusion and kinetics) of a well defined system (Reed, 1997).
Figure 3A. An example of a stacked reaction path modeling diagram: (A) Minerals formed in log moles. (B) pH and log total aqueous molality of the principal component species (i.e. $\Sigma\text{Fe}^{2+}$ represents the total of all aqueous Fe species). (C) Selected individual aqueous species in log molality (not log total aqueous molality). pH can be read directly from the Log total aq molality and Log molality axes of B and C respectively.
Figure 3B. An example of the same stacked reaction path modeling diagram presented in Figure 3A (except not in log form): (A) Minerals formed in moles. (B) pH and total aqueous molality of the principal component species (i.e. $\Sigma\text{Fe}^{2+}$ represents the total of all aqueous Fe species). (C) Selected individual aqueous species in molality (not total aqueous molality). pH can be read directly from the Total aq molality and Molality axes of B and C respectively.
(i) SOLVEQ

SOLVEQ is a FORTRAN computer-modeling program that can be used to compute the chemical equilibria in aqueous systems (Reed, 1982). It is mainly used for processing any type of water analyses in order to establish the consistency of such parameters as the input data and the total number of moles of $H^+$ in solution ($\text{MTOT H}^+$) (Spycher and Reed, 1998). The $\text{MTOT H}^+$ is required by CHILLER, and represents the initial pH of the solution in total moles. SOLVEQ calculates the activities of all aqueous species, the saturation indices of solids, and the fugacities of gases after the composition and temperature of the aqueous solution has been input (Spycher and Reed, 1998). These calculations are resolved using the Newton-Raphson numerical method which indirectly solves a system of mass-balance and mass-action equations (Reed, 1982; Sypcher and Reed, 1998).

(ii) SOLRUN, GEOCAL and SOLOUT

The SOLRUN file is used to run SOLVEQ and it contains all the data specific to each modeling run (Spycher and Reed, 1998). An existing SOLRUN file can be edited to run SOLVEQ or the program GEOCAL can be used to create a new SOLRUN file. GEOCAL is an interactive program that allows the programmer to specify the modeling input data in various units (ppm, mg/l, etc.) (Spycher and Reed, 1998). It asks simple questions regarding the model's aqueous composition and run conditions (i.e. temperature
and pH). Once SOLRUN is configured, SOLVEQ is run and, if there are no problems, convergence will be reached (refer to APPENDIX D for a description of the key components of the SOLRUN data file). If SOLVEQ fails to converge however, various error messages are built into the program that will help to determine the source of error (Spycher and Reed, 1998).

SOLOUT is the output file that contains the results of the calculations made by SOLVEQ (Spycher and Reed, 1998). The file contains a wide range of information such as: the number of iterations (loops) used to reach convergence, charge balance of the solution, temperature, speciation data for all aqueous species, and the characteristics of the component species.

(iii) CHILLER

CHILLER according to Reed (1982) is a FORTRAN computer modeling program that can be used to compute the chemical equilibria of a system among solids, gases, and an aqueous phase. This program can be used to model a variety of situations that include fluid-fluid mixing, gas or rock titrations, boiling, condensation, and evaporation (Reed and Spycher, 1998). CHILLER also applies the Newton-Raphson numerical method to indirectly solve a system of mass-balance and mass-action equations (Reed, 1982; Reed and Spycher, 1998). According to Reed and Spycher (1998) after the temperature, pressure, and total composition of a chemical system has been input, CHILLER computes the compositions of the solid, aqueous, and gas phases at equilibrium. To model geochemical processes, CHILLER allows for incremental changes in either temperature,
pressure, enthalpy or composition (Reed and Spycher, 1998). After each increment, CHILLER recalculates the equilibrium phase assemblage, mineral compositions and the aqueous composition of the system.

(iv) CHILLRUN and CHILLOUT

Before CHILLER is run, SOLVEQ should be used to calculate the homogeneous equilibrium on the solution that is to be used in CHILLER to ease convergence (Reed and Spycher, 1998). After getting the SOLVEQ output, the CHILLRUN file must be created by either running the program GEOCAL, or by editing an existing CHILLRUN file (Reed and Spycher, 1998). The CHILLRUN file contains all the data specific to each modeling run. Once CHILLRUN is set up, CHILLER is run and if there are no problems, convergence will be reached. After each successful equilibration, the values of SINC (step increment) and SLIM (step limit) are increased by a factor of ten (SINC and SLIM are titration parameters, refer to APPENDIX E for a description of the key components of the CHILLRUN data file), and CHILLER is run again. CHILLER usually reaches convergence without any problems when SINC and SLIM are increased by a factor of ten. When SINC and SLIM are increased by larger factors (i.e. 100 or 1000) the iterative method usually fails to reach convergence and the program stops. If CHILLER fails to converge at any point, various error messages are built into the program that will help determine the source of error (Reed and Spycher, 1998).

CHILLOUT is the output file that contains all of the run-specific CHILLRUN data, and the results of each titration and subsequent equilibration produced with
CHILLER (Reed and Spycher, 1998). The results are organized into a structured and thorough data file based upon the step increment (SINC) and the step limit (SLIM) set by the user. For each successful increment (titration) CHILLER outputs the equilibration data to CHILLOUT. Therefore, if SINC = 1 and SLIM = 10, CHILLOUT will contain data for nine increment steps as long as convergence is reached during each step. CHILLOUT contains a broad range of information for each step such as: the number of iterations (loops) used to reach convergence, charge balance of the solution, temperature, pressure, speciation data for all aqueous species, pH and the characteristics of the component species (Reed and Spycher, 1998).

(v) SOLTHERM and MINOX

SOLTHERM is the database used by CHILLER and SOLVEQ and contains all thermodynamic data for the aqueous, gas, and mineral species listed (Spycher and Reed, 1998; Reed and Spycher, 1990, 1998). This database supplies all of the thermodynamic data, (activity coefficients data, component species data, derived species data, gas data, mineral data and optional miscellaneous data), necessary to run CHILLER and SOLVEQ. The MINOX reactant data file contains reactant stoichiometries and molecular weights for the chemical components (oxides, minerals, gases, etc.) to be used as reactants in titration reactions (Reed and Spycher, 1998). Reactants are generally specified as oxides or minerals, but any other form of reactant may be entered into this file. MINOX is only read if the MINSOL option for titrations is enabled (MINSOL set to a non-zero value (1-4) in the CHILLRUN data file, see APPENDIX E) (Reed and Spycher, 1998).
(vi) Newton-Raphson Iteration and Convergence

Geochemical modeling programs like SOLVEQ and CHILLER provide insight into complex natural reactions. The simplified reactions run with these programs can be interpreted more easily than those occurring in nature if there is a balance between practicality and realism. With some basic geochemical knowledge, programs like CHILLER and SOLVEQ can be run without necessarily understanding the complexities of how each program internally calculates the equilibrated output. Programs like these solve a system of mass-balance and mass-action equations in order to reach equilibration. There is no direct general method however, for finding the solution of nonlinear equations, so these equations need to be solved indirectly by iteration (Bethke, 1996). According to Bethke (1996) Newton-Raphson iteration is the most effective approach for solving nonlinear equations reliably, especially in systems where the mass is distributed over minerals as well as dissolved species.

The Newton-Raphson iteration method works as follows (Bethke, 1996): the set of values that satisfies a group of equations is called the group’s root. The iterative method begins with a guess of the root’s value, and then proceeds to improve the value incrementally until it satisfies the equations to the desired accuracy. The first guess of the root is typically set by the model, which commonly assigns the guess 90 % of the mole numbers to the unknown variables. The desired accuracy is determined by the residual, which is a measure of the inequality between two sides of a system of equations Bethke (1996). Residuals are a measure of how far off the guess was from the root’s satisfying values. The Newton-Raphson iteration method attempts to make the residual
incrementally smaller by successively improving the guess of the root’s value. This process continues until some value of the root is reached at some iteration point that satisfies the system of equations to a desired accuracy, this is known as convergence (Bethke, 1996). Usually, convergence to a solution is rapid, however the model can “bomb” (stop) if convergence is not reached. A model that fails indicates that the residual cannot be improved to satisfy the root’s value for the specified modeling conditions. When this occurs, changes must be made to the modeling conditions in an attempt to reach convergence. As Reed and Spycher (1998) note however, some models may reach a numerical impossibility and never converge, or the chemical system that is being investigated may be impossible and the model cannot justify the chemistry.
(D) **Sulfide Oxidation**

Sulfide oxidation is a complicated process that involves a series of complex intertwined reactions, which may have a serious impact on the environment. With time, these reactions can become an environmental concern as the resulting effluent pH changes, ranging from less than 2 to as high as 8.5 (Mills, 1985). This broad range in pH values is related to the rate of sulfide oxidation, and the buffering capacity of the minerals present in the geologic setting (Mills, 1985). According to Ritchie (1994a), during the early stages (years to tens of years) of a sulfide-bearing tailings or waste-rock pile, the chemical composition of the pore water in the waste accumulation changes with time and depth. Several factors control these changes and they are dependent on such things as the rate of sulfide oxidation, the presence of acid-neutralizing gangue minerals, and the rate of pore water movement. Initially, the acid generated through sulfide oxidation is neutralized close to the source and the pore water pH is near neutral (Ritchie, 1994a). With time, the readily available acid-neutralizing minerals are consumed and the acid produced is transported away from the oxidation sites, decreasing the effluent pH. At this stage in the sulfide-bearing tailings or waste-rock piles history (tens to hundreds of years), the chemical composition of the effluent changes very slowly with time. It is this later stage drainage which is typically described as “acidic drainage” because the pH generally ranges from 2 to 4. Ritchie (1994a) also notes that the mine drainage from a sulfide-bearing waste pile may not have a low pH at all but can still be considered an environmental threat. If a sufficient amount of dolomite is present in this mine waste
pile, the acid produced through sulfide oxidation could be buffered to a near-neutral pH, however, the drainage would also have high levels of sulfate, calcium, and magnesium; common characteristics of AMD (without the earmark low pH).

Pyrite (FeS₂) and pyrrhotite (Fe₇₋₈S) are the most common sulfide minerals in base and precious metal tailings impoundments (Blowes et al., 1994). According to Ritchie (1994a), pyrite oxidation (the primary pollutant generating process in AMD) is controlled within the mine waste environment by several factors. These factors include (for example) temperature, pH, oxygen concentration, chemical composition of the pore water and microbial population. The relationships between the physical, chemical, and microbial environments within a mine waste dump affect the rate of pyrite oxidation. Consequently, the rate of pyrite oxidation affects the physical, chemical, and microbial environments within the dump. The processes involved in sulfide oxidation at any one mine waste site will vary considerably from any other depending on site specific conditions, and this is why modeling is difficult (Ritchie, 1994a).

(i) Pyrite Oxidation

The amount of information with regards to the mineralogy of oxidized sulfide-bearing mine waste is sparse. Several authors however, have proposed a series of generalized reactions that may lead to the formation of AMD. In this section, the proposed ideas of some of these authors will be examined. Although similarities exist between these proposed AMD reactions, each of the authors concepts are presented in their entirety.
The pyrite oxidation reactions responsible for AMD according to Singer and Stumm (1970) and Stumm and Morgan (1981) can be expressed as follows:

\[
\text{FeS}_2 + \frac{7}{2}\text{O}_2^0 + \text{H}_2\text{O} \rightleftharpoons \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \tag{2}
\]

*pyrite*

\[
\text{Fe}^{2+} + \frac{1}{4}\text{O}_2^0 + \text{H}^+ \rightleftharpoons \text{Fe}^{3+} + \frac{1}{2}\text{H}_2\text{O} \tag{3}
\]

\[
\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe(OH)}_3 + 3\text{H}^+ \tag{4}
\]

*ferrihydrite*

Pyrite is broken down and the sulfur is oxidized according to reaction 2 releasing Fe\(^{2+}\), SO\(_4^{2-}\) and H\(^+\). The subsequent oxidation of Fe\(^{2+}\) (reaction 3) and hydrolysis of Fe\(^{3+}\) (reaction 4) leads to the formation of ferrihydrite. The presence of Fe\(^{3+}\) can lead to the break down of pyrite and the direct oxidation of sulfur producing Fe\(^{2+}\), SO\(_4^{2-}\) and H\(^+\) according to reaction 5:

\[
\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightleftharpoons 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \tag{5}
\]

*pyrite*

The direct oxidation of the sulfur in 1 mole of pyrite by Fe\(^{3+}\) results in the release of 16 moles of H\(^+\) (reaction 5) versus the 2 moles of H\(^+\) released during the oxidation of the sulfur in pyrite by O\(_2^0\) (reaction 2). Reactions 2, 3, 4, and 5 regulate the amounts of H\(^+\) and Fe\(^{2+}\) released into solution.

*Thiobacillus ferrooxidans* (a species of bacterium) can act as a catalyst for reaction 3, and are most active between pH 1.5 - 5.0 (Rose and Daub, 1994). T.
ferrooxidans increase the rate at which Fe\textsuperscript{2+} is oxidized in comparison with inorganic rates (Singer and Stumm, 1970). As reaction 3 is considered to be the rate-controlling step, \textit{T. ferrooxidans} can increase the rate at which the characteristics of AMD are produced (Rose and Daub, 1994). Reactions 3 and 5 have been implicated as the problem reactions in extreme cases of AMD. Under extreme acidic conditions reaction 4 is the slowest of the four reactions thus limiting the rate at which additional acidity is produced in this reaction and reaction 5 (Rose and Daub, 1994).

The overall reaction for pyrite oxidation is presented in reaction 6, which represents the sum of reactions 2, 3, and 4 (Singer and Stumm, 1970; Stumm and Morgan, 1981):

$$\text{FeS}_2 + \frac{15}{4}\text{O}_2 + \frac{7}{2}\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 4\text{H}^+ \quad (6)$$

For each mole of pyrite oxidized in reaction 6 four moles of H\textsuperscript{+} are produced. According to Rose and Daub (1994) SO\textsubscript{4}\textsuperscript{2-} (reaction 6) is initially released during pyrite oxidation and this gives some indication to the amount of pyrite oxidized.

The following reactions according to Blowes et al. (1994) are responsible for the generation of AMD. Pyrite is broken down and the sulfur is oxidized according to reaction 2 producing Fe\textsuperscript{2+}, SO\textsubscript{4}\textsuperscript{2-}, and two moles of H\textsuperscript{+}:

$$\text{FeS}_2 + \frac{7}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \quad (2)$$
The oxidation and subsequent hydrolysis of Fe$^{2+}$ leads to the precipitation of Fe(OH)$_3$, yielding two addition moles of H$^+$ (reaction 6) (Blowes et al., 1994):

$$\text{FeS}_2 + ^{15/4}\text{O}_2^0 + ^{7/2}\text{H}_2\text{O} \rightleftharpoons \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 4\text{H}^+$$

(6)

**pyrite**  **ferrihydrite**

According to Bigham et al. (1990) and Blowes and Ptacek, (1994) (referring to reaction 6) goethite (FeOOH) or the precipitation of other Fe$^{3+}$-bearing phases may form in the place of Fe(OH)$_3$, releasing various amounts of H$^+$. Continued oxidation of the sulfur in pyrite by Fe$^{3+}$ (produced from the oxidation of Fe$^{2+}$, reaction 3, released from reaction 2) would lead to the release of more acid (reaction 5) (Blowes et al., 1994):

$$\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightleftharpoons 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+$$

(5)

**pyrite**

With Fe$^{3+}$ as the primary oxidant, each mole of pyrite oxidized yields 16 moles of acidity.

As a final example of the reactions involved in pyrite oxidation consider the following proposed by Ritchie (1994b):

$$\text{FeS}_2 + ^{7/2}\text{O}_2^0 + \text{H}_2\text{O} \rightleftharpoons \text{FeSO}_4 + \text{H}_2\text{SO}_4$$

(7)

**pyrite**

$$2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + ^{1/2}\text{O}_2^0 \rightleftharpoons \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$$

(8)

$$\text{FeS}_2 + \text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O} + 3\text{O}_2^0 \rightleftharpoons 3\text{FeSO}_4 + 2\text{H}_2\text{SO}_4$$

(9)

**pyrite**
\[ MS + \text{Fe}_2(\text{SO}_4)_3 + \frac{3}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{MSO}_4 + 2\text{FeSO}_4 + \text{H}_2\text{SO}_4 \]  
(10)

(where MS stands for any metal sulfide)

Reaction 7 (sum of reactions 8 and 9) shows that pyrite is oxidized in the presence of oxygen producing acid and sulfate. Reaction 10 is a general reaction illustrating the oxidation of any other metal sulfide. The rate of reaction 8 can be increased by a factor of about \(10^5\) (Singer and Stumm, 1968) if certain bacteria (i.e. \(\text{Thiobacillus ferrooxidans}\)) catalyze the oxidation of the ferrous iron in reaction 8 (Ritchie, 1994b). According to Ritchie (1994b) reaction 9 supports this process, at low acid pH values the oxidation of pyrite by \(\text{Fe}^{3+}\) is increased (about 10 to 100 times faster (Olson, 1991)) due to the presence of bacteria like \(T. \text{ferrooxidans}\).

The overall complexity of the reactions and mechanisms involved in the oxidation of sulfide minerals makes it difficult to describe all of the processes taking place at once (Ritchie, 1994b). The initial factors or conditions that begin the acidification process leading to AMD within the waste-rock/tailings pile are not completely understood. According to Nordstrom (1982) and Pronk et al. (1992) reactions like those reported by Singer and Stumm (1970), Stumm and Morgan (1981), Blowes (1994), and Ritchie (1994b) can be further complicated; \(T. \text{ferrooxidans}\) can also grow within an anaerobic environment. In order for the bacteria to survive under anaerobic conditions there must be a source of \(\text{Fe}^{3+}\) within the environment. Oxygen however, is required as described by reaction 8 for the continuing source of \(\text{Fe}^{3+}\) the bacteria require. It is obvious that oxygen cannot be present within an anaerobic environment. According to Nordstrom (1982) and Pronk et al. (1992) there is no conclusive evidence on the microorganisms ability to act as
a catalyst within the anaerobic environment. Kleinmann (1979) did however, find trace
growth of *T. ferrooxidans* in these saturated (anaerobic) environments. Nonetheless, with
the amount of research and experimentation involving water covers and other O₂ gas
diffusion barriers *T. ferrooxidans* likely do not act as good catalysts under these
conditions.

(ii) Pyrrhotite Oxidation

Very little information exists with regards to pyrrhotite oxidation compared to the
number of studies done on pyrite oxidation. Nicholson (1994) however, notes that the
amount of attention paid to pyrrhotite oxidation is increasing as pyrrhotite has been
recognized as an important waste mineral in many metal mine waste impoundments.
Aqueous pyrrhotite oxidation can be the dominant precursor to AMD in tailings
impoundments produced during the concentration and recovery of nickel (Blowes et al.,
1994). The complete oxidation of the sulfur in pyrrhotite may occur through reaction 11
(Blowes and Ptacek, 1994; Blowes et al., 1994; Nicholson, 1994):

\[
\text{Fe}_{(1-x)}S + (2-\frac{1}{2})\text{O}_2 + x\text{H}_2\text{O} \rightarrow (1-x)\text{Fe}^{2+} + \text{SO}_4^{2-} + 2x\text{H}^+ \quad (11)
\]

The stoichiometry of pyrrhotite affects the amount of H⁺ produced (Nicholson, 1994). If
x in reaction 11 is zero then pyrrhotite has a formula of FeS and no H⁺ will form during
oxidation. On the other hand, if x = 0.125 (the maximum value for x according to
Nicholson, 1994) then pyrrhotite will have a formula of Fe₇S₈ and the maximum amount
of acid will be produced. Partial completion of pyrrhotite oxidation will generate S⁰ and Fe²⁺ through the reaction (Blowes and Ptacek, 1994; Blowes et al., 1994):

\[
\text{Fe}_{(1-x)}S + (2-2x)\text{Fe}^{3+} \rightleftharpoons (3-3x)\text{Fe}^{2+} + S^0
\]

*pyrrhotite*

(12)

Sulfate (SO₄²⁻) may form if the elemental S⁰ is oxidized in reaction 12 (Blowes and Ptacek, 1994; Blowes et al., 1994). Elemental S⁰ has also been shown to form at the expense of H⁺ through reaction 13 (Ahonen and Tuovinen, 1994):

\[
\text{Fe}_{(1-x)}S + \left(\frac{1-x}{2}\right)\text{O}_2 + 2(1-x)\text{H}^+ \rightleftharpoons (1-x)\text{Fe}^{2+} + S^0 + (1-x)\text{H}_2\text{O}
\]

*pyrrhotite*

(13)

Burns and Fisher (1990) and Fisher and Burns (1990) have shown that the aqueous oxidation of sulfur in pyrrhotite can lead to the formation of pyrite, consider the following reaction:

\[
2\text{Fe}_{(1-x)}S + \left(\frac{1}{2}-x\right)\text{O}_2 + (2-4x)\text{H}^+ \rightleftharpoons \text{FeS}_2 + (1-2x)\text{Fe}^{2+} + (1-2x)\text{H}_2\text{O}
\]

*pyrrhotite*  *pyrite*

(14)

This reaction also consumes acid and with time the pyrite will undergo oxidation in the presence of oxygen (as seen in reaction 6). According to Nicholson (1994) pyrrhotite oxidation is 20 - 100 times faster than pyrite oxidation at 25 °C under atmospheric oxygen concentrations. Due to the greater sulfur content of pyrite however, more acid per mole is produced during pyrite oxidation than pyrrhotite oxidation.
(E) **Thiobacillus Ferrooxidans**

*Thiobacillus ferrooxidans* are a widely studied Fe$^{2+}$-, pyrite- and sulfur-oxidizing genus of microorganisms that contribute to AMD (Nordstrom, 1982). This gram-negative aerobic chemoautotrophic (produces its’ own food through oxidation) acidophilic (thrives within low pH environments) microbe obtains energy from some form of sulfur (i.e. metal sulfides or reduced sulfur compounds) (Nordstrom, 1982; Gould et al., 1994). Their optimal growth conditions according to Nordstrom (1982) are around a pH of 2 to 3, but they can survive within near-neutral pH environments. Gould et al. (1994) suggest that the pH range the *thiobacilli* thrive in is between 1 and 3.5 with the optimal near 2. Besides living under such harsh conditions as a low pH environment, *T. ferrooxidans* can also tolerate various deleterious metal ions and anions such as arsenate (Tuovinen and Kelly, 1972).

*T. ferrooxidans* play a significant role in the oxidation of sulfide minerals by acting as catalysts, accelerating the rate of sulfide oxidation and the rate in which Fe$^{3+}$ is generated from Fe$^{2+}$ (Nordstrom, 1982; Ritchie, 1994b; Nicholson, 1994; Gould et al., 1994). According to Singer and Stumm, (1968, 1970) and Nordstrom (1976) the bacterium increases the oxidation rate by a factor of about $10^5$. The presence of Fe$^{3+}$ at low pH allows for the direct oxidation of sulfides by Fe$^{3+}$, replacing O$_2$ as the primary oxidant (Nordstrom, 1982; Bigham, 1994).
(F) **Gangue Dissolution**

Gangue represents the valueless waste rock or minerals within an orebody that must be separated from the economic rocks and minerals during concentration (Bates and Jackson, 1984). The oxidation of sulfide minerals (within the gangue) and subsequent release of acid, sulfate, and dissolved metals into the impoundment effluent can persist for decades to centuries (Blowes and Ptacek, 1994). The dissolution of acid-neutralizing gangue minerals (carbonates and aluminosilicates) within a waste-rock/tailings environment act to buffer and neutralize the products of sulfide oxidation. The ultimate amount of acidity and deleterious elements released during sulfide oxidation relates to the amount of acid-generating minerals and acid-neutralizing minerals present in the gangue. If there are more acid-generating minerals present within the waste-rock/tailings pile then there is a greater chance of generating AMD. If there is a greater percentage of acid-neutralizing minerals within the waste-rock/tailings pile then the chances of generating AMD are decreased.

According to Blowes and Ptacek (1994) metal-bearing hydroxide and hydroxysulfate minerals can precipitate during the acid-neutralizing reactions. These minerals act as sponges, effectively removing dissolved metals from the pore water within the dump. If these acid neutralization and mineral precipitation reactions occur at the site of sulfide oxidation, then the rate of oxidation may be decreased by the formation of inhibitory mineral coatings (Blowes and Ptacek, 1994). Inhibitory minerals such as Fe(OH)$_3$ (ferrihydrite) can form according to reaction 15:

34
\[
\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe(OH)}_3 + 3\text{H}^+
\]

\textit{ferricydrite}

These mineral coatings can decrease the rate of sulfide oxidation by armoring the sulfide minerals but they do not prevent AMD (Blowes and Ptacek, 1994).

Consider several of the generally slow gangue dissolution reactions reported by Ritchie (1994b), they include muscovite, biotite, albite, anorthite, and K-feldspar:

\textbf{Muscovite Dissolution:}
\[
\begin{align*}
\text{KA}_2\text{[AlSi}_3\text{O}_{10}\text{(OH)}_2(s)} + \text{H}^+ + \frac{3}{2}\text{H}_2\text{O} & \rightleftharpoons \\
\text{K}^+ + \frac{3}{2}\text{Al}_2\text{Si}_2\text{O}_5\text{(OH)}_4(s) & \\
\end{align*}
\]

\textbf{Biotite Dissolution:}
\[
\begin{align*}
\text{KMg}_{1.5}\text{Fe}_{1.5}\text{AlSi}_3\text{O}_{10}\text{(OH)}_2(s) + 7\text{H}^+ + \frac{1}{2}\text{H}_2\text{O} & \rightleftharpoons \\
\text{K}^+ + 1.5\text{Mg}^{2+} + 1.5\text{Fe}^{2+} + 2\text{H}_4\text{SiO}_4^8 + \frac{1}{2}\text{Al}_2\text{Si}_2\text{O}_5\text{(OH)}_4(s) & \\
\end{align*}
\]

\textbf{Albite Dissolution:}
\[
\begin{align*}
\text{NaAlSi}_3\text{O}_6(s) + \text{H}^+ + \frac{9}{2}\text{H}_2\text{O} & \rightleftharpoons \\
\text{Na}^+ + 2\text{H}_4\text{SiO}_4^8 + \frac{1}{2}\text{Al}_2\text{Si}_2\text{O}_5\text{(OH)}_4(s) & \\
\end{align*}
\]

\textbf{Anorthite Dissolution:}
\[
\begin{align*}
\text{CaAl}_2\text{Si}_2\text{O}_6(s) + 2\text{H}^+ + \text{H}_2\text{O} & \rightleftharpoons \text{Ca}^{2+} + \text{Al}_2\text{Si}_2\text{O}_5\text{(OH)}_4(s) & \\
\end{align*}
\]

\textbf{K-feldspar Dissolution:}
\[
\begin{align*}
\text{KA}\text{[AlSi}_3\text{O}_8 (s)} + \text{H}^+ + \frac{9}{2}\text{H}_2\text{O} & \rightleftharpoons \\
\text{K}^+ + 2\text{H}_4\text{SiO}_4^8 + \frac{1}{2}\text{Al}_2\text{Si}_2\text{O}_5\text{(OH)}_4(s) & \\
\end{align*}
\]

According to Ritchie (1994b) these minerals represent some of the typical acid-neutralizing constituents present in gangue. Even though these reactions are slow in
comparison to carbonate dissolution reactions, their importance will be justified in time during the chemical evolution of the pore water within the dump (Ritchie, 1994b). With time, when all of the readily available carbonate has been removed through dissolution, the micas and feldspars will continue to neutralize the acid generated through sulfide oxidation. The concentrations of major ions such as Ca, Mg, Na, K, Al and sulfate within the drainage effluent are controlled by these reactions. In each case (reactions 16 to 20) the gangue mineral and H\(^+\) are consumed and the products of all the reactions include the formation of kaolinite (Al\(_2\)Si\(_2\)O\(_5\)(OH)\(_4\)) and silicic acid (H\(_4\)SiO\(_4\)) while releasing K\(^+\), Mg\(^{2+}\), Fe\(^{2+}\), Na\(^+\), and Ca\(^{2+}\) depending on the gangue minerals involved. Reactions 16 and 17 consume H\(^+\) and decrease the fluids acidity while yielding K\(^+\), and Mg\(^{2+}\) and K\(^+\) respectively. As the acidity of the solutions in reactions 18, 19, and 20 is decreased through dissolution, albite releases Na\(^+\), anorthite releases Ca\(^{2+}\), and K-feldspar releases K\(^+\).

(i) Feldspar (Aluminosilicate) Dissolution

Only under very low pH conditions after all other acid-neutralizing sources have been consumed (carbonates and simple hydroxides) does the dissolution of the feldspars become important (Blowes and Ptacek, 1994). As mentioned in the previous section the dissolution of the feldspars consumes H\(^+\) and contributes Ca, Na, and K, as well as Si and Al to the pore water and mine waste effluent. These reactions are generally slower than the rate of pore water movement throughout the tailings or waste-rock pile and are usually not rapid enough to attain equilibrium with the system (Blowes and Ptacek, 1994). The
significance of these more stable minerals becomes only more evident as the readily soluble carbonate minerals are depleted during the acid neutralization reactions (Blowes and Ptacek, 1994). The ability of such stable minerals to control AMD after all of the more readily consumed minerals are gone may play an important role in environmental remediation methods.

Within a tailings or waste-rock pile the factors governing feldspar dissolution and the subsequent neutralization of the acid generated through sulfide oxidation are complex. Complete acid neutralization may only occur where the feldspar to sulfide mineral ratio is high, the proportion of feldspar mineral surface areas with which to react with are large, and the rate of acid generation is slow (Morin and Hutt, 1994). The simplified neutralization reactions from Morin and Hutt (1994) have the following restrictions placed on them due to the complex nature of these feldspar dissolution reactions. For reactions 21 to 26, (1) all sulfur oxidizes to sulfate, (2) iron is oxidized and hydrolyzed as Fe(OH)₃, (3) the silicon from the feldspar converts to H₄SiO₄⁻ or SiO₂(s), (4) aluminum will only hydrolyze and precipitate as Al(OH)₃ around pH 7, and (5) the alkali metals (K⁺, Na⁺) and the alkaline earth metal (Ca²⁺) do not hydrolyze and precipitate between pH 3.5 and 7.

between 3.5 < pH < 4.5:

**Anorthite:**

\[
\begin{align*}
\text{FeS}_2 + \frac{3}{2} \text{H}_2 \text{O} + \frac{3}{2} \text{O}_2 &+ \text{CaAl}_2 \text{Si}_2 \text{O}_8 + 4 \text{H}^+ \rightarrow \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + \text{Ca}^{2+} + 2\text{Al}^{3+} + 2\text{H}_4\text{SiO}_4^{8} \\
\text{(21)}
\end{align*}
\]
K-Feldspar:

\[
\text{FeS}_2 + 11^{1/2}_{2}\text{H}_2\text{O} + 3^{3/4}_{4}\text{O}_2 + 2\text{KAlSi}_3\text{O}_8 + 4\text{H}^+ \rightleftharpoons \\
\text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 2\text{K}^+ + 2\text{Al}^{3+} + 6\text{H}_4\text{SiO}_4
\]  
(22)

Albite:

\[
\text{FeS}_2 + 11^{1/2}_{2}\text{H}_2\text{O} + 3^{3/4}_{4}\text{O}_2 + 2\text{NaAlSi}_3\text{O}_8 + 4\text{H}^+ \rightleftharpoons \\
\text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 2\text{Na}^+ + 2\text{Al}^{3+} + 6\text{H}_4\text{SiO}_4
\]  
(23)

around pH 7:

Anorthite:

\[
\text{FeS}_2 + 21^{1/2}_{2}\text{H}_2\text{O} + 3^{3/4}_{4}\text{O}_2 + 3\text{CaAl}_2\text{Si}_2\text{O}_8 + 2\text{H}^+ \rightleftharpoons \\
\text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 3\text{Ca}^{2+} + 6\text{Al(OH)}_3 + 6\text{H}_4\text{SiO}_4
\]  
(24)

K-Feldspar:

\[
\text{FeS}_2 + 38^{1/2}_{2}\text{H}_2\text{O} + 3^{3/4}_{4}\text{O}_2 + 5\text{KAlSi}_3\text{O}_8 + \text{H}^+ \rightleftharpoons \\
\text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 5\text{K}^+ + 5\text{Al(OH)}_3 + 15\text{H}_4\text{SiO}_4
\]  
(25)

Albite:

\[
\text{FeS}_2 + 38^{1/2}_{2}\text{H}_2\text{O} + 3^{3/4}_{4}\text{O}_2 + 5\text{NaAlSi}_3\text{O}_8 + \text{H}^+ \rightleftharpoons \\
\text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 5\text{Na}^+ + 5\text{Al(OH)}_3 + 15\text{H}_4\text{SiO}_4
\]  
(26)

For the reactions within the 3.5 < pH < 4.5 range less silicic acid and alkaline earth/alkali metals are produced per mole of pyrite consumed then at around pH 7. The silicic acid and alkaline earth/alkali metals produced at around pH 7 are 4 times greater per mole of pyrite consumed then what is produced within the 3.5 < pH < 4.5 range.
(ii) Carbonate Dissolution

Reactions 27 and 28 (Ritchie, 1994b) represent the dissolution of carbonate (generally present in gangue as calcite and dolomite) by sulfuric acid:

**Calcite Dissolution:**

\[
\text{CaCO}_3 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{CaSO}_4 + \text{H}_2\text{O} + \text{CO}_2
\]

*calcite*  

**Dolomite Dissolution:**

\[
\text{CaMg(CO}_3)_2 + 2\text{H}_2\text{SO}_4 \rightleftharpoons \text{CaSO}_4 + \text{MgSO}_4 + 2\text{H}_2\text{O} + 2\text{CO}_2
\]

*dolomite*  

The products of these dissolution reactions are CO₂, H₂O and calcium and magnesium sulfate. According to Ritchie (1994b) carbonate dissolution is relatively fast compared to the rate of other mechanisms that control pyrite oxidation and it buffers the pH of the waste-rock/tailings pore water at a near neutral pH. Chemical species containing many of the trace metals that are pollutants in AMD are not soluble at pH values above 4.5 (Ritchie, 1994b). As a result, the trace metal pollution is absent while the near-neutral pH-buffering action of the carbonates persists. Therefore, with carbonate dissolution the pore water chemistry of the dump can be maintained at a near neutral pH while lacking the presence of any heavy metals.
IV EXPERIMENTAL PROCEDURES

The initial intent of this study was to experimentally investigate how different feldspars neutralize the acid generated through aqueous sulfide oxidation. Column leaching experiments using triple distilled water, as the aqueous component, were set up to study these reactions. The sulfide and feldspar concentrations within the columns were varied and different feldspars were used (albite, anorthite and microcline) to see what affect they had on sulfide oxidation. The aim was to determine which feldspar and what concentration of that feldspar would most effectively neutralize the acidic drainage. These determinations were to be based upon the effluent that was collected daily from the columns. The effluent pH was monitored and measured regularly during the experiments and samples were collected for later analysis. These samples would be used to determine the concentrations of various dissolved metals as well as the concentrations of $\text{SO}_4^{2-}$ and $\text{SiO}_2^0$. The samples however, were not analyzed because the pH values measured from the leachate columns were always near neutral, whereas acidic conditions were expected. Even after approximately three months there was no significant change in the measured pH values. These experiments were repeated numerous times with sulfides that were donated and purchased, but the results were always the same.

To aid in the oxidation process, *Thiobacillus ferrooxidans* were purchased to act as catalyst’s for the sulfide oxidation reactions. After a brief introduction into the world of microbiology and numerous failed attempts, a culture of *T ferrooxidans* received from the American Type Culture Collection (ATCC) was successfully transferred and incubated in several test tubes of growth medium. After successful growth of a biofilm
within some of the leachate columns, the experiments were continued but the results were the same. The measured pH values of the various columns were still near neutral from day 1 and did not change with time.

As all attempts at modeling these reactions experimentally failed, it was decided to model/simulate these reactions using a computer. The program CHILLER was available and could be used to model these geochemical reactions. After over a year and with help from James L. Palandri (a Ph.D. candidate studying geochemistry with Professor Mark Reed’s research group) and Mark H. Reed (co-author of program CHILLER), the reactions were successfully modeled to simulate conditions within a submerged tailings pile (isolated from the atmosphere). Unfortunately, all attempts to model the same reactions open to the atmosphere failed. CHILLER could not model these reactions because the calculated ionic strengths (within CHILLOUT) would increase to excessive values and the corresponding activity coefficients would lose their meaning in the sulfate-dominated fluid (M.H. Reed, personal communication, 1998). Reed (personal communication, 1998) did suggest that the activity coefficient routine in CHILLER could be modified to take into account the sulfate-dominated fluid for a more refined treatment but unfortunately, due to time constraints this was not performed.
V MODELING and RESULTS

(A) CHILLRUN Setup Essentials

(i) Fluid Chemistry for the Water-Rock Titrations

The chemistry of the pore water fluid within tailings or waste-rock piles is site specific and dependent on numerous variables as was previously detailed. There is a common source however, for the water that infiltrates these mine waste accumulations - rainwater. It should be noted that the rainwater chemistry and oxygen content varies from region to region and this will affect the degree of sulfide oxidation within a mine waste accumulation. Therefore, in order to model these reactions properly, the actual rainwater chemistry for a specific region must be known. Although more accurate, this type of approach is somewhat limited only to that region and generalizations from region to region are difficult to make. In order to model sulfide oxidation reactions for a wider array of situations, an average global rainwater chemistry was used here. According to Lee and Fetter (1994), greater than 99 % of the solutes in natural groundwater are made up by less than twelve constituents. Seven ions make up the majority of these constituents: $\text{Ca}^{2+}$, $\text{Na}^+$, $\text{Mg}^{2+}$, $\text{K}^+$, $\text{HCO}_3^-$, $\text{SO}_4^{2-}$, and $\text{Cl}^{-}$; with some dissolved $\text{SiO}_2$. Lee and Fetter (1994) note that these constituents are routinely found in water sample analyses, so they can serve as the constituents to describe the chemistry of natural waters. The precipitation chemistry reported by Lee and Fetter (1994) was taken from Freeze and Cherry (1979), and these values where selected to represent the general rainwater chemistry for all the modeling performed with SOLVEQ and CHILLER (see Table 2).
The rainwater chemistry for the modeling runs was input into GEOCAL in mg/L and because the density of the solution was 1 g/cm³ (so 1 mg/L = 1 ppm) the oxygen concentration was input as a ppm value. The oxygen concentration of the water was set to 9 ppm for the reactions modeled because water which is fully saturated with air at 1 atmosphere and 20 °C contains about 9 ppm O₂⁰ (Brown et al, 1991).

(ii) Mineral Chemistry for the Water-Rock Titrations

In order for CHILLER to perform water-rock titrations, MINSOL in the CHILLRUN file must be set to a non-zero value (1, 2, 3, or 4) depending on whether the titration is in grams or moles. MINSOL was set to 1 for all of the reaction modeling completed in this study. MINSOL = 1 forces CHILLER to titrate the minerals in grams, with SINC and SLIM set in grams (refer to APPENDIX E for a description of the key components of the CHILLRUN data file). Once MINSOL is set to 1 in the CHILLRUN file the reactant minerals are input into NOMOX and their respective weight percents are

\[
\begin{array}{|c|c|}
\hline
\text{Constituent} & \text{Precipitation (mg/L)} \\
\hline
\text{Na}^+ & 0.6 \\
\text{K}^+ & 0.4 \\
\text{Ca}^{2+} & 0.9 \\
\text{Mg}^{2+} & 0.2 \\
\text{HCO}_3^- & 2.0 \\
\text{SO}_4^{2-} & 3.0 \\
\text{Cl}^- & 0.4 \\
\text{SiO}_2 & 0.1 \\
\hline
\end{array}
\]
entered into WTPC. For example, to titrate 80 % pyrite and 20 % albite into the aqueous phase of the CHILLRUN file, pyrite and albite are listed under NOMOX and their weight percents are input under WTPC as 80 % and 20 % respectively.

(iii) SINC and SLIM

SINC (step increment) is the incrementing parameter that defines how much mineral or rock reactant will be titrated into the aqueous phase of the CHILLRUN file (Reed and Spycher, 1998). SLIM (step limit) is the variable that tells CHILLER to stop once TOTMIX reaches SLIM. TOTMIX is the current amount of reactant added to the original solution in grams (Reed and Spycher, 1998). Therefore, if SINC = 1 and SLIM = 10, CHILLER will titrate 1 gram of the reactant into the aqueous phase of the CHILLRUN file and continue to do so as long as convergence is reached during each titration. CHILLER will stop execution once TOTMIX = SLIM. The CHILLRUN file must then be modified by increasing the SINC and SLIM values by a factor of 10 after each successful run in order to continue modeling. This procedure is continued until equilibrium is reached or until CHILLER fails to reach convergence, at which point the CHILLRUN file would have to be debugged. James Palandri (personal communication, 1998) suggested starting with SINC = 0.1x10⁻⁵ and SLIM = 0.1x10⁻⁴ as the initial CHILLRUN file parameters.
(B) **Sulfide Oxidation and Feldspar Dissolution Reactions**

(i) 100 % Pyrite

CHILLER was initially set up to simulate how pure pyrite would oxidize within an aqueous environment in which the water has a chemical composition equivalent to that in Table 2. Pyrite was titrated into the aqueous phase by CHILLER where it was immediately broken down and the sulfur was oxidized according to reaction 2, producing Fe$^{2+}$, SO$_4^{2-}$ and H$^+$ (Figure 4C).

$$\text{FeS}_2 + \text{H}_2\text{O} + \frac{7}{2}\text{O}_2 \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+$$  \hspace{1cm} (2)

(*pyrite*)

The H$^+$ liberated by reaction 2 acidifies the system and causes the pH to decrease from the initial value of 5.5. Goethite simultaneously precipitates according to reactions 3 and 29 (Figure 4A).

$$\text{Fe}^{2+} + \frac{1}{4}\text{O}_2 \rightarrow \text{Fe}^{3+} + \frac{1}{2}\text{H}_2\text{O}$$  \hspace{1cm} (3)

$$\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{FeO(OH)} + 3\text{H}^+$$  \hspace{1cm} (29)

(*goethite*)

The Fe$^{2+}$ produced in reaction 2 is oxidized according to reaction 3 into ferric iron (Fe$^{3+}$). The subsequent hydrolysis of Fe$^{3+}$ leads to the formation of goethite (reaction 29) (Figure 4A). Reactions 2 and 3 consume oxygen and deplete [O$_2^0$] within the system (Figure 4C).
Figure 4. Reaction of 100% pyrite (Appendix A, Figure 1) with water (Table 2) at 25 °C and no atmospheric contact. Mineral abbreviations can be found in the ‘List of Abbreviations’. (A) Minerals formed in log moles. (B) pH and log total aqueous molality of the principal component species (i.e. ΣFe²⁺ represents the total of all aqueous Fe species). (C) Selected individual aqueous species in log molality (not log total aqueous molality). (D) Shows graph (C) in its entirety. pH can be read directly from the Log total aq molality and Log molality axes of B and C respectively.
Figure 4. (Continued)

and D). The bisulfate species (HSO$_4^-$) increases in abundance prior to point 1 due to the protonation of SO$_4^{2-}$ (reaction 30). The increasing [H$^+$] drives reaction 30 to the right producing HSO$_4^-$.

$$H^+ + SO_4^{2-} \rightarrow HSO_4^-$$  \hspace{1cm} (30)

Point 1 / Interval 1-2

At point 1 [O$_2^0$] rapidly decreases (Figure 4C and D) in response to the rapidly increasing [Fe$^{2+}$] which drives reaction 3 to the right consuming O$_2^0$. The activity of Fe$^{2+}$ increases as it is produced more rapidly in reaction 2 than it is consumed through reaction 3. The bisulfate species (HSO$_4^-$) continues to increase in abundance, within interval 1-2, according to reaction 30.
Point 2

At point 2 FeSO$_4^0$ forms according to reaction 31; Fe$^{2+}$ and SO$_4^{2-}$ within the system have increased sufficiently to drive reaction 31 quantitatively to the right.

$$\text{Fe}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{FeSO}_4^0$$  (31)

H$_2$S$_0$ also forms at point 2 (reaction 32) due to the presence of H$^+$ and HS$^-$.  

$$\text{HS}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{S}_0$$  (32)

Pyrite oxidation ceases (or slows dramatically) as the available oxygen within the system has decreased significantly (Figure 4C and D). The low [O$_2^0$] inhibits the oxidation of ferrous to ferric iron in reaction 3. As a result, goethite does not form because ferric iron is required for its formation according to reaction 29. The initial pH of the fluid has decreased from 5.5 to approximately 3.5 at point 2 as a result of reactions 2, 3 and 29 (Figure 4B and C). At this point goethite is replaced by pyrite as the stable solid phase (reaction 33).

$$\text{FeO(OH)} + 2\text{SO}_4^{2-} + 4\text{H}^+ \rightleftharpoons \text{FeS}_2 + \frac{5}{2}\text{H}_2\text{O} + \frac{7.5}{2}\text{O}_2^0$$  (33)

\underline{goethite}  \hspace{5cm} \underline{pyrite}

Reaction 33 is the sum of reactions 2, 3 and 29. The relative stability of the two phases (pyrite and goethite) is controlled by [H$^+$] and [O$_2^0$], the increased H$^+$ and decreased O$_2^0$ concentrations force reaction 33 to the right where pyrite stabilizes. The pH increases slightly as a result of the H$^+$ consumed by reaction 33, yielding a final equilibrated pH of
approximately 3.8. Once equilibrium has been reached, pyrite simply accumulates as it is titrated into the system by CHILLET.

(ii) 100 % Pyrrhotite

CHILLET was also set up to simulate the oxidation of pure pyrrhotite within an aqueous environment. Pyrrhotite was titrated by CHILLET into the aqueous phase (see Table 2) where it was immediately broken down and the sulfur was oxidized according to reaction 11 (Blowes and Ptacek, 1994; Blowes et al., 1994; Nicholson, 1994).

\[
\text{Fe}_{1-x}\text{S} + x\text{H}_2\text{O} + (2-\frac{x}{2})\text{O}_2 \rightarrow (1-x)\text{Fe}^{2+} + \text{SO}_4^{2-} + 2x\text{H}^+ \tag{11}
\]

\text{pyrrhotite}

The products of reaction 11 (Fe}^{2+}, \text{SO}_4^{2-}\text{ and }\text{H}^+) accumulate within the aqueous phase (Figure 5C) and the system pH decreases from the initial value of 5.5. Goethite simultaneously precipitates (Figure 5A) as the Fe}^{2+} produced in reaction 11 is oxidized into Fe}^{3+} and hydrolyzed according to reactions 3 and 29. Bisulfate (HSO}_4^-) increases in abundance prior to point 1 due to the protonation of SO}^4_{2-} (reaction 30) (Figure 5C). The oxygen within the system is depleted by reactions 11 and 3 as it is consumed during the oxidation of pyrrhotite (Figure 5C and D).

Point 1 / Interval 1-2

At point 1 [O}_2^0] rapidly decreases (Figure 5C and D) as it did in the pyrite oxidation simulation. The rapidly increasing [Fe}^{2+}] continues to drive reaction 3 to the right, consuming O}_2^0 in the process while goethite is produced (reaction 29). The activity
Figure 5. Reaction of 100% pyrrhotite (Appendix A, Figure 11) with water (Table 2) at 25 °C and no atmospheric contact. Mineral abbreviations can be found in the 'List of Abbreviations'. (A) Minerals formed in log moles. (B) pH and log total aqueous molality of the principal component species (i.e. $\Sigma \text{Fe}^{2+}$ represents the total of all aqueous Fe species). (C) Selected individual aqueous species in log molality (not log total aqueous molality). (D) Shows graph (C) in its entirety. pH can be read directly from the Log total aq molality and Log molality axes of B and C respectively.
of $\text{HSO}_4^-$ continues to increase up to point 2 due to the protonation of $\text{SO}_4^{2-}$ (reaction 30).

**Point 2 and Point 3**

At point 2 the system pH has decreased to approximately 3.6 (Figure 5B and C) as a result of the $\text{H}^+$ produced through reaction 11. $\text{FeSO}_4^0$ forms (reaction 31) as $[\text{Fe}^{2+}]$ and $[\text{SO}_4^{2-}]$ continue to increase according to reaction 11. Goethite is replaced by pyrite at point 3 as the stable solid phase (reaction 33). The increased $[\text{H}^+]$ and decreased $[\text{O}_2^{0}]$ force reaction 33 to the right and pyrite stabilizes. The pH increases slightly to approximately 4.1 at point 3 as a result of the $\text{H}^+$ consumed by reaction 33.

**Interval 3-4**

The excess $[\text{H}^+]$ drives reaction 14 (Nicholson, 1994) to the right and pyrite forms as the sulfur in pyrrhotite is oxidized (Burns and Fisher, 1990; Fisher and Burns, 1990).
\[ 2\text{Fe}_{1-x}\text{S} + (2-4x)\text{H}^+ + (\frac{1}{2}-x)\text{O}_2^0 \rightleftharpoons \text{FeS}_2 + (1-2x)\text{Fe}^{2+} + (1-2x)\text{H}_2\text{O} \]  

The pH of the system increases to approximately 6.4 as a result of the \( \text{H}^+ \) consumed through reaction 14. Goethite re-precipitates within interval 3-4 as the \( \text{Fe}^{2+} \) is oxidized into \( \text{Fe}^{3+} \) (reaction 3) and hydrolyzed according to reaction 34.

\[ 5\text{Fe}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{FeO(OH)} + 4\text{Fe}^{2+} + 7\text{H}^+ + \text{O}_2^0 \]  

Reaction 34 acts as a decent pH buffer, holding the pH between 6.4 and 6.79 within interval 3-4. The \( \text{H}^+ \) produced in reaction 34 offsets the \( \text{H}^+ \) consumed through reaction 14. This buffer (reaction 34) however, fails when magnetite forms at point 4. The activity of \( \text{O}_2^0 \) is also buffered within this interval as the \( \text{O}_2^0 \) produced from reaction 34 offsets the \( \text{O}_2^0 \) consumed in reaction 14.

**Point 4**

Magnetite forms at point 4 (Figure 5A) as the decreasing \([\text{O}_2^0]\) (Figure 5C) drives reaction 35 to the right.

\[ \text{FeO(OH)} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Fe}_3\text{O}_4 + 3\text{Fe}^{2+} + \text{O}_2^0 + 9\text{H}^+ \]  

The \( \text{H}^+ \) produced in reaction 35 offsets the \( \text{H}^+ \) consumed in reaction 14. The formation of magnetite (reaction 35) acts as a good pH buffer, holding the pH at approximately 9.42 within interval 4-5. This buffer however, fails when all of the goethite has been
consumed (reaction 35) within interval 4-5. The concentration of the bisulfate species (HSO₄⁻) decreases at point 4 and, as a result, H⁺ and SO₄²⁻ are consumed according to reaction 30 as the reaction is driven to the right. The decreasing [Fe²⁺] and [SO₄²⁻] within interval 4-5 forces reaction 31 to the left consuming FeSO₄⁰ in the process.

While magnetite forms through reaction 35, and prior to the complete consumption of goethite, pyrrhotite stabilizes. The low [O₂⁰⁺] forces reaction 11 to the left and pyrrhotite forms as the stable solid phase. The system pH increases to a final equilibrated value of approximately 9.75 at point 5. Once equilibrium has been reached, pyrrhotite simply accumulates as it is titrated into the system by CHILLER.

(iii) Pyrite and Feldspar Reactions

Due to time constraints and the fact that the 100 % pyrrhotite reaction model (Figure 5) was buffered to higher pH values (by the formation of goethite and magnetite), pyrrhotite was not modeled with the addition of feldspars. The pH for the 100 % pyrite reaction model however, was buffered at a much lower value (3.8), so the main focus of this work was the investigation of how feldspars (and various proportions of these feldspars) affect pyrite oxidation. Models with ratios of 1:1, 1:4 and 4:1 pyrite:feldspar (albite, anorthite and microcline) were chosen to explore how these reactions would evolve, and to determine what affect increasing/decreasing the pyrite:feldspar ratio would have on the results. At a ratio of 1:4, CHILLER titrates 1 part sulfide for every 4 parts of feldspar into the aqueous phase. At a 1:1 ratio, equal parts of sulfide and feldspar are titrated into the aqueous phase and at the 4:1 ratio, 4 parts sulfide per 1 part of feldspar
are titrated into the aqueous phase. For brevity, this section deals with the models for the 1:1 ratios of pyrite:feldspar, showing how pyrite was buffered by the presence of the different feldspars. The results for the corresponding 1:4 and 4:1 pyrite:feldspar (albite, anorthite and microcline) reaction models can be found in Appendix C.

The following section describes the 1:1 reactions between pyrite + microcline (Figure 6), pyrite + albite (Figure 7), and pyrite + anorthite (Figure 8). Table 2 contains the composition of the initial aqueous phase for all of the modeled reactions. In all three situations, CHILLER titrates pyrite into the system where it reacts with the aqueous component to produce $\text{Fe}^{2+}$, $\text{SO}_4^{2-}$ and $\text{H}^+$ (Figures 6C, 7C and 8C) (reaction 2). Goethite precipitates as a result of reactions 3 and 29 as $\text{Fe}^{2+}$ is oxidized into $\text{Fe}^{3+}$ and $\text{Fe}^{3+}$ is hydrolyzed (Figures 6A, 7A and 8A). Goethite remains stable over intervals 1-3 (Figures 6A, 7A and 8A), but is replaced by pyrite (reaction 33) at point 3 as the stable solid phase. A minimum pH of approximately 3.7 is reached at point 3 for the 1:1 reactions involving pyrite + microcline and pyrite + albite (Figures 6B and 7B), while a minimum pH of approximately 3.8 is reached at point 3 for the 1:1 pyrite + anorthite reaction model (Figure 8B). The relative stability of the two phases (pyrite and goethite) is controlled by $[\text{H}^+]$ and $[\text{O}_2^0]$. The increased activity of $\text{H}^+$ and the decreased activity of $\text{O}_2^0$ forces reaction 33 to the right where pyrite stabilizes. Some $\text{H}^+$ is consumed as a result, and the pH increases slightly to approximately 4 within interval 3-4 (Figures 6B, 7B and 8B). The fluid then reaches equilibrium with pyrite and pyrite simply accumulates in the system as it is titrated by CHILLER.
(a) 50% Pyrite + 50% Microcline

The following minerals are initially undersaturated in the aqueous phase for the reaction of 50% pyrite and 50% microcline with rainwater: pyrite, goethite, diaspore, kaolinite, quartz, clinohore, daphnite, stilbite, muscovite, and microcline. Table 3 summarizes the main features/results of this reaction and illustrates the minerals present, produced and consumed, pH and buffering reactions (with buffered pH values where applicable) for the points and intervals of Figure 6.

Microcline is simultaneously titrated into the aqueous phase with pyrite where it dissolves congruently producing K\(^+\), Al\(^{3+}\), SiO\(_2\)^0, and AlO(OH)^0 (Figure 6B and C), the activities of which increase according to reaction 36.

\[
2\text{KAlSi}_3\text{O}_8 + 5\text{H}^+ \rightarrow \text{AlO(OH)}^0 + 2\text{K}^+ + 6\text{SiO}_2^0 + \text{Al}^{3+} + 2\text{H}_2\text{O} \tag{36}
\]

The increasing [H\(^+\)] (from pyrite oxidation) drives reaction 36 to the right, consuming microcline in the process. Although this reaction consumes H\(^+\), it does not consume H\(^+\) at a faster rate than it is produced through the oxidation of pyrite and the subsequent formation of goethite (see reactions 2, 3 and 29) and has no apparent visible affect on pH over intervals 1-3 (Figure 6B and C).

**Interval 1-2**

At point 1 diaspore saturates (Figure 6A) due to an increase in [Al\(^{3+}\)] and [AlO(OH)^0] (Figure 6C) that drives reaction 37 to the right.
\[
\begin{align*}
\text{Al}^{3+} + \text{AlO(OH)}^0 + 2\text{H}_2\text{O} & \rightarrow 2\text{AlO(OH)} + 3\text{H}^+ \\
\text{diaspore} & 
\end{align*}
\] (37)

The overall reaction for the formation of diaspore within this system is shown in reaction 38 (which is the sum of reactions 36 and 37). Diaspore forms as reaction 38 proceeds to the right (as a result of \([\text{H}^+]\)), consuming microcline in the process.

\[
\begin{align*}
2\text{KAISi}_3\text{O}_8 + 2\text{H}^+ & \rightarrow 2\text{AlO(OH)} + 2\text{K}^+ + 6\text{SiO}_2^0 \\
\text{microcline} & \rightarrow \text{diaspore} 
\end{align*}
\] (38)

Interval 2-3

Diaspore continues to form through reaction 38 until \([\text{SiO}_2^0]\) has increased sufficiently for kaolinite to saturate (reaction 39). Kaolinite forms at point 2 (Figure 6A) as the increasing \([\text{SiO}_2^0]\) (Figure 6C) drives reaction 39 to the right, completely consuming diaspore in the process.

\[
\begin{align*}
2\text{AlO(OH)} + 2\text{SiO}_2^0 + \text{H}_2\text{O} & \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \\
\text{diaspore} & \rightarrow \text{kaolinite} 
\end{align*}
\] (39)

Reaction 40 (which is the sum of reactions 38 and 39) now takes over as the main \(\text{H}^+\) consuming reaction (as diaspore has been consumed). Kaolinite is produced at the expense of microcline and \(\text{H}^+\) as reaction 40 proceeds to the right.

\[
\begin{align*}
2\text{KAISi}_3\text{O}_8 + \text{H}_2\text{O} + 2\text{H}^+ & \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{K}^+ + 4\text{SiO}_2^0 \\
\text{microcline} & \rightarrow \text{kaolinite} 
\end{align*}
\] (40)
Figure 6. Reaction of 50% pyrite and 50% microcline (Appendix A, Figure 4) with water (Table 2) at 25 °C and no atmospheric contact. Mineral abbreviations can be found in the ‘List of Abbreviations’. (A) Minerals formed in log moles. (B) pH and log total aqueous molality of the principal component species (i.e. $\Sigma Al^{3+}$ represents the total of all aqueous Al species). (C) Selected individual aqueous species in log molality (not log total aqueous molality). (D) Shows graph (C) in its entirety. pH can be read directly from the Log total aq molality and Log molality axes of B and C respectively.
**Figure 6.** (Continued)

**Interval 3-4**

At point 3 the amount of kaolinite produced increases as the excess $\text{H}^+$ and the $\text{H}_2\text{O}$ produced from goethite reacting out in reaction 36 drives reaction 40 to the right. Quartz saturates soon after point 3 (within interval 3-4) (Figure 6A) due to the increased [SiO$_2^0$]. As the activity of $\text{H}^+$ is relatively high within interval 3-4 and the amount of microcline titrated into the system is fairly low, $\text{H}^+$ is consumed slowly by reaction 40. Consequently, the PH appears to be buffered within interval 3-4 (Figure 6B and C) by reaction 40. The PH however, is not buffered within interval 3-4 and as more and more microcline is titrated into the system, $\text{H}^+$ is consumed rapidly. The resultant PH increases to approximately 6.2 at point 4 as $\text{H}^+$ is consumed by reaction 40, where daphnite and clinochlore precipitate.
The decrease in \([H^+]\) drives reaction 30 to the left consuming \(HSO_4^-\) along interval 3-4 (Figure 6C). The \(SO_4^{2-}\) produced from reaction 30 along with the \(Fe^{2+}\) in the system produces \(FeSO_4^0\) according to reaction 31. The activity of \(FeSO_4^0\) increases along interval 3-4 due to the increases in \([Fe^{2+}]\) and \([SO_4^{2-}]\) (Figure 6C) which drives reaction 31 to the right. The activity of \(HS^-\) increases along interval 3-4 at the expense of \([H_2S^0]\) due to the decrease in \([H^+]\) (Figure 6C). Referring back to reaction 32, the drop in \([H^+]\) drives reaction 32 to the left producing \(HS^-\).

**Interval 4-5**

As \([H^+]\) continues to decrease (Figure 6B) daphnite and clinoclore saturate at point 4 (Figure 6A) (reactions 41 and 42 respectively).

\[
2AlO(OH)^0 + 5Fe^{2+} + 3SiO_2^0 + 8H_2O \rightleftharpoons \quad (Fe)_{5}Al_{2}Si_{3}O_{10}(OH)_{8} + 10H^+

daphnite \tag{41}
\]

\[
2AlO(OH)^0 + 5Mg^{2+} + 3SiO_2^0 + 8H_2O \rightleftharpoons \quad (Mg)_{5}Al_{2}Si_{3}O_{10}(OH)_{8} + 10H^+

clinoclore \tag{42}
\]

The drop in \([H^+]\) forces both of these reactions to the right consuming \(Fe^{2+}\) and \(Mg^{2+}\) in the process. The \(H^+\) produced in reactions 41 and 42 offsets the \(H^+\) consumed in reaction 40 and buffers the pH between 6.25 and 6.5 within interval 4-5. The buffering effect of the chlorite pH buffers (Figure 6A) however, fails when \(\Sigma[Fe^{2+}]\) and \(\Sigma[Mg^{2+}]\) decrease (Figure 6B) as they are depleted by the precipitation of daphnite and clinoclore (reactions 41 and 42 respectively). \(Fe^{2+}\) is a balancing ion in reaction 41 and \(Mg^{2+}\) is a
balancing ion in reaction 42. The decline in $\Sigma[Fe^{2+}]$ and $\Sigma[Mg^{2+}]$ allows the pH to increase to about 7.1 in interval 4-5 (Figure 6B), where stilbite forms. The activity of FeSO$_4^0$ decreases as a result of the drop in $[Fe^{2+}]$ along interval 4-5 (Figure 6C) (see reaction 31). The drop in $[Fe^{2+}]$ forces reaction 31 to the left consuming [FeSO$_4^0$].

The stilbite-chlorite pH buffer also occurs within interval 4-5 (Figure 6A). The low [H$^+$] and the presence of Na$^+$, Ca$^{2+}$, SiO$_2^0$, and AlO(OH)$^0$ (Figure 6B and C) forces reaction 43 to the right where stilbite saturates.

\[
Na^+ + 2Ca^{2+} + 19SiO_2^0 + 9AlO(OH)^0 + 5Fe^{2+} + 5Mg^{2+} + 30H_2O \rightleftharpoons Clel + Dph + NaCa_2(Al_2Si_3O_3)_6 \cdot 14H_2O + 25H^+ \tag{43}
\]

The stilbite-chlorite pH buffer fails almost immediately as $\Sigma[Ca^{2+}]$ decreases in interval 4-5 (Figure 6B) due to the precipitation of stilbite (Ca$^{2+}$ is a balancing ion in reaction 43). The slope of [H$^+$] curve in interval 4-5 (Figure 6B) changes very slightly as stilbite forms. The H$^+$ produced in reaction 43 does little to offset the H$^+$ consumed in reaction 40. As a result, the pH increases to approximately 7.8 at point 5, where muscovite forms.

As a note, [Al$^{3+}$] rapidly decreases (within interval 4-5) (Figure 6C and D) and yet $\Sigma[Al^{3+}]$ increases in Figure 6B over the same interval. The increase in $\Sigma[Al^{3+}]$ within interval 4-5 (Figure 6B) is due to AlO$_2^-$, which is not shown on Figure 6C, for the sake of simplicity. The same peculiarity can also be observed in Figures 7 and 8 for the 1:1 reactions involving pyrite + albite and pyrite + anorthite.
Interval 5-6

Kaolinite continues to form through reaction 40 as microcline is titrated into the system until $[K^+]$ has increased sufficiently for muscovite to become stable (Figure 6A, point 5). Muscovite precipitates at point 5 as the excess $K^+$ drives reaction 44 to the right (consuming kaolinite).

\[
3\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{K}^+ \rightleftharpoons 2\text{KAl}_2\text{Si}_3\text{O}_{10}(\text{OH})_2 + 3\text{H}_2\text{O} + 2\text{H}^+ \quad (44)
\]

Reaction 45 (which is the sum of reactions 40 and 44) now takes over as the main $H^+$ consuming reaction. Muscovite is produced at the expense of microcline and $H^+$ as reaction 45 proceeds to the right.

\[
3\text{KAlSi}_3\text{O}_8 + 2\text{H}^+ \rightleftharpoons \text{KAl}_2\text{Si}_3\text{O}_{10}(\text{OH})_2 + 2\text{K}^+ + 6\text{SiO}_2^8 \quad (45)
\]

The kaolinite-muscovite-stilbite-chlorite pH buffer (reaction 46) briefly acts as a good pH buffer, holding the pH at approximately 7.8 within interval 5-6 (Figure 6B).

\[
3\text{Kln} + 2\text{K}^+ + \text{Na}^+ + 2\text{Ca}^{2+} + 19\text{SiO}_2^8 + 9\text{AlO(OH)}^8 + 5\text{Fe}^{2+} + 5\text{Mg}^{2+} + 27\text{H}_2\text{O} \rightleftharpoons 2\text{Ms} + \text{Cle} + \text{Dph} + \text{Stb} + 27\text{H}^+ \quad (46)
\]

The $H^+$ produced in reaction 46 balances the $H^+$ consumed in reaction 45. The kaolinite-muscovite-stilbite-chlorite pH buffer however, fails when all of the kaolinite is converted to muscovite in reaction 46. As a result, insufficient $H^+$ is produced (by reaction 46)
Table 3. A summary of the main features/results of the 1:1 Pyrite:Microcline reaction model illustrating the minerals present, produced and consumed, pH and buffering reactions (with buffered pH values where applicable) for the points and intervals of Figure 6.

<table>
<thead>
<tr>
<th>1:1 Py:Mc</th>
<th>Minerals Produced</th>
<th>Stable Minerals</th>
<th>Minerals Consumed</th>
<th>Buffering Reactions (and buffered pH, where applicable)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point 1</td>
<td>Dsp</td>
<td>Gt</td>
<td></td>
<td></td>
<td>5.49</td>
</tr>
<tr>
<td>Interval 1-2</td>
<td>Gt, Dsp</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Point 2</td>
<td>Kln</td>
<td>Gt</td>
<td>Dsp</td>
<td></td>
<td>4.57</td>
</tr>
<tr>
<td>Interval 2-3</td>
<td>Gt, Kln</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Point 3</td>
<td>Py</td>
<td>Kln</td>
<td>Gt</td>
<td></td>
<td>3.72</td>
</tr>
<tr>
<td>Interval 3-4</td>
<td>Qtz</td>
<td>Py, Kln</td>
<td></td>
<td>Mc-Kln-Qtz (3.98-4.3)</td>
<td></td>
</tr>
<tr>
<td>Point 4</td>
<td>Clcl, Dph</td>
<td>Py, Kln, Qtz</td>
<td></td>
<td></td>
<td>6.27</td>
</tr>
<tr>
<td>Interval 4-5</td>
<td>Stb</td>
<td>Py, Kln, Qtz, Clcl, Dph</td>
<td></td>
<td>Clcl-Dph (6.25-6.5) Stb-Clcl-Dph</td>
<td></td>
</tr>
<tr>
<td>Point 5</td>
<td>Ms</td>
<td>Py, Qtz, Clcl, Dph, Stb</td>
<td>Kln</td>
<td></td>
<td>7.86</td>
</tr>
<tr>
<td>Interval 5-6</td>
<td>Py, Qtz, Clcl, Dph, Stb, Ms</td>
<td></td>
<td>Kln</td>
<td>Kln-Ms-Stb-Clcl-Dph (7.86)</td>
<td></td>
</tr>
<tr>
<td>Point 6</td>
<td>Mc</td>
<td>Py, Qtz, Clcl, Dph, Stb, Ms</td>
<td></td>
<td>Mc-Ms-Stb-Clcl-Dph (8.34)</td>
<td>8.34</td>
</tr>
<tr>
<td>Beyond Point 6</td>
<td>Py, Qtz, Clcl, Dph, Stb, Ms, Mc</td>
<td></td>
<td></td>
<td>Mc-Ms-Stb-Clcl-Dph (8.34)</td>
<td>8.34</td>
</tr>
</tbody>
</table>
to balance the $H^+$ consumed through reaction 45.

The pH continues to increase as excess $H^+$ is consumed through reaction 45 (Figure 6B) until microcline dissolution ceases (or slows dramatically). At point 6 (Figure 6A) the system reaches equilibrium with microcline and the microcline-muscovite-stilbite-chlorite pH buffer (reaction 47) yields a final equilibrated pH of approximately 8.3.

$$3\text{Mc} + \text{Na}^+ + 2\text{Ca}^{2+} + 13\text{SiO}_2^0 + 9\text{AlO(OH)}^0 + 5\text{Fe}^{2+} + 5\text{Mg}^{2+} + 30\text{H}_2\text{O} \rightleftharpoons \text{Ms} + 2\text{K}^+ + \text{Clcl} + \text{Dph} + \text{Stb} + 23\text{H}^+ \quad (47)$$

Microcline continues to accumulate beyond point 6 (Figure 6A) as it is titrated into the system by CHILLER.

(b) 50 % Pyrite + 50 % Albite

The aqueous phase for the reaction of 50 % pyrite and 50 % albite with rainwater is initially undersaturated with respect to the following minerals: pyrite, goethite, diaspore, kaolinite, quartz, clinochlore, daphnite, stilbite, celadonite, paragonite, and albite. Table 4 summarizes the main features/results for this reaction and illustrates the minerals present, produced and consumed, pH and buffering reactions (with buffered pH values where applicable) for the points and intervals of Figure 7.

Albite is simultaneously titrated into the aqueous phase with pyrite where it dissolves congruently producing $\text{Na}^+$, $\text{Al}^{3+}$, $\text{SiO}_2^0$, and $\text{AlO(OH)}^0$ (Figure 7B and C), the activities of which increase according to reaction 48.
\[ 2\text{NaAlSi}_2\text{O}_8 + 5\text{H}^+ \rightleftharpoons \text{AlO(OH)}^0 + 2\text{Na}^+ + 6\text{SiO}_2^0 + \text{Al}^{3+} + 2\text{H}_2\text{O} \] (48)

\textit{albite}

The \text{H}^+ produced from the oxidation of pyrite drives reaction 48 to the right consuming albite. Although this reaction also consumes \text{H}^+, it does not consume \text{H}^+ at a faster rate than it is produced through the oxidation of pyrite (and the subsequent formation of goethite, reactions 2, 3 and 29) and has no apparent visible affect on pH over intervals 1-3 (Figure 7B and C).

\textbf{Interval 1-2}

Diaspore saturates at point 1 (Figure 7A) as [\text{Al}^{3+}] and [\text{AlO(OH)}^0] increase (Figure 7C) and drive reaction 37 to the right. Reaction 49 (which is the sum of reactions 37 and 48) represents the overall reaction for the formation of diaspore. Diaspore is produced as reaction 49 moves to the right, (driven by [\text{H}^+]), consuming albite.

\[ 2\text{NaAlSi}_2\text{O}_8 + 2\text{H}^+ \rightleftharpoons 2\text{AlO(OH)} + 2\text{Na}^+ + 6\text{SiO}_2^0 \] (49)

\textit{albite} \hspace{1cm} \textit{diaspore}

\textbf{Interval 2-3}

At point 2 [\text{SiO}_2^0] has increased sufficiently for kaolinite to saturate according to reaction 39. Kaolinite forms at point 2 (Figure 7A) because the increased [\text{SiO}_2^0] (Figure 7C) drives reaction 39 to the right, completely consuming diaspore. Reaction 50 (which is the sum of reactions 39 and 49) now represents the dominant \text{H}^+ consuming reaction. Kaolinite forms at the expense of microcline as the excess \text{H}^+ in the system drives reaction 50 to the right.
Figure 7. Reaction of 50 % pyrite and 50 % albite (Appendix A, Figure 2) with water (Table 2) at 25 °C and no atmospheric contact. Mineral abbreviations can be found in the 'List of Abbreviations'. (A) Minerals formed in log moles. (B) pH and log total aqueous molality of the principal component species (i.e. $\Sigma$Al$^{3+}$ represents the total of all aqueous Al species). (C) Selected individual aqueous species in log molality (not log total aqueous molality). (D) Shows graph (C) in its` entirety. pH can be read directly from the Log total aq molality and Log molality axes of B and C respectively.
2NaAlSi₃O₈ + H₂O + 2H⁺ ⇌ Al₂Si₂O₅(OH)₄ + 2Na⁺ + 4SiO₂⁻ (50)

*albite*  
*kaolinite*

**Interval 3-4**

The amount of kaolinite produced increases at point 3 as the excess H⁺ and the H₂O produced from the goethite reacting out in reaction 33 drives reaction 50 to the right. Quartz saturates within interval 3-4 (soon after point 3) (Figure 7A) due to the increased [SiO₂⁻]. As the activity of H⁺ is relatively high within interval 3-4 and the amount of albite titrated into the system is fairly low, H⁺ is consumed slowly by reaction 50. Consequently, the pH appears to be buffered within interval 3-4 (Figure 7B and C) as kaolinite forms according to reaction 50. The pH however, is not buffered within interval 3-4 and as more albite is titrated into the system, H⁺ is consumed more rapidly. The pH
increases to approximately 6.2 at point 4 as $H^+$ is consumed by reaction 50, where daphnrite and clinochlore precipitate.

$HSO_4^-$ is also consumed along interval 3-4 as the drop in $[H^+]$ drives reaction 30 to the left (Figure 7C). The $SO_4^{2-}$ produced through reaction 30 combines with the $Fe^{2+}$ in the system to produce $FeSO_4^{0}$ (Figure 7C) according to reaction 31. The activity of $FeSO_4^{0}$ increases along interval 3-4 as reaction 31 proceeds to the right. The activity of $HS^-$ also increases along interval 3-4 due to the decrease in $[H^+]$. Referring back to reaction 32, the drop in $[H^+]$ drives reaction 32 to the left and produces $HS^-$ while it consumes $H_2S^{0}$ (Figure 7C).

**Interval 4-5**

The decreasing $[H^+]$ (Figure 7B) causes daphnrite and clinochlore to saturate (Figure 7A) according to reactions 41 and 42 respectively. $Fe^{2+}$ and $Mg^{2+}$ are consumed as the decreased $[H^+]$ forces both of these reactions to the right. The $H^+$ consumed in reaction 50 is offset by the $H^+$ produced through reactions 41 and 42 and this causes the change in the slope of the $aH^+$ curve. The buffering effect of the chlorite pH buffers fails when $\Sigma[Fe^{2+}]$ and $\Sigma[Mg^{2+}]$ (Figure 7B) rapidly decrease as they are depleted by the formation of daphnrite and clinochlore (Figure 7A). $Fe^{2+}$ is a balancing ion for daphnrite (reaction 41) and $Mg^{2+}$ is a balancing ion for clinochlore (reaction 42). The drop in $\Sigma[Fe^{2+}]$ and $\Sigma[Mg^{2+}]$ allows the pH to increase to about 7.1 in interval 4-5 (Figure 7B), where stilbite forms.

The stilbite-chlorite pH buffer appears in interval 4-5 (Figure 7A). The decreased $[H^+]$ and the presence of $Na^+$, $Ca^{2+}$, $SiO_2^{0}$, and $AlO(OH)^0$ (Figure 7B and C) drive
reaction 43 to the right and stilbite forms. The stilbite-chlorite pH buffer fails almost immediately due to the drop in $\Sigma[Ca^{2+}]$ in interval 4-5 (Figure 7B) due to the formation of stilbite ($Ca^{2+}$ is a balancing ion in reaction 43). The $H^+$ produced in reaction 43 does little to offset the $H^+$ consumed in reaction 50 so the slope of the $aH^+$ curve in interval 4-5 (Figure 7B) changes very little. The pH increases to approximately 9.4 at point 5, where celadonite forms.

The activity of $FeSO_4^0$ decreases as a result of the drop in $[Fe^{2+}]$ along interval 4-5 (Figure 7C) (see reaction 31). The drop in $[Fe^{2+}]$ forces this reaction to the left consuming all of the $FeSO_4^0$ (Figure 7C). The activity of $HSO_4^-$ also decreases along interval 4-5 (Figure 7C) (see reaction 30). The decreased $[H^+]$ forces this reaction to the left consuming all of the $HSO_4^-$ (Figure 7C).

Interval 5-6

The celadonite-stilbite-chlorite mineral pH buffer occurs in interval 5-6 (Figure 7A) (reaction 51). Celadonite precipitates at point 5 (Figure 7A) as the low $[H^+]$ and the $K^+$ from the rainwater drive reaction 51 to the right.

$$Na^+ + 2Ca^{2+} + K^+ + Fe^{3+} + 23SiO_2^8 + 10AlO(OH)^8 + 6Fe^{2+} + 6Mg^{2+} + 34^{1/2}H_2O \rightarrow$$
$$Cdn + Clc + Dph + Stb + 2^{1/2}O_2^8 + 33H^+ \quad (51)$$

The celadonite-stilbite-chlorite pH buffer fails almost immediately as $\Sigma[Mg^{2+}]$, $\Sigma[K^+]$, $\Sigma[Fe^{2+}]$ and $\Sigma[Al^{3+}]$ (Figure 7B) all decrease in interval 5-6. The decrease of any of these balancing ions causes the celadonite-stilbite-chlorite pH buffer to fail. The $H^+$ produced
in reaction 51 does nothing to offset the H⁺ consumed in reaction 50. As a result, the pH increases to approximately 10.5 at point 6, where paragonite forms.

**Interval 6-7**

Kaolinite continues to form through reaction 50 as albite is titrated into the system until [Na⁺] has increased sufficiently and paragonite becomes stable (Figure 7A, point 6). Paragonite precipitates at point 6 as the excess Na⁺ drives reaction 52 to the right (consuming kaolinite).

\[
3\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{Na}^+ \rightleftharpoons 2\text{NaAl}_2(\text{AlSi}_3\text{O}_10)(\text{OH})_2 + 3\text{H}_2\text{O} + 2\text{H}^+ \quad (52)
\]

Reactions 53 now takes over as the main H⁺ consuming reaction; paragonite is produced as albite and H⁺ are consumed.

\[
3\text{NaAlSi}_3\text{O}_8 + 2\text{H}^+ \rightleftharpoons \text{NaAl}_2(\text{AlSi}_3\text{O}_10)(\text{OH})_2 + 2\text{Na}^+ + 6\text{SiO}_2^\circ \quad (53)
\]

The kaolinite-paragonite-celadonite-stilbite-chlorite pH buffer (reaction 54) briefly acts as a good pH buffer, holding pH at approximately 10.5 in interval 6-7 (Figure 7B).

\[
3\text{Kln} + 3\text{Na}^+ + 2\text{Ca}^{2+} + \text{K}^+ + \text{Fe}^{3+} + 23\text{SiO}_2^\circ + 10\text{AlO(OH)}^\circ + 6\text{Fe}^{2+} + 6\text{Mg}^{2+} + 31^{1/2}\text{H}_2\text{O} \rightleftharpoons 2\text{Pg} + \text{Cd}_n + \text{Clcl} + \text{Dph} + \text{Stb} + 2^{1/2}\text{O}_2^\circ + 35\text{H}^+ \quad (54)
\]
Table 4. A summary of the main features/results of the 1:1 Pyrite:Albite reaction model illustrating the minerals present, produced and consumed, pH and buffering reactions (with buffered pH values where applicable) for the points and intervals of Figure 7.

<table>
<thead>
<tr>
<th>1:1 Py:Ab</th>
<th>Minerals Produced</th>
<th>Stable Minerals</th>
<th>Minerals Consumed</th>
<th>Buffering Reactions (and buffered pH, where applicable)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point 1</td>
<td>Dsp</td>
<td>Gt</td>
<td></td>
<td></td>
<td>5.49</td>
</tr>
<tr>
<td>Interval 1-2</td>
<td></td>
<td>Gt, Dsp</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Point 2</td>
<td>Kln</td>
<td>Gt</td>
<td>Dsp</td>
<td></td>
<td>4.57</td>
</tr>
<tr>
<td>Interval 2-3</td>
<td></td>
<td>Gt, Kln</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Point 3</td>
<td>Py</td>
<td>Kln</td>
<td>Gt</td>
<td></td>
<td>3.72</td>
</tr>
<tr>
<td>Interval 3-4</td>
<td>Qtz</td>
<td>Py, Kln</td>
<td></td>
<td>Ab-Kln-Qtz (3.98-4.31)</td>
<td></td>
</tr>
<tr>
<td>Point 4</td>
<td>Clcl, Dph</td>
<td>Py, Kln, Qtz</td>
<td></td>
<td></td>
<td>6.27</td>
</tr>
<tr>
<td>Interval 4-5</td>
<td>Stb</td>
<td>Py, Kln, Qtz, Clcl, Dph</td>
<td>Clcl-Dph (6.25-6.5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Point 5</td>
<td>Cdn</td>
<td>Py, Kln, Qtz, Clcl, Dph, Stb</td>
<td></td>
<td></td>
<td>9.4</td>
</tr>
<tr>
<td>Interval 5-6</td>
<td></td>
<td>Py, Kln, Qtz, Clcl, Dph, Stb, Cdn</td>
<td>Cdn-Stb-Clcl-Dph</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Point 6</td>
<td>Pg</td>
<td>Py, Qtz, Clcl, Dph, Stb, Cdn</td>
<td>Kln</td>
<td></td>
<td>10.53</td>
</tr>
<tr>
<td>Interval 6-7</td>
<td></td>
<td>Py, Qtz, Clcl, Dph, Stb, Cdn, Pg</td>
<td>Kln</td>
<td>Kln-Pg-Cdn-Stb-Clcl-Dph (10.53)</td>
<td></td>
</tr>
<tr>
<td>Point 7</td>
<td>Ab</td>
<td>Py, Qtz, Clcl, Dph, Stb, Cdn, Pg</td>
<td>Ab</td>
<td>Ab-Pg-Cdn-Stb-Clcl-Dph (10.75)</td>
<td>10.75</td>
</tr>
<tr>
<td>Beyond Point 7</td>
<td></td>
<td>Py, Qtz, Clcl, Dph, Stb, Cdn, Pg, Ab</td>
<td>Ab</td>
<td>Ab-Pg-Cdn-Stb-Clcl-Dph (10.75)</td>
<td>10.75</td>
</tr>
</tbody>
</table>
The \( H^+ \) produced in reaction 54 balances the \( H^+ \) consumed in reaction 53. The kaolinite-paragonite-celadonite-stilbite-chlorite pH buffer fails when all of the kaolinite is converted to paragonite (reaction 54). As a result, there is not enough \( H^+ \) produced to offset the \( H^+ \) consumed in reaction 53.

The pH continues to increase as excess \( H^+ \) is consumed in reaction 53 (Figure 7B) until albite dissolution ceases (or slows dramatically). At point 7 (Figure 7A) the fluid reaches equilibrium with albite and the albite-paragonite-celadonite-stilbite-chlorite pH buffer (reaction 55) yields a final equilibrated pH of approximately 10.7.

\[
3\text{Ab} + 2\text{Ca}^{2+} + \text{K}^+ + \text{Fe}^{3+} + 17\text{SiO}_2^6^- + \\
10\text{AlO(OH)}^0 + 6\text{Fe}^{2+} + 6\text{Mg}^{2+} + 34^{1/2}\text{H}_2\text{O}^{2-} \\
\text{Pg} + \text{Cd} + \text{Cl} + \text{Dph} + \text{Stb} + \text{Na}^+ + 2^{1/2}\text{O}_2^6^- + 31\text{H}^+ 
\]

(55)

Albite continues to accumulate beyond point 7 (Figure 7A) as it is titrated into the system by CHILLER.

\( \text{(c) \hspace{1cm} 50 \% \text{Pyrite} + 50 \% \text{Anorthite}} \)

The following minerals are initially undersaturated in the aqueous phase for the reaction of 50 \% pyrite and 50 \% anorthite with rainwater: pyrite, goethite, diaspore, kaolinite, clinochlore, daphnite, stilbite, laumontite, margarite, calcite and anorthite. Table 5 summarizes the main features/results of this reaction and illustrates the minerals present, produced and consumed, pH and buffering reactions (with buffered pH values where applicable) for the points and intervals of Figure 8.
Anorthite is simultaneously titrated into the aqueous phase with pyrite where it dissolves congruently producing Ca\(^{2+}\), Al\(^{3+}\), SiO\(_2\)^0, and AlO(OH)^0 (Figure 8B and C), their activities increase according to reaction 56.

\[
\text{CaAl}_2\text{Si}_2\text{O}_8 + 5\text{H}^+ \rightarrow \text{AlO(OH)}^0 + \text{Ca}^{2+} + 2\text{SiO}_2^0 + \text{Al}^{3+} + 2\text{H}_2\text{O} \quad (56)
\]

*anorthite*

The activity of H\(^+\) (which has increased due to the oxidation of pyrite) drives reaction 56 to the right and anorthite is consumed. Although reaction 56 consumes H\(^+\), it does not consume H\(^+\) at a faster rate than it is produced through the oxidation of pyrite and the subsequent formation of goethite (see reactions 2, 3 and 29). The amount of H\(^+\) consumed by reaction 56 appears to have no apparent visible affect on pH over intervals 1-3 (Figure 8B and C).

**Interval 1-2**

At point 1 diaspore saturates (Figure 8A) in response to the increased [Al\(^{3+}\)] and [AlO(OH)^0] (Figure 8C), driving reaction 37 to the right. The overall reaction for the formation of diaspore is shown in reaction 57 (which is the sum of reactions 37 and 56). Diaspore is produced as reaction 57 moves to the right (due to [H\(^+\)]), consuming anorthite.

\[
\text{CaAl}_2\text{Si}_2\text{O}_8 + 2\text{H}^+ \rightarrow 2\text{AlO(OH)} + \text{Ca}^{2+} + 2\text{SiO}_2^0 \quad (57)
\]

*anorthite*  
*diaspore*
Interval 2-3

Kaolinite saturates at point 2 (Figure 8A) because of an increase in $[\text{SiO}_2^0]$ which drives reaction 39 to the right. As a result, diaspore is completely consumed in interval 2-3 (Figure 8A). Now, the main $\text{H}^+$ consuming reaction involves the formation of kaolinite as the excess $\text{H}^+$ drives reaction 58 (which is the sum of reactions 39 and 57) to the right.

\[
\text{CaAl}_2\text{Si}_2\text{O}_8 + \text{H}_2\text{O} + 2\text{H}^+ \rightarrow 2\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Ca}^{2+}
\]

\[\text{anorthite} \quad \text{kaolinite}\] (58)

Interval 3-4

At point 3, diaspore saturates (Figure 8A) due to an increase in $[\text{AlOOH}^0]$ (Figure 8C) which drives reaction 37 to the right. The increase in $[\text{AlOOH}^0]$, observed only within interval 3-4 of this model/simulation, can be attributed to the fact that there are 2 moles of $\text{Al}^{3+}$ released per mole of anorthite consumed (while only 1 mole of $\text{Al}^{3+}$ is produced per mole of albite or microcline consumed). The increase in $[\text{AlOOH}^0]$ drives reaction 37 to the right, producing diaspore. In addition, the amount of kaolinite increases at point 3 as the excess $\text{H}^+$ and the $\text{H}_2\text{O}$ produced as a result of the goethite reacting out (see reaction 33) drives reaction 58 to the right.

As the activity of $\text{H}^+$ is relatively high within interval 3-4 and the amount of anorthite titrated into the system is fairly low, $\text{H}^+$ is consumed slowly by reaction 58. Consequently, the pH appears to be buffered within interval 3-4 (Figure 8B and C) by reaction 58. The pH however, is not buffered within interval 3-4 and as more anorthite is
Figure 8. Reaction of 50 % pyrite and 50 % anorthite (Appendix A, Figure 3) with water (Table 2) at 25 °C and no atmospheric contact. Mineral abbreviations can be found in the ‘List of Abbreviations’. (A) Minerals formed in log moles. (B) pH and log total aqueous molality of the principal component species (i.e. $\Sigma$Al$^{3+}$ represents the total of all aqueous Al species). (C) Selected individual aqueous species in log molality (not log total aqueous molality). (D) Shows graph (C) in its entirety. pH can be read directly from the Log total aq molality and Log molality axes of B and C respectively.
titrated into the system, H⁺ is consumed rapidly. The H⁺ consumed by reaction 58 causes the pH to increase to approximately 6.3 at point 4, where daphnite and clinochlore precipitate.

The decrease in [H⁺] drives reaction 30 to the left consuming HSO₄⁻ along interval 3-4 (Figure 8C). The SO₄²⁻ produced from this reaction along with [Fe²⁺] in the system produces FeSO₄⁰ according to reaction 31. The activity of FeSO₄⁰ increases along interval 3-4 as reaction 31 proceeds to the right (Figure 8C). The activity of HS⁻ also increases along interval 3-4 due to the decrease in [H⁺]. Referring back to reaction 32, the drop in [H⁺] drives reaction 32 to the left producing HS⁻ while it consumes [H₂S⁰] (Figure 8C).
**Interval 4-5**

The decrease in \([H^+]\) (Figure 8B) causes daphnite and clinochlore to saturate (Figure 8A) according to reactions 41 and 42 (respectively). The drop in \([H^+]\) drives both of these reactions to the right consuming \(Fe^{2+}\) and \(Mg^{2+}\) in the process. The \(H^+\) produced through reactions 41 and 42 offsets the \(H^+\) consumed in reaction 58. The buffering effect of the chlorite pH buffers (Figure 8A) however, fails as \(\Sigma[Fe^{2+}]\) and \(\Sigma[Mg^{2+}]\) decrease rapidly in interval 4-5 (Figure 8B) due to the precipitation of daphnite and clinochlore. \(Fe^{2+}\) is a balancing ion for daphnite (reaction 41) and \(Mg^{2+}\) is a balancing ion for clinochlore (reaction 42). The drop in \(\Sigma[Fe^{2+}]\) and \(\Sigma[Mg^{2+}]\) allows the pH to increase to about 8.9 in interval 4-5 (Figure 8B), where stilbite forms.

Kaolinite is consumed in interval 4-5 (Figure 8A) (see reaction 39) due to the drop in \([SiO_2^6]\) (Figure 8C). As \([SiO_2^6]\) decreases reaction 39 is driven to the left and diaspore forms.

The stilbite-chlorite-kaolinite-diaspore pH buffer also occurs in interval 4-5 (Figure 8A). The depleted \([H^+]\) (Figure 8B and C) drives reaction 59 to the right and stilbite forms.

\[
\begin{align*}
Kln + Na^+ + 2Ca^{2+} + 17SiO_2^6 + \ 9AlO(OH)^6 + 5Fe^{2+} + 5Mg^{2+} + 29H_2O & \rightarrow \\
Clcl + Dph + Stb + 2Dsp + 25H^+ & \quad (59)
\end{align*}
\]

The stilbite-chlorite-kaolinite-diaspore pH buffer acts as a good pH buffer, holding the pH at approximately 8.9 (Figure 8B and C) because the \(H^+\) produced in
reaction 59 balances the $H^+$ consumed in reaction 57. This pH buffer (reaction 59) however, fails at point 5 once all of the kaolinite has been consumed (Figure 8A).

The activity of $FeSO_4^0$ decreases as a result of the drop in $[Fe^{2+}]$ along interval 4-5 (Figure 8C) (see reaction 31). The drop in $[Fe^{2+}]$ forces this reaction to the left consuming all of the $FeSO_4^0$. The activity of $HSO_4^-$ also decreases along interval 4-5 and continues to do so into interval 5-6 (Figure 8C) (see reaction 30). The decreased $[H^+]$ forces this reaction to the left consuming all of the $HSO_4^-$ in interval 5-6 (Figure 8C).

**Interval 5-6**

The low $[H^+]$ (Figure 8B and C) within the system drives reaction 60 to the right producing laumontite at point 5 (Figure 8A).

\[
\begin{align*}
An + Stb + 4AlO(OH)^8 + 3SiO_2^0 + & \\ 5Fe^{2+} + 5Mg^{2+} + 16H_2O + Al^{3+} & \rightarrow & \\ Cl_{cl} + Dph + 3Lmt + 2Dsp + Na^+ + 22H^+ & (60)
\end{align*}
\]

The laumontite-stilbite-chlorite-diaspore pH buffer (reaction 60) also acts as a good pH buffer, holding the pH at approximately 9 in interval 5-6 (Figure 8B and C). Reaction 61 now takes over as the dominant $H^+$ consuming reaction as diaspore and laumontite form.

\[
\begin{align*}
2CaAl_2Si_2O_8 + 2H^+ + 4H_2O & \rightleftharpoons 2Dsp + Lmt + Ca^{3+} & (61)
\end{align*}
\]

The $H^+$ produced in reaction 60 balances the $H^+$ consumed in reaction 61. This pH buffer fails within interval 5-6 once all of the stilbite has been converted into laumontite through
reaction 60 (Figure 8A). As a result, the pH increases to approximately 10.3 at point 6 (Figure 8B and C), where calcite forms.

**Interval 6-7**

Calcite saturates at point 6 (Figure 8A) due to an increase in $\Sigma[Ca^{2+}]$ and a decrease in $[H^+]$ (Figure 8B). The increase in $\Sigma[Ca^{2+}]$ and the decrease in $[H^+]$ drives reaction 62 to the right producing calcite.

\[
Ca^{2+} + HCO_3^- \rightleftharpoons CaCO_3 + H^+
\]

(calcite) \hspace{2cm} (62)

Calcite does not buffer the pH at all, and as a result, the pH decreases to approximately 11.9 at point 7, where margarite forms.

**Interval 7-8**

Diaspore continues to form (reaction 61) as anorthite is titrated into the system until $\Sigma[Ca^{2+}]$ has sufficiently increased and margarite stabilizes (Figure 8A, point 7). Margarite saturates at point 7 as $\Sigma[Ca^{2+}]$ increases (Figure 8B) driving reaction 63 to the right, consuming diaspore.

\[
2An + 6Dsp + Ca^{2+} + 5Fe^{2+} + 5Mg^{2+} + 8SiO_2^8 + HCO_3^- + 20H_2O \rightleftharpoons Mrg + Cal + Lmt + Dph + Clei + 21H^+ \]

(63)
Table 5. A summary of the main features/results of the 1:1 Pyrite:Anorthite reaction model illustrating the minerals present, produced and consumed, pH and buffering reactions (with buffered pH values where applicable) for the points and intervals of Figure 8.

<table>
<thead>
<tr>
<th>1:1 Py:An</th>
<th>Minerals Produced</th>
<th>Stable Minerals</th>
<th>Minerals Consumed</th>
<th>Buffering Reactions (and buffered pH, where applicable)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point 1</td>
<td>Dsp</td>
<td>Gt</td>
<td></td>
<td></td>
<td>5.49</td>
</tr>
<tr>
<td>Interval 1-2</td>
<td></td>
<td>Gt, Dsp</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Point 2</td>
<td>Kln</td>
<td>Gt</td>
<td>Dsp</td>
<td></td>
<td>4.46</td>
</tr>
<tr>
<td>Interval 2-3</td>
<td></td>
<td>Gt, Kln</td>
<td>Dsp</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Point 3</td>
<td>Py, Dsp</td>
<td>Kln</td>
<td>Gt</td>
<td></td>
<td>3.85</td>
</tr>
<tr>
<td>Interval 3-4</td>
<td></td>
<td>Py, Kln, Dsp</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Point 4</td>
<td>Clcl, Dph</td>
<td>Py, Kln, Dsp</td>
<td></td>
<td></td>
<td>6.37</td>
</tr>
<tr>
<td>Interval 4-5</td>
<td>Stb</td>
<td>Py, Dsp, Clcl, Dph</td>
<td>Kln</td>
<td>Clcl-Dph (6.15-6.5) Stb-Clcl-Dph (8.9)</td>
<td></td>
</tr>
<tr>
<td>Point 5</td>
<td>Lmt</td>
<td>Py, Dsp, Clcl, Dph</td>
<td>Stb</td>
<td></td>
<td>8.9</td>
</tr>
<tr>
<td>Interval 5-6</td>
<td></td>
<td>Py, Dsp, Clcl, Dph, Lmt</td>
<td>Stb</td>
<td>Lmt-Stb-Clcl-Dph-Dsp (9.07)</td>
<td></td>
</tr>
<tr>
<td>Point 6</td>
<td>Cal</td>
<td>Py, Dsp, Clcl, Dph, Lmt</td>
<td></td>
<td></td>
<td>10.3</td>
</tr>
<tr>
<td>Interval 6-7</td>
<td></td>
<td>Py, Dsp, Clcl, Dph, Lmt, Cal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Point 7</td>
<td>Mrg</td>
<td>Py, Clcl, Dph, Lmt, Cal</td>
<td>Dsp</td>
<td></td>
<td>11.92</td>
</tr>
<tr>
<td>Interval 7-8</td>
<td></td>
<td>Py, Clcl, Dph, Lmt, Cal, Mrg</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Point 8</td>
<td>An</td>
<td>Py, Clcl, Dph, Lmt, Cal, Mrg</td>
<td></td>
<td>Mrg-Lmt-Cal-Clcl-Dph-Dsp (11.92)</td>
<td>13.52</td>
</tr>
<tr>
<td>Beyond Point 8</td>
<td></td>
<td>An, Py, Clcl, Dph, Lmt, Cal, Mrg</td>
<td></td>
<td>An-Mrg-Lmt-Cal-Clcl-Dph (13.52)</td>
<td>13.52</td>
</tr>
</tbody>
</table>

79
The margarite-laumontite-calcite-chlorite-diaspore pH buffer (reaction 63) (Figure 8A) briefly acts as a good pH buffer holding pH at approximately 11.9 in interval 7-8. The $H^+$ produced in reaction 63 balances the $H^+$ consumed in reaction 61, however, this buffer fails when all of the diaspore in the system is converted to margarite (Figure 8A) (reaction 63). Reaction 64 now takes over as the main $H^+$ consuming reaction, producing margarite and laumontite.

$$3\text{An} + 2H^+ + 4H_2O \rightleftharpoons \text{Mrg} + \text{Lmt} + Ca^{2+}$$  \hspace{1cm} (64)

The pH continues to increase as the excess $H^+$ is consumed in reaction 64 (Figure 8B) until anorthite dissolution ceases (or slows dramatically). At point 8 (Figure 8A) the fluid reaches equilibrium with anorthite and the anorthite-margarite-laumontite-calcite-chlorite pH buffer (reaction 65) yields a final equilibrated pH of approximately 13.5.

$$3\text{An} + 4\text{AlO(OH)}^8 + 5\text{Fe}^{2+} + 5\text{Mg}^{2+} + 20H_2O + \text{HCO}_3^- + 6\text{SiO}_2^6 \rightleftharpoons \text{Mrg} + \text{Lmt} + \text{Cal} + \text{Dph} + \text{Clcl} + 19H^+$$  \hspace{1cm} (65)

Anorthite accumulates beyond point 8 (Figure 8A) as it is titrated into the system by CHILLER.
VI DISCUSSION

Numerical practicality according to Reed (1997) dictates why water/rock reactions are typically calculated by titrating rock into water. Because of this approach, the initial water/rock ratios (w/r) are large as the amount of rock titrated into the system is so small (initially) compared to the amount of water (in the initial aqueous phase). Consequently, the results are usually expressed with the w/r changing from a large to a small value as graphs are read from left to right (Figure 8). This corresponds to an increasing amount of rock being titrated into the system as the graph is read from left to right. To reiterate, the models presented within this text represent how the chemistry of a receptacle (containing 1 kg of rainwater) would evolve as rock is incrementally titrated into the system. After each titration the rock and the fluid are allowed to equilibrate before the next incremental addition of rock. This process continues as more and more rock is incrementally titrated into the repository (refer Figure 1), until final equilibration is reached.

(A) 100 % Pyrite and 100 % Pyrrhotite

The 100 % pyrite and 100 % pyrrhotite reaction models produced very different results. The model involving 100 % pyrite proceeded in a predictable manner, similar to that described by Bethke (1996). Pyrite is oxidized and goethite forms as long as there is sufficient oxygen available within the system (Figure 4). Goethite is one of the principal secondary products formed during the oxidation of pyrite or pyrrhotite within a tailings environment (Jambor, 1994; Blowes and Ptacek, 1994). The pH within the system
becomes acidic (decreases) as \( H^+ \) is produced during the breakdown of pyrite according to reaction 2. Figure 9 (which is a graph comparing the activity of \( H^+ \) from both models) illustrates this point. The pH decreases up to point 1 (Figure 9) at which point pyrite oxidation ceases (or slows dramatically) and equilibrium is reached within the system.

The model for 100 \% pyrrhotite, on the other hand, behaved in quite a different fashion. Up to point 1 (Figure 9) the oxidation of pyrrhotite produced results that were very similar to the results produced in the model for 100 \% pyrite. Pyrrhotite is oxidized and goethite forms as \( Fe^{2+} \) is oxidized and hydrolyzed (Figure 5) (reactions 11, 3 and 29 respectively). Beyond point 2 (Figure 9) however, the pyrrhotite reaction model proceeded in a very different manner. The subsequent formation of different pH-buffering minerals altered the shape of the \([H^+]\) curve giving it a distinctive step-like appearance indicative of good pH buffers. Referring to Figure 5, goethite buffers the pH between 6.4 and 6.79 (interval 3-4) and magnetite buffers the pH at approximately 9.42 (interval 4-5). Where the curve flattens out, the pH is buffered by the formation of a new alteration mineral phase or assemblage. The initial pH for both of these systems was 5.5 and the final equilibrated pH values for the models (100 \% pyrite and 100 \% pyrrhotite) were 3.8 and 9.75 respectively.

The resultant activities of \( Fe^{2+} \) and \( SO_4^{2-} \) are also different for the models involving 100 \% pyrite and 100 \% pyrrhotite (Figures 10 and 11 respectively). \( Fe^{2+} \) and \( SO_4^{2-} \) both increase up to point 1 as they accumulate in response to reaction 2 (the breakdown of pyrite and the oxidation of sulfur) and reaction 11 (the breakdown of

82
Figure 9. The activity curves for $H^+$ from the 100 % Pyrite and 100 % Pyrrhotite reactions modeled with CHILLER (Figures 4 and 5 respectively). pH can be read directly from the y-axis (Log molality). The selected individual aqueous specie is expressed in log molality (not log total aqueous molality).

Figure 10. The activity curves for $Fe^{2+}$ from the 100 % Pyrite and 100 % Pyrrhotite reactions modeled with CHILLER (Figures 4 and 5 respectively). The selected individual aqueous specie is expressed in log molality (not log total aqueous molality).
Figure 11. The activity curves for $\text{SO}_4^{2-}$ from the 100 % Pyrite and 100 % Pyrrhotite reactions modeled with CHILLER (Figures 4 and 5 respectively). The selected individual aqueous specie is expressed in log molality (not log total aqueous molality).

pyrrhotite and the oxidation of sulfur). With pyrite (reaction 2), $\text{Fe}^{2+}$ and $\text{SO}_4^{2-}$ no longer accumulate beyond point 1 (Figures 10 and 11) as equilibrium has been reached. Both $\text{Fe}^{2+}$ and $\text{SO}_4^{2-}$ however, decrease beyond point 1 for the pyrrhotite reaction model and equilibrium is not reached until after point 2 (Figures 10 and 11). The decrease in the activities of both $\text{Fe}^{2+}$ and $\text{SO}_4^{2-}$ are a result of the reactions involved in pyrrhotite oxidation and the subsequent formation of pyrite, goethite and magnetite (Figure 5). Magnetite has been suggested by Alpers et al. (1994) to form as a secondary mineral within the mine waste environment.

The differences between the 100 % pyrite and 100 % pyrrhotite reaction models are due to the distinct mineral assemblages that buffer the pH to different values. For the pyrite reaction model, the goethite-pyrite pH buffer (reaction 33) buffers the pH to a final
equilibrated value of approximately 3.8. The pyrrhotite reaction model however, proceeds through a series of mineral pH buffers that alter the shape of the [H\(^+\)] curve. Reaction 34 (the goethite-pyrite pH buffer) buffers the pH between 6.4 and 6.79, but, eventually fails and gives way to reaction 35 (the goethite-pyrite-magnetite pH buffer). Reaction 35 temporarily buffers the pH at 9.42, but, also fails and gives way to the final mineral pH buffer, reaction 11. The pyrite-magnetite-pyrrhotite pH buffer (reaction 11), buffers the pH for the 100 % pyrrhotite reaction model to a final equilibrated value of approximately 9.75.

(B) 1:1 Pyrite + Albite, Pyrite + Anorthite, Pyrite + Microcline

The results produced from the modeled reactions between 1:1 pyrite:albite, pyrite:anorthite and pyrite:microcline were all similar in appearance (Figures 6, 7 and 8). As expected, pyrite was broken down and the sulfur was oxidized to produce H\(^+\), Fe\(^{2+}\) and SO\(_4^{2-}\), until [O\(_2^0\)] decreased significantly to the point at which the reaction ceased (or slowed dramatically). The corresponding feldspar was broken down through dissolution and as a result, H\(^+\) was consumed. A series of mineral pH-buffering assemblages formed from the products of the feldspar dissolution reactions, buffering the acidity within the system to different values. The steps in the [H\(^+\)] curve of Figures 6, 7 and 8 B and C coincide with the formation of these mineral pH-buffering assemblages. Each step begins with the formation of a new alteration mineral, which acts as a good pH buffer. The steps end with the breakdown of the mineral pH buffer by dissolution or by depletion of the balancing cations activity as the alteration mineral forms.

85
The graphs in Figures 12 through 17 compare the activities of $H^+$, $O_2^0$, $Al^{3+}$, $Fe^{2+}$, $SO_4^{2-}$ and $AlO(OH)^0$ (respectively) from each model. The differences between the activities of these species are due to the particular feldspar involved in the reaction. The cation released by the feldspar in each model (albite—$Na^+$, anorthite—$Ca^{2+}$ and microcline—$K^+$) influences the mineral assemblages that form. A different mineral assemblage forms for each of the modeled reactions (1:1 pyrite:albite, 1:1 pyrite:anorthite and 1:1 pyrite:microcline) because of the particular cation ($Na^+$, $Ca^{2+}$ or $K^+$) involved. Therefore, the activities of $H^+$, $O_2^0$, $Al^{3+}$, $Fe^{2+}$, $SO_4^{2-}$ and $AlO(OH)^0$ are different in each model because of the differences that exist between the resultant mineral assemblages.

The pH (Figure 12) for all three models decreases up to point 1 after which a series of pH-buffering minerals forms, altering the [$H^+$] curves. The decrease in pH (for each model) was due to the $H^+$ produced from the oxidation of pyrite. The reaction between 1:1 pyrite:microcline is the first modeled reaction to reach equilibrium (Figure 12, point 2) and has a final equilibrated pH of approximately 8.3. The 1:1 pyrite:anorthite reaction model takes the longest to reach equilibrium (Figure 12, point 3) and has a final equilibrated pH of approximately 13.5. Based on these results, if a near-neutral pH is desired, microcline would be the preferred feldspar to use as a mineral pH buffer under these conditions. Anorthite however, would be a more appropriate mineral pH buffer, if at some point in time, more $H^+$ was generated in the system. Under these conditions, anorthite would have a greater potential to neutralize any acid released into the system (with time) because it has a much higher final equilibrated pH.
All three models consume oxygen at approximately the same rate (Figure 13). At point 1 the rate of $O_2^0$ consumption promptly increases as the amount of pyrite titrated into the system has reached a critical value, rapidly consuming the $O_2^0$ as pyrite is oxidized. The products produced from the oxidation of pyrite increase as a result. Besides the increase in $[H^+]$ (as previously discussed), the activities of $Fe^{2+}$ and $SO_4^{2-}$ also increase up to point 1 (Figures 14 and 15 respectively) as pyrite is oxidized. The activity of $Fe^{2+}$ decreases beyond point 1 due to the formation of $FeSO_4^0$ and iron-bearing minerals, daphnite (for the models involving microcline and anorthite) and daphnite and celadonite (for the albite reaction model). The activity of $SO_4^{2-}$ (Figure 15) is essentially the same for all three models. The feldspar modeled for each system does not appear to affect, differently, the amount of $SO_4^{2-}$ released into the system.

The activity of $Al^{3+}$ increases up to point 1 (Figure 16) as it is produced through feldspar dissolution. Beyond this point, $[Al^{3+}]$ decreases as various Al-bearing alteration minerals precipitate (i.e. kaolinite, the chlorites, the micas, and the zeolites). Comparisons of the behavior of $[Al^{3+}]$ (Figure 16) with $[H^+]$ (Figure 12) yield an interesting finding. There appears to be a direct relationship between the activities of $H^+$ and $Al^{3+}$ produced from the 1:1 reactions between pyrite:microcline, pyrite:albite and pyrite:anorthite (Figures 12 and 16, respectively). The corresponding $H^+$ and $Al^{3+}$ graphs for each of these reactions appear to be virtually identical. The relationship that exists between these species can be explained by examining the equilibrium constant ($K$).

According to the law of mass action, the relative activities of the reactants and products of a reaction at equilibrium can be expressed in terms of the equilibrium
Figure 12. The activity curves for $H^+$ from the 50 % Pyrite and 50 % Feldspar (microcline, albite and anorthite) reactions modeled with CHILLER (Figures 6, 7 and 8 respectively). pH can be read directly from the y-axis (Log molality). The selected individual aqueous specie is expressed in log molality (not log total aqueous molality).

Figure 13. The activity curves for $O_2^0$ from the 50 % Pyrite and 50 % Feldspar (microcline, albite and anorthite) reactions modeled with CHILLER (Figures 6, 7 and 8 respectively). The selected individual aqueous specie is expressed in log molality (not log total aqueous molality).
**Figure 14.** The activity curves for $\text{Fe}^{2+}$ from the 50% Pyrite and 50% Feldspar (microcline, albite and anorthite) reactions modeled with CHILLER (Figures 6, 7 and 8 respectively). The selected individual aqueous specie is expressed in log molality (not log total aqueous molality).

**Figure 15.** The activity curves for $\text{SO}_4^{2-}$ from the 50% Pyrite and 50% Feldspar (microcline, albite and anorthite) reactions modeled with CHILLER (Figures 6, 7 and 8 respectively). The selected individual aqueous specie is expressed in log molality (not log total aqueous molality).
constant. Consider reaction 37, K relates to the H⁺ and Al³⁺ species as follows:

\[
K = \frac{[H^+]^3}{[Al^{3+}]}\]

As K is a constant, the concentrations of the reactants and products must increase or decrease in order for K to remain constant. Therefore, because the activity curves for H⁺ and Al³⁺ (Figures 12 and 16, respectively) are so similar in appearance, it can be concluded that as H⁺ increases (pH decreases) the corresponding activity of Al³⁺ must also increase in order for K to remain constant. Conversely, as H⁺ decreases (pH increases) the corresponding activity of Al³⁺ must also decrease in order for K to remain constant.

The activity of AIO(OH)⁰ behaves similarly for the 1:1 pyrite:microcline and pyrite:albite reaction models (Figure 17). Up to point 1 (Figure 17), the activity of AIO(OH)⁰ remains stable due to the formation of diaspore but decreases beyond point 1 because diaspore is no longer stable. The activity of AIO(OH)⁰ for the 1:1 pyrite:anorthite reaction model remains stable due to the formation of diaspore but decreases beyond point 2 because diaspore is no longer stable. The activity of AIO(OH)⁰ increases again at point 3, however, after decreasing within interval 2-3, because diaspore is again stable until point 4. As previously discussed, the activity of AIO(OH)⁰ increases again due to the fact that there are 2 moles of Al³⁺ released per mole of anorthite consumed. The excess Al³⁺ causes an increase in [AIO(OH)⁰] within the aqueous phase and diaspore re-precipitates at point 3.
Figure 16. The activity curves for Al$^{3+}$ from the 50% Pyrite and 50% Feldspar (microcline, albite and anorthite) reactions modeled with CHILLER (Figures 6, 7 and 8 respectively). The selected individual aqueous specie is expressed in log molality (not log total aqueous molality).

Figure 17. The activity curves for A1O(OH)$^{0}$ from the 50% Pyrite and 50% Feldspar (microcline, albite and anorthite) reactions modeled with CHILLER (Figures 6, 7 and 8 respectively). The selected individual aqueous specie is expressed in log molality (not log total aqueous molality).
The majority of the minerals formed through these modeled reactions have been reported from waste rock accumulations. Goethite and kaolinite (although uncertainty exists as to the latter’s identification as a secondary mineral) are reported to form from the oxidation of coal wastes (Jambor, 1994). Kaolinite, goethite and micas (vermiculite and mixed-layer mica-vermiculite) have been identified as secondary minerals in sulfide rich tailings (Jambor, 1994). According to Blowes and Ptacek (1994) goethite, chlorite, muscovite and feldspars have been identified as principal pH-buffering phases in tailings piles. Zeolites often form as a result of the alteration of feldspars according to Mason and Berry (1968). Therefore, zeolites may form through the dissolution of feldspars within a tailings pile, though none have been reported from these environments.

The minerals formed during the modeling reactions with CHILLER are all identified as minerals that exist within tailings environments or have the potential to exist under those conditions. Initial test runs with CHILLER however, had resulted in the formation of several minerals that were questionable, as far as their existence, within these environments. As a result, these minerals had to be suppressed from forming during modeling by listing them under the SUPNAM feature in the CHILLRUN data file for each of the modeled reactions. SUPNAM is used to prevent the formation of any questionable minerals, based on the user’s knowledge (Reed and Spycher, 1998) (refer to APPENDIX E for a description of the key components of the CHILLRUN data file). Some of the minerals suppressed from forming during these modeling reactions were: andradite, staurolite, vesuvianite, zoisite, tilleyite, diopside, larnite and merwinite to name a few.
Although not identified as secondary minerals, paragonite, margarite and celadonite (all micas) could all form under appropriate conditions. These minerals may already form within tailings piles, especially those known to contain micas (vermiculite and mixed-layer mica-vermiculite), but they may not be present in sufficient quantities and therefore, not yet identified. On the other hand, no one may have looked at the possibility of their existence, or the simulations modeled with CHILLER are incorrect. The same rational can be applied to the zeolites (laumontite and stilbite); they may exist as a byproduct of feldspar dissolution, but remain to be discovered. As noted earlier, the amount of information regarding the mineralogy (primary and secondary) of mine waste tailings piles and waste rock accumulations is scant.

One has to bear in mind that the results from CHILLER do not actually dictate which minerals would form but rather which minerals could form under the specified conditions. This has to be kept in mind when reviewing the results from CHILLER, as with all other geochemical models, the results are not absolute. Geochemical reaction modeling serves only as a tool that hopefully leads to further, more refined investigations, whether it be in the laboratory or in nature. The reactions presented within this study testify to the complexity of the types of possible geochemical reactions that can take place within mine waste accumulations during the formation of acidic mine drainage.

(C) 1:4, 1:1 and 4:1 Pyrite + Feldspar Ratios

The pyrite and feldspar reactions were modeled at ratios of 1:1, 1:4 and 4:1 to determine the effect of increasing/decreasing the pyrite:feldspar ratio. The results
indicate that increasing or decreasing the pyrite:feldspar ratio had no affect on the sequence of alteration minerals formed; the resultant buffering reactions, buffered pH values and final equilibrated pH were the same for each group of modeled reactions. The results of the pyrite:albite modeling reactions (1:4, 1:1 and 4:1) were all the same, as were the results from the pyrite:anorthite and pyrite:microcline modeling reactions. This conclusion is not surprising because all that is being altered within the CHILLRUN file is the amounts of pyrite and feldspar titrated into the systems.

Increasing/decreasing the pyrite:feldspar ratio only affected the point at which the reactions occurred. As time is not a factor expressed in the results from CHILLER, the point at which these reactions occur will be related to the water/rock ratio. To illustrate this point, refer to the activity diagram for H⁺ (Figure 18) from the 1:4, 1:1 and 4:1 pyrite:microcline reaction models. As can be seen in Figure 18, pyrite oxidation ceases (or slows dramatically) at point 1 (log w/r = 5) for the 4:1 pyrite:microcline reaction model while in the 1:4 pyrite:microcline reaction model pyrite oxidation does not cease (or slow dramatically) until point 3 (log w/r = 4.38). Therefore, the 4:1 pyrite:microcline reaction model is the first modeled reaction in which pyrite oxidation ceases (or slows dramatically) while the 1:4 pyrite:microcline reaction model is the last modeled reaction to reach this stage. All three models (1:4, 1:1 and 4:1 pyrite:microcline) reach a minimum pH at different w/r ratios (Figure 18 points 1, 2 and 3), and this is directly related to the pyrite:feldspar titration ratio. At a ratio of 4:1 pyrite:feldspar, more pyrite is titrated into the system per titration than in the other modeled reactions (1:1 and 4:1 pyrite:feldspar). As a result, the available oxygen within the system (9 ppm O₂) is
consumed more rapidly by the 4:1 pyrite:feldspar reaction models and they are the first modeled reactions in which pyrite oxidation ceases (or slows dramatically). Conversely, the 1:4 pyrite:microcline reaction model is the first modeled reaction to reach equilibrium (Figure 18 point 4 versus points 5 and 6) because more feldspar (microcline) is titrated into the system per titration than in the other modeled reactions (1:1 and 4:1 pyrite:microcline). As a result, $H^+$ is consumed more rapidly by the 1:4 pyrite:feldspar reaction models and they are the first modeled reactions in which equilibrium is reached.

**Figure 18.** The activity curves for $H^+$ from the 1:4, 1:1 and 4:1 Pyrite:Microcline reactions modeled with CHILLER. pH can be read directly from the y-axis (Log molality). The selected individual aqueous specie is expressed in log molality (not log total aqueous molality).
VII CONCLUSIONS

The principal conclusions from the results of this study are:

1. The 100 % pyrite reaction model was buffered by the goethite-pyrite pH buffer to a final equilibrated pH of approximately 3.8.

2. The 100 % pyrrhotite reaction model was buffered by three distinct mineral pH buffers, altering the shape of the [aH+] curve. The pH was initially buffered between 6.4 and 6.79 by the goethite-pyrite pH buffer, then it was buffered at 9.42 by the goethite-pyrite-magnetite pH buffer. The model was buffered to a final equilibrated pH of approximately 9.75 by the pyrite-magnetite-pyrrhotite pH buffer.

3. The mineral assemblages produced by each of the modeled reactions (1:1 pyrite:albite, 1:1 pyrite:anorthite and 1:1 pyrite:microcline) were different because of the particular cation (Na+, Ca2+ or K+) involved. Consequently, the activities of species produced from these reactions (i.e. H+, O2 0, Al3+) were different in each of the models because of the differences that existed between the resultant mineral assemblages.

4. The 1:1 pyrite:microcline reaction model is the first modeled reaction to reach equilibrium with a final equilibrated pH of approximately 8.3. The 1:1 pyrite:anorthite reaction model took the longest to reach equilibrium and buffered the pH to the highest final equilibrated value of approximately 13.5.
5. The minerals formed during the modeling reactions with CHILLER have been shown to exist within tailings environments or have the potential to exist under those conditions.

The following minerals formed from the 1:1 pyrite:microcline reaction model:

- goethite, diaspore, kaolinite, quartz, clinochlore, daphnite, stilbite and muscovite.

The 1:1 pyrite:albite reaction model produced the following minerals:

- goethite, diaspore, kaolinite, quartz, clinochlore, daphnite, stilbite, celadonite and paragonite.

The minerals that formed from the 1:1 pyrite:anorthite reaction model were:

- goethite, diaspore, kaolinite, clinochlore, daphnite, stilbite, laumontite, calcite and margarite.

6. Increasing or decreasing the pyrite:feldspar ratio did not affect the sequence of alteration minerals formed, so the resultant buffering reactions, buffered pH values and final equilibrated pH were the same for each group of modeled reactions. Increasing or decreasing the pyrite:feldspar ratio only affected the point at which the reactions occurred (with respect to the water/rock ratio). To illustrate, in all three groups of models the 1:4 (pyrite:feldspar) reaction models reached final equilibration first (at a higher w/r) while, the 4:1 (pyrite:feldspar) reaction models were the last to reach final equilibration (at a lower w/r).
VIII RECOMMENDATIONS

All of the reactions were successfully modeled isolated from the atmosphere, simulating how sulfide oxidation generates acid or AMD and feldspar dissolution neutralizes/buffers the acid produced in a closed environment. To expand upon this research, the same reactions should also be modeled without removing the atmospheric buffers in CHILLER. The results of modeling these same reactions open to the atmosphere would show how pyrite oxidation proceeds indefinitely with an inexhaustible source of oxygen and unlimited amounts of pyrite. This type of model could then be used to predict the minimum percentage of feldspar (depending on type) required to buffer and neutralize the acid generated under certain conditions. In general, if there are more acid-consuming minerals in the mine waste, the resulting pH will be near neutral to basic. CHILLER would have to be modified however, because with previous modeling attempts, the calculated ionic strengths (within CHILLOUT) would increase to excessive values and the corresponding activity coefficients would lose their meaning in the sulfate-dominated fluid (M.H. Reed, personal communication, 1998). Reed (personal communication, 1998) suggests that the activity coefficient routine in CHILLER could be altered to take into account the sulfate-dominated fluid for a more refined treatment.

Further attempts at modeling the reactions could be made in the laboratory. If successful, CHILLER could then be used in conjunction with the laboratory experiments to predict the outcome of certain reactions, which could then be tested in a series of experiments. This approach would produce more reliable predictions, since they were corroborated experimentally.
Actual site specific data reported from mining companies consisting of mine waste composition, pore fluid chemistry and effluent chemistry could be used by CHILLER to predict how their present remediation techniques will fare with time or model potential mixing remediation strategies. If the results produced with CHILLER are accurate, the modeler could use CHILLER to model and predict how the effluent chemistry from newly accumulated mine waste piles would change with time. This advance would establish CHILLER as a predictive tool for acid mine drainage.
REFERENCES


100


Itzkovitch, I.J., and Feasby, D.G., (1993), Le programme de neutralisation des eaux de drainage dans l'environnement minier, Colloque sur le programme de neutralisation des eaux de drainage dans l'environnement minier, Val d'Or, NEDEM 93, pp. 1-16.


Olson, G.J., (1991), Rate of Bioleaching by *Thiobacillus ferroxidans*; Results of an Interlabatory Comparison, Applied Environmental Microbiology 57, pp 642-644.


APPENDICES
APPENDIX A

CHILLRUN files used to run CHILLER
LIST OF FIGURES FOR APPENDIX A

Figure 1: Chillrun1.dat (Chillrun file for the reaction between 100 % pyrite and water with no atmospheric contact). ..............................................110

Figure 2: Chillrun2.dat (Chillrun file for the reaction between 50 % pyrite + 50 % albite and water with no atmospheric contact). .................111

Figure 3: Chillrun3.dat (Chillrun file for the reaction between 50 % pyrite + 50 % anorthite and water with no atmospheric contact). ..........112

Figure 4: Chillrun4.dat (Chillrun file for the reaction between 50 % pyrite + 50 % microcline and water with no atmospheric contact). ......113

Figure 5: Chillrun5.dat (Chillrun file for the reaction between 20 % pyrite + 80 % albite and water with no atmospheric contact). ..........114

Figure 6: Chillrun6.dat (Chillrun file for the reaction between 20 % pyrite + 80 % anorthite and water with no atmospheric contact). ......115

Figure 7: Chillrun7.dat (Chillrun file for the reaction between 20 % pyrite + 80 % microcline and water with no atmospheric contact). ....116

Figure 8: Chillrun8.dat (Chillrun file for the reaction between 80 % pyrite + 20 % albite and water with no atmospheric contact). ..........117

Figure 9: Chillrun9.dat (Chillrun file for the reaction between 80 % pyrite + 20 % anorthite and water with no atmospheric contact) ........118

Figure 10: Chillrun10.dat (Chillrun file for the reaction between 80 % pyrite + 20 % microcline and water with no atmospheric contact). ....119

Figure 11: Chillrun11.dat (Chillrun file for the reaction between 100 % pyrrhotite and water with no atmospheric contact) ..................120
Figure 1: Chillrun1.dat (Chillrun file for the reaction between 100% pyrite and water with no atmospheric contact).

Median precipitation values of seven sites worldwide; hundreds of analyses. Precipitation values (1kg H2O) + pyrite; (9ppm O2 aq. @ 25 degrees C & 1 bar)

<table>
<thead>
<tr>
<th>erpc</th>
<th>ph</th>
<th>pfluid</th>
<th>temp</th>
<th>tempc</th>
<th>volbox-1</th>
<th>rhofresh</th>
</tr>
</thead>
<tbody>
<tr>
<td>.100E-11</td>
<td>.00000</td>
<td>1.00000</td>
<td>25.00000</td>
<td>.00000</td>
<td>.00000</td>
<td>.00000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>sinc</th>
<th>slim</th>
<th>totmix</th>
</tr>
</thead>
<tbody>
<tr>
<td>.10E-05</td>
<td>.10E-04</td>
<td>.0000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>enth</th>
<th>senth</th>
<th>denth</th>
<th>totwat</th>
<th>solmin</th>
<th>rm</th>
<th>aggrm</th>
<th>suprnt</th>
</tr>
</thead>
<tbody>
<tr>
<td>.00000</td>
<td>.00000</td>
<td>.00000</td>
<td>.00000</td>
<td>.000E+00</td>
<td>.00000</td>
<td>.00000</td>
<td>.1000E-10</td>
</tr>
</tbody>
</table>

----- c ifra ipun nloo iste lims loco ient itre idea ipsa incr incp mins neut
| 0 | 3 | 0 | 0 | 70 | 0 | 1 | 0 | 0 | 0 | 1 | 0 | 0 | 1 | 0 |

<table>
<thead>
<tr>
<th>saq</th>
<th>name</th>
<th>mtot</th>
<th>mtry</th>
<th>gamma</th>
<th>comtot</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 H+</td>
<td>.3185000E-04</td>
<td>.3162278E-05</td>
<td>1.0000</td>
<td>.00000E+00</td>
<td></td>
</tr>
<tr>
<td>2 H2O</td>
<td>.9999834E+00</td>
<td>.1000000E+01</td>
<td>1.0000</td>
<td>.00000E+00</td>
<td></td>
</tr>
<tr>
<td>3 Cl-</td>
<td>.3430500E-04</td>
<td>.1000000E-03</td>
<td>1.0000</td>
<td>.00000E+00</td>
<td></td>
</tr>
<tr>
<td>4 SO4--</td>
<td>.3122996E-04</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.00000E+00</td>
<td></td>
</tr>
<tr>
<td>5 HCO3-</td>
<td>.3277614E-04</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.00000E+00</td>
<td></td>
</tr>
<tr>
<td>7 SiO2</td>
<td>.1664447E-05</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.00000E+00</td>
<td></td>
</tr>
<tr>
<td>9 Ca++</td>
<td>.2245509E-04</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.00000E+00</td>
<td></td>
</tr>
<tr>
<td>10 Mg++</td>
<td>.8226390E-05</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.00000E+00</td>
<td></td>
</tr>
<tr>
<td>11 Fe++</td>
<td>.0000000E-05</td>
<td>.0000000E-18</td>
<td>1.0000</td>
<td>.00000E+00</td>
<td></td>
</tr>
<tr>
<td>12 K+</td>
<td>.1022966E-04</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.00000E+00</td>
<td></td>
</tr>
<tr>
<td>13 Na+</td>
<td>.2609853E-04</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.00000E+00</td>
<td></td>
</tr>
<tr>
<td>31 O2</td>
<td>.2812500E-03</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.00000E+00</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>min</th>
<th>mintry</th>
</tr>
</thead>
</table>

<nomox> < wtpc >
pyrit-ox | .1000E+03 |

<supnam>
FCO2-3.0
FCO2-3.5
FO2-0.7
hematite

<dontfr>
Figure 2: Chillrun2.dat (Chillrun file for the reaction between 50% pyrite + 50% albite and water with no atmospheric contact).

Median precipitation values of seven sites worldwide; hundreds of analyses. Precipitation values (1 kg H2O) + pyrite & albite, (1:1); (9 ppm O2 825°C & 1 bar)

<table>
<thead>
<tr>
<th>erpc</th>
<th>ph</th>
<th>pfluid</th>
<th>temp</th>
<th>tempc</th>
<th>&lt;volbox-1&gt;</th>
<th>&lt;rhofresh&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00E-11</td>
<td>.00000</td>
<td>1.00000</td>
<td>25.00000</td>
<td>.00000</td>
<td>.00000</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>sinc</th>
<th>slim</th>
<th>totmix</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0E-05</td>
<td>.10E-04</td>
<td>.0000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>enth</th>
<th>senth</th>
<th>d enth</th>
<th>totwat</th>
<th>solmin</th>
<th>rm</th>
<th>aqgrm</th>
<th>suprnt</th>
</tr>
</thead>
<tbody>
<tr>
<td>.00000</td>
<td>.00000</td>
<td>.00000</td>
<td>.00000</td>
<td>.0000E+00</td>
<td>.00000</td>
<td>.0000E+00</td>
<td></td>
</tr>
</tbody>
</table>

-------
c ifra ipun nlOO iste lims looc ient itre idea ipsa incr incp mins neut

| 0 3 0 0 70 | 0 1 0 | 0 0 0 | 0 1 0 1 0 |

<table>
<thead>
<tr>
<th>saq</th>
<th>&lt; name &gt;</th>
<th>&lt; mthot</th>
<th>&lt; mtry</th>
<th>&lt; gamma</th>
<th>&lt; comtot</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H+</td>
<td>.3185000E-04</td>
<td>.3162278E-05</td>
<td>1.0000</td>
<td>.0000E+00</td>
</tr>
<tr>
<td>2</td>
<td>H2O</td>
<td>.9999834E+00</td>
<td>.1000000E+01</td>
<td>1.0000</td>
<td>.0000E+00</td>
</tr>
<tr>
<td>3</td>
<td>Cl-</td>
<td>.3430500E-04</td>
<td>.1000000E-03</td>
<td>1.0000</td>
<td>.0000E+00</td>
</tr>
<tr>
<td>4</td>
<td>SO4---</td>
<td>.3122999E-04</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.0000E+00</td>
</tr>
<tr>
<td>5</td>
<td>HCO3-</td>
<td>.3277614E-04</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.0000E+00</td>
</tr>
<tr>
<td>7</td>
<td>SiO2</td>
<td>.1664447E-05</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.0000E+00</td>
</tr>
<tr>
<td>8</td>
<td>Al+++</td>
<td>.0000000E-05</td>
<td>.1000000E-12</td>
<td>1.0000</td>
<td>.0000E+00</td>
</tr>
<tr>
<td>9</td>
<td>Ca++</td>
<td>.2245509E-04</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.0000E+00</td>
</tr>
<tr>
<td>10</td>
<td>Mg+++</td>
<td>.8226390E-05</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.0000E+00</td>
</tr>
<tr>
<td>11</td>
<td>Fe++</td>
<td>.0000000E-05</td>
<td>.1000000E-18</td>
<td>1.0000</td>
<td>.0000E+00</td>
</tr>
<tr>
<td>12</td>
<td>K+</td>
<td>.1022966E-04</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.0000E+00</td>
</tr>
<tr>
<td>13</td>
<td>Na+</td>
<td>.2609853E-04</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.0000E+00</td>
</tr>
<tr>
<td>31</td>
<td>O2 aq.</td>
<td>.2812500E-03</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.0000E+00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>&lt; min</th>
<th>&lt; mintry &gt;</th>
</tr>
</thead>
</table>

<nomox> < wtpc >
pyrit-oX  .5000E+02
albite   .5000E+02

<supnam>
FO2-3.0
FO2-3.5
FO2-0.7
hematite
<dontfr>
Figure 3: Chillrun3.dat (Chillrun file for the reaction between 50% pyrite + 50% anorthite and water with no atmospheric contact).

Median precipitation values of seven sites worldwide; hundreds of analyses.

Precipitation values (1kg H2O) + pyrite-anorthite, (1:1); (9ppm O2 @ 25C & 1bar)

<table>
<thead>
<tr>
<th>Name</th>
<th>mH2O</th>
<th>mH2O</th>
<th>mH2O</th>
<th>mH2O</th>
<th>mH2O</th>
<th>mH2O</th>
<th>mH2O</th>
<th>mH2O</th>
<th>mH2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>H+</td>
<td>.3185000E-04</td>
<td>.3162278E-05</td>
<td>1.0000</td>
<td>.0000E+00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2O</td>
<td>.9999834E+00</td>
<td>.1000000E+01</td>
<td>1.0000</td>
<td>.0000E+00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl-</td>
<td>.3430500E-04</td>
<td>.1000000E-03</td>
<td>1.0000</td>
<td>.0000E+00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO4--</td>
<td>.3122996E-04</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.0000E+00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCO3-</td>
<td>.3277614E-04</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.0000E+00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO2</td>
<td>.1664447E-05</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.0000E+00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al+++</td>
<td>.0000000E-05</td>
<td>.1000000E-12</td>
<td>1.0000</td>
<td>.0000E+00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca++</td>
<td>.2245509E-04</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.0000E+00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg++</td>
<td>.8226390E-05</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.0000E+00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe++</td>
<td>.0000000E-05</td>
<td>.0000000E-18</td>
<td>1.0000</td>
<td>.0000E+00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K+</td>
<td>.1022966E-04</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.0000E+00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na+</td>
<td>.2609853E-04</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.0000E+00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O2 aq.</td>
<td>.2812500E-03</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.0000E+00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

< min > < mtry >

< supname>
FCO2=3.0
FCO2=3.5
FO2=0.7
hematite
lawsonit
andradite
grossula
pumpelly
prehnite
clinozois
epid-ord
vesuvian
zoisite
wollasto
woll-psd
tilleyit
epido-Fe
rankinit
diopside
heidenber
spurrite
portland
larnite
gehlenit
merwinit
<dontfr>
Figure 4: Chillrun4.dat (Chillrun file for the reaction between 50% pyrite + 50% microcline and water with no atmospheric contact).

Median precipitation values of seven sites worldwide: hundreds of analyses. Precipitation values (1 kg H2O) + pyrite K-feldspar, (1:1); (9 ppm O2 @25°C & 1 bar)

< erpc >< ph >< pfluid >< temp >< tempc >< volbox-1>< rhofresh >
.1000E-11 .00000 1.00000 25.00000 .00000 .00000 .00000

< snc >< slim >< totmix >
.10E-05 .10E-04 .0000

< enth >< enth >< denth >< totwat >< solmin >< rm >< aqgrm >< suprnt >
.00000 .00000 .00000 .00000 .00000 .00000 .1000E-10

----- c i fra i pun nlo o iste lys loc o int itre ide a ipsa incr incp mins neut
0 3 0 0 70 0 1 0 0 0 0 1 0 0 1 0

saq> < name > < mtot >< mtry >< gamma > < comtot >
1 H+ .3185000E-04 .3162278E-05 1.0000 .0000E+00
2 H2O .9999834E+00 .1000000E+01 1.0000 .0000E+00
3 Cl- .3430500E-04 .1000000E-03 1.0000 .0000E+00
4 SO4-- .3122996E-04 .1000000E-06 1.0000 .0000E+00
5 HCO3- .3277614E-04 .1000000E-06 1.0000 .0000E+00
7 SiO2 .1664447E-05 .1000000E-06 1.0000 .0000E+00
8 Al+++ .0000000E+00 .1000000E-12 1.0000 .0000E+00
9 Ca++ .2245509E-04 .1000000E-06 1.0000 .0000E+00
10 Mg++ .8226390E-05 .1000000E-06 1.0000 .0000E+00
11 Fe++ .0000000E-05 .0000000E-18 1.0000 .0000E+00
12 K+ .1022966E-04 .1000000E-06 1.0000 .0000E+00
13 Na+ .2609853E-04 .1000000E-06 1.0000 .0000E+00
31 O2 aq. .2812500E-03 .1000000E-06 1.0000 .0000E+00

< min > < m tr y >

<nom ox > < wtpc >
pyrit-ox .5000E+02
microcli .5000E+02

< supnam >
FCO2-3.0
FCO2-3.5
F02-0.7
hematite
celad-Fe

dontfr>
Figure 5: Chillrun5.dat (Chillrun file for the reaction between 20% pyrite + 80% albite and water with no atmospheric contact).

Median precipitation values of seven sites worldwide; hundreds of analyses. Precipitation values (1 kg H2O) + pyrite + albite, (1:4); (9 ppm O2 @25°C & 1 bar)
< erpc  > < ph  > < pfluid > < temp > < tempc > < volbox-1 > < rhofresh >
0.1000E-11 0.0000 1.00000 25.000000 0.0000 0.0000 0.0000
< sinc  > < slim > < totmix >
0.10E-05 0.10E-04 0.0000
< enth > < senth > < denth > < totwat > < solmin > < rm > < aqgrm > < suprant >
0.0000 0.0000 0.0000 0.0000 0.0000E+00 0.0000 0.0000 0.1000E-10

----- c ifra ipun nloo iste lims looc ient itre idea ipsa incr incp mins neut
0 3 0 0 70 0 1 0 0 0 0 1 0 0 1 0

< saq> < name > < mtot > < mtry > < gamma > < comtot >
1 H+ 0.3185000E-04 0.3162278E-05 1.0000 0.0000E+00
2 H2O 0.9999834E+00 0.1000000E+01 1.0000 0.0000E+00
3 Cl- 0.3430500E-04 0.1000000E-03 1.0000 0.0000E+00
4 SO4-- 0.3122996E-04 0.1000000E-06 1.0000 0.0000E+00
5 HCO3- 0.3277614E-04 0.1000000E-06 1.0000 0.0000E+00
7 SiO2 0.1664447E-05 0.1000000E-06 1.0000 0.0000E+00
8 Al+++ 0.0000000E-05 0.1000000E-12 1.0000 0.0000E+00
9 Ca++ 0.2245509E-04 0.1000000E-06 1.0000 0.0000E+00
10 Mg++ 0.8226390E-05 0.1000000E-06 1.0000 0.0000E+00
11 Fe++ 0.0000000E-05 0.0000000E-18 1.0000 0.0000E+00
12 K+ 0.1022966E-04 0.1000000E-06 1.0000 0.0000E+00
13 Na+ 0.2609853E-04 0.1000000E-06 1.0000 0.0000E+00
31 O2 aq. 0.2812500E-03 0.1000000E-06 1.0000 0.0000E+00

< min > < mintry >
< nomox > < wtpc >
pyrit-ox 0.2000E+02
albite 0.8000E+02
< supnam>
FCO2=3.0
FCO2=3.5
FO2=0.7
hematite
staur-Mg
< dontfr>
Figure 6: Chillrun6.dat (Chillrun file for the reaction between 20% pyrite + 80% anorthite and water with no atmospheric contact).

Median precipitation values of seven sites worldwide; hundreds of analyses. Precipitation values (1 kg H2O) + pyrite & anorthite, (1:4); (9 ppm O2 @ 25°C & 1 bar)

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; erpc &gt;</td>
<td>&lt; ph &gt;</td>
<td>&lt; pfluid &gt;</td>
<td>&lt; temp &gt;</td>
<td>&lt; tempc &gt;</td>
<td>&lt; volbox-1 &gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>.1000E-11</td>
<td>.00000</td>
<td>1.00000</td>
<td>25.00000</td>
<td>.00000</td>
<td>.00000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>&lt; sinc &gt;</th>
<th>&lt; slim &gt;</th>
<th>&lt; totmix &gt;</th>
<th>&lt; 10E-05 &gt;</th>
<th>&lt; 10E-04 &gt;</th>
<th>&lt; 0000 &gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; enth &gt;</td>
<td>&lt; senth &gt;</td>
<td>&lt; denth &gt;</td>
<td>&lt; totwat &gt;</td>
<td>&lt; solmin &gt;</td>
<td>&lt; rm &gt;</td>
<td>&lt; aggrm &gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>.00000</td>
<td>.00000</td>
<td>.00000</td>
<td>.00000</td>
<td>.0000E+00</td>
<td>.0000</td>
<td>.0000</td>
</tr>
</tbody>
</table>

---

**saq** | < name > | < mttot > | < mtry > | < gamma > | < comtot > |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1 H+</td>
<td>.3185000E-04</td>
<td>.3162278E-05</td>
<td>1.00000</td>
<td>.0000E+00</td>
<td></td>
</tr>
<tr>
<td>2 H2O</td>
<td>.9999834E+00</td>
<td>1.0000000E+01</td>
<td>1.0000</td>
<td>.0000E+00</td>
<td></td>
</tr>
<tr>
<td>3 Cl-</td>
<td>.3430500E-04</td>
<td>.1000000E-03</td>
<td>1.0000</td>
<td>.0000E+00</td>
<td></td>
</tr>
<tr>
<td>4 SO4--</td>
<td>.3122996E-04</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.0000E+00</td>
<td></td>
</tr>
<tr>
<td>5 HCO3-</td>
<td>.3277614E-04</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.0000E+00</td>
<td></td>
</tr>
<tr>
<td>7 SiO2</td>
<td>.1664447E-05</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.0000E+00</td>
<td></td>
</tr>
<tr>
<td>8 Al+++</td>
<td>.0000000E-05</td>
<td>.1000000E-12</td>
<td>1.0000</td>
<td>.0000E+00</td>
<td></td>
</tr>
<tr>
<td>9 Ca++</td>
<td>.2245509E-04</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.0000E+00</td>
<td></td>
</tr>
<tr>
<td>10 Mg++</td>
<td>.8226390E-05</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.0000E+00</td>
<td></td>
</tr>
<tr>
<td>11 Fe++</td>
<td>.0000000E-05</td>
<td>.0000000E-18</td>
<td>1.0000</td>
<td>.0000E+00</td>
<td></td>
</tr>
<tr>
<td>12 K+</td>
<td>.1022966E-04</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.0000E+00</td>
<td></td>
</tr>
<tr>
<td>13 Na+</td>
<td>.2609853E-04</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.0000E+00</td>
<td></td>
</tr>
<tr>
<td>31 O2 aqu.</td>
<td>.2812500E-03</td>
<td>.1000000E-06</td>
<td>1.0000</td>
<td>.0000E+00</td>
<td></td>
</tr>
</tbody>
</table>

**min** | < mintry > |
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; nomox &gt;</td>
<td>&lt; wtco &gt;</td>
</tr>
<tr>
<td>pyrit-ox</td>
<td>.2000E+02</td>
</tr>
<tr>
<td>anorthit</td>
<td>.8000E+02</td>
</tr>
</tbody>
</table>

**<supnam>**
FCO2-3.0
FCO2-3.5
FO2-0.7
hematite
lawsonit
andradit
grossula
pumpelly
prehnite
clinzoai
epid-ord
vesuvian
zoisite
wollasto
woll-psd
tilleyit
epdo-Fe
rankinit
diopside
hedenber
spurrite
portland
larnite
gehlenit
merwinit
staur-Mg
<dontfr>

115
Figure 7: Chillrun7.dat (Chillrun file for the reaction between 20% pyrite + 80% microcline and water with no atmospheric contact).

Median precipitation values of seven sites worldwide; hundreds of analyses.
Precipitation values (kg H2O) + pyrite & K-feldspar, (1:4); (9 ppm O2 @ 25°C & 1 bar)
< erpc << ph << pfluid >< temp %> < tempc > < volbox-1 > < rhofresh >
.1000E-11 .00000 1.00000 25.00000 .00000 .00000 .00000
< sinc >> slim >> totmix >
.10E-05 .10E-04 .0000
< enth >> enth > < denth > < totwat > < solmin > < rm > < aqgrm > < suprnt >
.00000 .00000 .00000 .00000 .0000E+00 .00000 .00000 .1000E-10

----- c ifra ipun nloo iste lims looc ient itre idea ipsa incr incp mins neut
0 3 0 0 70 0 1 0 0 0 0 1 0 0 1 0

< name > < mtot > < mtry > < gamma > < comtot >
1 H+ .3185000E-04 .3162278E-05 1.0000 .0000E+00
2 H2O .9999834E+00 .1000000E+01 1.0000 .0000E+00
3 Cl- .3430500E+04 .1000000E-03 1.0000 .0000E+00
4 SO4- .3122996E-04 .1000000E-06 1.0000 .0000E+00
5 HCO3- .3277614E-04 .1000000E-06 1.0000 .0000E+00
7 SiO2 .1664447E-05 .1000000E-06 1.0000 .0000E+00
8 Al+++ .0000000E-05 .1000000E-12 1.0000 .0000E+00
9 Ca++ .2245509E-04 .1000000E-06 1.0000 .0000E+00
10 Mg++ .8226390E-05 .1000000E-06 1.0000 .0000E+00
11 Fe++ .0000000E-05 .0000000E-18 1.0000 .0000E+00
12 K+ .1022966E-04 .1000000E-06 1.0000 .0000E+00
13 Na+ .2609853E-04 .1000000E-06 1.0000 .0000E+00
31 O2 aq. .2812500E-03 .1000000E-06 1.0000 .0000E+00

< min > < mintry >
< nomox > < wtpc >
pyrit-ox .2000E+02
microcli .8000E+02
< supnam>
FCO2-3.0
FCO2-3.5
FO2-0.7
hematite
celad-Fe
staur-Mg
< dontfr>
Figure 8: Chillrun8.dat (Chillrun file for the reaction between 80% pyrite + 20% albite and water with no atmospheric contact).

Median precipitation values of seven sites worldwide; hundreds of analyses. Precipitation values (kg H2O) + pyrite & albite, (4:1); (9 ppm O2 @ 25°C & 1 bar)

< erpc >> ph >> pfluid >> temp >> tempc >> volbox-l >> rhotfresh >
.1000E-11  .00000  1.00000  25.00000  .00000  .00000  .00000

< sinc >> slim >> totmix >
.10E-05   .10E-04  .0000

< enth >> senth >> denth >> totwat >> solmin >> rm >> aqgrm >> suprnt >
.00000  .00000  .00000  .00000  .00000  .00000  .000E-10

----- c ifra ipun nloo iste lims looc lten itre idea ipsa incr incp mins neut
 0 3 0 0 70 0 1 0 0 0 0 0 1 0 0 0

< name > < mtot > < mtry > < gamma > < comtot >
 1 H+   .3185000E-04  .3162278E-05  1.0000  .00000E+00
 2 H2O  .9999834E+00  .1000000E+01  1.0000  .00000E+00
 3 Cl-  .3430500E-04  .1000000E-03  1.0000  .00000E+00
 4 SO4-- .3122996E-04  .1000000E-06  1.0000  .00000E+00
 5 HCO3--.3277614E-04  .1000000E-06  1.0000  .00000E+00
 7 SiO2 .1664447E-05  .1000000E-06  1.0000  .00000E+00
 8 Al+++ .0000000E-05  .1000000E-12  1.0000  .00000E+00
 9 Ca++ .2245509E-04  .1000000E-06  1.0000  .00000E+00
10 Mg++ .8226390E-05  .1000000E-06  1.0000  .00000E+00
11 Fe++ .0000000E-05  .0000000E-18  1.0000  .00000E+00
12 K+  .1022966E-04  .1000000E-06  1.0000  .00000E+00
13 Na+ .2609853E-04  .1000000E-06  1.0000  .00000E+00
31 O2 ag. .2812500E-03  .1000000E-06  1.0000  .00000E+00

< min > < mintry >

<nomox > < wtpc >
pyrit-ox  .8000E+02
albite   .20000E+02

<supnam>
FCO2=3.0
FCO2=3.5
FO2=0.7
hematite

<dontfr>
Figure 9: Chillrun9.dat (Chillrun file for the reaction between 80% pyrite + 20% anorthite and water with no atmospheric contact).

Median precipitation values of seven sites worldwide; hundreds of analyses. Precipitation values (1kg H2O) + pyrite & anorthite (4:1); (9ppm O2 @25°C & 1 bar)

< erpc > < ph > < pfluid > < temp > < tempc > < volbox-1 > < rhofresh >
.1000E-11   0.00000   1.00000   25.00000   .00000   .00000   .00000
< sinc > < slim > < totmix >
.10E-05    .10E-04   .0000
< enth > < enth > < denth > < totwat > < solmin > < rm > < aggrm > < suprnt >
.000000   .000000   .000000   .000000   .000000E+00   .000000   .000000   .10000E-10

-----
c ifra ipun nloq iste lims looc ient itre idea ipsa incr incp mins neut
0 3 0 0 70 0 1 0 0 0 0 0 1 0 0 0 1 0 0

<saq> < name > < mtot > < mtry > < gamma > < cmtot >
1 H+   .3185000E-04   .3162278E-05   1.0000   .00000E+00
2 H2O   .9998348E+00   .1000000E+01   1.0000   .00000E+00
3 Cl-   .3430500E-04   .1000000E-03   1.0000   .00000E+00
4 SO4--  .3122996E-04   .1000000E-06   1.0000   .00000E+00
5 HCO3-  .3277614E-04   .1000000E-06   1.0000   .00000E+00
7 SiO2   .1664447E-05   .1000000E-06   1.0000   .00000E+00
8 Al+++  .0000000E-05   .1000000E-12   1.0000   .00000E+00
9 Ca++  .2245509E-04   .1000000E-06   1.0000   .00000E+00
10 Mg++  .8226390E-05   .1000000E-06   1.0000   .00000E+00
11 Fe+++  .0000000E-05   .0000000E-18   1.0000   .00000E+00
12 K+   .1022966E-04   .1000000E-06   1.0000   .00000E+00
13 Na+  .2600853E-04   .1000000E-06   1.0000   .00000E+00
31 O2aq.  .2812500E-03   .1000000E-06   1.0000   .00000E+00

< min > < mintry >
<nomox > < wtpc >
p yrit-ox   .80000E+02
anorthit   .20000E+02

<supnam>
FCO2-3.0
FCO2-3.5
FO2-0.7
hematite
lawsonit
andradit
grossula
pumpey
prehnite
clinozoi
epid-ord
vesuvian
zoisite
wollast
woll-psd
tilleyit
epido-Fe
rankinit
diopside
hedenber
spurrte
portalnd
larnite
tienit
merwinit
<dontfr>

118
Figure 10: Chillrun10.dat (Chillrun file for the reaction between 80 % pyrite + 20 % microcline and water with no atmospheric contact).

Median precipitation values of seven sites worldwide; hundreds of analyses. Precipitation values (1 kg H2O) + pyrite + K-feldspar, (4:1); (9 ppm O2 @ 25°C & 1 bar)

< erpc > < ph > < pfluid > < temp > < tempc > < volbox-1 > < rhofresh >
.1000E-11  .00000  1.00000  25.00030  .00000  .00000  .00000

< sin < < slim > < totmix >
.10E-05   .10E-04    .0000

< enth > < senth > < denth > < totwat > < solmin > < rm > < aqgrm > < suprnt >
.00000  .00000  .00000  .00000  .00000  .00000  .00000  .1000E-10

----- c ifra ipun nloo iste lims looc ient itre idea ipsa incr incp mins neut
0  3  0  0  70  0  1  0  0  1  0  0  0  1  0  1  0

saq> < name > < mtot > < mtry > < gamma > < contot >
1  H+   .3185000E-04  .3162278E-05  1.0000  .0000E+00
2  H2O  .9999834E+00  .1000000E+01  1.0000  .0000E+00
3  Cl-  .3430500E-04  .1000000E+03  1.0000  .0000E+00
4  SO4---.3122996E-04  .1000000E-06  1.0000  .0000E+00
5  HCO3-  .3277614E-04  .1000000E-06  1.0000  .0000E+00
7  SiO2  .1664447E-05  .1000000E-06  1.0000  .0000E+00
8  Al+++  .0000000E-05  .1000000E-12  1.0000  .0000E+00
9  Ca++  .2245509E-04  .1000000E-06  1.0000  .0000E+00
10  Mg++ .8226390E-05  .1000000E-06  1.0000  .0000E+00
11  Fe++  .0000000E-05  .0000000E-18  1.0000  .0000E+00
12  K+   .1022966E-04  .1000000E-06  1.0000  .0000E+00
13  Na+  .2609853E-04  .1000000E-06  1.0000  .0000E+00
31  O2 aq.  .2812500E-03  .1000000E-06  1.0000  .0000E+00

< min > < mintry >
< nomox > < wtpc >
pyrit-ox .8000E+02
microcl. .2000E+02

< supnam >
FCO2-3.0
FCO2-3.5
FO2-0.7
hematite
celad-Fe

< dontfr >
Figure 11: Chillrun11.dat (Chillrun file for the reaction between 100% pyrrhotite and water with no atmospheric contact).

Median precipitation values of seven sites worldwide; hundreds of analyses. Precipitation values (kg H2O) + pyrrhotite; (9ppm O2aq. 025 degreesC & 1 bar)

< erpc << ph >> pfluid << temp >> tempc << volbox-l << rhofresh >
.1000E-11 .00000 1.00000 25.00000 .00000 .00000 .00000

< sinc << slim << totmix >
.10E-05 .10E-04 .0000

< enth << senth << denth << totwat << solmin << rm >> aqgrm << suprnt >
.00000 .00000 .00000 .00000 .00000 .00000 .1000E-10

----- c ifra ipun nloo iste lims looc intre idea ipsa incr incp mins neut
0 3 0 0 70 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0

< saq > < name > < mtot > < mtry > < gamma > < comtot >
1 H+ .3185000E-04 .3162278E-05 1.0000 .0000E+00
2 H2O .9999834E+00 .1000000E+01 1.0000 .0000E+00
3 Cl- .3430500E-04 .1000000E-03 1.0000 .0000E+00
4 SO4-- .3122996E-04 .1000000E-06 1.0000 .0000E+00
5 HCO3- .3277614E-04 .1000000E-06 1.0000 .0000E+00
7 SiO2 .1664447E-05 .1000000E-06 1.0000 .0000E+00
9 Ca++ .2245509E-04 .1000000E-06 1.0000 .0000E+00
10 Mg++ .8226390E-05 .1000000E-06 1.0000 .0000E+00
11 Fe++ .0000000E-05 .0000000E-18 1.0000 .0000E+00
12 K+ .1022966E-04 .1000000E-06 1.0000 .0000E+00
13 Na+ .2609853E-04 .1000000E-06 1.0000 .0000E+00
31 O2 aq. .2812500E-03 .1000000E-06 1.0000 .0000E+00

< min > < mintry >

< nomox > < wtpc > pyrrhoti .1000E+03

< supnam>
FCO2-3.0
FCO2-3.5
FO2-0.7
hematite
ccl1-Alf
antigor

< dontfr>
APPENDIX B

SINC and SLIM values for the CHILLRUN files in Appendix A
(Included are the increment (SINC) and corresponding pH values sampled)
LIST OF FIGURES FOR APPENDIX B

Figure 1: SINC and SLIM values for Chillrun1.dat (Reaction between 100 % pyrite and water with no atmospheric contact).................................123

Figure 2: SINC and SLIM values for Chillrun2.dat (Reaction between 50 % pyrite + 50 % albite and water with no atmospheric contact). ......124

Figure 3: SINC and SLIM values for Chillrun3.dat (Reaction between 50 % pyrite + 50 % anorthite and water with no atmospheric contact). .........................................................................................125

Figure 4: SINC and SLIM values for Chillrun4.dat (Reaction between 50 % pyrite + 50 % microcline and water with no atmospheric contact). .........................................................................................126

Figure 5: SINC and SLIM values for Chillrun5.dat (Reaction between 20 % pyrite + 80 % albite and water with no atmospheric contact). ......127

Figure 6: SINC and SLIM values for Chillrun6.dat (Reaction between 20 % pyrite + 80 % anorthite and water with no atmospheric contact). .........................................................................................128

Figure 7: SINC and SLIM values for Chillrun7.dat (Reaction between 20 % pyrite + 80 % microcline and water with no atmospheric contact). .........................................................................................129

Figure 8: SINC and SLIM values for Chillrun8.dat (Reaction between 80 % pyrite + 20 % albite and water with no atmospheric contact). ......130

Figure 9: SINC and SLIM values for Chillrun9.dat (Reaction between 80 % pyrite + 20 % anorthite and water with no atmospheric contact). .........................................................................................131

Figure 10: SINC and SLIM values for Chillrun10.dat (Reaction between 80 % pyrite + 20 % microcline and water with no atmospheric contact). .........................................................................................132

Figure 11: SINC and SLIM values for Chillrun11.dat (Reaction between 100 % pyrrhotite and water with no atmospheric contact). ..........133
Figure 1: SINC and SLIM values for Chillrun1.dat (Reaction between 100 % pyrite and water with no atmospheric contact).

<table>
<thead>
<tr>
<th>SINC</th>
<th>SLIM</th>
<th>Sampled @</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) 0.1x10^{-5}</td>
<td>0.1x10^{-4}</td>
<td>0.000099</td>
<td>5.4810</td>
</tr>
<tr>
<td>(2) 0.1x10^{-4}</td>
<td>0.1x10^{-3}</td>
<td>0.000299</td>
<td>5.3018</td>
</tr>
<tr>
<td>(3) 0.1x10^{-3}</td>
<td>0.1x10^{-2}</td>
<td>0.005099</td>
<td>4.9950</td>
</tr>
<tr>
<td>(4) 0.1x10^{-1}</td>
<td>0.1</td>
<td>0.009599</td>
<td>4.5000</td>
</tr>
<tr>
<td>(5) 1.0</td>
<td>10</td>
<td>0.009999</td>
<td>4.0847</td>
</tr>
<tr>
<td>(6) 10</td>
<td>100</td>
<td>3.7934</td>
<td></td>
</tr>
<tr>
<td>(7) 100</td>
<td>1000</td>
<td>3.5501</td>
<td></td>
</tr>
<tr>
<td>(8) 1000</td>
<td>10000</td>
<td>3.5830</td>
<td></td>
</tr>
<tr>
<td>(9) 10000</td>
<td></td>
<td>3.7990</td>
<td></td>
</tr>
<tr>
<td>(10) 10000</td>
<td></td>
<td>3.8234</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.8234</td>
<td></td>
</tr>
</tbody>
</table>

123
Figure 2: SINC and SLIM values for Chillrun2.dat (Reaction between 50 % pyrite + 50 % albite and water with no atmospheric contact).

<table>
<thead>
<tr>
<th>Sampled @</th>
<th>SINC</th>
<th>SLIM</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000001</td>
<td>0.1x10^{-5}</td>
<td>0.1x10^{-4}</td>
<td>5.4990</td>
</tr>
<tr>
<td>0.000003</td>
<td>0.1x10^{-4}</td>
<td>0.1x10^{-3}</td>
<td>5.4974</td>
</tr>
<tr>
<td>0.000399</td>
<td>0.1x10^{-3}</td>
<td>0.1x10^{-2}</td>
<td>5.1685</td>
</tr>
<tr>
<td>0.006999</td>
<td>0.1x10^{-2}</td>
<td>0.1x10^{-1}</td>
<td>4.8510</td>
</tr>
<tr>
<td>0.001999</td>
<td>0.1x10^{-1}</td>
<td>0.22</td>
<td>4.5743</td>
</tr>
<tr>
<td>0.002999</td>
<td>1.0</td>
<td>10</td>
<td>4.4120</td>
</tr>
<tr>
<td>0.009999</td>
<td></td>
<td></td>
<td>3.9399</td>
</tr>
<tr>
<td>0.017999</td>
<td>10</td>
<td>100</td>
<td>3.7261</td>
</tr>
<tr>
<td>0.018999</td>
<td>100</td>
<td>1000</td>
<td>3.9044</td>
</tr>
<tr>
<td>0.019999</td>
<td>1000</td>
<td>10000</td>
<td>3.9879</td>
</tr>
<tr>
<td>0.022999</td>
<td></td>
<td></td>
<td>4.0020</td>
</tr>
<tr>
<td>0.055999</td>
<td></td>
<td></td>
<td>4.3108</td>
</tr>
<tr>
<td>0.073999</td>
<td></td>
<td></td>
<td>4.7387</td>
</tr>
<tr>
<td>0.081999</td>
<td></td>
<td></td>
<td>5.2509</td>
</tr>
<tr>
<td>0.086999</td>
<td></td>
<td></td>
<td>5.8144</td>
</tr>
<tr>
<td>0.091999</td>
<td></td>
<td></td>
<td>6.2773</td>
</tr>
<tr>
<td>0.148999</td>
<td></td>
<td></td>
<td>6.5050</td>
</tr>
<tr>
<td>0.176999</td>
<td></td>
<td></td>
<td>6.8969</td>
</tr>
<tr>
<td>0.182999</td>
<td></td>
<td></td>
<td>7.1656</td>
</tr>
<tr>
<td>0.205999</td>
<td></td>
<td></td>
<td>7.5314</td>
</tr>
<tr>
<td>0.214999</td>
<td></td>
<td></td>
<td>7.9446</td>
</tr>
<tr>
<td>0.219999</td>
<td></td>
<td></td>
<td>8.4124</td>
</tr>
<tr>
<td>0.222999</td>
<td>0.2x10^{-9}</td>
<td>0.2x10^{-8}</td>
<td>9.0152</td>
</tr>
<tr>
<td>0.249999</td>
<td></td>
<td></td>
<td>9.4065</td>
</tr>
<tr>
<td>0.299999</td>
<td></td>
<td></td>
<td>9.8024</td>
</tr>
<tr>
<td>0.429999</td>
<td></td>
<td></td>
<td>10.2061</td>
</tr>
<tr>
<td>0.709999</td>
<td></td>
<td></td>
<td>10.5388</td>
</tr>
<tr>
<td>0.999999</td>
<td></td>
<td></td>
<td>10.5388</td>
</tr>
<tr>
<td>1.999999</td>
<td>0.1x10^{-9}</td>
<td>0.1x10^{-8}</td>
<td>10.7517</td>
</tr>
<tr>
<td>9.999999</td>
<td></td>
<td></td>
<td>10.7517</td>
</tr>
<tr>
<td>99.999999</td>
<td></td>
<td></td>
<td>10.7517</td>
</tr>
<tr>
<td>999.999999</td>
<td></td>
<td></td>
<td>10.7517</td>
</tr>
<tr>
<td>9999.99999</td>
<td></td>
<td></td>
<td>10.7517</td>
</tr>
</tbody>
</table>
Figure 3: SINC and SLIM values for Chillrun3.dat (Reaction between 50 % pyrite + 50 % anorthite and water with no atmospheric contact).

<table>
<thead>
<tr>
<th></th>
<th>SINC</th>
<th>SLIM</th>
<th>Sampled @</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1x10^-5</td>
<td>0.1x10^-4</td>
<td>0.000001</td>
<td>5.4992</td>
</tr>
<tr>
<td>2</td>
<td>0.1x10^-4</td>
<td>0.1x10^-3</td>
<td>0.000002</td>
<td>5.4985</td>
</tr>
<tr>
<td>3</td>
<td>0.1x10^-3</td>
<td>0.1x10^-2</td>
<td>0.000399</td>
<td>5.2014</td>
</tr>
<tr>
<td>4</td>
<td>0.1x10^-2</td>
<td>0.1x10^-1</td>
<td>0.000999</td>
<td>4.8983</td>
</tr>
<tr>
<td>5</td>
<td>0.1x10^-2</td>
<td>0.1</td>
<td>0.002999</td>
<td>4.4645</td>
</tr>
<tr>
<td>6</td>
<td>0.1x10^-2</td>
<td>0.22</td>
<td>0.007999</td>
<td>4.1399</td>
</tr>
<tr>
<td>7</td>
<td>0.1x10^-1</td>
<td>1.0</td>
<td>0.009999</td>
<td>4.0595</td>
</tr>
<tr>
<td>8</td>
<td>1.0</td>
<td>10</td>
<td>0.017999</td>
<td>3.8504</td>
</tr>
<tr>
<td>9</td>
<td>5.0</td>
<td>100</td>
<td>0.018999</td>
<td>4.0906</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
<td>1000</td>
<td>0.019999</td>
<td>4.1999</td>
</tr>
<tr>
<td>11</td>
<td>1000</td>
<td>10000</td>
<td>0.034999</td>
<td>4.5222</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.040999</td>
<td>4.9011</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.043999</td>
<td>5.3500</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.045999</td>
<td>5.7823</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.047999</td>
<td>6.1669</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.049999</td>
<td>6.3712</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.070999</td>
<td>6.5059</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.090999</td>
<td>6.8359</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.097999</td>
<td>7.4351</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.099999</td>
<td>7.7621</td>
</tr>
<tr>
<td>6</td>
<td>0.102999</td>
<td></td>
<td>8.2765</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.104999</td>
<td></td>
<td>8.7421</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.106999</td>
<td></td>
<td>8.9084</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.115999</td>
<td></td>
<td>8.9084</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.140999</td>
<td></td>
<td>8.9084</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.141999</td>
<td></td>
<td>8.9612</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.143999</td>
<td></td>
<td>9.0723</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.173999</td>
<td></td>
<td>9.0723</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.196999</td>
<td></td>
<td>9.0933</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.197999</td>
<td></td>
<td>9.3718</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.206999</td>
<td></td>
<td>9.6121</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.269999</td>
<td></td>
<td>10.0514</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.329999</td>
<td></td>
<td>10.3059</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.539999</td>
<td></td>
<td>10.7171</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.999999</td>
<td></td>
<td>11.0850</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1.999999</td>
<td></td>
<td>11.4250</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.999999</td>
<td></td>
<td>11.7293</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.999999</td>
<td></td>
<td>11.9237</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.999999</td>
<td></td>
<td>11.9237</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.999999</td>
<td></td>
<td>11.9418</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>29.999999</td>
<td></td>
<td>12.3662</td>
<td></td>
</tr>
<tr>
<td></td>
<td>99.999999</td>
<td></td>
<td>12.7973</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>399.99999</td>
<td></td>
<td>13.2713</td>
<td></td>
</tr>
<tr>
<td></td>
<td>899.99999</td>
<td></td>
<td>13.5292</td>
<td></td>
</tr>
<tr>
<td></td>
<td>999.99999</td>
<td></td>
<td>13.5292</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>9999.99999</td>
<td></td>
<td>13.5292</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4: SINC and SLIM values for Chillrun4.dat (Reaction between 50% pyrite + 50% microcline and water with no atmospheric contact).

<table>
<thead>
<tr>
<th>SINC</th>
<th>SLIM</th>
<th>Sampled @</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 x 10^{-5}</td>
<td>0.1 x 10^{-4}</td>
<td>0.000001</td>
<td>5.4989</td>
</tr>
<tr>
<td>0.1 x 10^{-4}</td>
<td>0.1 x 10^{-3}</td>
<td>0.000003</td>
<td>5.4974</td>
</tr>
<tr>
<td>0.1 x 10^{-3}</td>
<td>0.1 x 10^{-2}</td>
<td>0.000099</td>
<td>5.4095</td>
</tr>
<tr>
<td>0.1 x 10^{-2}</td>
<td>0.1 x 10^{-1}</td>
<td>0.000399</td>
<td>5.1664</td>
</tr>
<tr>
<td>0.1 x 10^{-1}</td>
<td>0.2</td>
<td>0.009999</td>
<td>4.8481</td>
</tr>
<tr>
<td>1.0</td>
<td>10</td>
<td>0.019999</td>
<td>4.5713</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
<td>0.029999</td>
<td>4.4105</td>
</tr>
<tr>
<td>100</td>
<td>1000</td>
<td>0.099999</td>
<td>3.9397</td>
</tr>
<tr>
<td>1000</td>
<td>10000</td>
<td>0.179999</td>
<td>3.7257</td>
</tr>
<tr>
<td>0.189999</td>
<td>3.9022</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.199999</td>
<td>3.9834</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.023999</td>
<td>3.9997</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.058999</td>
<td>4.3047</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.070999</td>
<td>4.5164</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.082999</td>
<td>4.9485</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.088999</td>
<td>5.4506</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.093999</td>
<td>5.9785</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.097999</td>
<td>6.2781</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.117999</td>
<td>6.3314</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.156999</td>
<td>6.4976</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.184999</td>
<td>6.8186</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.193999</td>
<td>7.1637</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.199999</td>
<td>7.2161</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.219999</td>
<td>7.5731</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.229999</td>
<td>7.8686</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.309999</td>
<td>7.8686</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.319999</td>
<td>7.9245</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.329999</td>
<td>8.3438</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.999999</td>
<td>8.3438</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.999999</td>
<td>8.3438</td>
<td></td>
<td></td>
</tr>
<tr>
<td>99.999999</td>
<td>8.3438</td>
<td></td>
<td></td>
</tr>
<tr>
<td>999.999999</td>
<td>8.3438</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9999.999999</td>
<td>8.3437</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 5: SINC and SLIM values for Chillrun5.dat (Reaction between 20 % pyrite + 80 % albite and water with no atmospheric contact).

<table>
<thead>
<tr>
<th></th>
<th>SINC</th>
<th>SLIM</th>
<th>Sampled @</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>0.1x10^{-4}</td>
<td>0.1x10^{-4}</td>
<td>0.000001</td>
<td>5.4998</td>
</tr>
<tr>
<td>(2)</td>
<td>0.1x10^{-4}</td>
<td>0.1x10^{-3}</td>
<td>0.000002</td>
<td>5.4997</td>
</tr>
<tr>
<td>(3)</td>
<td>0.1x10^{-3}</td>
<td>0.1x10^{-2}</td>
<td>0.009999</td>
<td>5.2856</td>
</tr>
<tr>
<td>(4)</td>
<td>0.1x10^{-2}</td>
<td>0.1x10^{-1}</td>
<td>0.001999</td>
<td>5.1072</td>
</tr>
<tr>
<td>(5)</td>
<td>0.5x10^{-2}</td>
<td>0.4x10^{-1}</td>
<td>0.009999</td>
<td>4.4720</td>
</tr>
<tr>
<td>(6)</td>
<td>0.5x10^{-2}</td>
<td>0.1</td>
<td>0.014999</td>
<td>4.2995</td>
</tr>
<tr>
<td>(7)</td>
<td>0.5x10^{-2}</td>
<td>0.21</td>
<td>0.044999</td>
<td>3.8822</td>
</tr>
<tr>
<td>(8)</td>
<td>0.1</td>
<td>1.0</td>
<td>0.045499</td>
<td>3.9365</td>
</tr>
<tr>
<td>(9)</td>
<td>1.0</td>
<td>10</td>
<td>0.047499</td>
<td>4.3732</td>
</tr>
<tr>
<td>(10)</td>
<td>10</td>
<td>100</td>
<td>0.047999</td>
<td>4.6671</td>
</tr>
<tr>
<td>(11)</td>
<td>100</td>
<td>1000</td>
<td>0.048499</td>
<td>4.9128</td>
</tr>
<tr>
<td>(12)</td>
<td>1000</td>
<td>10000</td>
<td>0.051499</td>
<td>5.2914</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.053999</td>
<td>5.7476</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.057499</td>
<td>6.2773</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.072999</td>
<td>6.3502</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.087999</td>
<td>6.4546</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.099999</td>
<td>6.5966</td>
</tr>
<tr>
<td>(7)</td>
<td></td>
<td></td>
<td>0.109999</td>
<td>6.8654</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.114999</td>
<td>7.1742</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.129999</td>
<td>7.5994</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.134999</td>
<td>8.0175</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.139999</td>
<td>8.7423</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.149999</td>
<td>9.2666</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.154999</td>
<td>9.3815</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.179999</td>
<td>9.7340</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.209999</td>
<td>9.9592</td>
</tr>
<tr>
<td>(8)</td>
<td></td>
<td></td>
<td>0.309999</td>
<td>10.3166</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.509999</td>
<td>10.5388</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.609999</td>
<td>10.5388</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.709999</td>
<td>10.5846</td>
</tr>
<tr>
<td>(9)</td>
<td>1.909999</td>
<td>10.7517</td>
<td>9.909999</td>
<td>10.7517</td>
</tr>
<tr>
<td></td>
<td>9.909999</td>
<td>10.7517</td>
<td>9.909999</td>
<td>10.7517</td>
</tr>
<tr>
<td>(10)</td>
<td>99.909999</td>
<td>10.7517</td>
<td>99.909999</td>
<td>10.7517</td>
</tr>
<tr>
<td>(11)</td>
<td>999.909999</td>
<td>10.7517</td>
<td>999.909999</td>
<td>10.7517</td>
</tr>
<tr>
<td>(12)</td>
<td>9999.909999</td>
<td>10.7517</td>
<td>9999.909999</td>
<td>10.7517</td>
</tr>
</tbody>
</table>

127
Figure 6: SINC and SLIM values for Chillrun6.dat (Reaction between 20 % pyrite + 80 % anorthite and water with no atmospheric contact).

<table>
<thead>
<tr>
<th>SINC</th>
<th>SLIM</th>
<th>Sampled @</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) 0.1x10^2</td>
<td>0.1x10^4</td>
<td>0.000001</td>
<td>5.5001</td>
</tr>
<tr>
<td>(2) 0.1x10^4</td>
<td>0.1x10^3</td>
<td>0.009999</td>
<td>5.4435</td>
</tr>
<tr>
<td>(3) 0.1x10^3</td>
<td>0.1x10^2</td>
<td>0.019999</td>
<td>5.3880</td>
</tr>
<tr>
<td>(4) 0.1x10^2</td>
<td>0.1x10^1</td>
<td>0.009999</td>
<td>5.3038</td>
</tr>
<tr>
<td>(5) 0.5x10^2</td>
<td>0.44x10^4</td>
<td>0.024999</td>
<td>4.6818</td>
</tr>
<tr>
<td>(6) 0.1x10^1</td>
<td>0.47x10^1</td>
<td>0.040999</td>
<td>4.5002</td>
</tr>
<tr>
<td>(7) 0.1x10^2</td>
<td>0.65x10^1</td>
<td>0.044899</td>
<td>4.4590</td>
</tr>
<tr>
<td>(8) 0.1x10^3</td>
<td>0.66x10^1</td>
<td>0.045599</td>
<td>4.9576</td>
</tr>
<tr>
<td>(9) 0.2x10^2</td>
<td>0.1</td>
<td>0.045799</td>
<td>5.4024</td>
</tr>
<tr>
<td>(10) 0.1x10^2</td>
<td>0.14</td>
<td>0.045999</td>
<td>5.9795</td>
</tr>
<tr>
<td>(11) 0.1x10^1</td>
<td>1.0</td>
<td>0.046099</td>
<td>6.2298</td>
</tr>
<tr>
<td>(12) 1.0</td>
<td>10</td>
<td>0.046299</td>
<td>6.5726</td>
</tr>
<tr>
<td>(13) 5</td>
<td>100</td>
<td>0.046999</td>
<td>6.5706</td>
</tr>
<tr>
<td>(14) 100</td>
<td>1000</td>
<td>0.047999</td>
<td>6.5679</td>
</tr>
<tr>
<td>(15) 1000</td>
<td>10000</td>
<td>0.048999</td>
<td>6.5824</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.058999</td>
<td>7.0019</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.061999</td>
<td>7.6405</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.063999</td>
<td>8.1445</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.064999</td>
<td>8.5288</td>
</tr>
<tr>
<td>(9)</td>
<td>0.065999</td>
<td>8.8404</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.067999</td>
<td>8.9084</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.087999</td>
<td>8.9084</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.089999</td>
<td>9.0723</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.099999</td>
<td>9.0723</td>
<td></td>
</tr>
<tr>
<td>(10)</td>
<td>0.122999</td>
<td>9.0723</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.123999</td>
<td>9.1092</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.129999</td>
<td>9.3951</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.139999</td>
<td>9.6670</td>
<td></td>
</tr>
<tr>
<td>(11)</td>
<td>0.169999</td>
<td>10.0626</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.209999</td>
<td>10.3245</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.319999</td>
<td>10.6798</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.539999</td>
<td>11.0055</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.719999</td>
<td>11.1587</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.999999</td>
<td>11.3207</td>
<td></td>
</tr>
<tr>
<td>(12)</td>
<td>1.999999</td>
<td>11.6341</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.999999</td>
<td>11.9237</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.999999</td>
<td>11.9253</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.999999</td>
<td>12.1277</td>
<td></td>
</tr>
<tr>
<td>(13)</td>
<td>24.999999</td>
<td>12.4719</td>
<td></td>
</tr>
<tr>
<td></td>
<td>49.999999</td>
<td>12.7195</td>
<td></td>
</tr>
<tr>
<td></td>
<td>99.999999</td>
<td>12.9592</td>
<td></td>
</tr>
<tr>
<td>(14)</td>
<td>299.999999</td>
<td>13.3341</td>
<td></td>
</tr>
<tr>
<td></td>
<td>599.999999</td>
<td>13.5292</td>
<td></td>
</tr>
<tr>
<td></td>
<td>999.999999</td>
<td>13.5292</td>
<td></td>
</tr>
</tbody>
</table>
Figure 7: SINC and SLIM values for Chillrun7.dat (Reaction between 20 % pyrite + 80 % microcline and water with no atmospheric contact).

<table>
<thead>
<tr>
<th></th>
<th>SINC</th>
<th>SLIM</th>
<th>Sampled @</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>0.1x10^{-5}</td>
<td>0.1x10^{-4}</td>
<td>0.000001</td>
<td>5.4997</td>
</tr>
<tr>
<td>(2)</td>
<td>0.1x10^{-4}</td>
<td>0.1x10^{-3}</td>
<td>0.000002</td>
<td>5.4997</td>
</tr>
<tr>
<td>(3)</td>
<td>0.1x10^{-3}</td>
<td>0.1x10^{-2}</td>
<td>0.009999</td>
<td>5.2759</td>
</tr>
<tr>
<td>(4)</td>
<td>0.1x10^{-2}</td>
<td>0.1x10^{-1}</td>
<td>0.001999</td>
<td>5.0921</td>
</tr>
<tr>
<td>(5)</td>
<td>0.5x10^{-3}</td>
<td>0.1</td>
<td>0.004999</td>
<td>4.7452</td>
</tr>
<tr>
<td>(6)</td>
<td>0.1x10^{-2}</td>
<td>0.21</td>
<td>0.009999</td>
<td>4.4522</td>
</tr>
<tr>
<td>(7)</td>
<td>0.1</td>
<td>1.0</td>
<td>0.015499</td>
<td>4.2660</td>
</tr>
<tr>
<td>(8)</td>
<td>1.0</td>
<td>10</td>
<td>0.029999</td>
<td>4.0060</td>
</tr>
<tr>
<td>(9)</td>
<td>10</td>
<td>100</td>
<td>0.044999</td>
<td>3.8659</td>
</tr>
<tr>
<td>(10)</td>
<td>100</td>
<td>1000</td>
<td>0.047999</td>
<td>4.5351</td>
</tr>
<tr>
<td>(11)</td>
<td>1000</td>
<td>10000</td>
<td>0.048499</td>
<td>4.7038</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.053499</td>
<td>5.1262</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.055999</td>
<td>5.5146</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.058499</td>
<td>5.9398</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.060999</td>
<td>6.2771</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.086499</td>
<td>6.4033</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.099999</td>
<td>6.5173</td>
</tr>
<tr>
<td>(6)</td>
<td>0.117999</td>
<td>6.9275</td>
<td>0.120999</td>
<td>7.1606</td>
</tr>
<tr>
<td></td>
<td>0.136999</td>
<td>7.5477</td>
<td>0.141999</td>
<td>7.8686</td>
</tr>
<tr>
<td></td>
<td>0.169999</td>
<td>7.8686</td>
<td>0.198999</td>
<td>7.8686</td>
</tr>
<tr>
<td></td>
<td>0.199999</td>
<td>7.9244</td>
<td>0.201999</td>
<td>8.1042</td>
</tr>
<tr>
<td></td>
<td>0.204999</td>
<td>8.3438</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(7)</td>
<td>0.909999</td>
<td>8.3438</td>
<td>9.909999</td>
<td>8.3438</td>
</tr>
<tr>
<td>(8)</td>
<td>9.909999</td>
<td>8.3438</td>
<td>99.909999</td>
<td>8.3438</td>
</tr>
<tr>
<td>(9)</td>
<td>999.909999</td>
<td>8.3438</td>
<td>9999.909999</td>
<td>8.3438</td>
</tr>
<tr>
<td>(10)</td>
<td>9999.909999</td>
<td>8.3438</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(11)</td>
<td>99999.909999</td>
<td>8.3438</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Figure 8:** SINC and SLIM values for Chillrun8.dat (Reaction between 80 % pyrite + 20 % albite and water with no atmospheric contact).

<table>
<thead>
<tr>
<th>SINC</th>
<th>SLIM</th>
<th>Sampled @</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1x10^-5</td>
<td>0.1x10^-4</td>
<td>0.000001</td>
<td>5.4982</td>
</tr>
<tr>
<td>0.1x10^-4</td>
<td>0.1x10^-3</td>
<td>0.000007</td>
<td>5.4888</td>
</tr>
<tr>
<td>0.1x10^-3</td>
<td>0.1x10^-2</td>
<td>0.000299</td>
<td>5.0853</td>
</tr>
<tr>
<td>0.1x10^-2</td>
<td>0.1x10^-1</td>
<td>0.000999</td>
<td>4.6262</td>
</tr>
<tr>
<td>0.1x10^-1</td>
<td>0.013</td>
<td>0.001999</td>
<td>4.3461</td>
</tr>
<tr>
<td>0.1x10^-1</td>
<td>0.1</td>
<td>0.004999</td>
<td>3.9502</td>
</tr>
<tr>
<td>0.2x10^-1</td>
<td>1.0</td>
<td>0.009999</td>
<td>3.6528</td>
</tr>
<tr>
<td>0.5</td>
<td>10</td>
<td>0.011199</td>
<td>3.6044</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
<td>0.011999</td>
<td>3.9033</td>
</tr>
<tr>
<td>100</td>
<td>1000</td>
<td>0.012099</td>
<td>3.9352</td>
</tr>
<tr>
<td>1000</td>
<td>10000</td>
<td>0.022999</td>
<td>3.9626</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.062999</td>
<td>4.0157</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.092999</td>
<td>4.1032</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.112999</td>
<td>4.1776</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.172999</td>
<td>4.5772</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.192999</td>
<td>4.8902</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.212999</td>
<td>5.6092</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.232999</td>
<td>6.2803</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.372999</td>
<td>6.5064</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.432999</td>
<td>6.7928</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.472999</td>
<td>7.2244</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.512999</td>
<td>7.5071</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.532999</td>
<td>7.8342</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.552999</td>
<td>8.5306</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.572999</td>
<td>8.9871</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.592999</td>
<td>9.2096</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.612999</td>
<td>9.3445</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.732999</td>
<td>9.7649</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.992999</td>
<td>10.1362</td>
</tr>
<tr>
<td>1.992999</td>
<td>10.5388</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.492999</td>
<td>10.5388</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.992999</td>
<td>10.6109</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.492999</td>
<td>10.7517</td>
<td></td>
<td></td>
</tr>
<tr>
<td>99.992999</td>
<td>10.7517</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9999.992999</td>
<td>10.7517</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 9: SINC and SLIM values for Chillrun9.dat (Reaction between 80% pyrite + 20% anorthite and water with no atmospheric contact).

<table>
<thead>
<tr>
<th></th>
<th>SINC</th>
<th>SLIM</th>
<th>Sampled @</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1x10^2</td>
<td>0.1x10^4</td>
<td>0.000001</td>
<td>5.4983</td>
</tr>
<tr>
<td>2</td>
<td>0.1x10^4</td>
<td>0.1x10^3</td>
<td>0.000004</td>
<td>5.4939</td>
</tr>
<tr>
<td>3</td>
<td>0.1x10^3</td>
<td>0.1x10^2</td>
<td>0.000299</td>
<td>5.0939</td>
</tr>
<tr>
<td>4</td>
<td>0.1x10^2</td>
<td>0.1x10^1</td>
<td>0.009999</td>
<td>4.6368</td>
</tr>
<tr>
<td>5</td>
<td>0.1x10^1</td>
<td>0.14x10^1</td>
<td>0.010199</td>
<td>4.3710</td>
</tr>
<tr>
<td>6</td>
<td>0.1x10^0</td>
<td>1.0</td>
<td>0.008999</td>
<td>4.0018</td>
</tr>
<tr>
<td>7</td>
<td>0.1x10^1</td>
<td>0.25</td>
<td>0.011199</td>
<td>3.7051</td>
</tr>
<tr>
<td>8</td>
<td>0.1x10^0</td>
<td>1.0</td>
<td>0.012099</td>
<td>4.0343</td>
</tr>
<tr>
<td>9</td>
<td>0.2</td>
<td>10</td>
<td>0.043999</td>
<td>4.1725</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>100</td>
<td>0.073999</td>
<td>4.3597</td>
</tr>
<tr>
<td>11</td>
<td>100</td>
<td>1000</td>
<td>0.094999</td>
<td>4.6672</td>
</tr>
<tr>
<td>12</td>
<td>200</td>
<td>10000</td>
<td>0.105999</td>
<td>5.0717</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.111999</td>
<td>5.5214</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.117999</td>
<td>6.0203</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.122999</td>
<td>6.3674</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.162999</td>
<td>6.4600</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.191999</td>
<td>6.5635</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.238999</td>
<td>7.0987</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.244999</td>
<td>7.4352</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.249999</td>
<td>7.7622</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.259999</td>
<td>8.5291</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.269999</td>
<td>8.9084</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.319999</td>
<td>8.9084</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.349999</td>
<td>8.9084</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.359999</td>
<td>9.0723</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.469999</td>
<td>9.0723</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.489999</td>
<td>9.0723</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.499999</td>
<td>9.1690</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.549999</td>
<td>9.6121</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.669999</td>
<td>10.0399</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.829999</td>
<td>10.3122</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.999999</td>
<td>10.4875</td>
</tr>
<tr>
<td>9</td>
<td>1.799999</td>
<td>10.9007</td>
<td>4.599999</td>
<td>11.3865</td>
</tr>
<tr>
<td></td>
<td>9.999999</td>
<td>11.7293</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>19.999999</td>
<td>11.9237</td>
<td>29.999999</td>
<td>12.0148</td>
</tr>
<tr>
<td></td>
<td>59.999999</td>
<td>12.2828</td>
<td>99.999999</td>
<td>12.4719</td>
</tr>
<tr>
<td>11</td>
<td>299.999999</td>
<td>12.8604</td>
<td>799.999999</td>
<td>13.1951</td>
</tr>
<tr>
<td>12</td>
<td>1999.99999</td>
<td>13.5144</td>
<td>2199.99999</td>
<td>13.5292</td>
</tr>
<tr>
<td></td>
<td>9999.99999</td>
<td>13.5292</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 10: SINC and SLIM values for Chillrun10.dat (Reaction between 80 % pyrite + 20 % microcline and water with no atmospheric contact).

<table>
<thead>
<tr>
<th>SINC</th>
<th>SLIM</th>
<th>Sampled @</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1x10^-2</td>
<td>0.1x10^-4</td>
<td>0.000001</td>
<td>5.4982</td>
</tr>
<tr>
<td>0.1x10^-4</td>
<td>0.1x10^-3</td>
<td>0.000001</td>
<td>5.4888</td>
</tr>
<tr>
<td>0.1x10^-3</td>
<td>0.1x10^-2</td>
<td>0.000299</td>
<td>5.0848</td>
</tr>
<tr>
<td>0.1x10^-2</td>
<td>0.1x10^-1</td>
<td>0.000999</td>
<td>4.6256</td>
</tr>
<tr>
<td>0.5x10^-3</td>
<td>0.1</td>
<td>0.001999</td>
<td>4.3431</td>
</tr>
<tr>
<td>0.1x10^-2</td>
<td>0.25</td>
<td>0.004999</td>
<td>3.9470</td>
</tr>
<tr>
<td>0.1x10^-1</td>
<td>1.0</td>
<td>0.009999</td>
<td>3.6496</td>
</tr>
<tr>
<td>1.0</td>
<td>10</td>
<td>0.010199</td>
<td>3.6089</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
<td>0.011999</td>
<td>3.8966</td>
</tr>
<tr>
<td>100</td>
<td>1000</td>
<td>0.012499</td>
<td>3.9318</td>
</tr>
<tr>
<td>1000</td>
<td>10000</td>
<td>0.015999</td>
<td>3.9650</td>
</tr>
<tr>
<td>0.180999</td>
<td>4.5500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.209999</td>
<td>5.0106</td>
<td>0.024999</td>
<td>3.9626</td>
</tr>
<tr>
<td>0.222999</td>
<td>5.4725</td>
<td>0.059999</td>
<td>3.9997</td>
</tr>
<tr>
<td>0.232999</td>
<td>5.9007</td>
<td>0.099999</td>
<td>4.1073</td>
</tr>
<tr>
<td>0.439999</td>
<td>6.6646</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.489999</td>
<td>7.1799</td>
<td>0.789999</td>
<td>7.8686</td>
</tr>
<tr>
<td>0.559999</td>
<td>7.7245</td>
<td>0.799999</td>
<td>7.9245</td>
</tr>
<tr>
<td>0.569999</td>
<td>7.8686</td>
<td>0.819999</td>
<td>8.3438</td>
</tr>
<tr>
<td>0.679999</td>
<td>7.8686</td>
<td>0.999999</td>
<td>8.3438</td>
</tr>
<tr>
<td>0.789999</td>
<td>7.8686</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.819999</td>
<td>8.3438</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.999999</td>
<td>8.3438</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.999999</td>
<td>8.3438</td>
<td>99.999999</td>
<td>8.3438</td>
</tr>
<tr>
<td>999.999999</td>
<td>8.3438</td>
<td>9999.99999</td>
<td>8.3438</td>
</tr>
</tbody>
</table>
**Figure 11:** SINC and SLIM values for Chillrun11.dat (Reaction between 100% pyrrhotite and water with no atmospheric contact).

<table>
<thead>
<tr>
<th>SINC</th>
<th>SLIM</th>
<th>Sampled @</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) 0.1x10^-5</td>
<td>0.1x10^-4</td>
<td>0.000001</td>
<td>5.4983</td>
</tr>
<tr>
<td>(2) 0.1x10^-4</td>
<td>0.1x10^-3</td>
<td>0.000399</td>
<td>5.0286</td>
</tr>
<tr>
<td>(3) 0.1x10^-3</td>
<td>0.1x10^-2</td>
<td>0.000999</td>
<td>4.6641</td>
</tr>
<tr>
<td>(4) 0.1x10^-3</td>
<td>0.2x10^-1</td>
<td>0.002399</td>
<td>4.2855</td>
</tr>
<tr>
<td>(5) 0.1x10^-2</td>
<td>0.79x10^-1</td>
<td>0.006599</td>
<td>3.8469</td>
</tr>
<tr>
<td>(6) 0.1x10^-2</td>
<td>0.1</td>
<td>0.010999</td>
<td>3.6311</td>
</tr>
<tr>
<td>(7) 0.1x10^-4</td>
<td>0.107</td>
<td>0.011899</td>
<td>4.1036</td>
</tr>
<tr>
<td>(8) 0.1</td>
<td>1.0</td>
<td>0.012199</td>
<td>4.5586</td>
</tr>
<tr>
<td>(9) 1.0</td>
<td>10</td>
<td>0.012299</td>
<td>4.9498</td>
</tr>
<tr>
<td>(10) 10</td>
<td>100</td>
<td>0.012399</td>
<td>5.5308</td>
</tr>
<tr>
<td>(11) 100</td>
<td>1000</td>
<td>0.012999</td>
<td>5.9859</td>
</tr>
<tr>
<td>(12) 1000</td>
<td>6000</td>
<td>0.013699</td>
<td>6.4012</td>
</tr>
<tr>
<td>(13) 10</td>
<td>10000</td>
<td>0.019999</td>
<td>6.4320</td>
</tr>
<tr>
<td>(5) 0.057999</td>
<td>6.7876</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.069999</td>
<td>7.2562</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.071999</td>
<td>7.5741</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.072999</td>
<td>8.0480</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.073999</td>
<td>8.6146</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.075999</td>
<td>9.0584</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.078999</td>
<td>9.3563</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(6) 0.080499</td>
<td>9.4261</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.085099</td>
<td>9.4261</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.090099</td>
<td>9.4261</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.090199</td>
<td>9.4269</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.099999</td>
<td>9.6550</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(7) 0.106969</td>
<td>9.7524</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.106999</td>
<td>9.7524</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(9) 9.906999</td>
<td>9.7524</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(11) 999.906999</td>
<td>9.7524</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(12) 5999.906999</td>
<td>9.7533</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(13) 9989.906999</td>
<td>9.7533</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX C

1:4 and 4:1 (Pyrite:Feldspar (Ab, An and Mc)) Graphs
**LIST OF FIGURES FOR APPENDIX C**

| Figure 1: | Reaction of 20 % pyrite and 80 % albite. | 136 |
| Figure 2: | Reaction of 20 % pyrite and 80 % anorthite. | 138 |
| Figure 3: | Reaction of 20 % pyrite and 80 % microcline. | 140 |
| Figure 4: | Reaction of 80 % pyrite and 20 % albite. | 142 |
| Figure 5: | Reaction of 80 % pyrite and 20 % anorthite. | 144 |
| Figure 6: | Reaction of 80 % pyrite and 20 % microcline. | 146 |
Figure 1. Reaction of 20% pyrite and 80% albite (Appendix A, Figure 5) with water (Table 2) at 25 °C and no atmospheric contact. Mineral abbreviations can be found in the `List of Abbreviations`. (A) Minerals formed in log moles. (B) pH and log total aqueous molality of the principal component species (i.e. $\Sigma \text{Al}^{3+}$ represents the total of all aqueous Al species). (C) Selected individual aqueous species in log molality (not log total aqueous molality). (D) Shows graph (C) in its entirety. pH can be read directly from the Log total aq molality and Log molality axes of B and C respectively.
Figure 1.  (Continued)
Figure 2. Reaction of 20 % pyrite and 80 % anorthite (Appendix A, Figure 6) with water (Table 2) at 25 °C and no atmospheric contact. Mineral abbreviations can be found in the 'List of Abbreviations'. (A) Minerals formed in log moles. (B) pH and log total aqueous molality of the principal component species (i.e. $\Sigma Al^{3+}$ represents the total of all aqueous Al species). (C) Selected individual aqueous species in log molality (not log total aqueous molality). (D) Shows graph (C) in its entirety. pH can be read directly from the Log total aq molality and Log molality axes of B and C respectively.
Figure 2. (Continued)
Figure 3. Reaction of 20% pyrite and 80% microcline (Appendix A, Figure 7) with water (Table 2) at 25 °C and no atmospheric contact. Mineral abbreviations can be found in the ‘List of Abbreviations’. (A) Minerals formed in log moles. (B) pH and log total aqueous molality of the principal component species (i.e. ΣAl³⁺ represents the total of all aqueous Al species). (C) Selected individual aqueous species in log molality (not log total aqueous molality). (D) Shows graph (C) in its entirety. pH can be read directly from the Log total aq molality and Log molality axes of B and C respectively.
Figure 4. Reaction of 80 % pyrite and 20 % albite (Appendix A, Figure 8) with water (Table 2) at 25 °C and no atmospheric contact. Mineral abbreviations can be found in the 'List of Abbreviations'. (A) Minerals formed in log moles. (B) pH and log total aqueous molality of the principal component species (i.e. ΣAl^3+ represents the total of all aqueous Al species). (C) Selected individual aqueous species in log molality (not log total aqueous molality). (D) Shows graph (C) in its entirety. pH can be read directly from the Log total aq molality and Log molality axes of B and C respectively.
Figure 4. (Continued)
Figure 5. Reaction of 80 % pyrite and 20 % anorthite (Appendix A, Figure 9) with water (Table 2) at 25 °C and no atmospheric contact. Mineral abbreviations can be found in the ‘List of Abbreviations’. (A) Minerals formed in log moles. (B) pH and log total aqueous molality of the principal component species (i.e. $\Sigma Al^{3+}$ represents the total of all aqueous Al species). (C) Selected individual aqueous species in log molality (not log total aqueous molality). (D) Shows graph (C) in its entirety. pH can be read directly from the Log total aq molality and Log molality axes of B and C respectively.
Figure 5. (Continued)
Figure 6. Reaction of 80 % pyrite and 20 % microcline (Appendix A, Figure 10) with water (Table 2) at 25 °C and no atmospheric contact. Mineral abbreviations can be found in the 'List of Abbreviations'. (A) Minerals formed in log moles. (B) pH and log total aqueous molality of the principal component species (i.e. ΣAl^{3+} represents the total of all aqueous Al species). (C) Selected individual aqueous species in log molality (not log total aqueous molality). (D) Shows graph (C) in its entirety. pH can be read directly from the Log total aq molality and Log molality axes of B and C respectively.
Figure 6. (Continued)
APPENDIX D

Key Components of SOLRUN
Key Components of SOLRUN

The key components of SOLRUN that best define how SOLVEQ was used for this study are highlighted (BOLD CAPS) in Figure 1. This sample SOLRUN file is followed by brief descriptions of the key components (Spycher and Reed, 1998). All other components are either non-essential default values or they are not applicable to these reactions.

Rainwater (1kg) with 9ppm O2; pH = 5.5
Data from Freeze and Cherry, 1979.

\[ \text{< eprc > < PH > < unac > < alkalin > < TEMPC > < rm > < pr_min >} \]
\[ .100E-11.550E+01.000E+00.000E+00.250E+02.00E+00 \]

\[ \text{ntem nmtt ipri ichb NLOC C nsun igeo itre neut} \]
\[ 0 0 0 0 1 40 3 0 0 0 0 \]

\[ \text{SAQ > < NAME > < MTOT > < MTRY > < gamma >} \]
\[ 1 \text{ H+} \quad .0000000E+00 \quad .3162278E-05 \quad 1.0000 \]
\[ 2 \text{ H2O} \quad .9999834E+00 \quad .1000000E+01 \quad 1.0000 \]
\[ 3 \text{ Cl-} \quad .1128254E-04 \quad .1000000E-03 \quad 1.0000 \]
\[ 4 \text{ SO4--} \quad .3122996E-04 \quad .1000000E-06 \quad 1.0000 \]
\[ 5 \text{ HCO3-} \quad .3277614E-04 \quad .1000000E-06 \quad 1.0000 \]
\[ 7 \text{ SiO2} \quad .1664474E-05 \quad .1000000E-06 \quad 1.0000 \]
\[ 9 \text{ Ca++} \quad .2245509E-04 \quad .1000000E-06 \quad 1.0000 \]
\[ 10 \text{ Mg++} \quad .8226390E-05 \quad .1000000E-06 \quad 1.0000 \]
\[ 12 \text{ K+} \quad .1022966E-04 \quad .1000000E-06 \quad 1.0000 \]
\[ 13 \text{ Na+} \quad .2609853E-04 \quad .1000000E-06 \quad 1.0000 \]
\[ 31 \text{ O2 aq.} \quad .2812500E-03 \quad .1000000E-06 \quad 1.0000 \]

\[ \text{< eqnam > ieq} \]

Figure 1. SOLRUN file - this file computes the MTOT of \( \text{H}^+ \) (pH=5.5) for rainwater (key components in BOLD CAPS), precipitation constituents from Freeze and Cherry, 1979.
**PH**

If PH is given, the total molar amount of H⁺ is calculated. If PH = zero, the pH is calculated from the amount of H⁺ provided.

**TEMPC**

TEMPC = the temperature (in °C) of the system at which equilibrium is calculated.

**NLOOP or NLOO**

(NLOOP = "number of loops"). NLOOP is the maximum number of Newton-Raphson iterations that SOLVEQ will use to converge the solution. If convergence is not reached after NLOOP iterations, the program ceases and non-convergence is assumed. NLOOP is normally set to 40 and it is generally accepted that if a case is not solved within 70 iterations, it will not converge.

**C**

(C = "charge" balance). The numerical value for C corresponds to the selected ion from the component species in solution that is used for charge balancing. The total molality of this ion is adjusted if a charge imbalance occurs within the solution.

**SAQ**

(SAQ = “sequence, aqueous”). The numeric values for SAQ are preset and correspond to specific component species (from the sequence of component
species) within the SOLTHERM data file. SAQ tells SOLVEQ the positions of the component species, required for the calculations, within SOLTHERM.

**NAME**

The names of the selected component species identified by SAQ are listed under NAME. These names only serve as a visual aid for the reader as he/she reads the SOLRUN data file.

**MTOT**

(MTOT = "moles, total"). MTOT represents the total number of moles for the component species within the SOLRUN file and defines the overall chemical composition of the system. MTOT for water is designated as the amount of water (in kilograms) within the system.

**MTRY**

(MTRY = "molality trial" value). MTRY contains the estimated trial molalities for the component species. Default MTRY values are 1x10^{-10}. As SOLVEQ is used to calculate the actual (unknown) molalities, the closer the preliminary MTRY values are to the actual molalities the better are the chances for convergence. The MTRY value for water is in kilograms and is preset by SOLVEQ to 1 kg.
APPENDIX E

Key Components of CHILRUN
Key Components of CHILLRUN

The key components of CHILLRUN that best define how CHILLER was used for this study are highlighted (BOLD CAPS) in Figure 1. This sample CHILLRUN file is followed by brief descriptions of the key components (Reed and Spycher, 1998). All other components are either non-essential default values or they are not applicable to these water-rock titration reactions.

Figure 1. CHILLRUN file - this file illustrates the rock titration (MINSOL = 1) capabilities of CHILLER. Pyrite is titrated into the aqueous phase at a rate of 0.1x10⁻⁵ g (SINC) until the value of SLIM (0.1x10⁻⁴ g) is reached at which point program CHILLER stops (key components in BOLD CAPS).

153
**PH**

If PH is zero, the system pH is calculated from the H⁺ ions in solution, and is allowed to fluctuate with changes in fluid chemistry. If PH is non-zero (1-14), the pH remains fixed at that value during the run.

**PFLUID**

Pressure of the system in bars.

**TEMP**

Temperature of the system in °C.

**SINC**

(SINC = “step increment”). SINC represents the incremental quantity of reactant to be titrated into the aqueous phase. For modeling rock titration reactions (MINSOL = 1), SINC is input as the amount of reactant in grams. For each subsequent CHILLRUN file SINC is typically increased by a factor of ten.

**SLIM**

(SLIM = “step limit”). SLIM represents the total quantity of reactant that can be titrated into the aqueous phase for that specific CHILLRUN file. Once SINC = SLIM program CHILLER stops and a new value for SLIM most be input into the succeeding CHILLRUN file in order for CHILLER to run. For each subsequent CHILLRUN file SLIM is also typically increased by a factor of ten.
**TOTMIX**

(TOTMIX = ‘total mixture’). For modeling rock titration reactions (MINSOL = 1), TOTMIX represents the total amount of reactant added to the solution, in grams.

**C**

(C = “charge” balance). The numerical value for C corresponds to the selected ion from the component species in solution that is used for charge balancing. The total molality of this ion may be adjusted if a charge imbalance occurs within the solution.

**NLOOP or NLOOP**

(NLOOP = “number of loops”). NLOOP is the maximum number of Newton-Raphson iterations that CHILLER will use to converge the solution. If convergence is not reached after NLOOP iterations, the program ceases and non-convergence is assumed. NLOOP is normally set to 70 and it is generally accepted that if a case is not solved within 70 iterations, it will not converge. For some redox calculations however, an NLOOP value as large as 150 is required.

**MINS or MINSOL**

MINSOL is used to activate the titration capabilities of CHILLER. With MINSOL set to 1, SINC and SLIM are entered into the CHILLRUN data file in grams. All reactants are therefore titrated into the aqueous phase in grams.
**SAQ**

(SAQ = "sequence, aqueous"). The numeric values for SAQ are preset and correspond to specific component species (from the sequence of component species) within the SOLThERM data file. SAQ tells CHILLER the positions of the component species, required for the calculations, within SOLThERM.

**NAME**

The names of the selected component species identified by SAQ are listed under NAME. These names only serve as a visual aid for the reader as he/she reads the CHILLRUN data file.

**MTOT**

(MTOT = "moles, total"). MTOT represents the total number of moles for the component species within the CHILLRUN file and defines the overall chemical composition of the system. MTOT for water is designated as the amount of water (in kilograms) within the system.

**MTRY**

(MTRY = "molality trial" value). MTRY contains the estimated trial molalities for the component species. Default MTRY values are 1x10^{-10}. As CHILLER is used to calculate the actual (unknown) molalities, the closer the preliminary MTRY values are to the actual molalities the better are the chances for convergence. The MTRY value for water is in kilograms and is preset by CHILLER to 1 kg.
MIN or SATMIN

(SATMIN = “saturated mineral”). SATMIN lists all of the minerals and (or) gases that are saturated within the system.

MINTRY

(MINTRY = “mineral moles, trial”). MINTRY contains the molar amounts of the minerals or gases listed within SATMIN. Default MINTRY values are $1 \times 10^{-9}$.

NOMOX

(NOMOX = “name, oxide”). NOMOX contains the names of the minerals (reactants) used for the rock titration reactions.

WTPC

(WTPC = “weight percent”). WTPC contains the weight percents of the minerals listed under NOMOX.

SUPNAM

(SUPNAM = “suppression name”). SUPNAM lists the names of the minerals that are suppressed during the CHILLER calculations. This feature (which is user specified) is used to suppress the formation of any questionable minerals.
APPENDIX F
List of Reactions
\[
\begin{align*}
\text{Reaction} & \quad \text{Equation} \\
(1) & \quad \text{pyrite} \quad \text{FeS}_2 + \frac{5}{2} \text{H}_2\text{O} + \frac{15}{4} \text{O}_2{}^8 \Rightarrow \text{FeOOH} + 4\text{H}^+ + 2\text{SO}_4{}^2^- \\
(2) & \quad \text{pyrite} \quad \text{FeS}_2 + \frac{7}{2} \text{O}_2{}^8 + \text{H}_2\text{O} \Rightarrow \text{Fe}^{2+} + 2\text{SO}_4{}^2^- + 2\text{H}^+ \\
(3) & \quad \text{Fe}^{2+} + \frac{1}{4} \text{O}_2{}^8 + \text{H}^+ \Rightarrow \text{Fe}^{3+} + \frac{1}{2} \text{H}_2\text{O} \\
(4) & \quad \text{ferricydrite} \quad \text{Fe}^{3+} + 3\text{H}_2\text{O} \Rightarrow \text{Fe(OH)}_3 + 3\text{H}^+ \\
(5) & \quad \text{pyrite} \quad \text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \Rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4{}^2^- + 16\text{H}^+ \\
(6) & \quad \text{ferricydrite} \quad \text{FeS}_2 + \frac{15}{4} \text{O}_2{}^8 + \frac{7}{2} \text{H}_2\text{O} \Rightarrow \text{Fe(OH)}_3 + 2\text{SO}_4{}^2^- + 4\text{H}^+ \\
(7) & \quad \text{pyrite} \quad \text{FeS}_2 + \frac{7}{2} \text{O}_2{}^8 + \text{H}_2\text{O} \Rightarrow \text{FeSO}_4 + \text{H}_2\text{SO}_4 \\
(8) & \quad \text{FeSO}_4 + \text{H}_2\text{SO}_4 + \frac{1}{2} \text{O}_2{}^8 \Rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O} \\
(9) & \quad \text{pyrite} \quad \text{FeS}_2 + \text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O} + 3\text{O}_2{}^8 \Rightarrow 3\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 \\
(10) & \quad \text{MS} + \text{Fe}_2(\text{SO}_4)_3 + \frac{3}{2} \text{O}_2{}^8 + \text{H}_2\text{O} \Rightarrow \text{MSO}_4 + 2\text{FeSO}_4 + \text{H}_2\text{SO}_4 \\
& \quad \text{(where MS stands for any metal sulfide)}
\end{align*}
\]
\[
\begin{align*}
Fe_{(1-x)}S + (2\cdot\frac{3}{2})O_2^8 + xH_2O & \rightleftharpoons (1-x)Fe^{2+} + SO_4^{2-} + 2xH^+ \quad (11) \\
pyrrhotite \\

Fe_{(1-x)}S + (2-2x)Fe^{2+} & \rightleftharpoons (3-3x)Fe^{2+} + S^0 \quad (12) \\
pyrrhotite \\

Fe_{(1-x)}S + (1-x)/2 O_2^8 + 2(1-x)H^+ & \rightleftharpoons (1-x)Fe^{2+} + S^0 + (1-x)H_2O \quad (13) \\
pyrrhotite \\

2Fe_{(1-x)}S + (1/2-x)O_2^8 + (2-4x)H^+ & \rightleftharpoons \\
pyrrhotite \quad FeS_2 + (1-2x)Fe^{2+} + (1-2x)H_2O \quad (14) \\
pyrite \\

Fe^{3+} + 3H_2O & \rightleftharpoons Fe(OH)_3 + 3H^+ \quad (15) \\
ferricyanide \\

KAl_2[AlSi_3O_{10}](OH)_2(s) + H^+ + 3/2 H_2O & \rightleftharpoons \\
K^+ + 3/2 Al_2Si_2O_5(OH)_4(s) \quad (16) \\

KMg_{1.5}Fe_{1.5}AlSi_3O_{10}(OH)_2(s) + 7H^+ + 1/2 H_2O & \rightleftharpoons \\
K^+ + 1.5Mg^{2+} + 1.5Fe^{2+} + 2H_4SiO_4^9 + 1/2 Al_2Si_2O_5(OH)_4(s) \quad (17) \\

NaAlSi_3O_6(s) + H^+ + 9/2 H_2O & \rightleftharpoons \\
Na^+ + 2H_4SiO_4^9 + 1/2 Al_2Si_2O_5(OH)_4(s) \quad (18) \\

CaAl_2Si_2O_8(s) + 2H^+ + H_2O & \rightleftharpoons Ca^{2+} + Al_2Si_2O_5(OH)_4(s) \quad (19) \\

KAlSi_3O_8(s) + H^+ + 9/2 H_2O & \rightleftharpoons \\
K^+ + 2H_4SiO_4^9 + 1/2 Al_2Si_2O_5(OH)_4(s) \quad (20) \\

\end{align*}
\]

160
\[
\begin{align*}
\text{FeS}_2 + 3^{1/2}\text{H}_2\text{O} + 3^{3/4}\text{O}_2 + \text{CaAl}_2\text{Si}_2\text{O}_8 + 4\text{H}^+ &= \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + \text{Ca}^{2+} + 2\text{Al}^{3+} + 2\text{H}_4\text{SiO}_4^0 \\
(21) \\
\text{FeS}_2 + 11^{1/2}\text{H}_2\text{O} + 3^{3/4}\text{O}_2 + 2\text{KAlSi}_3\text{O}_8 + 4\text{H}^+ &= \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 2\text{K}^+ + 2\text{Al}^{3+} + 6\text{H}_4\text{SiO}_4^0 \\
(22) \\
\text{FeS}_2 + 11^{1/2}\text{H}_2\text{O} + 3^{3/4}\text{O}_2 + 2\text{NaAlSi}_3\text{O}_8 + 4\text{H}^+ &= \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 2\text{Na}^+ + 2\text{Al}^{3+} + 6\text{H}_4\text{SiO}_4^0 \\
(23) \\
\text{FeS}_2 + 21^{1/2}\text{H}_2\text{O} + 3^{3/4}\text{O}_2 + 3\text{CaAl}_2\text{Si}_2\text{O}_8 + 2\text{H}^+ &= \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 3\text{Ca}^{2+} + 6\text{Al(OH)}_3 + 6\text{H}_4\text{SiO}_4^0 \\
(24) \\
\text{FeS}_2 + 38^{1/2}\text{H}_2\text{O} + 3^{3/4}\text{O}_2 + 5\text{KAlSi}_3\text{O}_8 + \text{H}^+ &= \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 5\text{K}^+ + 5\text{Al(OH)}_3 + 15\text{H}_4\text{SiO}_4^0 \\
(25) \\
\text{FeS}_2 + 38^{1/2}\text{H}_2\text{O} + 3^{3/4}\text{O}_2 + 5\text{NaAlSi}_3\text{O}_8 + \text{H}^+ &= \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 5\text{Na}^+ + 5\text{Al(OH)}_3 + 15\text{H}_4\text{SiO}_4^0 \\
(26) \\
\text{CaCO}_3 + \text{H}_2\text{SO}_4 &= \text{CaSO}_4 + \text{H}_2\text{O} + \text{CO}_2 \\
\text{calcite} \\
(27) \\
\text{CaMg(CO}_3)_2 + 2\text{H}_2\text{SO}_4 &= \text{CaSO}_4 + \text{MgSO}_4 + 2\text{H}_2\text{O} + 2\text{CO}_2 \\
\text{dolomite} \\
(28) \\
\text{Fe}^{3+} + 2\text{H}_2\text{O} &= \text{Fe(OH)}_3 + 3\text{H}^+ \\
\text{goethite} \\
(29) \\
\text{H}^+ + \text{SO}_4^{2-} &= \text{HSO}_4^- \\
(30)
\end{align*}
\]
\[ \text{Fe}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{FeSO}_4^0 \]  \hspace{1cm} (31)

\[ \text{HS}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{S}^0 \]  \hspace{1cm} (32)

\[ \text{FeO(OH)} + 2\text{SO}_4^{2-} + 4\text{H}^+ \rightleftharpoons \text{FeS}_2 + \frac{5}{2}\text{H}_2\text{O} + \frac{7}{2}\text{O}_2^0 \]  
\[ \text{goethite} \hspace{1cm} \text{pyrite} \]  \hspace{1cm} (33)

\[ 5\text{Fe}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{FeO(OH)} + 4\text{Fe}^{2+} + 7\text{H}^+ + \text{O}_2^0 \]  
\[ \text{goethite} \]  \hspace{1cm} (34)

\[ \text{FeO(OH)} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Fe}_3\text{O}_4 + 3\text{Fe}^{2+} + \text{O}_2^0 + 9\text{H}^+ \]  
\[ \text{goethite} \hspace{1cm} \text{magnetite} \]  \hspace{1cm} (35)

\[ 2\text{KAlSi}_3\text{O}_8 + 5\text{H}^+ \rightleftharpoons \text{AlO(OH)}^0 + 2\text{K}^+ + 6\text{SiO}_2^0 + \text{Al}^{3+} + 2\text{H}_2\text{O} \]  
\[ \text{microcline} \]  \hspace{1cm} (36)

\[ \text{Al}^{3+} + \text{AlO(OH)}^0 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{AlO(OH)} + 3\text{H}^+ \]  
\[ \text{diaspore} \]  \hspace{1cm} (37)

\[ 2\text{KAlSi}_3\text{O}_8 + 2\text{H}^+ \rightleftharpoons 2\text{AlO(OH)} + 2\text{K}^+ + 6\text{SiO}_2^0 \]  
\[ \text{microcline} \hspace{1cm} \text{diaspore} \]  \hspace{1cm} (38)

\[ 2\text{AlO(OH)} + 2\text{SiO}_2^0 + \text{H}_2\text{O} \rightleftharpoons \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \]  
\[ \text{diaspore} \hspace{1cm} \text{kaolinite} \]  \hspace{1cm} (39)

\[ 2\text{KAlSi}_3\text{O}_8 + \text{H}_2\text{O} + 2\text{H}^+ \rightleftharpoons \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{K}^+ + 4\text{SiO}_2^0 \]  
\[ \text{microcline} \hspace{1cm} \text{kaolinite} \]  \hspace{1cm} (40)
\[
2\text{AlO(OH)}^0 + 5\text{Fe}^{2+} + 3\text{SiO}_2^0 + 8\text{H}_2\text{O} \rightleftharpoons \\
(\text{Fe})_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8 + 10\text{H}^+ \\
\text{daphnite}
\]

\[
2\text{AlO(OH)}^0 + 5\text{Mg}^{2+} + 3\text{SiO}_2^0 + 8\text{H}_2\text{O} \rightleftharpoons \\
(\text{Mg})_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8 + 10\text{H}^+ \\
\text{clinochlore}
\]

\[
\text{Na}^+ + 2\text{Ca}^{2+} + 19\text{SiO}_2^0 + 9\text{AlO(OH)}^0 + 5\text{Fe}^{2+} + 5\text{Mg}^{2+} + 30\text{H}_2\text{O} \rightleftharpoons \\
\text{Clcl} + \text{Dph} + \text{NaCa}_2(\text{Al}_2\text{Si}_3\text{O}_{36}) \cdot 14\text{H}_2\text{O} + 25\text{H}^+ \\
\text{stilbite}
\]

\[
3\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{K}^+ \rightleftharpoons 2\text{KAl}_5\text{Si}_3\text{O}_{10}(\text{OH})_2 + 3\text{H}_2\text{O} + 2\text{H}^+ \\
\text{kaolinite} \\
\text{muscovite}
\]

\[
3\text{KAlSi}_3\text{O}_8 + 2\text{H}^+ \rightleftharpoons \text{KAl}_5\text{Si}_3\text{O}_{10}(\text{OH})_2 + 2\text{K}^+ + 6\text{SiO}_2^0 \\
\text{microcline} \\
\text{muscovite}
\]

\[
3\text{Kln} + 2\text{K}^+ + \text{Na}^+ + 2\text{Ca}^{2+} + 19\text{SiO}_2^0 + \\
9\text{AlO(OH)}^0 + 5\text{Fe}^{3+} + 5\text{Mg}^{2+} + 27\text{H}_2\text{O} \rightleftharpoons \\
2\text{Ms} + \text{Clcl} + \text{Dph} + \text{Stb} + 27\text{H}^+ \\
\text{K-feldspar} \\
\text{muscovite}
\]

\[
3\text{Mc} + \text{Na}^+ + 2\text{Ca}^{2+} + 13\text{SiO}_2^0 + \\
9\text{AlO(OH)}^0 + 5\text{Fe}^{2+} + 5\text{Mg}^{2+} + 30\text{H}_2\text{O} \rightleftharpoons \\
\text{Ms} + 2\text{K}^+ + \text{Clcl} + \text{Dph} + \text{Stb} + 23\text{H}^+ \\
\text{K-feldspar} \\
\text{muscovite}
\]

\[
2\text{NaAlSi}_3\text{O}_8 + 5\text{H}^+ \rightleftharpoons \\
\text{albite} \\
\text{AlO(OH)}^0 + 2\text{Na}^+ + 6\text{SiO}_2^0 + \text{Al}^{3+} + 2\text{H}_2\text{O} \\
\text{albite}
\]

\[
2\text{NaAlSi}_3\text{O}_8 + 2\text{H}^+ \rightleftharpoons 2\text{AlO(OH)} + 2\text{Na}^+ + 6\text{SiO}_2^0 \\
\text{albite} \\
\text{diaspore}
\]

163
\[ 2\text{NaAlSi}_3\text{O}_8 + \text{H}_2\text{O} + 2\text{H}^+ \rightleftharpoons \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{Na}^+ + 4\text{SiO}_2^0 \]  
\textit{albite} \hspace{1cm} \textit{kaolinite}  

\[ \text{Na}^+ + 2\text{Ca}^{2+} + \text{K}^+ + \text{Fe}^{3+} + 23\text{SiO}_2^0 + 10\text{AlO(OH)}^0 + 6\text{Fe}^{2+} + 6\text{Mg}^{2+} + 34^{1/2}\text{H}_2\text{O} \rightleftharpoons \text{Cdn} + \text{Clcl} + \text{Dph} + \text{Stb} + 2^{1/2}\text{O}_2^0 + 33\text{H}^+ \]  

\[ 3\text{Al}_2\text{Si}_2\text{O}_8(\text{OH})_4 + 2\text{Na}^+ \rightleftharpoons \]  
\textit{kaolinite} \hspace{1cm} \text{2NaAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2 + 3\text{H}_2\text{O} + 2\text{H}^+ \]  
\textit{paragonite}  

\[ 3\text{NaAlSi}_3\text{O}_8 + 2\text{H}^+ \rightleftharpoons \text{NaAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2 + 2\text{Na}^+ + 6\text{SiO}_2^0 \]  
\textit{albite} \hspace{1cm} \textit{paragonite}  

\[ 3\text{Kln} + 3\text{Na}^+ + 2\text{Ca}^{2+} + \text{K}^+ + \text{Fe}^{3+} + 23\text{SiO}_2^0 + 10\text{AlO(OH)}^0 + 6\text{Fe}^{2+} + 6\text{Mg}^{2+} + 31^{1/2}\text{H}_2\text{O} \rightleftharpoons \]  
\text{2Pg} + \text{Cdn} + \text{Clcl} + \text{Dph} + \text{Stb} + 2^{1/2}\text{O}_2^0 + 35\text{H}^+ \]  

\[ 3\text{Ab} + 2\text{Ca}^{2+} + \text{K}^+ + \text{Fe}^{3+} + 17\text{SiO}_2^0 + 10\text{AlO(OH)}^0 + 6\text{Fe}^{2+} + 6\text{Mg}^{2+} + 34^{1/2}\text{H}_2\text{O} \rightleftharpoons \]  
\text{Pg} + \text{Cdn} + \text{Clcl} + \text{Dph} + \text{Stb} + \text{Na}^+ + 2^{1/2}\text{O}_2^0 + 31\text{H}^+ \]  

\[ \text{CaAl}_2\text{Si}_2\text{O}_8 + 5\text{H}^+ \rightleftharpoons \text{AlO(OH)}^0 + \text{Ca}^{2+} + 2\text{SiO}_2^0 + \text{Al}^{3+} + 2\text{H}_2\text{O} \]  
\textit{anorthite}  

\[ \text{CaAl}_2\text{Si}_2\text{O}_8 + 2\text{H}^+ \rightleftharpoons 2\text{AlO(OH)} + \text{Ca}^{2+} + 2\text{SiO}_2^0 \]  
\textit{anorthite} \hspace{1cm} \textit{diaspore}  

\[ \text{CaAl}_2\text{Si}_2\text{O}_8 + \text{H}_2\text{O} + 2\text{H}^+ \rightleftharpoons \text{Al}_2\text{Si}_3\text{O}_5(\text{OH})_4 + \text{Ca}^{2+} \]  
\textit{anorthite} \hspace{1cm} \textit{kaolinite}
Kln + Na\(^+\) + 2Ca\(^{2+}\) + 17SiO\(_2\)\(^6\) +

\[9\text{AlO(OH)}\]\(^6\) + 5Fe\(^{2+}\) + 5Mg\(^{2+}\) + 29H\(_2\)O ⇄

Clc + Dph + Stb + 2Dsp + 25H\(^+\) \hspace{1cm} (59)

An + Stb + 4AlO(OH)\(^6\) + 3SiO\(_2\)\(^6\) +

5Fe\(^{2+}\) + 5Mg\(^{2+}\) + 16H\(_2\)O + Al\(^{3+}\) ⇄

Clc + Dph + 3Lmt + 2Dsp + Na\(^+\) + 22H\(^+\) \hspace{1cm} (60)

2CaAl\(_2\)Si\(_2\)O\(_8\) + 2H\(^+\) + 4H\(_2\)O ⇄ 2Dsp + Lmt + Ca\(^{2+}\)

anorthite \hspace{1cm} (61)

Ca\(^{2+}\) + HCO\(_3\)\(^-\) ⇄ CaCO\(_3\) + H\(^+\)

calcite \hspace{1cm} (62)

2An + 6Dsp + Ca\(^{2+}\) + 5Fe\(^{2+}\) + 5Mg\(^{2+}\) +

8SiO\(_2\)\(^6\) + HCO\(_3\)\(^-\) + 20H\(_2\)O ⇄

Mrg + Cal + Lmt + Dph + Clc + 21H\(^+\) \hspace{1cm} (63)

3An + 2H\(^+\) + 4H\(_2\)O ⇄ Mrg + Lmt + Ca\(^{2+}\) \hspace{1cm} (64)

3An + 4AlO(OH)\(^6\) + 5Fe\(^{2+}\) + 5Mg\(^{2+}\) +

20H\(_2\)O + HCO\(_3\)\(^-\) + 6SiO\(_2\)\(^6\) ⇄

Mrg + Lmt + Cal + Dph + Clc + 19H\(^+\) \hspace{1cm} (65)
VITA AUCTORIS

NAME: Christopher Kenneth Lauzon

PLACE OF BIRTH: Windsor, Ontario, Canada

DATE OF BIRTH: October 18/1967

EDUCATION:

Riverside Secondary School
1981-1986

St. Clair College of Applied Arts and Technology, Windsor, Ontario, Canada
1986-1988 Industrial Control Systems Technician

University of Windsor, Windsor, Ontario, Canada
1989-1994 B.Sc. Honors Geology

University of Windsor, Windsor, Ontario, Canada