EVALUATION OF SOLUTION-MINERAL EQUILIBRIA
IN THE
SMALL SCALE SOLUTION MINING
OF COPPER

by

Robert W. Smith

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ABSTRACT

Solution mining of copper is becoming an increasingly important source of domestic copper. The solution mining of copper is presently carried out with little regard for the interaction of the acid with silicate gangue. Theoretical calculations and experimental works show that low grade biotite-bearing porphyry type copper ores, when leached with strongly acidic solutions, undergo extensive alteration to clay minerals and amorphous aluminosilicates. However, the use of solution-mineral equilibrium techniques enables leach solutions to be prepared that are near equilibrium with the gangue minerals. This minimizes the alteration of the silicates. These stabilized leach solutions have pH's in the range of four to five and contain high concentrations of sodium or potassium ions or both.

The ores used in this study had chalcopyrite as the predominate copper sulfide. Leaching of chalcopyrite was kinetically unfavorable using stabilized leach solutions. It is believed that this is the result of $Fe(OH)_3$ or $Fe_4SO_4(OH)_{10}$ coating the chalcopyrite grains.

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LIST OF ABBREVIATIONS

Abbreviations and mineral compositions used in Figures 1, 2, 3, 4, 5, 8, 9, and 10.

ABBREVIATION	MINERAL FORMULA
ALB	albite $NaAlSi_3O_8$
CHLOR	chlorite $Mg_5Al_2Si_3O_{10}(OH)_8$
CRIST	"β-cristobalite" SiO_2
KAOL	kaolinite $Al_2Si_2O_5(OH)_4$
Mg-MONT	magnesium beidellite $Mg_{.167}Al_{2.33}Si_{3.67}O_{10}(OH)_2$
MICRO	microcline $KAlSi_3O_8$
MUSC	muscovite $KAl_3Si_3O_{10}(OH)_2$
Na-MONT	sodium beidellite $Na_{.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$
PHLOG	phlogopite $KMg_3AlSi_3O_{10}(OH)_2$
PYROPH	pyrophyllite $Al_2Si_4O_{10}(OH)_2$
QTZ	quartz SiO_2

INTRODUCTION

Solution chemistry and mineralogy play a very important role in the solution mining of low grade copper ores. Often however, leaching is carried out with no consideration of solution-rock interaction. It is felt by some (Bruynestein, Duvain and Ballard, 1977) that dump leaching of copper ores can be evaluated and modeled with little or no consideration of the leach solution's interaction with the silicate gangue. Recent work by Beane and Popp (in press) has shown that leaching efficiency can be increased, and acid consumption decreased by leaching with a solution that is near equilibrium with the rock. This thesis is an application of the principles outlined by Beane and Popp (in press) to rocks with more complex mineralogies. Table 1 compares the mineralogy of the Tyrone ore used by Beane and Popp to that of Pinto Valley and Duval-Sierrita rock used in this leach study. The presence of biotite and plagioclase introduces the necessity for consideration of ions other than potassium in the stabilized leach solution. Table 2 is a comparison of the chemical compositions of the three rocks. In all three of the rocks the copper content is 0.31 wt% or less, however unlike the Tyrone rock, which had chalcocite as the predominate copper mineral, the Duval-Sierrita and Pinto Valley rocks had chalcopyrite as the predominate copper containing mineral.

SOLUTION-SULFIDE INTERACTIONS

In this study chalcopyrite and pyrite were the principle sulfide minerals. The oxidation of these two minerals in a waste dump environ-

TABLE I

Comparative mineralogies of Tyrone ore (Beane and Popp, in press) and the ores used in this study.

TYRONE		DUVAL-SIERRITA		PINTO VALLEY	
MINERALS	EST. VOL. %	MINERALS	EST. VOL. %	MINERALS	EST. VOL %
quartz	40	quartz	26	quartz	35
opaque	8	opaque	3	opaque	3
K-feldspar (highly altered to sericite)	30	K-feldspar	20	K-feldspar	27
		plagioclase Ab_{70}	35	plagioclase Ab_{70}	15
		biotite (Fe:Mg, atomic)	12 (1:2)	biotite (Fe:Mg, atomic)	10 (1:1)
kaolinite	trace				
jarosite	trace				
sericite	22			sericite	10
				zircon	trace
		zoisite	4		

TABLE 2

Comparative chemical analysis of Tyrone ore (Beane and Popp, in press) and ores used in this study.

	TYRONE*	DUVAL-SIERRITA	PINTO VALLEY
SiO_2	61.2	72	72.9
Al_2O_3	16.2	14	12.4
Fe_2O_3	--	1.40	1.64
MgO	.30	.44	.64
CaO	.04	1.4	1.00
K_2O	4.4	3.7	5.54
Na_2O	.30	3.2	1.73
loss on ignition	5.1	1.3	1.8
CO_2	N.D.	N.D.	N.D.
Fe	6.9	1.76	1.47
Cu	.29	.31	.21
S	7.4	2.02	1.69
	102.1	101.5	101.0

N.D. - not detected

*wt. %

ment occurs according to the following equations (Cathles and Apps, 1975):

$$(1) \quad CuFeS_2 + \frac{5}{2}O_2 + 2H^+ = Cu^{2+} + Fe^{2+} + SO_4{}^{2-} + H_2O + S^0$$

and

$$(2) \quad FeS_2 + \frac{7}{2}O_2 + H_2O = Fe^{2+} + 2SO_4{}^{2-} + 2H^+$$

The oxidation of chalcopyrite can be carried out using ferric iron as the oxidizing agent via:

$$(3) \quad CuFeS_2 + 10Fe^{3+} + 2H^+ = Cu^{2+} + 11Fe^{2+} + SO_4{}^{2-} + S^0$$

However the use of ferric iron as an oxidizing agent requires a pH of less than 2.3 to maintain an activity of ferric iron of 10^{-2} molal, as a result of the low solubility of $Fe(OH)_3$ (Garrels and Christ, 1965).

A pH of two would result in alteration of the rock forming silicates to acid stable clays and oxides. For example, consider the conversion of biotite to kaolinite:

$$(4) \quad 2KFeMg_2AlSi_3O_{10}(OH)_2 + H_2O + 14H^+ = Al_2Si_2O_5(OH)_4 + 2K^+ + 4Mg^{2+} + 2Fe^{2+} + 4H_4SiO_4$$

or under stronger acid conditions; hydrolysis of biotite:

$$(5) \quad KFeMg\ AlSi_3O_{10}(OH)_2 + 10H^+ = K^+ + Fe^{2+} + 2Mg^{2+} + Al^{3+} + 3H_4SiO_4$$

As can be seen from the above reactions. both the dissolution reaction or the conversion to clays of primary silicate minerals consume acid and cause the pH to rise. To overcome the acid consumption by the rock and maintain low pH values, large amounts of acid (at least initially) must be added to the leach solution. In addition to consuming large amounts of acid, a reduction in permeability could occur as a result of stoichiometric precipitation of silica and clays.

The presence of high concentrations of ferric iron could result in the formation of jarosite, or "basic ferric sulfate":

$$(6)\quad K^{+} + 3Fe^{3+} + 6H_2O + 2SO_4{}^{2-} + KFe_3(OH)_6(SO_4)_2 + 6H^{+}$$

or

$$(7)\quad 4Fe^{3+} + 10H_2O + SO_4{}^{2-} = Fe_4(OH)_{10}SO_4 + 10H^{+}$$

The precipitation of these minerals could result in a decrease in permeability and also could coat the chalcopyrite and thus remove it from contact with the solution.

SOLUTION-SILICATE INTERACTIONS

Minerals -

Silica Polymorphs - Silica (SiO_2) exists in several polymorphs (Deer, Howie, and Zussman, 1966). This discussion shall be limited to three of the polymorphs, namely α-quartz, "β-cristobalite" and amorphous silica. Of these three, α-quartz has the lowest free energy and is the least soluble silica polymorph at 25° C. Based on strictly thermodynamic considerations of the reaction below (Helgeson, 1969);

$$(8)\quad SiO_{2\,(qtz)} + 2H_2O = H_4SiO_{4\,(aq)} \qquad \log K = -4.00$$

defining the activity of the solid phase as one and assuming an activity of unity for water, the above expression reduces to;

$$(9)\quad \log a_{H_4SiO_{4\,(aq)}} = -4.00$$

or 6 ppm as SiO_2 ($\gamma_{H_4SiO_4}$ = 1). Observation of natural waters at surface conditions show that supersaturatuon with respect to quartz is extremely common (Siever, 1957, Garrels and Christ, 1965, p. 361, and Popp, Smith, and Laquer, in prep). Previous work done by Beane and Popp (in press) and Riese (1978) show that both acidic and basic solutions used for solution mining become supersaturated with respect to quartz.

There is disagreement over the free energy value of amorphous silica as is shown by the reaction and data given below:

$$(10) \quad SiO_{2\,(am)} + 2H_2O = H_4SiO_{4\,(aq)}$$

log K = -2.72 Walther and Helgeson (1970)
= -2.97 Mel'nik (1972)
= -3.02 Robie and Walbaum (1968)
= -2.65 Ulbrich and Merino (1974)
= -2.96 Robie, Hemingway, and Fisher (1978)

From the above data the log K values for "amorphous" silica form two groups, one with a value of log K ∿ -3.0, and the other with a value of log K ∿ -2.7.

In order to reconcile the values for amorphous silica there are two possible explanations: 1) the value of log K = -2.7 is supersaturated with amorphous silica, or 2) the value of log K = -3.0 is for an ordered (cryptocrystalline) polymorph of SiO_2. The second explanation is much more plausible than the first as the values of Robie and Walbaum (1968) and Robie, Hemingway and Fisher (1978) were based on SiO_2 glass which could have been somewhat ordered.

Data from Beane and Popp (in press) and Popp (personal communication) indicated that log $a_{H_4SiO_4}$ for all copper leach solutions in which the pH was approximately four had values of -3.0 or less. Work by Riese (1978) dealing with laboratory scale solution mining of uranium had maximum values of $10^{-3.0}$ m for aqueous silica. This investigator also found that the upper limit of silica solubility was $10^{-3.0}$. The above observations and the observations of Garrels and Christ (1965, p. 361) indicate that the maximum activity of silica in a solution is not controlled by amorphous silica, but rather by some ordered phase. This could be an explanation of the log K = -3.0 values for amorphous silica discussed earlier. Because of the good agreement between the observed values of maximum silica activity ($10^{-3.0}$) and the value predicted by Walther and Helgeson (1977) for "β-cristobalite;

(11) $SiO_{2\,(crist)} + 2H_2O = H_4SiO_4$ $\qquad$ $\log K = -3.01$

$\log a_{H_4SiO_4} = -3.01$

the thermodynamic data and also the molar volume of "β-cristobalite", will be used for the ordered silica phase. Throughout this introductory discussion the maximum solubility of silica will be assumed to be controlled by "β-cristobalite" (cryptocrystalline?).

Pyrophyllite - The stability of pyrophyllite in preference to kaolinite at 25° C in the presence of an aqueous solution is dependent upon the activity of silica in the solution by the following reaction:

(12) $Al_2Si_4O_{10}(OH)_2 + 5H_2O = Al_2Si_2O_5(OH)_4 + 2H_4SiO_4$

Using free energy data for kaolinite from Helgeson (1969) and for pyrophyllite from Ulbrich and Merino (1974), log K_{eq} for the above reaction is

-5.79. Calculating the activity of H_4SiO_4, defining $a_{solids} = 1$ and assuming unit activity for water, yields:

(13a) $2\log a_{H_4SiO_4} = -5.79$

(13b) $\log a_{H_4SiO_4} = -2.90$

This indicates that pyrophyllite will not form if the maximum silica activity is controlled by "β-cristobalite".

Biotite - Biotite is a ternary solid solution of three ideal end members; phlogopite ($KMg_3AlSi_3O_{10}(OH)_2$), annite ($KFe_3^{2+}AlSi_3O_{10}(OH)_2$), and proton deficient oxyannite ($KFe_3^{3+}AlSi_3O_{12}(H_{-1})$) (Beane, 1972). Beane (1972) has shown that the binary solid solution between annite and phlogopite is nearly ideal. He has also indicated that the biotite formed in the potassic alteration zone of porphyry copper deposits contains none or only a small mole fraction of PD oxyannite (Beane, 1974). Based on the above information biotite will be assumed to be a binary solid solution of annite and phlogopite. Furthermore, for simplicity in modeling, the Fe^{2+} component will initially be ignored.

Mineral Stability (Activity-Activity) Diagrams - The stability of minerals in the presence of an aqueous phase can be represented graphically in terms of the activity of aqueous silica and the activity ratio of a cation to the hydrogen ion ($\log \frac{a_{K^+}}{a_{H^+}}$, $\log \frac{a_{Mg^{2+}}}{(a_{H^+})^2}$, etc.) (Garrels and Christ, 1965, pp. 359-362). Mineral stability diagrams used in this paper are constructed such that aluminum is conserved in solid phases. In a review and re-interpretation of kinetic work, Helgeson (1971) indicated that mass transfer among silicates and an aqueous phase is accomplished by the mobilization of alkali metal and alkaline earth elements in addition to silica out of the reacting mineral grain. The solution reacts with the aluminum rich rind (gibbsite or boehmite) to form an alteration mineral. For example the following reaction of albite to montmorillonite can be considered:

$$(14)\quad 7NaAlSi_3O_8 + 20H_2O + 6H^+ = 3Na_{.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 10H_4SiO_4 + 6Na^+$$

$$(15)\quad \log \frac{(a_{MONT})^3\ (a_{H_4SiO_4})^{10}\ (a_{Na^+})^6}{(a_{ALB})^7\ (a_{H_2O})^{20}\ (a_{H^+})^6} = \log K$$

By defining the activity of the solid phases as unity and assuming a value of unity for water, the law of mass action statement for the above reaction reduces to:

$$(16)\quad \log \frac{a_{Na^+}}{a_{H^+}} = \frac{\log K - 10 \log a_{H_4SiO_4}}{6}$$

The above expression defines the equilibrium boundary between albite and pure Na-montmorillonite on a mineral stability diagram such as Figure 1.

Using available thermodynamic data (Helgeson, 1969, Walther and Helgeson, 1977, Ulbrich and Merino, 1974, and Nesbitt, 1977), summarized in appendix A, mineral stability diagrams in terms of $\log \frac{a_{Na^+}}{a_{H^+}}$ vs $\log a_{H_4SiO_4}$ (Figure 1), $\log \frac{a_{K^+}}{a_{H^+}}$ vs $\log a_{H_4SiO_4}$ (Figure 2), and $\log \frac{a_{Mg^{2+}}}{(a_{H^+})^2}$ vs $\log \frac{a_{K^+}}{a_{H^+}}$ at fixed activity of dissolved silica (Figure 3), have been prepared.

Mineral Stability diagrams are useful in predicting what mineral phase or phases are in equilibrium with a solution of known composition.

FIGURE 1

The system Na_2O-Al_2O_3-SiO_2-H_2O in the presence of an aqueous phase at 25° C and one atmosphere pressure in terms of $\log \frac{a_{Na^+}}{a_{H^+}}$ and $\log a_{H_4SiO_4}$.

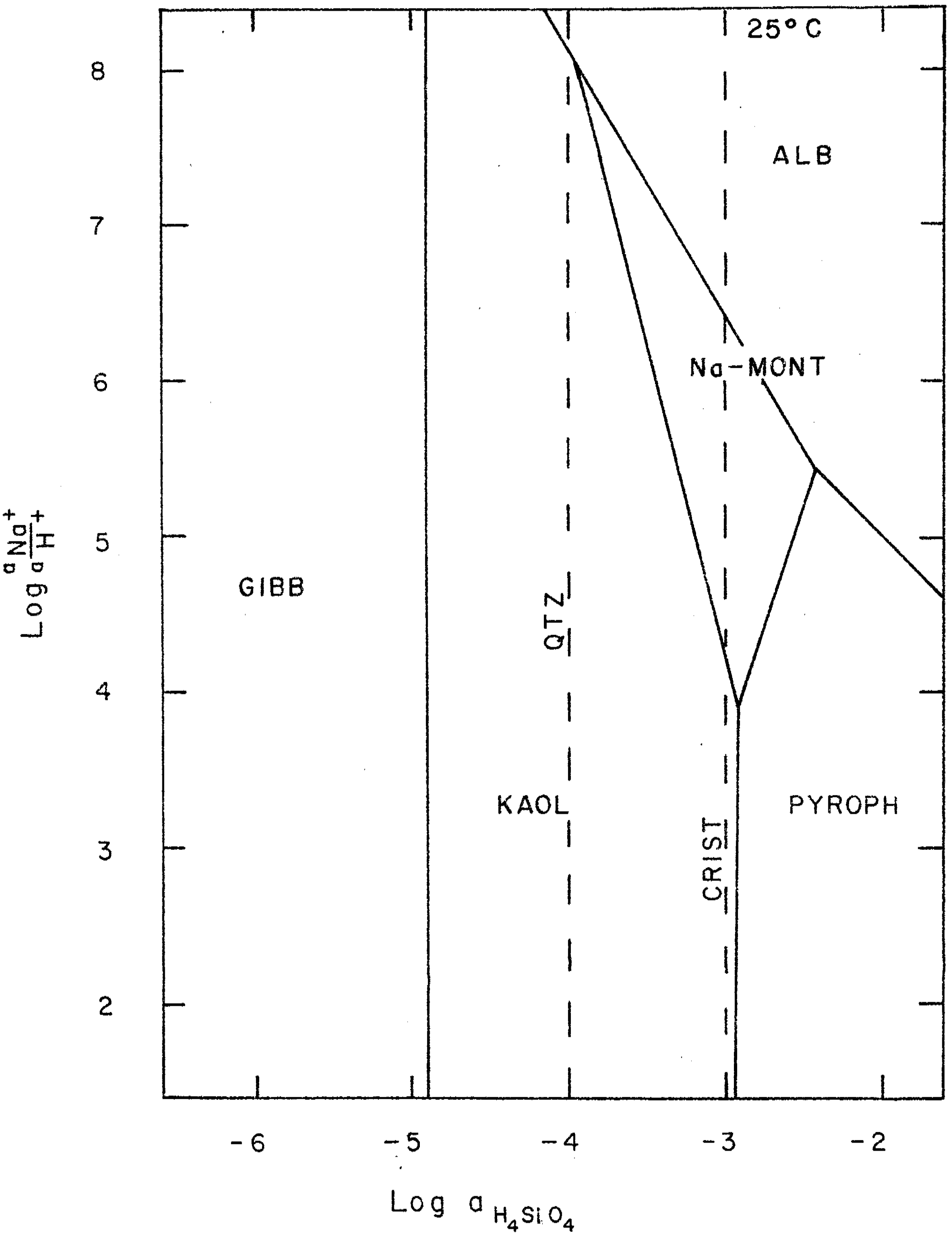

25° C
ALB
Na-MONT
GIBB
QTZ
KAOL
CRIST
PYROPH
8
7
6
5
4
3
2
-6
-5
-4
-3
-2
$\mathrm{Log}\ \frac{a_{Na^+}}{a_{H^+}}$
$\mathrm{Log}\ a_{H_4SiO_4}$

FIGURE 2

The system K_2O-Al_2O_3-SiO_2-H_2O in the presence of an aqueous phase at 25° C and one atmosphere pressure in terms of $\log \frac{a_{K^+}}{a_{H^+}}$ and $\log a_{H_4SiO_4}$.

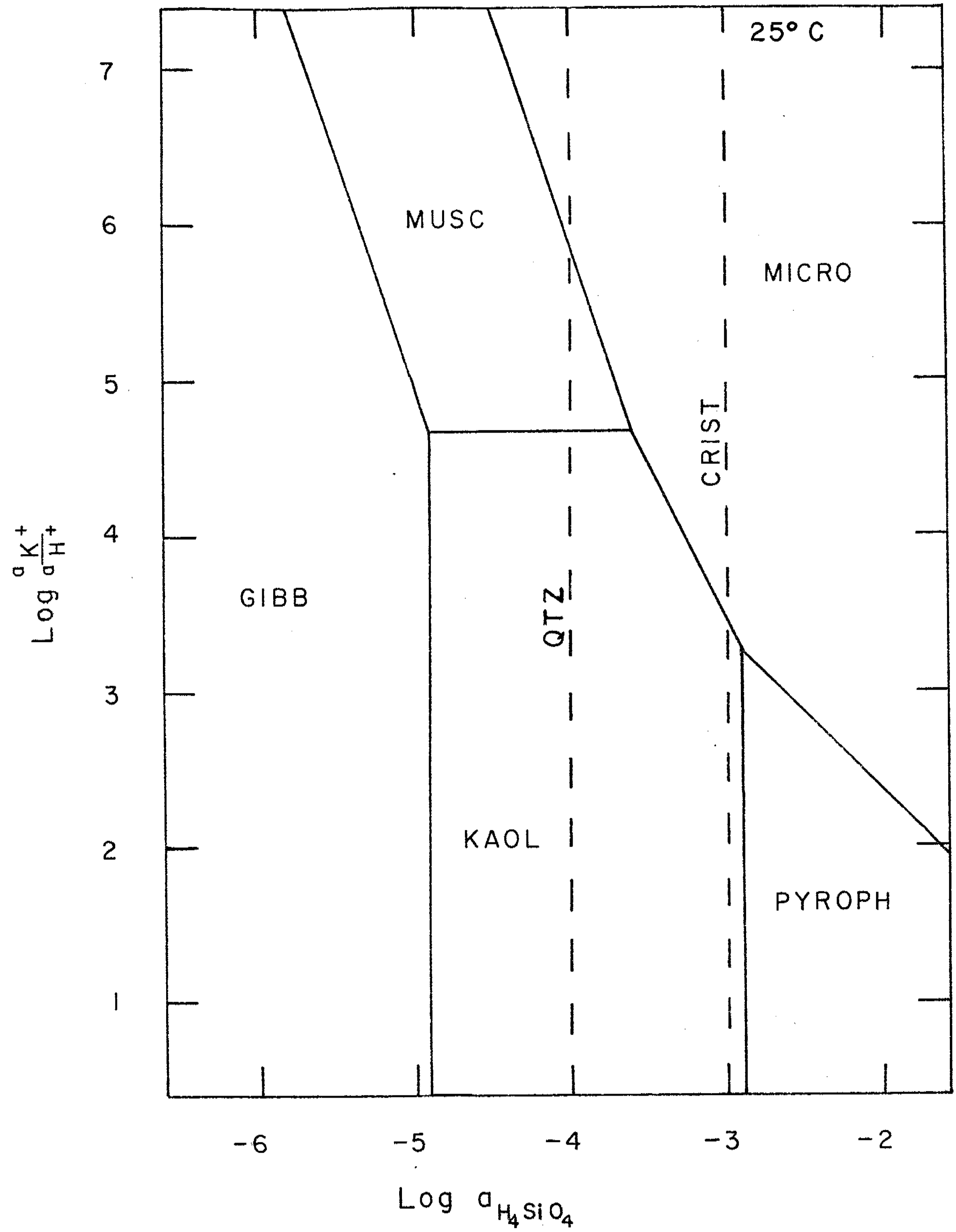
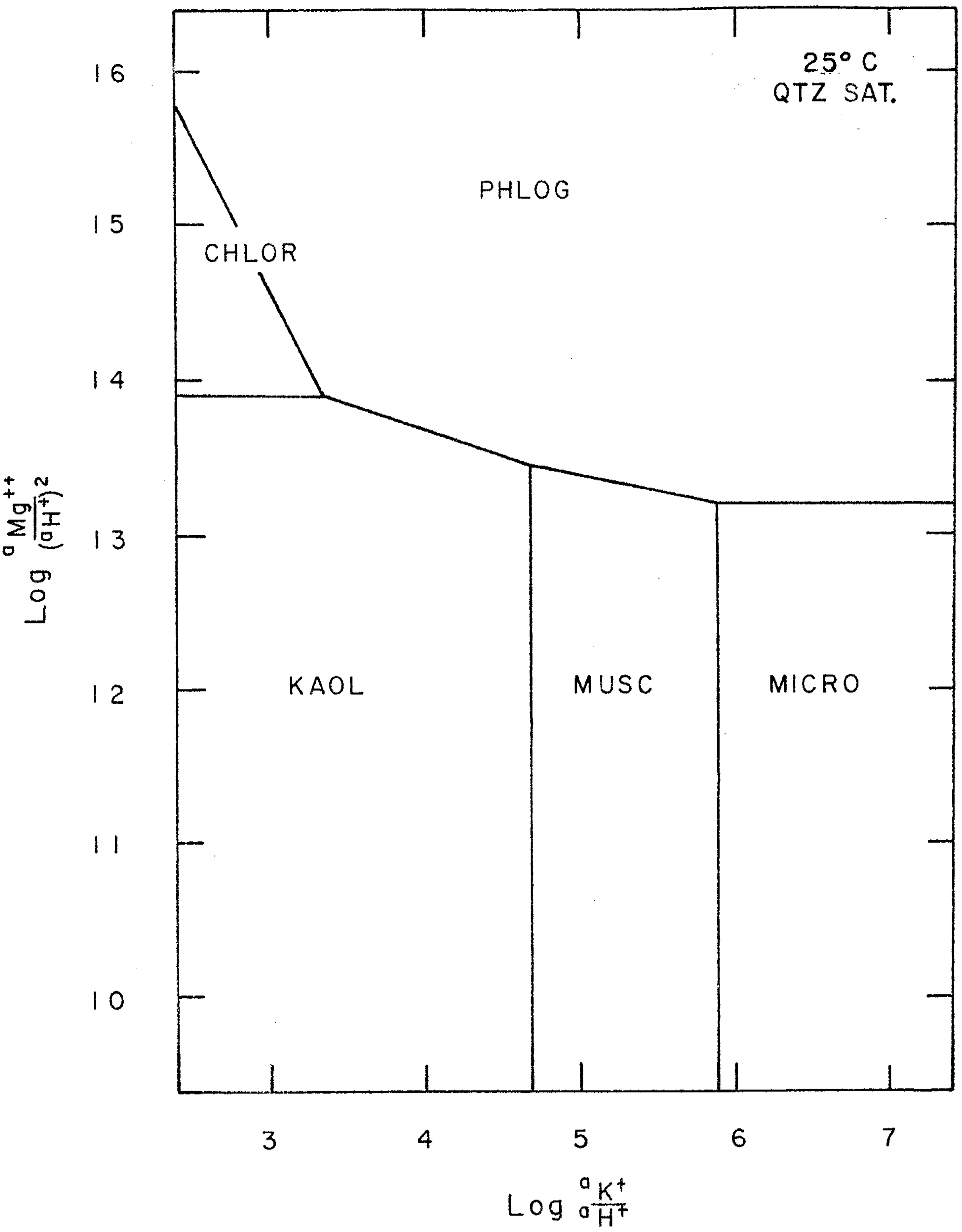

25° C
MUSC
MICRO
CRIST
GIBB
QTZ
KAOL
PYROPH
7
6
5
4
3
2
1
-6
-5
-4
-3
-2
$\log \frac{a_{K^+}}{a_{H^+}}$
$\log a_{H_4SiO_4}$

FIGURE 3

The system K_2O-MgO-Al_2O_3-SiO_2-H_2O in the presence of an aqueous phase and quartz at 25° C and one atmosphere pressure in terms of $\log \frac{a_{K^+}}{a_{H^+}}$ and $\log \frac{a_{Mg^{2+}}}{(a_{H^+})^2}$.


25° C
QTZ SAT.
PHLOG
CHLOR
KAOL
MUSC
MICRO
16
15
14
13
12
11
10
3
4
5
6
7
$\mathrm{Log}\ \frac{a_{Mg^{++}}}{(a_{H^+})^2}$
$\mathrm{Log}\ \frac{a_{K^+}}{a_{H^+}}$

The use of these diagrams, however, requires conversion of concentration to activity by the use of stoichiometric individual ion activity coefficients ($\dot{\gamma}_i$) by the relationship:

(17) $a_i = \dot{\gamma}_i \times m_i$

where a_i equals the activity of *ith* species considering solvent-ion interaction and ion pair formation and m_i is the total molality of the *ith* species.

Irreversible Reactions - Helgeson and others (Helgeson, 1968, Helgeson, Garrels and MacKenzie, 1969, and Helgeson, Brown, Nigrini, and Jones, 1970) have outlined methods by which systems containing a mineral and an aqueous phase in heterogeneous disequilibrium can be evaluated as the system moves to heterogeneous equilibrium (homogeneous equilibrium among solutions species was assumed at all times).

Beane and Popp (in press) have applied the above mentioned method to copper bearing rock from Tyrone, New Mexico, assuming sericite (muscovite) to be the most reactive mineral. The two rocks (Pinto Valley and Duval-Sierrita) used in this study, unlike the Tyrone rock, contained biotite. It has been shown that biotite is one hundred times more reactive than other silicate gangue minerals in porphyry type copper deposits (Cathles and Apps, 1975). Because of this, with the aid of a computer, the interaction of the biotite bearing copper ore and an acid solution can be modeled, as described by Helgeson (1968), assuming disequilibrium between biotite (phlogopite) and an acid solution, and assuming an open system.

If a ground water with a pH equal to 8.4, magnesium concentration of 24 ppm, potassium concentration of 2.22 ppm, and dissolved silica concentration of 36 ppm were acidified with sulfuric acid to a pH of two it would plot at point A on Figure 4. This solution is clearly out of equilibrium with phlogopite, and even though the projected solution composition plots in the kaolinite stability field, kaolinite is not stable as the aluminum activity is not high enough to allow the formation of kaolinite from the solution. As a result phlogopite will hydrolize by the following reaction:

(18) $KMg_3AlSi_3O_{10}(OH)_2 + 10H^+ = K^+ + 3Mg^{2+} + Al^{3+} + 3H_4SiO_4$

As can be seen fron the above reaction, the solution will increase in potassium, magnesium, aluminum, and dissolved silica, and move towards point B.

At point B the solution becomes saturated with "β-cristobalite" ($\log{}_{H_4SiO_4} = -3.01$) and this mineral phase will precipitate via the following reaction:

(19) $KMg_3AlSi_3O_{10}(OH)_2 + 10H^+ = Al^{3+} + 3Mg^{2+} + K^+ + 3SiO_2 + 3H_2O$

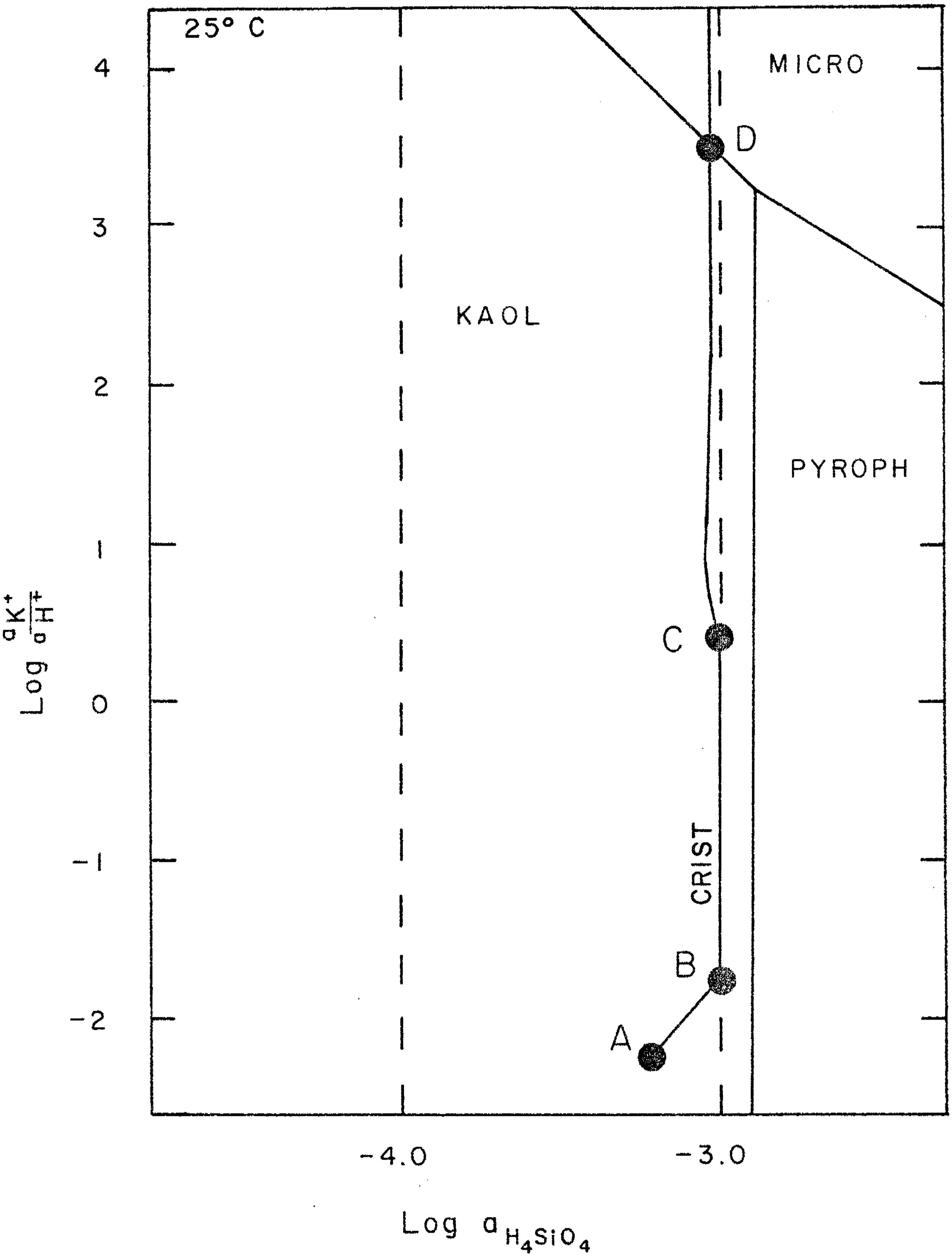
As the phlogopite continues to dissolve at fixed silica activity, the solution composition moves to point C (Figure 4). At this point the solution has a pH of 3.43 and an aluminum concentration of $10^{-2.96}$ which is high enough to allow formation of kaolinite by the reaction:

(20) $2KMg_3AlSi_3O_{10}(OH)_2 + H_2O + 14H^+ = 2K^+ + 6Mg^{2+} + Al_2Si_2O_5(OH)_4$
$+ 4H_4SiO_4$

Although the above reaction indicates that the silica content of the

FIGURE 4

Projection onto a log $\frac{a_{K^+}}{a_{H^+}}$ vs log $a_{H_4SiO_4}$ diagram of solution compositions resulting from the irreversible reaction of phlogopite with an acid solution as described in text. The upper limit of silica solubility is controlled by "β-cristobalite". Curvature of the path projected from point C to point D is exaggerated for clarity. Point D of this figure represents the same solution as point D on Figure 5.


25° C
MICRO
D
KAOL
PYROPH
C
CRIST
B
A
4
3
2
1
0
-1
-2
Log $\frac{a_{K^+}}{a_{H^+}}$
-4.0
-3.0
Log $a_{H_4SiO_4}$

solution will increase, "β-cristobalite" will not form because of the stoichiometric precipitaion of kaolinite by the following reaction:

(21) $2Al^{3+} + 2H_4SiO_4 + H_2O = Al_2Si_2O_5(OH)_4 + 6H^+$

The results of the reactions (20) and (21) will be that the silica content will initially decrease, reach a minimum value of $10^{-3.05}$, and then increase to a maximum of $10^{-3.03}$ as the homogeneous precipitation becomes less significant. Upon continued reaction the solution will reach point D (Figure 4). At point D the solution has a silica concentration of $10^{-3.03}$ molal, a pH of 6.4 and a $\log \frac{a_{K^+}}{a_{H^+}}$ of 3.54. Figure 5 is a $\log \frac{a_{Mg^{2+}}}{(a_{H^+})^2}$ vs $\log \frac{a_{K^+}}{a_{H^+}}$ diagram with the activity of silica fixed at $\log a_{H_4SiO_4}$ equal to -3.03. Point D on this diagram (Figure 5) corresponds to point D of Figure 4. As the solution continues to react with phlogopite, microcline will form by the reaction:

(22) $KMg_3AlSi_3O_{10}(OH)_2 + 6H^+ = KAlSi_3O_8 + 3Mg^{2+} + 4H_2O$

Continued reaction of phlogopite with the solution would result in increase of the $\log \frac{a_{Mg^{2+}}}{(a_{H^+})^2}$ and the $\log \frac{a_{K^+}}{a_{H^+}}$ until point E is reached. At point E the solution has a pH of 7.83 and a value of $\log \frac{a_{Mg^{2+}}}{(a_{H^+})^2}$ of 13.20 and is in equilibrium with phlogopite. Table 3 lists the chemical composition of the solution at points A, B, C, D, and E (Figures 4 and 5). As can be seen from Table 3, the initial acid solution reacted with phlogopite resulting in increased concentration of potassium, magnesium and

FIGURE 5

Projection onto a $\log \frac{a_{Mg^{2+}}}{(a_{H^+})^2}$ vs $\log \frac{a_{K^+}}{a_{H^+}}$ diagram of solution compositions resulting from the irreversible reaction of phlogopite with solution described in text. The activity of silica in the solution is $10^{-3.03}$ molal. Point D of this figure represents the same solution as point D on Figure 4.

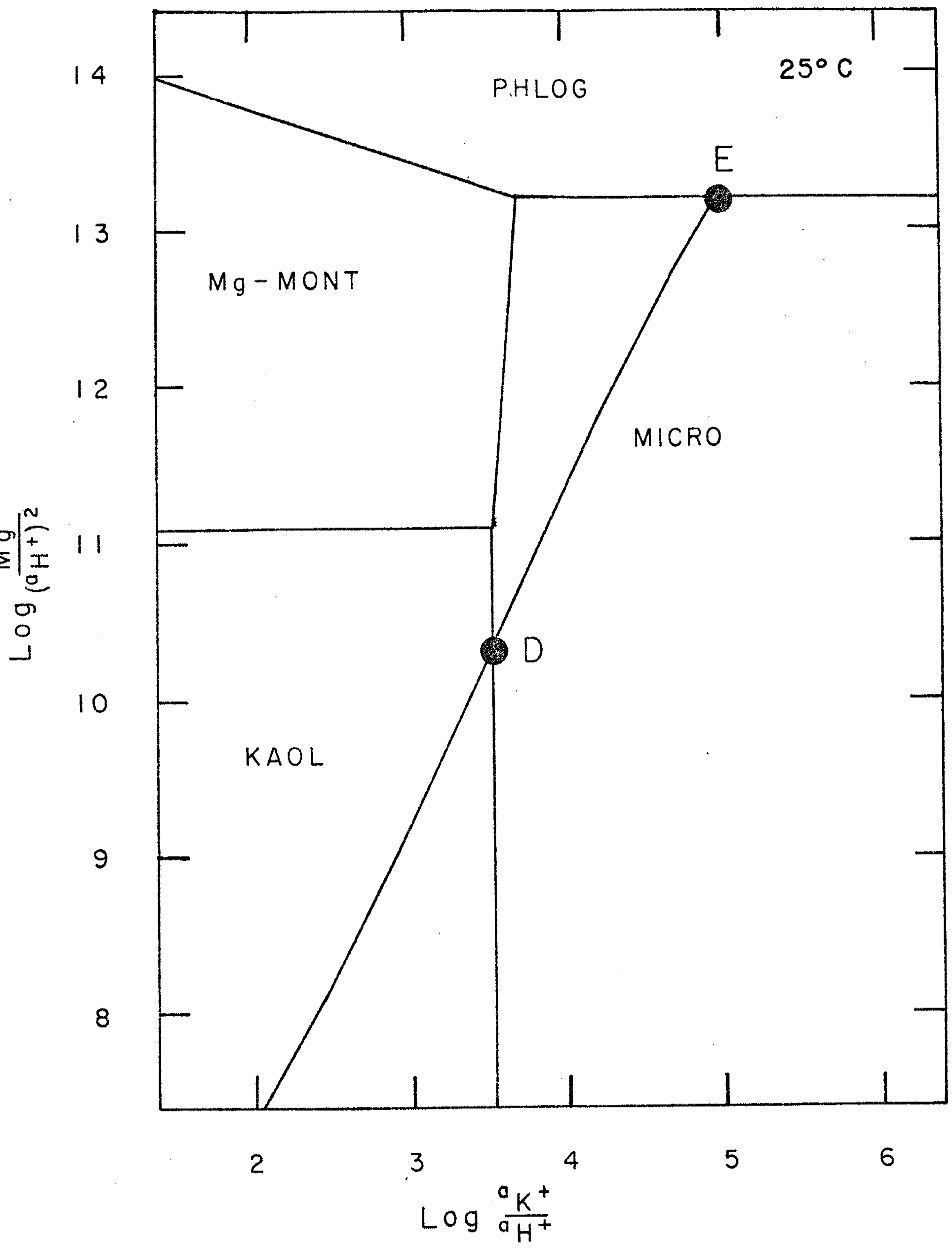

25° C
PHLOG
Mg - MONT
MICRO
KAOL
E
D
14
13
12
11
10
9
8
2
3
4
5
6
$\log \frac{a_{Mg^{++}}}{(a_{H^+})^2}$
$\log \frac{a_{K^+}}{a_{H^+}}$

TABLE 3

Summary of solution compositions for an acid leach solution reacting irreversibly with phlogopite.

Values calculated as described in text.

POINT	pH	Mg	K	$\sum$ Al	$\log \frac{a_{K^+}}{a_{H^+}}$	$\log \frac{a_{Mg^{2+}}}{(a_{H^+})^2}$	$\log a_{H_4SiO_4}$
A	2.01	9.8×10^{-4}	6.4×10^{-5}	4.3×10^{-5}	-2.26	.78	-3.22
B	2.06	1.4×10^{-3}	1.9×10^{-4}	1.3×10^{-4}	-1.74	1.02	-3.01
C	3.43	4.2×10^{-3}	1.1×10^{-3}	1.1×10^{-3}	.42	4.26	-3.01
D	6.40	5.8×10^{-3}	1.7×10^{-3}	1.4×10^{-10}	3.54	10.33	-3.03
E	7.83	5.8×10^{-3}	1.7×10^{-3}	1.1×10^{-10}	4.99	13.20	-3.03

silica. Also, and more importantly, there would be a tremendous reduction in the acid content of the leaching solution.

Table 4 summarizes the molar and volume changes of the solid phases. This table shows that the alteration of phlogopite would result in a zone of decreased volume of the solid (resulting in increased porosity) as a result of leaching all the cations, leaving only cristobalite. The leached zone is followed by a zone of decreased porosity (and permeability) as a result of the conversion of phlogopite to kaolinite. The permeability of the upper portion of the zone could be further reduced by the stoichiometric precipitation of kaolinite.

The predicted changes in solution composition according to this model could differ from those observed experimentally for several reasons, among them being solid solution of phlogopite with annite, formation of a metastable phase (for example, halloysite instead of kaolinite), and kinetic effects. In addition, if consideration for sulfate would have been made, alunite would have formed between point B and C (Figure 4) by the reactions (Hemley, Hostetler, Gude and Mountjoy, 1969):

$$(23)\quad 3KMg_3AlSi_3O_{10}(OH)_2 + 2SO_4^{2-} + 24H^+ = KAl_3(OH)_6(SO_4)_2 + 2K^+ + 9Mg^{2+} + 9SiO_2 + 12H_2O$$

and

$$(24)\quad K^+ + 3Al^{3+} + 2SO_4^{2-} + 6H_2O = KAl_3(OH)_6(SO_4)_2 + 6H^+$$

These reactions would result in a lower $\frac{K^+}{Mg^{2+}}$ ratio than for the nonsulfate case, and Mg-montmorillonite could form instead of microcline during the last stages of alteration.

TABLE 4

Summary of moles of minerals produced and consumed and volume changes of the "rock" for the irreversible reaction of an acid solution and biotite, as described in text.

	moles reacted / kg H_2O				(cm^3)
SEGMENT	phlogopite	cristobalite	kaolinite	K-feldspar	$^*\Delta$ volume
A-B	-1.26×10^{-4}	--	--	--	-1.89×10^{-2}
B-C	-9.55×10^{-4}	2.87×10^{-3}	--	--	-6.93×10^{-2}
C-D	-5.20×10^{-4}	--	8.02×10^{-4}	--	1.86×10^{-3}
D-E	-1.96×10^{-7}	--	--	1.96×10^{-7}	-8.07×10^{-6}
total	-1.60×10^{-3}				

* - molar volumes from Robie, Hemingway, and Fisher (1978)

+ produced

- consumed

A great deal of work involving the alteration of silicate minerals to clays has been done (Ebel and Hower, 1975, Iglesia, Martin-Vivaldt and Aguayo, 1976, Oberlin and Couty, 1970, Kittrick, 1970, and Wolast, 1967).

The study by Schoen, White, and Hemley (1974) of the clay minerals resulting from descending acid water at Steamboat Springs, Nevada, because of its similarity of conventional acid leaching, will be discussed in some detail.

In their paper dealing with argillization by descending acid water, Schoen and others (op. cit.) suggested sources for sulfuric acid which are:

1) Formation of sulfuric acid from hydrogen sulfide dissolved at depth under pressure which is oxidized as the ascending thermal meteoric water approaches the surface via

$$H_2S + 2O_2 = 2H^+ + SO_4^{2-}$$

2) Formation of sulfuric acid at the surface from native sulfur by the action of *Thiobacillus* bacteria via

$$S^0 + \frac{3}{2}O_2 + H_2O = 2H^+ + SO_4^{2-}$$

These acid waters are nearly at atmospheric temperatures, and thus can well represent the type of water rock interaction expected with prolonged solution mining.

Drill hole GS-7 of the study by Schoen and others (op. cit.) was in an altered biotite bearing granodiorite. The observed alteration sequence was very similar to that calculated earlier in this paper, and is as follows:

1) The upper 111 feet consist of opal (β-cristobalite to fifty feet becoming amorphous below) and residual quartz. From 111 to 114 feet amorphous opal fills all interstices.

2) At the water table alunite predominates with small amounts of residual quartz.

3) Kaolinite increases from 120 to 132 feet as alunite decreases.

4) Below 132 feet alunite is gone and the mineral assemblage consists of 14 Å montmorillonite which may have magnesium in the inter layer site, illite, residual quartz, orthoclase, and plagioclase as well as sporadic biotite.

Schoen and others (op. cit.) feel that the presence of montmorillonite and illite below 133 feet indicates that the effects of hypogene alteration supercedes those of supergene alteration (descending acid). However, the same alteration could result from a descending acid solution that is near neutral because of kaolinization of the rock above. From the above discussion, it is very clear that the interaction of a strong acid solution with phlogopite (or other silicates) will result in production of silica and clay minerals with a marked decrease in the acidity, and hence ability to leach and transport copper, of the solution.

Effects of Biotite Solid Solution - Biotite exists as a solid solution with Mg^{2+}, Fe^{2+}, and Fe^{3+} substituting in trioctahedral sites. The stability of biotite in an acid solution is very dependent upon the composition of the biotite (Beane and Popp, 1976).

Beane (1972) has shown that the solid solution of annite (KFe_3^{2+}-$AlSi_3O_{10}(OH)_2$) and phlogopite ($KMg_3AlSi_3O_{10}(OH)_2$) is nearly ideal. He has also shown that the introduction of ferric iron coupled with the loss of a proton results in a large negative excess free energy of solution for the solid solution, especially in biotite with low mole fraction of phlogopite.

As has been shown earlier (Irreversible Reactions) phlogopite is in equilibrium with microcline with a log $\frac{a_{\mathrm{Mg}^{2+}}}{(a_{\mathrm{H}^+})^2}$ of 13.2. Beane and Popp (in press) have shown that stabilization of minerals in acid leaching solutions are possible by the addition of appropriate cations. Application of these concepts show that at leachable pH's (less than five) a minimum activity of $10^{3.2}$ molal Mg^{2+} is required to stabilize phlogopite in the presence of microcline. Conversion of the phase to some other magnesium mineral, for example montmorillonite, would require approximately 1 molal Mg^{2+} to be stable in the presence of kaolinite, microcline and cristobalite, at a pH of five. However, the conversion of biotite (phlogopite) to montmorillonite is not feasible as the alteration via the following reaction consumes approximately seven moles of hydrogen ion for every mole of phlogopite reacted:

$$(25)\quad 14\mathrm{KMgAlSi_3O_{10}(OH)_2} + 96\mathrm{H}^+ = 6\mathrm{Mg_{.167}Al_{2.33}Si_{3.67}O_{10}(OH)_2} + 14\mathrm{K}^+ + 41\mathrm{Mg}^{2+} + 16\mathrm{H_2O} + 20\mathrm{H_4SiO_4}$$

An alternative reaction to the conversion of biotite to a more acid-stable magnesium mineral would be the conversion of the magnesium rich biotite to an iron rich biotite by the following reaction:

$$(26)\quad \mathrm{KMg_3AlSi_3O_{10}(OH)_2} + 3\mathrm{Fe}^{2+} = \mathrm{KFe_3}^{2+}\mathrm{AlSi_3O_{10}(OH)_2} + 3\mathrm{Mg}^{2+}$$

Annite in equilibrium with microcline has an ion activity ratio of $\frac{a_{\mathrm{Fe}^{2+}}}{(a_{\mathrm{H}^+})^2}$ equal to $10^{8.4}$. A solution with a pH of five would require a ferrous iron concentration of $10^{-1.6}$ molal to be stable. This stability can be depressed even further by making the biotite a member of the PD oxy-annite-annite solid solution by the oxidation-reduction reaction:

(27) $KFe_3{}^{2+}AlSi_3O_{10}(OH)_2 + \frac{1}{2}O_2 = KFe_3{}^{3+}AlSi_3O_{12} + H_2O$

The introduction of 20 mole per cent PD oxyannite would result in the biotite-microcline equilibrium being shifted to a value of $\log \frac{a_{Fe^{2+}}}{(a_{H^+})^2}$ of less than eight (using an activity for annite of 0.05, Beane, 1972). Because the above reactions involve only substitution of ions in tri-octahedral sites, no strictural rearrangement in the tetrahedral layers will occur. This means that only a minute amount of the biotite would be involved in the reaction as the result of early formation of a stable annite surface layer. This substitution would also result in the biotite-microcline equilibrium being shifted to a much lower value because the Mg^{2+} componet would be removed from contact with the leach solution.

Idealized Leach Solution Compositions - It has been shown that a leach solution could be stabilized with respect to kaolinite and microcline at a pH of four, and still transport large amounts of copper (Beane and Popp, in press). Using a pH of four and calculating the amount of potassium needed to stabilize kaolinite and microcline in the presence of cristobalite yields a potassium ion activity of $10^{-0.5}$ or a concentration of KCl of approximately 0.35 molal.

Work by Beane and Popp (Popp, personal communication) with smectite containing sandstone uranium ores indicate that the equilibrium $\frac{Na^+}{K^+}$ ratio for microcline-Na-montmorillonite-solution is twenty to one. Assuming the ideal value of $\log \frac{a_{K^+}}{a_{H^+}}$ is equal to four (Beane and Popp, in press) coupled with the above information for smectite, a pH of four would require twenty molal NaCl and one molal KCl to meet the above ratio. However, at a pH of five, two molal NaCl, and 0.1 molal KCl would satisfy the twenty to one ratio assuming that the silica activity will rapidly adjust to equilibrium conditions. At a pH of five and low sulfate activity, the solution should still transport $10^{-0.8}$ molal copper (Garrels and Christ, 1965). Table 5 summarizes the two idealized leach solutions.

Summary of Theoretical Rock-Water Interactions - Several statements regarding the interaction of an acid leach solution with the gangue minerals present in porphyry copper ores can be made:

1) "β-cristobalite" or amorphous aluminosilicates limit the solubility fo H_4SiO_4 in the leach solution.
2) Pyrophyllite will not be an alteration product if "β-cristobalite" controls H_4SiO_4 activity.
3) Biotite is the most reactive gangue mineral in porphyry copper ores.
4) Interaction of a strongly acidic solution with phlogopite (biotite) results in the formation of clays and a substantial decrease in solution pH.
5) Conversion of magnesium rich biotite to a ferrous rich biotite followed by oxidation of the ferrous iron increases the acid stability of biotite.
6) Leach solutions capable of transporting greater than 10,000 ppm of copper can be equilibrated with rock-forming minerals found in porphyry copper ores.

TABLE 5

Summary of the idealized leach solution compositions for the solution mining of copper.

	pH	K^+	Na^+	H_4SiO_4
K	4	.35m	-	$10^{-3.0}$m
Na + K	5	.1m	2m	*

* allowed to equilibrate with the rock.

EXPERIMENTAL

In order to experimentally evaluate the forgoing theoretical solution-rock interactions, small scale (1.5-2 Kg) "bench top" leach tests were performed using the Pinto Valley and Duval-Sierrita rocks. Four columns were run, the conditions for each column are summarized below:

1) A column of Pinto Valley and a column of Duval-Sierrita rocks were leached with no attempt to equilibrate the solutions within the rocks. The pH's of these two columns were adjusted daily to approximately 2.0, to simulate normal leaching practices.
2) A column of Duval-Sierrita rock was initially treated with a ferrous iron solution ($Fe^{2+} = 10^{-2}$ molal) in order to form a surface layer of annite on the biotite present in the rock. The rock was then treated with hydrogen peroxide to oxidize the annite, and thus make it more acid stable. A leach solution that was near equilibrium with microcline, kaolinite and "β-cristobalite" (pH = 4, KCl = 0.5 molal, and $H_4SiO_4 = 10^{-3.5}$ molal) was used to leach the rock.
3) Finally, a column of Pinto Valley ore was leached using a solution containing a 20:1 $\frac{Na^+}{K^+}$ ratio (pH = 5, NaCl = 2 molal, and KCl = 0.1 molal) to evaluate the effect of the sodium component of the rock on solution pH and leaching efficiency.

During the course of the experiment, the solutions were analyzed periodically for aluminum, calcium, magnesium, potassium, sodium, silica, copper, iron, Eh, pH, sulfate, and chloride. Total solution concentrations were charge balanced with sulfate (unstabilized acid columns) or chloride (all others), and converted to free ion activities of the individual solution species, considering solvent--solvent, solvent--ion (Debye-Huckel), and ion--ion (complexing) interactions using a computer code described by Beane and Popp (in press). It employed conservation of mass and homogeneous equilibrium among solution species to calculate distribution and activities of solution species. Converting concentration to activity allows the use of mineral stability diagrams (such as Figures 1 and 2) containing ion activities as variables to represent solution compositions. The equation used to calculate activity coefficients (γ_i) was a two term Debye-Huckel expression (Helgeson, 1969):

$$(28) \quad \log \gamma_i = \frac{-Az_i^{\,2}\,\bar{I}^{\frac{1}{2}}}{1 + \mathring{a}_i B\,\bar{I}^{\frac{1}{2}}} + B\cdot\bar{I}$$

where A and B are constant dependent upon temperature, density, and dielectric constant of the solvent; z_i is the charge of the species; $\mathring{a}_i$ is the hydrated radius of the species; and $\bar{I}$ is the true ionic strength, considering complex ion formation. B• is the deviation function and may be determined from:

$$(29) \quad B\cdot = \frac{\log \gamma_{\pm} + A|z_1 z_2|I^{\frac{1}{2}} / (1 + \mathring{a}BI^{\frac{1}{2}})}{I}$$

where $\gamma_{\pm}$ is the mean ionic activity coefficient. Comparison of this equation to the Stokes-Robinson equation (Stokes and Robinson, 1948), which is as follows;

$$(30) \quad \log \gamma_{\pm} = -\frac{A|z_1 z_2|I^{\frac{1}{2}}}{1 + \mathring{a}BI^{\frac{1}{2}}} - \frac{h}{\nu}\log a_{H_2O} - \log\,[1 - 0.018m(\nu - h)]$$

where ν is the number of ions per mole of solute, h is the average number of water molecules coordinated to ν ions in solution, and m is equal to the dissociated molality of the electrolyte, shows that:

$$(31)\ B \cdot I = -\frac{h}{\nu} \log a_{H_2O} - \log [1 - 0.018m(\nu - h)]$$

In a solution in which one electrolyte contributes the majority of the ionic strength, the activity of water and the number of coordinated waters is a function soley of the supporting electrolyte. Evaluation of the deviation functions for the concentrations of the supporting electrolytes used in this study (NaCl or KCl) yield values of 0.041 (Helgeson, 1969) for NaCl and 0.014 (Stokes and Robinson, 1948) for KCl.

Solution species with a charge of zero (H_4SiO_4) were assigned an activity coefficient equivalent to an activity coefficient for H_2CO_3 in a sodium chloride solution of equal ionic strength (Helgeson, 1969).

The leaching columns in this study were made of either glass or lucite with six cm inside diameter and a length of approximately 50 cm and were mounted vertically. The leach solutions were circulated to the top of the columns using a Cole-Parmer tubing pump and allowed to gravity drain into a filter flask reservoir. The solution was circulated for approximately eight hours a day. The ore was crushed with a quarter-inch jaw crusher and one to two kilograms of crushed ore were used in each column. The columns were closed via rubber stoppers with glass tubing inserted to permit solution flow. The bottom of the columns contained a glass wool "plug" to prevent the fine materials from being washed from the columns.

The pH was measured with a glass electrode against a saturated calomel reference using an Orion model 601 Ionanalyzer pH meter. The Eh was measured with a platinum electrode versus the saturated calomel using a Corning model 5 pH meter. The metal ions and dissolved silica were determined using a Perkin-Elmer model 403 Atomic Absorption Spectrophotometer. Sulfate was determined gravimetrically as barium sulfate (Rand, Green, and Taras, 1976, p 495-496). Chloride was determined by titration with mercuric nitrate (op. cit., p 304-306), but was later done using a chloride (Orion model 94-17) ion specific electrode with a double junction (Orion model 90-02) reference electrode and an Orion model 601 Ionanalyzer.

The whole rock chemistry for the Duval-Sierrita rock was done using hydrofluoric acid pressure digestion that was stabilized with boric acid (see method A in Appendix B). The whole rock chemistry of the Pinto Valley ore was done, with modification, by the method of Shapiro and Brannock (1962) (see method B in Appendix B). Sulfur was determined in both ores gravimetrically, as barium sulfate, using a sodium carbonate fusion (Volbroth, 1967, pp. 131-133). Water was determined as loss on ignition to 800° C. Carbon dioxide determinations were done by gas displacement (Leo, 1963).

CLAY MINERALOGIES

Clay separations and mineralogies were done on the two ores in their original conditions as received and again done after the leaching experiments were completed. The clay separations were done by the method of Caroll (1970) with modification (see Appendix C).

Two columns (Pinto Valley unstabilized and Duval-Sierrita unstabilized) required chemical treatments in order to keep the clay minerals from flocculating. The clay and silt materials, after being separated from the crushed ore, were treated with boiling EDTA according to the method of Bodine and Fernalld (1973) to remove the gypsum (?) that had formed during leaching.

CLAY MINERAL IDENTIFICATION

Four clay minerals were identified by X-ray diffraction using the clay separations that were done. These minerals were identified on the following criteria:

Illite - Illite was identified on the basis of a strong 10 Å (001) diffraction and a weak 5 Å (002) diffraction. This mineral identified as illite showed no changes in peak location by heating or glycolation.

Smectite - Descrete smectite was observed at 15.2 Å and 12.3 Å. Upon glycol treatment these peaks shifted to 17 Å and upon heating to 350° C were displaced to 10 Å. Based on basal d spacings the 15.2 Å smectite was concluded to be from calcium ions in exchangeable sites. The 12.3 Å smectite was concluded to be from a monovalent cation, probably sodium, in the exchangeable sites

Kaolinite - Kaolinite was identified on the basis of the 7.15 Å (001) and the 3.75 Å (002) peaks. These peaks did not change locations with glycol treatment. Heating to 550° C resulted in the loss of the (002) peak and a reduced intensity for the (001) peak (see Figure 6). The 7.15 Å peak that remained after heating was attributed to the (002) peak of chlorite (also present in the clays).

Chlorite - Chlorite was characterized by peaks at 14 Å (001) and 4.7 Å (003) that did not shift upon glycolation or heating. Also the thermal integrity and presence of a 7 Å (002) peak after the kaolinite was destroyed indicated the presence of chlorite. Figure 7 is a trace of the X-ray diffractometer graph for the less than two micrometer fraction of

FIGURE 6

X-ray diffractometer diagrams of the Pinto Valley rock clay fraction, as received. This figure shows the effects of heating to 550° C on the (001) and (002) peaks of kaolinite.

Q - quartz
I - illite
K - kaolinite
C - chlorite

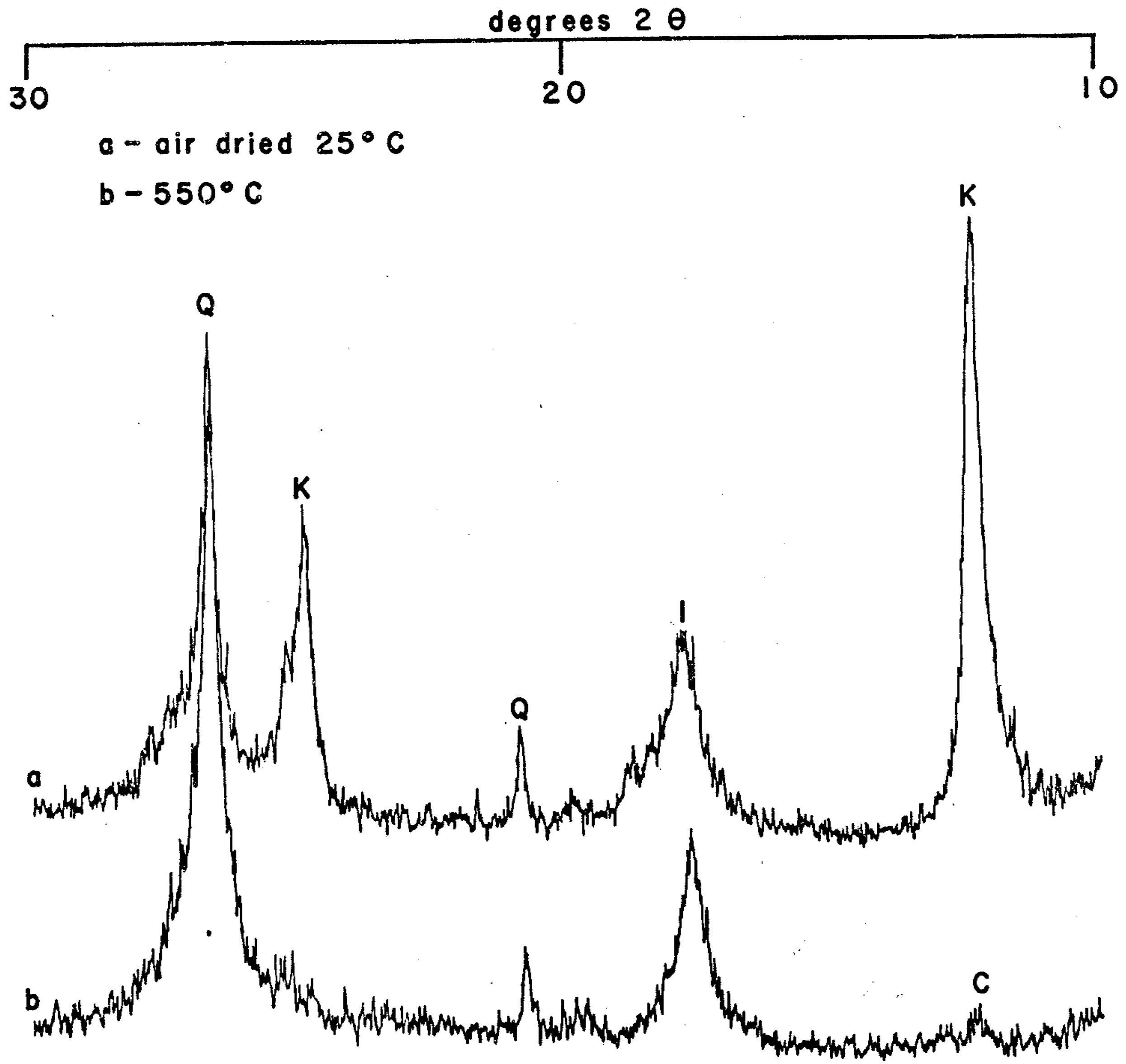
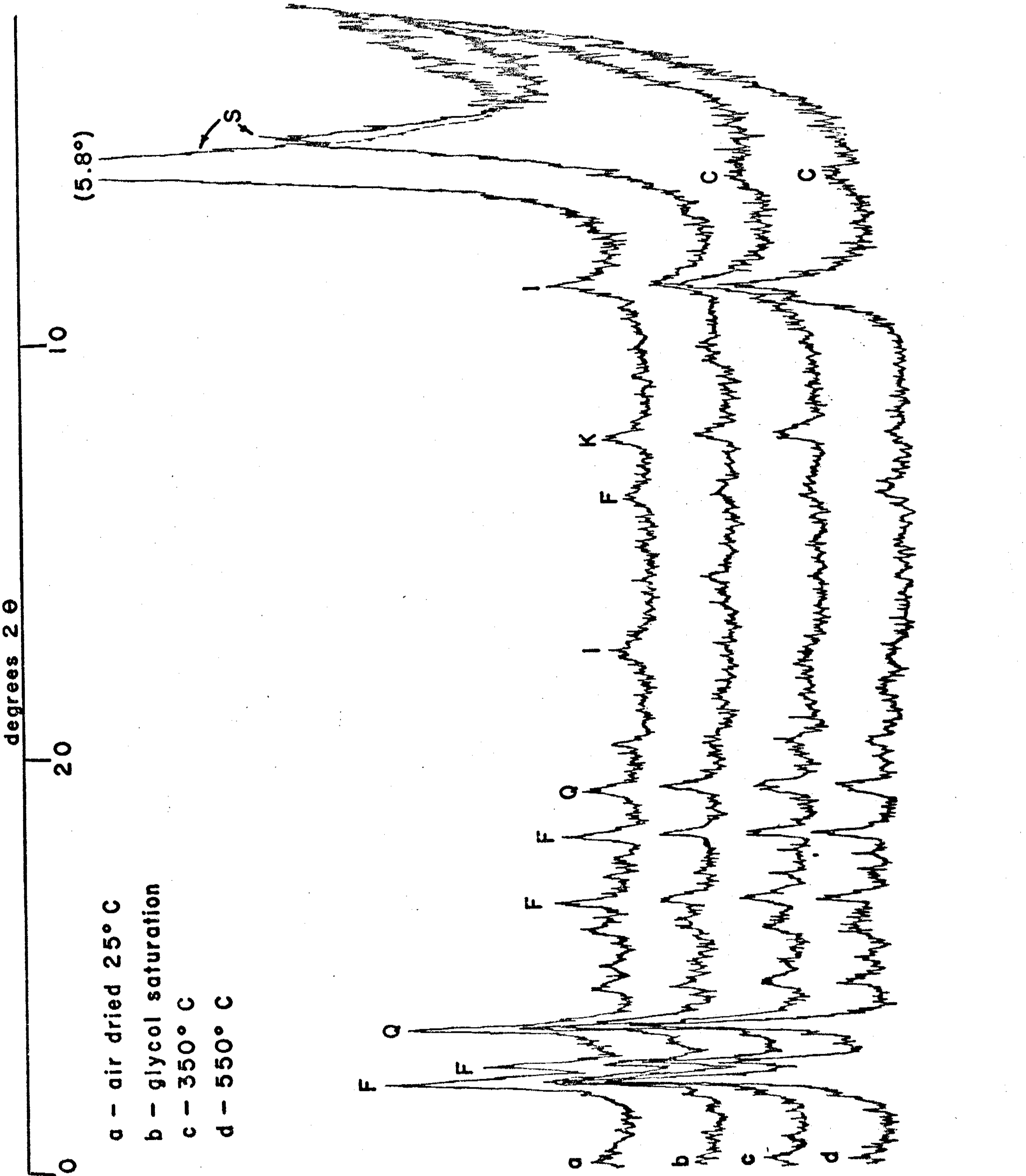

degrees 2 θ
30
20
10
a – air dried 25° C
b – 550° C
Q
K
Q
I
K
a
b
C

FIGURE 7

X-ray diffractometer diagrams of the Duval-Sierrita clay fraction, as received. This figure shows the effect of the treatments used for clay identification on the position and intensity of the peaks.

Q - quartz
I - illite
K - kaolinite
C - chlorite
S - smectite
F - feldspar


degrees 2 θ
30
20
10
a – air dried 25° C
b – glycol saturation
c – 350° C
d – 550° C
a
b
c
d
F
F
Q
F
F
Q
I
F
K
I
C
C
(5.8°)
S

the Duval-Sierrita rock, showing the effects of the treatments used on peak locations and intensities.

Rock mineralogy was done using a petrographic microscope and thin sections. Minerals were identified based on optical properties given by Kerr (1959) with plagioclase composition determined by Michel-Levy's method (op. cit. p. 258).

EXPERIMENTAL RESULTS

Tables 6, 7, 8, and 9 list the compositions of effluent solutions for the Duval-Sierrita acid leach (Table 6), the Duval-Sierrita potassium stabilized leach (Table 7), the Pinto Valley acid leach (Table 8), and the Pinto Valley sodium-potassium stabilized leach (Table 9). Tables 10, 11, 12, and 13 list ion activity ratios and activities of H_4SiO_4 for the solutions listed in Tables 6, 7, 8, and 9. Table 14 lists the clay mineralogies for the two original unaltered rocks, as well as the clay mineralogies for the four leached rocks.

TABLE 6

Effluent solution compositions for the Duval-Sierrita acid leached column. Values in ppm except Eh (mv) and pH.

DATE	K^+	Cu^{2+}	Fe	Al^{3+}	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	pH	Eh^*	SiO_2
09-20-76	113	1.3	.2	8	1450	570	73	80	4.27	675	75
10-11-76	63	2.6	.1	31	1695	700	59	64	4.07	835	114
10-25-76	80	45	.2	90	2156	410	50	57	3.89	735	159
11-17-76	80	70	1.3	150	2535	340	70	140	3.44	705	184
11-29-76	60	125	3.0	170	2691	271	90	60	3.21	775	210
01-18-77	80	330	180	340	5210	340	150	60	2.32	975	319
06-21-77	57	800	250	500	5263	1100	250	33	2.16	910	300

* - corrected for saturated calomel reference electrode.

TABLE 7

Effluent solution compositions for the Duval-Sierrita potassium stabilized leach. Values in ppm except Eh (mv) and pH.

DATE	K^+	Cu^{2+}	Fe	Al^{3+}	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	pH	Eh^*	SiO_2
09-10-76	18,800	8.5	0.9	4.3	1464	700	7	48	4.55	655	39
09-22-76	16,300	19	4.0	9.5	1066	660	10	98	3.89	665	69
10-06-76	14,400	180	0.3	8.6	1202	510	11	33	3.90	705	56
10-15-76	11,300	140	0.8	13.4	1200	420	9	25	4.30	655	56
10-22-76	8,200	360	0.3	15	1235	370	8.2	102	4.10	695	51
10-25-76	9,200	400	1.6	21	1699	470	11.7	34	4.16	645	49

* - corrected (see Table 6).

TABLE 8

Effluent compositions for the Pinto Valley acid leach. Values in ppm except Eh (mv) and pH.

DATE	K^+	Cu^{2+}	Fe	Al^{3+}	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	Eh^*	pH	SiO_2
08-03-78	6	251	790	530	6279	299	111	10	795	2.25	101
08-04-78	6	241	810	540	6366	312	113	10	785	2.30	124
08-07-78	7	235	780	530	6617	334	113	11	775	2.28	133
08-08-78	6	242	860	560	6642	348	118	11	785	2.25	139
08-10-78	6	235	820	580	6740	391	135	10	795	2.20	144

* - corrected (see Table 6).

TABLE 9

Effluent compositions for the Pinto Valley sodium-potassium stabilized leach. Values in ppm except Eh (mv) and pH.

DATE	K^+	Cu^{2+}	Fe	Al^{3+}	SO_4^{2-}	Cl^-	Ca^{2+}	Mg^{2+}	Na^+	pH	Eh*	SiO_2
08-04	6,900	45	.5	2	502	61,900	280	11	32,000	4.90	625	2
08-08	7,400	54	.3	1	983	58,800	290	11	33,000	5.10	625	21
08-30	7,700	70	.2	2	564	63,000	280	11	37,000	5.15	635	30
09-27	7,700	90	.4	2	570	68,000	310	11	34,000	4.70	615	28
------------ new solution ------------												
09-30	4,700	20	.1	1	148	68,000	160	1.7	41,000	4.40	595	28
10-17	4,500	24	.4	1	290	68,000	74	1.9	42,000	5.15	625	26
10-21	4,200	41	.6	1	226	67,000	38	2.3	42,000	5.14	625	26
10-26	4,600	47	.9	1	242	68,000	93	2.2	42,000	5.15	620	28
10-31	4,300	50	.8	0	238	70,00	100	2.2	43,000	4.77	660	30
11-04	4,400	70	.7	1	321	70,000	120	2.3	43,000	5.00	635	30
11-07	4,300	80	.7	0	354	69,000	101	2.3	43,000	4.90	635	30

* - corrected (see Table 6).

TABLE 10

Ion activity ratios and activities of H_4SiO_4 for solutions listed in Table 6 (Duval-Sierrita acid leached).*

DATE	$\log \frac{a_{K^+}}{a_{H^+}}$	$\log a_{H_4SiO_4}$
09-20-76	1.64	-2.90
10-11-76	1.16	-2.72
10-25-76	1.03	-2.57
11-17-76	.62	-2.50
11-29-76	.26	-2.46
01-18-77	-.55	-2.25
06-21-77	-1.89	-2.26

* - The initial solution was distilled H_2O with pH adjusted to two with H_2SO_4.

TABLE 11

Ion activity ratios and activities of H_4SiO_4 for solutions listed in Table 7 (Duval-Sierrita potassium stabilized).

DATE	$\log \frac{a_{K^+}}{a_{H^+}}$	$\log a_{H_4SiO_4}$
initial solution	3.50	-3.44
09-10-76	4.02	-3.13
09-22-76	3.41	-2.89
10-06-76	3.28	-2.99
10-15-76	3.58	-3.00
10-22-76	3.25	-3.04
10-25-76	3.35	-3.05

TABLE 12

Ion activity ratios and activities of H_4SiO_4 for solutions listed in Table 8 (Pinto Valley acid leach).*

DATE	$\log \frac{a_{K^+}}{a_{H^+}}$	$\log \frac{a_{Na^+}}{a_{H^+}}$	$\log a_{H_4SiO_4}$
08-03-78	-1.77	-1.32	-2.74
08-04-78	-1.72	-1.28	-2.65
08-07-78	-1.67	-1.25	-2.62
08-08-78	-1.77	-1.29	-2.60
08-10-78	-1.83	-1.38	-2.59

* - The initial solution was distilled H_2O with pH adjusted to two with H_2SO_4.

TABLE 13

Ion activity ratios and activities of H_4SiO_4 for solutions listed in Table 9 (Pinto Valley sodium-potassium stabilized).

DATE	$\log \frac{a_{K^+}}{a_{H^+}}$	$\log \frac{a_{Na^+}}{a_{H^+}}$	$\log a_{H_4SiO_4}$
08-04	3.92	4.86	-4.29
08-08	4.15	5.08	-3.29
08-30	4.22	5.18	-3.13
09-27	3.77	4.77	-3.15
------------------------ new solution ------------------------			
09-30	3.26	4.48	-3.15
10-17	3.99	5.23	-3.19
10-21	3.95	5.22	-3.19
10-26	4.00	5.24	-3.15
10-31	3.59	4.87	-3.12
11-04	3.83	5.10	-3.12
11-07	3.72	5.00	-3.12

TABLE 14

Clay mineralogies of Pinto Valley and Duval-Sierrita rocks as received and after leaching

PINTO VALLEY

As Received	Acid	Na-K Stabilized
12.3 Å smectite	12.3 Å smectite	12.3 Å smectite
kaolinite	kaolinite	kaolinite
illite	illite	illite
chlorite	chlorite	chlorite

DUVAL-SIERRITA

As Received	Acid	K Stabilized
15.2 Å smectite	12.3 Å smectite	
kaolinite	kaolinite	kaolinite
illite	illite	illite
chlorite	chlorite	chlorite

DISCUSSION AND CONCLUSIONS

BIOTITE

One of the concerns of this study was the effect of biotite on leach solution compositions. The Duval-Sierrita potassium stabilized column was initially treated with ferrous iron and subsequently oxidized with hydrogen peroxide as described earlier (see Experimental). No attempt was made to stabilize the biotite in any of the other leach columns. Comparison of the magnesium concentrations in the four leach solutions (Tables 6, 7, 8, and 9) shows that the two acid columns had much higher magnesium concentrations than either the Duval-Sierrita potassium stabilized or the Pinto Valley sodium-potassium stabilized columns. High magnesium concentrations in the acid column were expected as a result of the continual hydrolysis of the biotite. The magnesium concentrations of the biotite treated column (Duval-Sierrita, table 7) and the Pinto Valley sodium-potassium stabilized column remained relatively constant and very low (less than 10^{-3} molal). Also when a new solution was added to the Pinto Valley sodium-potassium stabilized leach column (table 9, 9-30) the magnesium concentration approached 10^{-4} molal (one fifth the magnesium concentration of the original Pinto Valley solution). Possible reasons for the apparant stabilization of the solutions with magnesium are:

1) The solutions are stabilized with the biotite in the rock. The dissolution of pyrite in the Pinto Valley sodium-potassium stabilized column produced enough ferrous iron in the solution to replace magnesium on the biotite's surface, thus stabilization is via a natural mechanism.

2) The biotite is not stabilized with the solution, but in solutions with pH's in the range of four to five the rate at which the biotite hydrolyzes may be slow compared to the duration of the experiment and magnesium concentration could be controlled by the reaction of smectite with the solution. The magnesium reduction by a factor of five between the two sodium-potassium stabilized solutions used with the Pinto Valley ore could indicate that initially the high sodium solution reacted with the smectite present in the rock and reduced the mole fraction of the Mg-component via:

$$(32) \quad 2Na^+ + 6Mg_{.167}Al_{2.33}Si_{3.67}O_{10}(OH)_2 = Mg^{2+} + 6Na_{.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$$

When a new solution was added (Table 9, 9-30), the decreased activity of the Mg-smectite required a lower activity of magnesium for equilibrium to exist.

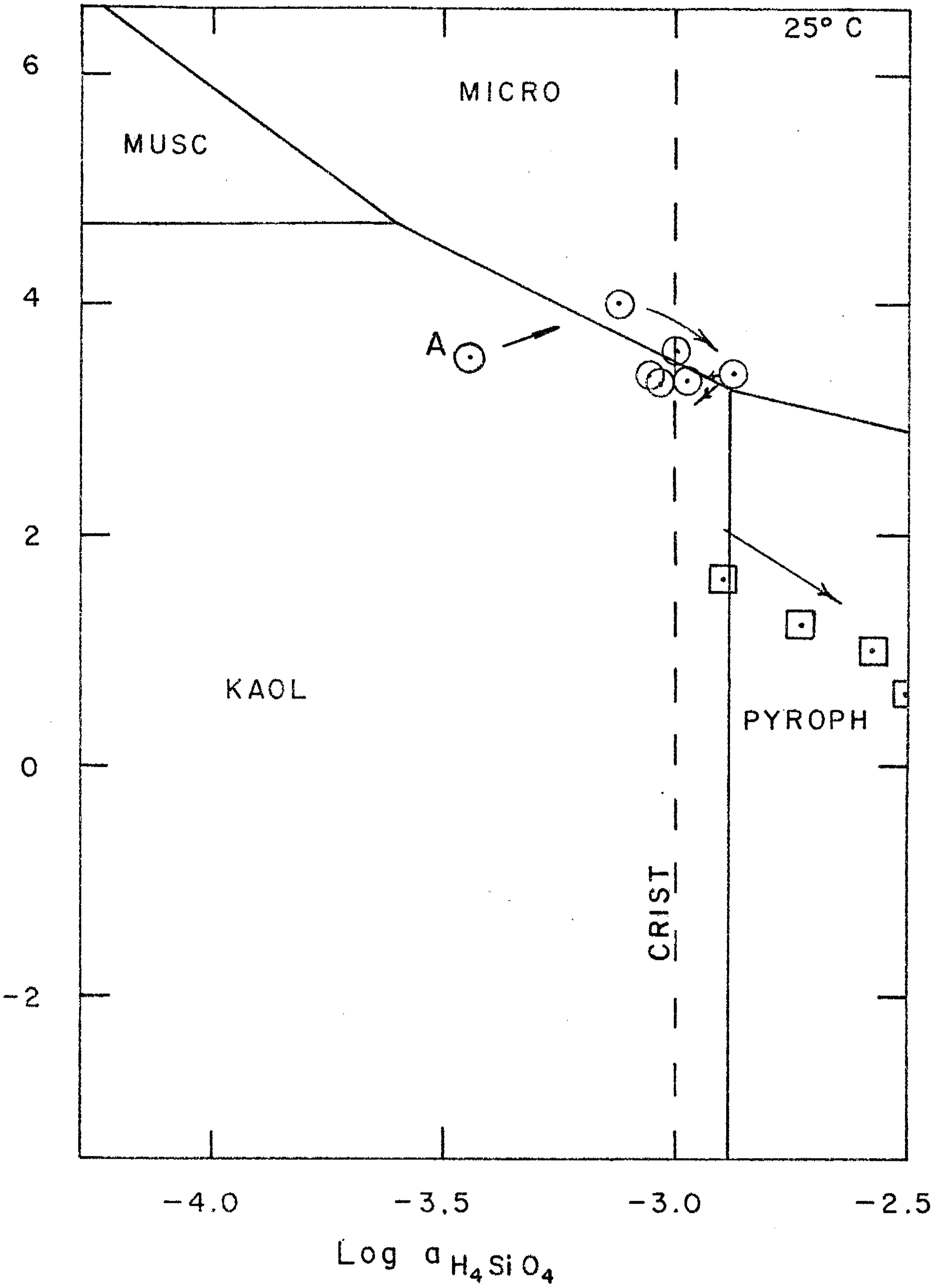
If the latter of these two reasons was true, it would mean that dump leaching of ores containing biotite can be carried out, with no attempt to stabilize the minerals with the leach solution, and with only minimal acid consumption, provided the pH is in the range of four to five if the kinetic problems of chalcopyrite leaching can be solved.

POTASSIUM STABILIZED LEACH

A solution with its composition adjusted near equilibrium with kaolinite, microcline, and "β-cristobalite" was used to leach the Duval-Sierrita rock. The log $\frac{a_{K^+}}{a_{H^+}}$ and log $a_{H_4SiO_4}$ information from Table 11 was plotted on an activity-activity diagram (Figure 8). The solution initially plotted at point A and was kept to a constant volume of 0.5 liter by the addition of distilled water after sampling. Because of the dilution

FIGURE 8

Plot of log $\frac{a_{K^+}}{a_{H^+}}$ and log $a_{H_4SiO_4}$ values for effluent solutions used to leach Duval-Sierrita rock. Circles correspond to potassium stabilized leach solution and squares correspond to the acid leach solution. Point A represents the initial solution composition.



25° C
MICRO
MUSC
KAOL
PYROPH
CRIST
A
6
4
2
0
-2
$\text{Log}\,\frac{a_{K^+}}{a_{H^+}}$
-4.0
-3.5
-3.0
-2.5
$\text{Log}\ a_{H_4SiO_4}$

factor, the potassium concentration (Table 7) fell to lower values as the experiment proceeded. Regardless of the dilution effect, the solution became slightly supersaturated with respect to "β-cristobalite" and then decreased to saturation with "β-cristobalite". The value for log $\frac{a_{K^+}}{a_{H^+}}$ increased initially (due to a rise in the pH) and then fell to values near the microcline-kaolinite stability boundary. Earlier it was suggested that biotite reacted very slowly with a solution in the pH range of four to five. The source of the increased silica in the solution therefore, would be from either the feldspars or the clays. Helgeson (1971) has suggested that the kinetics of silicates reacting with a solution follows a simple parabolic rate law at fixed pH. This would indicate a diffusion controlled mechanism for the reaction. Thus, minerals with increased surface area would have faster rates of reaction. This would tend to favor the clays, because of their large surface area, as the source of the silica, via the reaction:

$$(33)\quad 6Ca_{.167}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 2H^+ + 23H_2O = 7Al_2Si_2O_5(OH)_4 + 8H_4SiO_4 + Ca^{2+}$$

Also, since most of the original calcium is in the plagioclase, the Ca-montmorillonite in the Duval-Sierrita rock resulted from the alteration of plagioclase. The plagioclase probably has an outer rind of Ca-montmorillonite and this rind would therefore remove plagioclase from contact with the solution. Garrels (1967) has indicated that in the presence of biotite and plagioclase, microcline and quartz are relatively inert. Clay minerals, because of their size, are much more important in controlling solution chemistry than the feldspars and biotite in the pH range of four to five.

The aluminum concentration in the solution steadily rose. This rise may have resulted from the alteration of Ca-montmorillonite to kaolinite.

The aluminum activity may have been controlled by a reaction intermediate such as gibbsite (Helgeson, 1971). The formation of polymetric aluminum hydroxide solution species (Smith, 1971) may have resulted in erroneously high calculated aluminum activities. However, the solution apparently became supersaturated with respect to kaolinite.

SODIUM-POTASSIUM STABILIZED LEACH

A solution with a composition near equilibrium with Na-montmorillonite, kaolinite and microcline was used to leach one column of the Pinto Valley ore. The log $\frac{a_{K^+}}{a_{H^+}}$, log $\frac{a_{Na^+}}{a_{H^+}}$, and log $a_{H_4SiO_4}$ data (see Table 13) are plotted on Figures 9 and 10. The solution that was initially used (Table 9, 8-04) had a $\frac{Na^+}{K^+}$ ratio of eight to one. This solution, after a short time, was replaced with a solution containing a $\frac{Na^+}{K^+}$ ratio more near the twenty to one ratio observed by Beane and Popp (Popp, personal communication). Both solutions after a short period of time were in equilibrium with kaolinite, microcline and Na-montmorillonite. The sodium and the potassium in this column remained constant as both were initially added in high concentrations. The variations in magnesium concentrations were discussed earlier. The variations in Ca^{2+} (trend towards increase) is probably due to 1) the result of the exchange of sodium for calcium in the smectite present in the Pinto Valley rock, and 2) the slow conversion of plagioclase to montmorillonite or kaolinite. The aluminum concentrations listed in Table 9 are near the lower limit of detection for the method used.

FIGURE 9

Plot of log $\frac{a_{K^+}}{a_{H^+}}$ and log $a_{H_4SiO_4}$ values for effluent solutions used to leach Pinto Valley rock. Circles correspond to sodium-potassium stabilized leach solution and squares correspond to the acid leached solution.

A - 08-04 Table 13

B - 09-30 Table 13

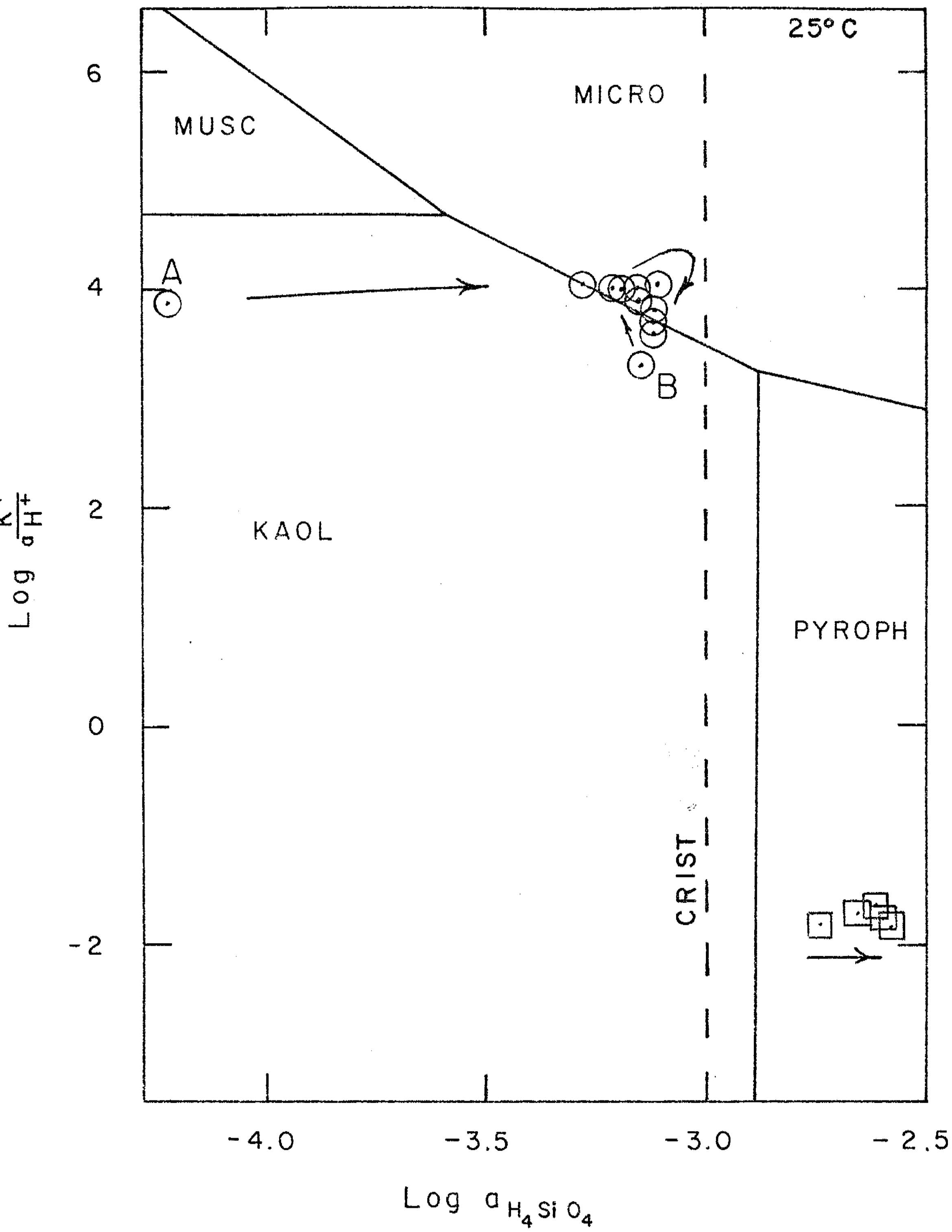
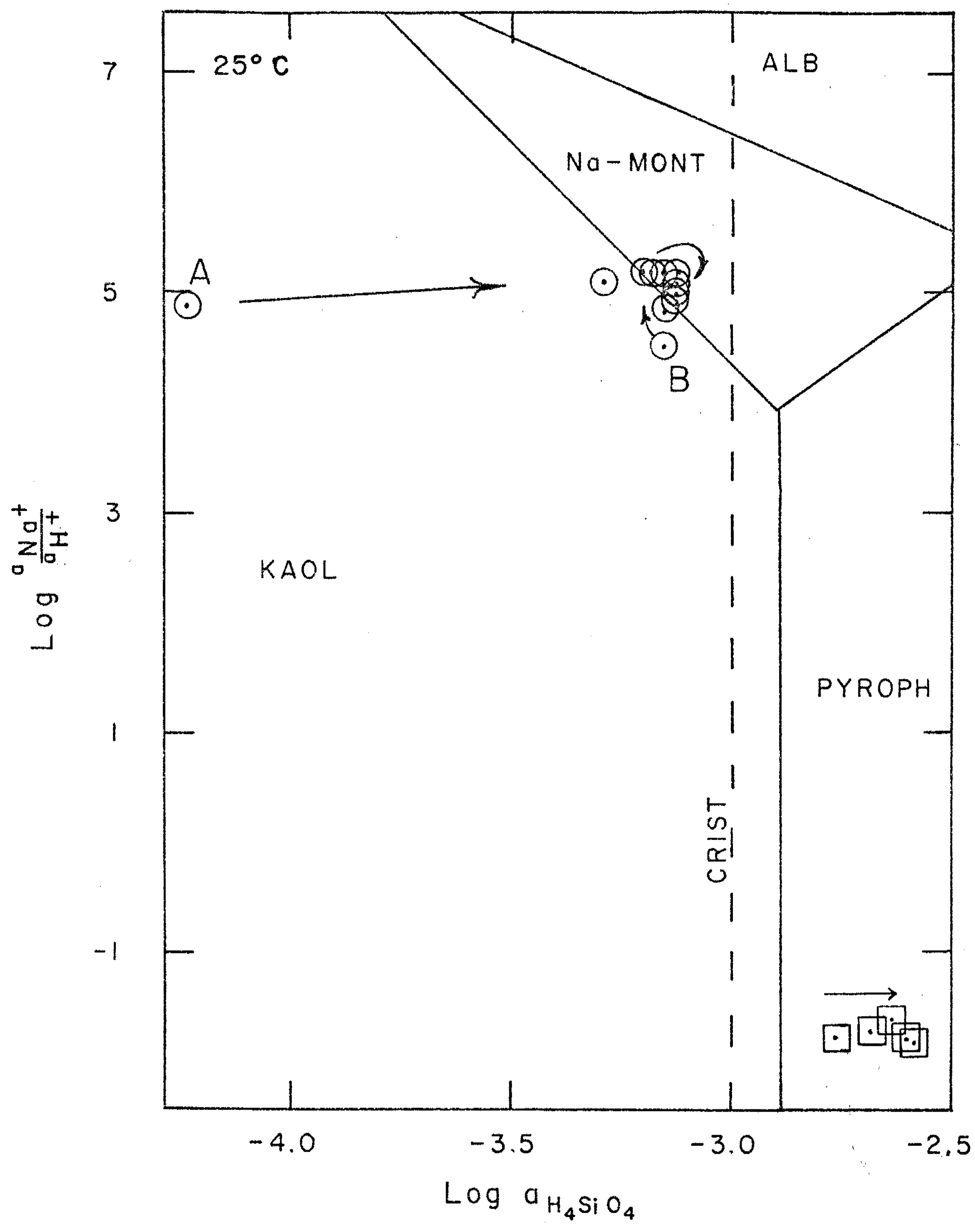

25° C
MUSC
MICRO
KAOL
PYROPH
CRIST
A
B
6
4
2
0
-2
-4.0
-3.5
-3.0
-2.5
Log $\frac{a_{K^+}}{a_{H^+}}$
Log $a_{H_4SiO_4}$

FIGURE 10

Plot of log $\frac{a_{Na^+}}{a_{H^+}}$ and log $a_{H_4SiO_4}$ values for effluent solutions used to leach Pinto Valley rock. Circles correspond to the sodium-potassium stabilized leach solution and squares correspond to the acid leached solution.

A - 08-04 Table 13

B - 09-30 Table 13


25° C
ALB
Na - MONT
A
B
KAOL
PYROPH
CRIST
7
5
3
1
-1
-4.0
-3.5
-3.0
-2.5
Log $\frac{a_{Na^+}}{a_{H^+}}$
Log $a_{H_4SiO_4}$

UNSTABILIZED ACID LEACH

The log $\frac{a_{K^+}}{a_{H^+}}$ and log $a_{H_4SiO_4}$ data for the Duval-Sierrita acid leach (see table 10) are plotted on Figure 8 (squares). As the solution was cycled, it moved towards progressively lower values of log $\frac{a_{K^+}}{a_{H^+}}$ and higher values of log $a_{H_4SiO_4}$. It passed from the kaolinite stability field into the pyrophyllite stability field and eventually became supersaturated with amorphous silica (log $a_{H_4SiO_4} = -2.72$). Supersaturation with respect to amorphous silica is due to the formation of colloidal silica, and since no method was found to successfully remove the colloidal silica, no reliable silica activities could be determined for the solutions with more than 60 ppm SiO_2 ("β-cristobalite").

The log $\frac{a_{K^+}}{a_{H^+}}$, log $\frac{a_{Na^+}}{a_{H^+}}$, and log $a_{H_4SiO_4}$ data for the Pinto Valley acid solution (Table 12) are plotted on Figures 9 and 10. Addition of one ml of concentrated H_2SO_4 to 0.5ℓ of the leach solution resulted in effluent pH's of approximately two. With this column, as with the Duval-Sierrita acid leach column, the silica activity became greater than allowed by amorphous silica.

In both of the acid leached columns the sodium and potassium concentrations remained relatively constant (the value of 140 ppm for Na on 11-17-76 in Table 6 was attributed to an analytical error). Aluminum concentrations of both solutions rose as the rock reacted with the acid solution. The calcium and magnesium concentrations were variable in the Duval-Sierrita acid leach, and steadily increased in the Pinto Valley acid leach. But in both cases magnesium concentrations were much higher in the final solution than in the initial solution, indicating the hydrolysis of magnesium minerals. The calcium activity of both solutions appeared to be controlled by saturation with gypsum.

CLAY MINERALOGY

Table 14 lists the mineralogy of the less than two micrometer fraction for the two rocks as received and also the mineralogy for all columns upon completion of leaching.

The clay mineralogy for the Duval-Sierrita rock leached with a potassium stabilized solution shows the loss of the 15 Å smectite peak. The loss of this peak was attributed to two things; 1) the alteration of Ca-smectite to kaolinite, as already discussed, and 2) the exchange of potassium for calcium resulting in the loss of the 15 Å peak as non-expandable illitic clays are formed.

The smectite in the Duval-Sierrita acid leach column showed a basal d-spacing of 12.3 Å. This spacing indicates the substitution of a monovalent cation (sodium or potassium) for calcium, or the early hydrolysis of the less acid-stable calcium smectite, leaving the monovalent smectite. It is known that smectite, through ion exchange, acts to buffer the potassium (and sodium?) contents found in soils (Grim, 1967, pp. 320-323). This buffering ability of the smectite may possibly account for the relatively constant concentrations of sodium and potassium in the Duval-Sierrita acid leach solution (see Table 6).

The Pinto Valley clay mineralogy shows no change in the kind of minerals present after leaching (Table 14). This was expected since the rock was leached with sodium-potassium stabilized solutions. As the solution composition was adjusted to equilibrium with sodium-montmorillonite, the Pinto Valley acid leached rocks also showed no change in clay mineralogy. The inability to do quantitative clay analysis makes changes in amounts of clay minerals very difficult to determine, unless the solutions are cycled long enough to eliminate a phase, or the minerals (smectites) undergo rapid cation exchange with the solution. No changes in the Pinto Valley acid leach were observed since the duration of this experiment was several weeks instead of several months.

"β-CRISTOBALITE"

"β-cristobalite" was not detected in any of the columns. Three possible reasons why this phase was not detected are 1) only a very small amount of the mineral need be present to fix the silica activity, and "β-cristobalite" may have been present in quantities too small to be detected by X-ray diffraction, or 2) the preparation of samples for X-ray required "washing" the materials with large quantities of water. This may have resulted in the hydrolysis of any small amounts of "β-cristobalite" present, or 3) an amorphous aluminosilicate, not "β-cristobalite", controlled the silica activity.

ORE MINERAL STABILITY

The primary copper mineral in both the Duval-Sierrita and Pinto Valley rocks was chalcopyrite. Chalcopyrite was not efficiently extracted by the stabilized leach solution. This is shown by the low amounts of copper extracted from the rocks (10 per cent after eighteen months). After the Duval-Sierrita acid column was neutralized, the rate of copper extraction increased (7 per cent in four months). A reason for this may be that the mechanism for the dissolution of chalcopyrite is dependent on the ability of the solution to transport iron. The Eh data for the Duval-Sierrita potassium stabilized and the Pinto Valley sodium-potassium stabilized leach solutions showed that the iron solubility was controlled by the precipitation of ferric hydroxide. Hence, the solution was capable of transporting only small amounts of iron.

The final X-ray mineralogy from the leach columns showed the presence of a "basic ferric sulfate" ("BFS"), $Fe_4(SO_4)(OH)_{10}$ (A.S.T.M. Card No. 19-630) in the Duval-Sierrita potassium stabilized column. This mineral was not observed in the acid column as the pH's of the solutions were low enough to allow the transport of the ferric iron. The Pinto Valley sodium-potassium stabilized column did not show "BFS", possibly because this column was run one-fifth as long as the Duval-Sierrita potassium stabilized column. Based on the presence of "BFS" and the low iron concentration of the two stabilized solutions (see Tables 7 and 9) it can be concluded that iron is conserved in solid phases. Assuming conservation of iron, reaction (1) can be rewritten:

$$(34)\quad CuFeS_2 + \frac{11}{4}O_2 + \frac{1}{2}H^+ + H_2O = Cu^{2+} + \frac{3}{4}SO_4{}^{2-} + S^0 + \frac{1}{4}Fe_4SO_4(OH)_{10}$$

or

$$(35)\quad CuFeS_2 + \frac{11}{4}O_2 + \frac{3}{2}H_2O = Cu^{2+} + SO_4{}^{2-} + S^0 + Fe(OH)_3$$

Two possible mechanisms for the above reactions are:

1) Dissolved oxygen from the solution diffuses into a chalcopyrite grain and oxidizes the sulfide sulfur to native sulfur and sulfate. The charge imbalance enables the copper and ferrous iron to enter the solution. The ferrous iron in the solution is oxidized to ferric iron and homogenous precipitation of "BFS", or ferric hydroxide, occurs.
2) Dissolved oxygen from the solution diffuses into a chalcopyrite grain and oxidizes the sulfur as above. In addition, the ferrous iron is oxidized to ferric iron and reacts with some of the sulfate to form a rind of "BFS". This rind would effectively remove chalcopyrite from contact with the solution.

Both mechanisms for chalcopyrite dissolution at pH's between four and five would result in the formation of an insoluble ferric iron mineral covering the chalcopyrite. Since the rate of dissolution of chalcopyrite is controlled by the diffusion of oxygen into and ions out of the mineral grain, the formation of a stable surface mineral on chalcopyrite grains will increase the distance the ions must diffuse, and thus reduce the rate of the reaction.

APPENDIX A

HYDROLYSIS REACTIONS FOR SILICATE MINERALS USED IN THIS STUDY

$SiO_2 + 2H_2O = H_4SiO_4$

quartz log K = -4.00 a,b

"β-cristobalite" = -3.01 b

amorphous silica = -2.72 b

$KAlSi_3O_8 + 4H^+ + 4H_2O = K^+ + Al^{3+} + 3H_4SiO_4$

microcline log K = 1.29 a

$NaAlSi_3O_8 + 4H^+ + 4H_2O = Na^+ + Al^{3+} + 3H_4SiO_4$

low albite log K = 3.94 a

$3Na_{.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 22H^+ + 8H_2O = Na^+ + 7Al^{3+} + 11H_4SiO_4$

Na-montmorillonite log K = 19.06 a,c

$6Mg_{.167}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 4H^+ + 16H_2O = Mg^{2+} + 14Al^{3+} + 22H_4SiO_4$

Mg-montmorillonite log K = 40.26 c

$Al_2Si_2O_5(OH)_4 + 6H^+ = 2Al^{3+} + 2H_4SiO_4 + H_2O$

kaolinite log K = 7.63 a

$Al_2Si_4O_{10}(OH)_2 + 6H^+ + 4H_2O = 2Al^{3+} + 4H_4SiO_4$

pyrophyllite log K = 1.84 d

$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O$

gibbsite log K = 8.73 d

$Mg_5Al_2Si_3O_{10}(OH)_8 + 16H^+ = 5Mg^{2+} + 2Al^{3+} + 3H_4SiO_4 + 6H_2O$

Mg-chlorite log K = 73.20 a

$KAl_3Si_3O_{10}(OH)_2 + 10H^+ = 3Al^{3+} + K^+ + 3H_4SiO_4$

muscovite log K = 16.11 d

$KMg_3AlSi_3O_{10}(OH)_2 + 10H^+ = K^+ + 3Mg^{2+} + Al^{3+} + 3H_4SiO_4$

phlogopite log K = 40.89 e

$KFe_3^{2+}AlSi_3O_{10}(OH)_2 + 10H^+ = K^+ + 3Fe^{2+} + Al^{3+} + 3H_4SiO_4$

annite log K = 26.5 f

a Helgeson (1969)
b Walther and Helgeson (1977)
c Nesbitt (1977)
d Ulbrich and Merino (1974)
e Beane (1976, written communication)
f Beane (1974)

APPENDIX B

WHOLE ROCK CHEMICAL PROCEDURES

Method A: This procedure for whole rock chemistry made use of a hydrofluoric acid/boric acid digestion. This was first reported by Bernas in 1968 and further devedoped by him in 1972 (Bernas, 1968, 1972).

Procedure: an one hundred mg sample of the mixed and ground ($^+$ 80 mesh) ore was placed in a thirty ml teflon-lined pressure reaction vessel (Parr # 4745). The sample was wetted with two ml of concentrated nitric acid. Three ml of hydrofluoric acid were then added and the vessel was closed. It was then heated for two hours at 120° C. After the vessel cooled the contents were placed in a 250 ml plastic disposable beaker with 2.8 g of boric acid. Enough deionized water was added to bring the total volume to 30 ml. It is very important that the total volume at this point does not exceed 30 ml, as this would inhibit the formation of HBF_4. The mixture was allowed to stir covered up overnight. It was then diluted to 100 ml with deionized water. All dilutions were made with a matrix solution of 30 ml of HF and 28 g of boric acid per liter.

The following elements were analyzed for on a Perkin-Elmer model 403 Atomic Absorption Spectrophotometer (flame-type in parentheses: A-A: air acetylene; N-A: nitrous oxide acetylene); silicon (N-A), aluminum (N-A), iron (A-A), copper (A-A), magnesium (N-A), calcium (N-A), sodium (A-A), and potassium (A-A). In addition to these elements, Bernas (1972) reports successes in determining these additional elements; antomony, lead, titanium, vanadium, molybdenum, zinc, cobalt, manganese, nickle and barium. This method has an overall accuracy of about five per cent.

Method B: This method was not as fast as method A but it was more accurate. It made use of a sodium hydroxide fusion for silicon and aluminum and an acid digestion for the other metals (Shapiro and Brannock, 1962).

SILICON AND ALUMINUM PROCEDURE

The rock sample was crushed to pass 80 mesh (this was done with steel grinding equipment). One hundred to two hundred mg of the sample and 1.5 g of sodium hydroxide were placed into a 35 ml zirconium crucible. The crucible, sample and hydroxide were then put into a cold muffle furnace and heated to 850° C for fifteen minutes. A reagent blank was also prepared. The crucible was removed from the furnace and quenched in water and the fusion cake was dissolved in 100 ml of 6 molar HCl. The resulting solution was then transferred quantitatively to a one liter volumetric flask and diluted to volume. The solution was stored in a one liter polyethylene bottle.

Aluminum was determined by A.A. and silica was determined colormetrically using three ml of the fusion solution dilůted to 50 ml.

OTHER METALS

Procedure: Two hundred mg of the crushed rock sample was digested in a 250 milliliter teflon beaker, with ten ml of hydrofluoric acid, ten ml of hydrochloric acid, and five ml of nitric acid. The digestion was then evaporated to dryness. The salts were next dissolved in 25 ml of concentrated hydrochloric acid and diluted to 250 ml. The metals were then determined by A.A. as described earlier.

APPENDIX C

CLAY SEPARATION

Procedure: approximately 500 g of the crushed rock were placed in a one liter bowl. Then one-half liter of deionized water was added to the crushed ore and the mixture was stirred and allowed to settle for 45 seconds. The water-clay-silt slurry was decanted into a two liter beaker. This procedure was repeated until 1) the beaker was full or 2) after 45 seconds of settling the water contained none or only a small amount of clay. The beaker was then covered with plastic film and allowed to settle undisturbed for 24 hours. The water was decanted to the drain and replaced.

After the 24 hours on distilled water, all but 500 ml of the water was decanted into the drain. The clay material was next mixed well with the remaining water and placed in two 250 ml centrifuge bottles and centrifuged at 2500 RPM for ten minutes. The supernatant liquid was decanted to the drain and then water was added and the procedure repeated. After the clays no longer flocculated, the two bottles were combined and the volume was brought up to 250 ml. The clay material was suspended using a sonic cell disrupter. The water clay suspension was placed into a 250 ml graduated cylinder.

The time necessary for the settling and separation of the less than two micrometer fraction was calculated from Folk's (1968) equation. The suspension containing the desired size fraction was pipetted onto glass slides and the water allowed to evaporate. These slides were then X-rayed using a Norelco Diffractionmeter (CuK_α radiation) under the following conditions:

1) Untreated; air dried 25° C.
2) Glycol saturation; 60° C for two hours.
3) Untreated; air dried 375° C for one hour.
4) Untreated; air dried 550° C for one hour.

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This thesis is accepted on behalf of the faculty of the Institute by the following committee:

Carl J Popp 4/30/79

Marc W. Bodine Jr. 4/30/79

R E Beane 5/4/79

Date ______________________