


**DISSOLUTION OF HALOGENATED BIOTITE FROM
AN ACID-MINE-DRAINAGE SITE IN GLOBE-MIAMI, ARIZONA,
AND ITS CONTRIBUTIONS TO GROUND-WATER CHEMISTRY**

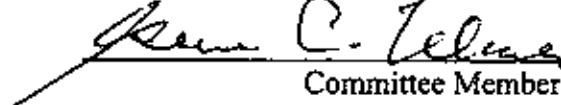
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ABSTRACT

Dissolution kinetics and ion-release rates were measured for a halogenated, trioctahedral biotite isolated from stream alluvium down-gradient from an acidic metal-enriched plume in Pinal Creek Basin, Arizona. Experiments were performed using flow-through columns in which unground 150-250 μm biotite and bulk alluvial sediment from Pinal Creek basin were reacted with a solution of dilute sulfuric acid (pH 3.4 and 2.9) for five months under flowing argon gas at 25°C. The dissolution rate of the halogenated biotite was $2.16 \times 10^{-13} \text{ mol m}^{-2} \text{ s}^{-1}$ at pH 3. After 1400 hours, mineral dissolution was constant and congruent. The order of the biotite dissolution reaction with respect to hydrogen ion activity (n) was 0.52 for output pH values between 3.1 and 3.5. Dissolution rates for this study were slightly slower than rates previously measured for biotite and phlogopite in the same pH ranges, possibly due to sample composition, preparation and/or reactor design. This study is one of the few where Cl release rates were measured and averaged $0.08 \text{ picomol m}^{-2} \text{ s}^{-1}$.

Inverse geochemical modeling of ground-water evolution between wells in Pinal Creek basin by Glynn and Brown (1996) suggested that an additional chloride source was necessary in some model simulations to achieve chloride mass balance. A model calculation of Cl input from biotite dissolution along the flow path modeled by Glynn and Brown (1996) using the biotite dissolution rate and the rate of Cl released determined in this study determined that Cl contribution from the dissolution of halogenated biotite can be as much as 10 mg/L.

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INTRODUCTION

Pinal Creek basin is located in east central Arizona (Figure 1), about 100 km east of the Phoenix metropolitan area. Ground-water contamination of the surficial aquifer in the basin is due to acid-mine drainage resulting from more than a century of copper mining of granite porphyry deposits in the basin. The basin spans 516 square kilometers, of which the surficial aquifer occupies 170 square kilometers (Figure 2). Acidic, metal-enriched drainage in the basin is due to (1) the oxidation of pyrite and other sulfide-rich minerals in mine tailings, which cover approximately 27 square kilometers of the basin, and (2) leakage of acidic wastewater from Webster Lake, an unconfined surface-water impoundment that existed from 1940 until it was drained in 1988 by the U.S. Environmental Protection Agency (USEPA; Brown, and Eychaner, 1996). Just prior to being drained, the pH of Webster Lake was 2.7 with concentrations of dissolved iron (Fe) and sulfate (SO_4), respectively, in excess of 6,000 and 20,000 milligrams per liter (mg/L; Glynn and Brown, 1996). At its maximum size, Webster Lake held 7 million cubic meters of wastewater generated from the processing of ore. The slow seepage of acidic drainage and mine waste into the regional aquifer gave rise to an acidic, metal-enriched-ground-water plume over 15 km long, which migrated southeast under Webster Gulch and then northward under Miami Wash and Pinal Creek. The plume flows primarily through the unconsolidated alluvial aquifer, but also extends into the upper portion of the underlying, and less permeable, consolidated basin fill. The acidic part of the plume (pH 3 to 4) contains high concentrations of dissolved ions. For example, contaminated ground water from the alluvial aquifer had 1,100 mg/L of dissolved iron and 7,000 mg/L of dissolved sulfate in 1988 (Brown, 1990).

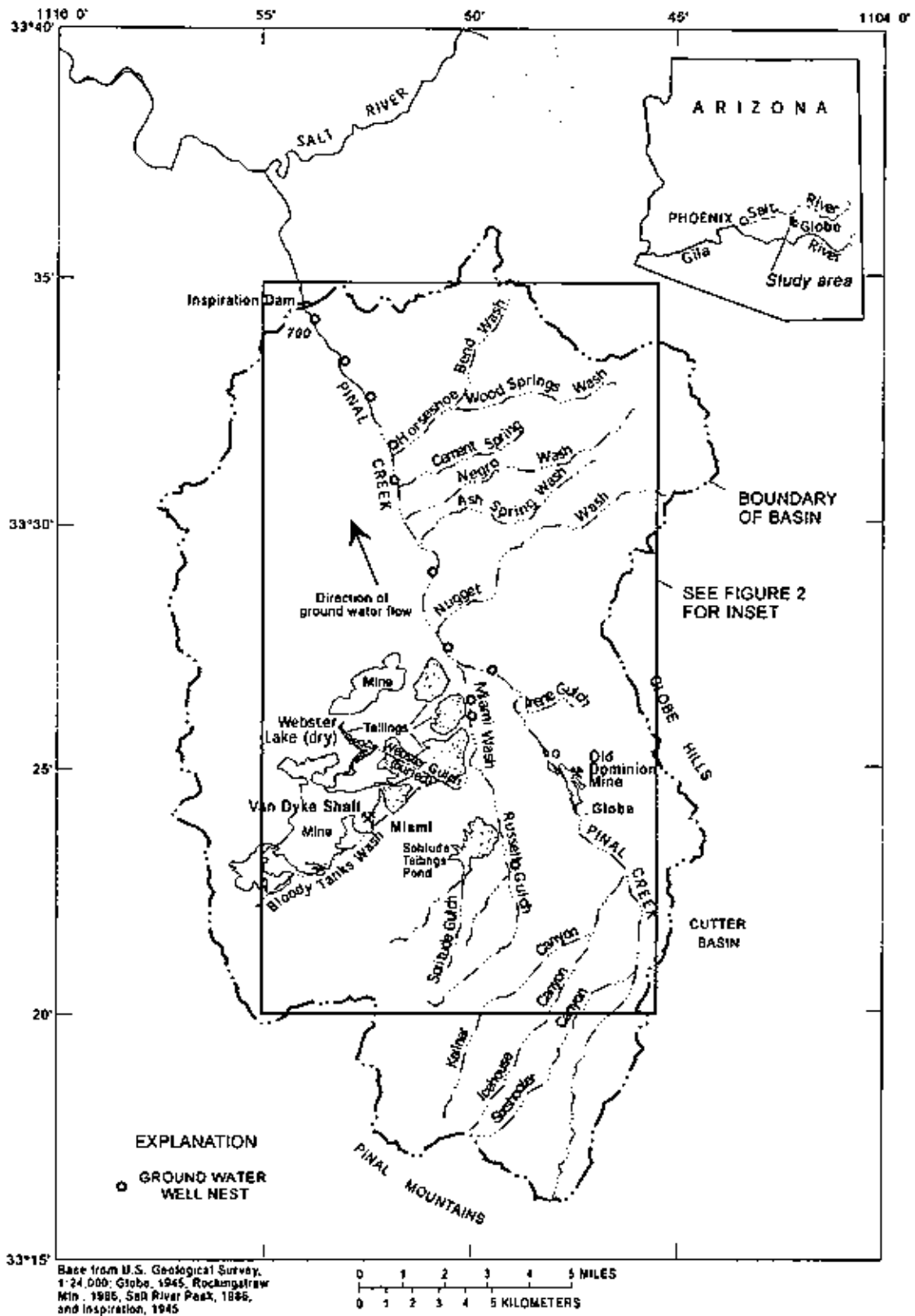


Figure 1. Study area. Map showing the location of Pinal Creek basin, Arizona (modified from Brown and Eychaner, 1996)

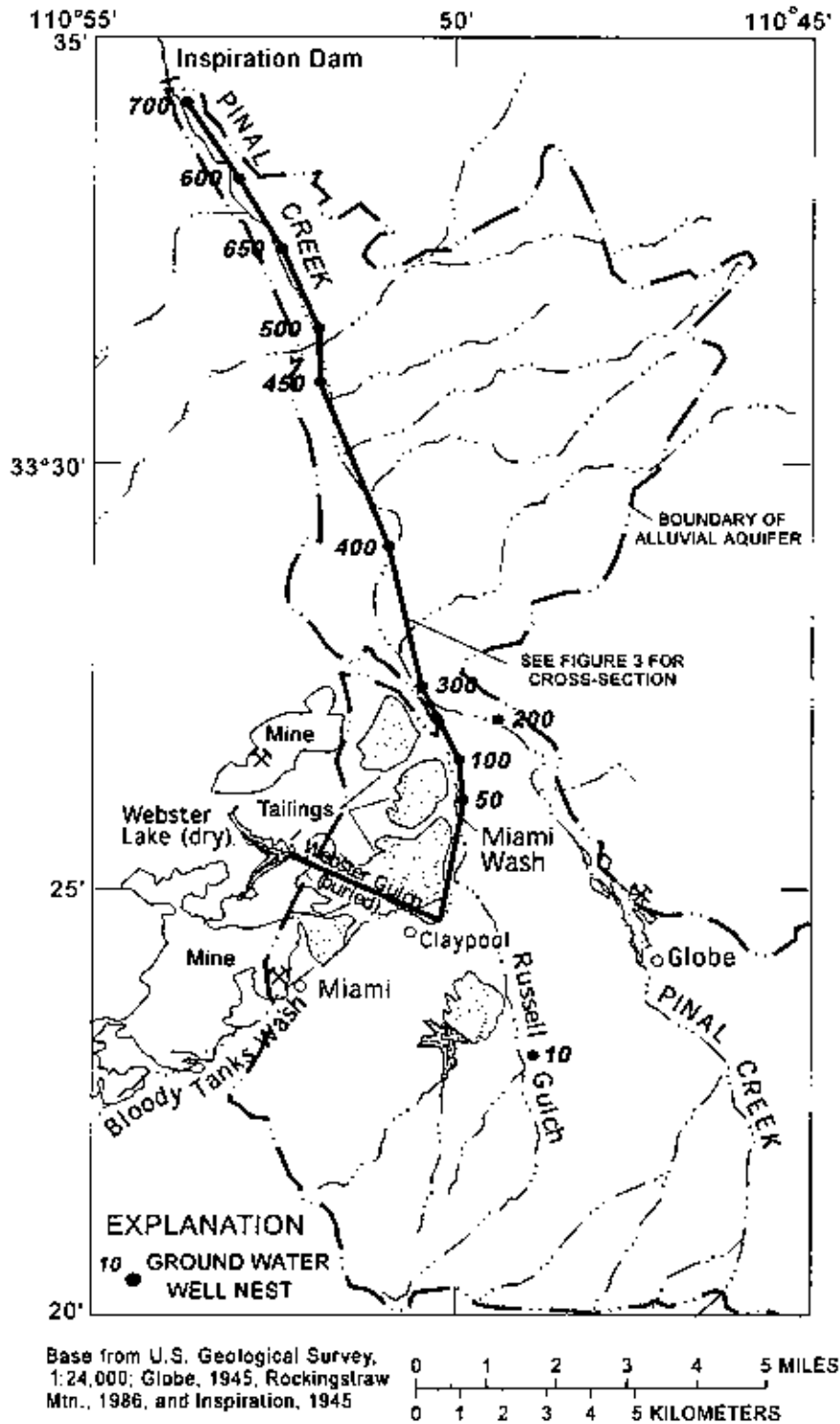


Figure 2. Ground-water well locations. Map showing the extent of the alluvial aquifer and location of ground-water monitoring wells in proximity to mine tailings and the former Webster Lake (modified from Brown and Eychaner, 1996)

Background Information

The geochemical evolution of contaminated ground water in Pinal Creek is complex; as ground water moves through the alluvial aquifer and basin fill, it is (1) diluted by mixing with uncontaminated "background" ground water, and (2) neutralized by reaction with carbonate minerals in the aquifer. Neutralization increases the pH from a range of 3-4 to a range of about 5-6 (Figure 3), causing metallic ions to precipitate out and/or adsorb onto mineral surfaces in the aquifer. The alluvium contains less carbonate minerals than the basin fill, which is composed of the carbonate-cemented Gila Conglomerate, providing a greater acid-neutralizing capacity to contaminated groundwater than the overlying alluvial aquifer. Aquifer confinement near well group 500 forces the ground water to the surface where it is discharged as perennial flow to Pinal Creek.

Contamination of the alluvial aquifer in Pinal Creek basin was first reported in the 1930's, but surface-water contamination was not detected until the 1960's (Envirologic Systems, Inc., 1983 as cited by Brown and Eychaner, 1996). In 1989, the Arizona Department of Environmental Quality (ADEQ) included Pinal Creek in its Water Quality Revolving Fund (WQARF), a state Superfund cleanup program. Numerous government agencies and universities have conducted research at the site¹; in particular, the U.S. Geological Survey (USGS) has studied ground water and surface water from the basin since 1984. Since that time, the USGS has maintained over 30 ground-water monitoring wells in the basin. These well are distributed among ten well nest sites, shown in Figure 2, and are screened to admit ground water at various selected depths in the

¹ See the Pinal Creek web site at <http://az.water.usgs.gov/pinal/index.html>

unconsolidated alluvial aquifer and the underlying consolidated basin fill (Figure 3). The well nests are located along Miami Wash and Pinal Creek with distance down gradient of Webster Lake and the tailings piles (Brown and Eychaner, 1996).

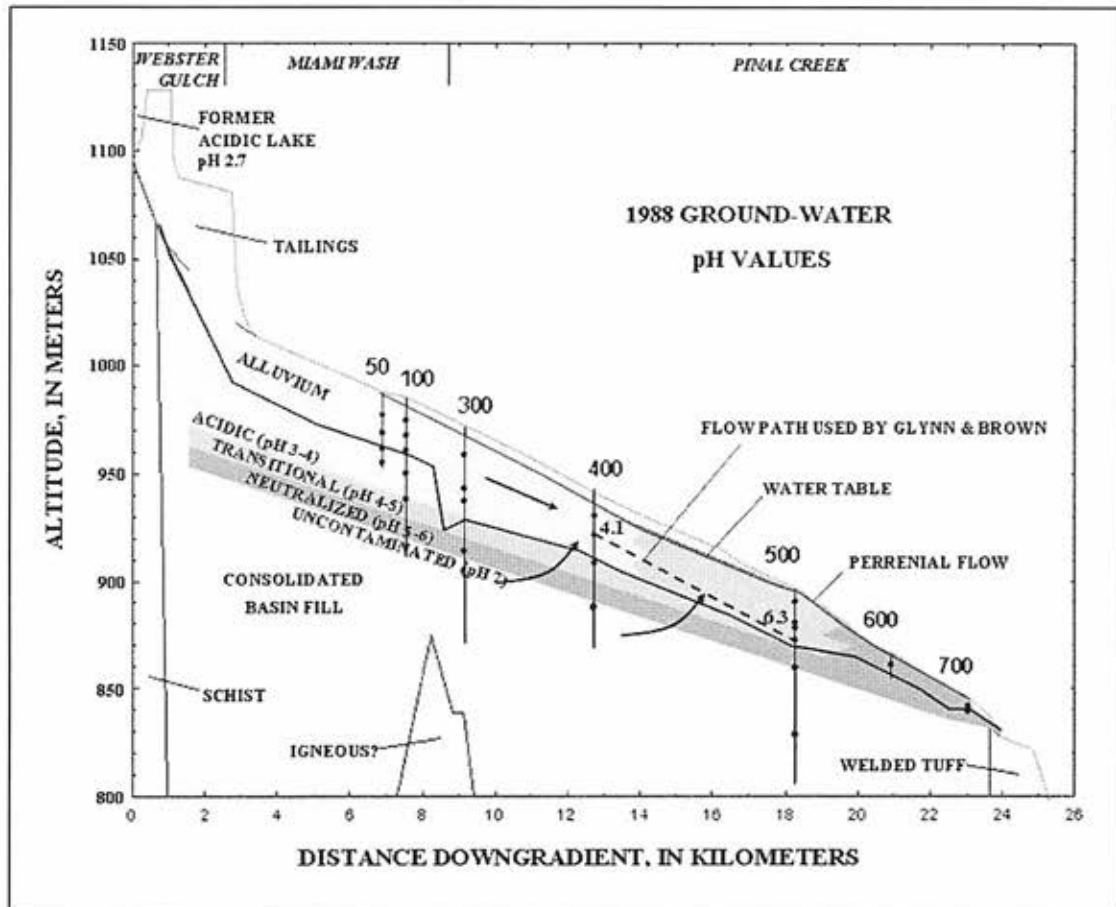


Figure 3. Cross-section of ground water pH values. A cross-section showing variation in 1988 pH values with depth in the alluvium and basin fill (figure modified from Brown and Eychaner, 1996, with data from Brown, 1990).

Mass Balance Problems in Pinal Creek Ground Water

The U.S. Geological Survey Toxic Substances Hydrology Program boasts over 80 publications related to Pinal Creek (*i.e.*; Stollenwerk and Eychaner, 1987; Eychaner, 1989; Lind and Stollenwerk, 1993; Stollenwerk, 1996; Brown and Eychaner, 1996;

Glynn and Brown, 1996; and Brown and Glynn, 2003). As part of this research, Glynn and Brown (1996) used PHREEQC (pH-Redox-Equilibrium; Parkhurst and Appelo, 1995), an inverse geochemical modeling program, to examine the evolution of contaminated ground water from Pinal Creek basin. Inverse geochemical modeling can be used to predict the stability of potential mineral phases in the chemical evolution of related ground waters along a flow path. In this type of modeling, reactions calculated are constrained by user-defined assumptions about hydrology (*i. e.*, flow rate, transport, and flow path delineation), and geochemistry (*i. e.*, evolutionary history of the ground water, and geochemical reactions known to occur).

Glynn and Brown (1996) ran multiple simulations of the evolution of acidic ground water between well 402 (pH 4.13) and well 503 (pH 5.59; see Figure 3 for flow path location). Decreases in the concentrations of conservative ions, such as chloride (Cl) and sodium (Na), indicate dilution of ground water along the flow path. Dilution occurs as uncontaminated ground water from the basin fill mixes with acidic ground water in the alluvium. To simulate this dilution, Glynn and Brown (1996) used a mixing fraction of ground water from well 503, an uncontaminated ground water in the basin fill.

Simulations were run using various geochemical constraints, as well as different mixing fractions of background diluting water. Mixing fractions of back-ground water used ranged from 0.216 to 0.347, and were calculated based on Cl, Na and SO₄ concentrations.

When Cl ion was used to determine the mixing fractions, a Na ion sink was required by the model to accommodate inputs from the dissolution of silicate minerals. Aquifer ion exchange could be a potential Na sink, since mineral dissolution in acidic ground-water regions is known to increase the cation exchange capacity of aquifer

material. However, the coarseness of Pinal Creek sediment, and its relatively small amount of clay suggest that this sink is limited and unable to accommodate the amount of Na required by the model. Therefore, Glynn and Brown (1996) concluded that there might be an additional source of Cl in the basin.

Ground Water Mixing Fractions

The concentration of Cl in ground water decreases from 140 to 112 mg/L between wells 402 and 503 (Table 1). If ground water from 402 is diluted by background water with a Cl concentration of 9.7, then the mixing fraction of background water (f_{504}) necessary to produce a Cl concentration of 112 at well 503 can be calculated using the equation:

$$f_{504} = \frac{C_{402} - C_{503}}{C_{504} - C_{402}}, \quad (1)$$

where,

f_{504} is the fraction of background water from well 504,

C_{402} is the concentration of an ion in acidic ground water from well 402,

C_{503} is the concentration of an ion in neutralized ground water from well 503, and

C_{504} is the concentration of an ion in uncontaminated ground water from well 504.

The mixing fractions calculated from Cl concentrations are:

$$79\% \text{ Well 402} + 21\% \text{ Well 504} = 100\% \text{ Well 503}$$

To examine the possibility that Cl is not conservative in the evolution of Pinal Creek ground water, we must identify a different conservative tracer and calculate a new mixing fraction. If Na is assumed conservative, the mixing fractions calculated from Na concentrations given in Table x are:

$$65\% \text{ Well 402} + 35\% \text{ Well 504} = 100\% \text{ Well 503}$$

Using these mixing percentages and Cl values for wells 402 and 504, well 503 should have a Cl concentration of 94 mg/L. However, the Cl measured for well 530 was 112 mg/L, a difference of 18 mg/L. This suggests an 18 mg/L source of Cl in the basin. This calculation assumes that these wells are on the same flowpath.

Chloride in Pinal Creek Biotite

Much of the chloride found in continental interior ground water originates from cyclic salts, and the dissolution of Cl-bearing silicates, such as amphibole and biotite (Kullerud, 2000). It was suggested that since some Pinal Creek sediments are hydrothermal in origin, the dissolution of halogenated biotite in the aquifer sediments might provide a significant chloride source (Dr. Pierre Glynn, U.S. Geological Survey, personal communication, 1999). Scanning electron microscopy (SEM) examination of basin sediments (Dr. Owen Bricker, U.S. Geological Survey, personal communication, 1998) indicated that the biotite contained amounts of chloride detectable by energy

dispersive x-ray spectroscopy (EDXS); thus biotite dissolution seemed a possible Cl source. Within this study, previous laboratory and field studies of biotite dissolution have been reviewed (*i.e.*, Lin and Clemency, 1981b; Velbel, 1985; Acker and Bricker, 1992; Swoboda-Colberg and Drever, 1993; Suarez and Wood, 1996; Kalinowski and Schweda, 1996; Malmstrom and Banwart, 1997; Murphy *et al.*, 1998; and Taylor *et al.*, 2000). Although a lot of work has been done in this area, not much attention has been given to Cl concentrations in biotite or its effect on dissolution rates. Therefore, the value of the Cl source-term at Pinal Creek could not be assessed.

Study Objectives

This study used a flow-through column experiment to examine dissolution of biotite isolated from uncontaminated stream alluvium in Pinal Creek basin, Arizona. The purpose of this study is to determine if the Cl imbalance in Pinal Creek ground water identified by Glynn and Brown (1996) could be due to the dissolution of biotite in the alluvial aquifer. This objective is accomplished by:

- 1) Determining the percent of biotite in alluvial stream sediment from Pinal Creek basin.
- 2) Characterizing the biotite in the alluvium using BET surface area, x-ray diffraction (XRD), x-ray fluorescence (XRF), and SEM techniques.
- 3) Reacting the biotite and alluvial sediment with a weak SO_4 solution in a flow-through column for 2000 hours.
- 4) Examining dissolution kinetics and ion-release rates from the biotite based on ion composition in output solutions from the flow-through columns.

- 5) Comparing biotite dissolution rates in this study with those of previous dissolution studies.
- 6) Quantifying the amount of Cl released from the biotite, and assessing its contribution to ground-water chemistry in Pinal Creek basin, based on the percent of biotite in the alluvium.

STUDY AREA

Pinal Creek Basin is situated in the Basin and Range mountain province of central Arizona (Figure 4), a mountainous region formed by numerous periods of volcanic activity, uplift, erosion, deposition, and metamorphism. The study area is a region that has been actively mined for silver and copper for over a century. The Globe-Miami copper district lies within the study area and includes the *Inspiration* and *Old Dominion* Copper Mines. A simplified geologic map and stratigraphic section of the area are shown in Figure 5 and Table 1. Pinal Creek is located in a graben enclosed by the Globe Hills block to the east and the Inspiration block to the west. Topographic highs in the area include the Pinal Mountains (2,392 meters at Pinal Peak) to the south, the Apache Peaks and Globe Hills (1,000 meters) to the east, and Webster Mountain (17,000 meters) to the west. The lower basin receives 40-50 centimeters of rainfall annually, with precipitation accumulations increasing with elevation in the basin (Brown and Eyehaner, 1996).

Geology

The geologic history of the Globe-Miami district has been summarized by Ransome (1903) and Peterson (1962). Among the oldest rocks in the area is the 1.71 billion years old (Ga), Early Proterozoic Pinal Schist (generally equivalent to the Vishnu Schist found in the Grand Canyon), which contains abundant biotite and biotite, altered to chlorite (Peterson, 1962). The Pinal Schist underwent deformation during the Mazatzal Orogeny (1.6 to 1.65 Ga) and subsequent igneous intrusion during the Mesozoic and Tertiary ages. Pinal Schist outcrops in the Pinal Mountains, south and the south west of the study area. Other Early Proterozoic formations include the Madera Diorite (1.58 to

1.66 Ga), a granodiorite found in the Pinal Mountains; the Solitude Granite, a muscovite-rich granite west of the Pinal Mountains; and the Ruin Granite, a coarse grained porphyritic rock extensively exposed in the northern section of the study area.

Early Proterozoic rocks are overlain by the Apache Group, a Middle Proterozoic sequence including the Scanlan Conglomerate, the Pioneer Formation (quartzite), the Barnes Conglomerate, the Dripping Springs Quartzite, and the Mescal Limestone, which range in age from 1.1 to 1.4 Ga (Peterson, 1962; Nations and Stump, 1996). The Apache Group is overlain by basalt flows and the Troy Quartzite, deposited between 0.9 and 1.1 Ga. Outcrops of the Apache Group occur in the Apache Peaks, east of the study area.

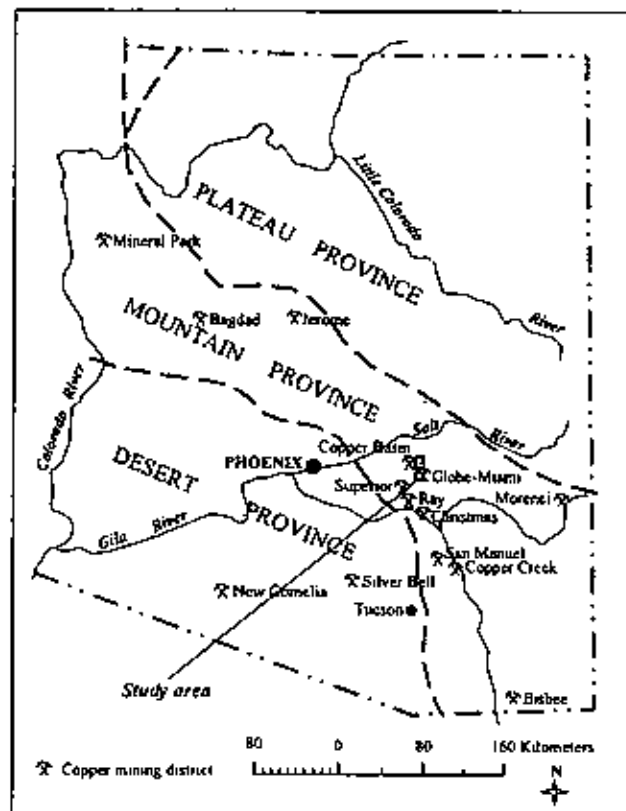


Figure 4. Physiographic map of Arizona. Map showing the study area location in the mineral belt region of Arizona's mountain province (modified from Peterson, 1962).

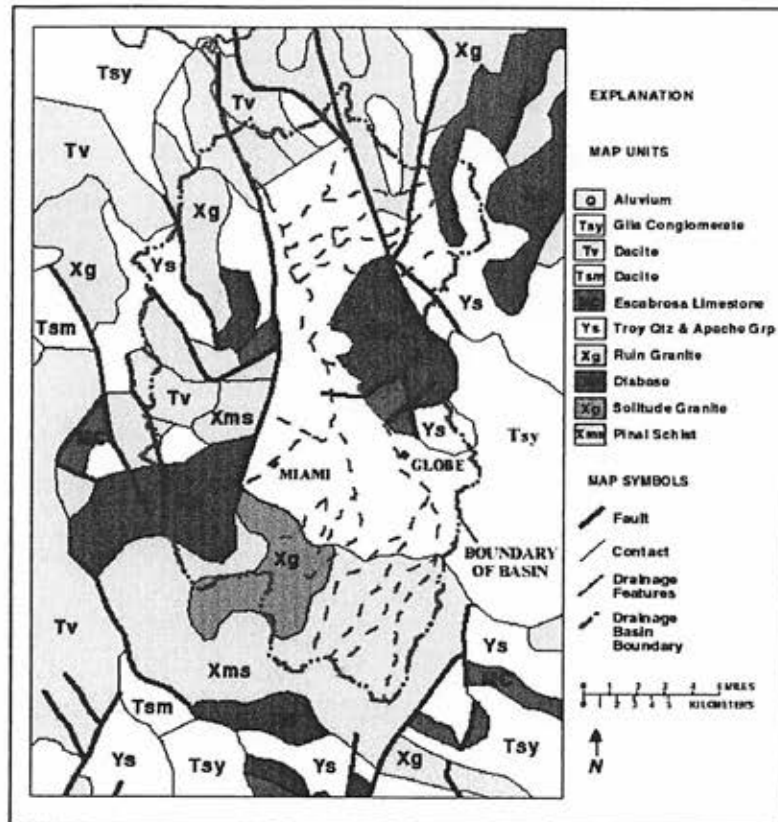


Figure 5. Simplified geologic map of the study area. Geologic formations are shown in relation to the boundary of Pinal Creek basin and its major drainage features (modified from Nations and Stump, 1996).

The Paleozoic Era is characterized by carbonate rocks deposited in a shallow marine environment. The Martin Formation is a sequence of Devonian limestones (408 to 360 million years ago, Ma) that lie unconformably atop Middle Proterozoic rocks. Mississippian age Escabrosa Limestone (360 to 320 Ma) lies conformably atop the Martin Formation, and is found west of Pinal Creek near the town of Claypool. Uplift and erosion at the end of the Mississippian led to the disconformable deposition of the Naco Limestone in the Pennsylvanian (320 to 286 Ma). The last marine transgression occurred in the Late Cretaceous period, leading to erosion and nonmarine sedimentation.

Table 1. Geologic units in Pinal Creek basin, Arizona (values from Peterson, 1962; and Nations and Stump, 1996) [Ma, million years age]

| ERA | PERIOD | Ma | FORMATION | |
|-----------------------|-------------------------|------|----------------------------------|----------------------------|
| Cenozoic | Quaternary | | Alluvium | |
| | Quaternary/ Tertiary | 2 | Gila Conglomerate | |
| | Tertiary | 32 | Dacite Whitetail Conglomerate | |
| Cenozoic/ Mesozoic | Tertiary/ Cretaceous | 80 | Shultz Granite | |
| | | | Diorite Porphyry | |
| | | | Diabase | |
| | | | Lost Gulch Monzonite | |
| | | | Widow Spring Grandodiorite | |
| Paleozoic | Pennsylvanian | 320 | Naco Limestone | |
| | Mississippian | 360 | Escobrosa Limestone | |
| | Devonian | 406 | Martin Formation | |
| Proterozoic | Late Precambrian | 1100 | Troy Quartzite | |
| | Middle Precambrian | 1400 | Apache Group | Mescal Limestone |
| | | | | Dripping Springs Quartzite |
| | | | | Barnes Conglomerate |
| | | | | Pioneer Formation |
| | | | | Scanlan Conglomerate |
| | Early Precambrian | 1700 | | Ruin Granite |
| | | | | Diabase |
| | | | | Solitude Granite |
| | | | | Madera Diorite |
| | | | Pinal Schist | |

Volcanic activity associated with the Laramide Orogeny (50 to 80 Ma) during the Cretaceous and Tertiary age is responsible for the emplacement of granitic porphyry intrusions. The Lost Gulch Quartz Monzonite, an intrusive found west of Pinal Creek, contains eight percent biotite present in aggregates and as books, both being 2.5 to 8 millimeters in diameter (Peterson, 1962). Diabase intrusions occur east of Pinal Creek,

where it forms the Globe Hills, and west of Pinal Creek, where it forms the Gerald Hills. The Shultz Granite (58 to 61 Ma) is a granite porphyry exposed near Bloody Tanks Wash. Volcanic activity associated with the emplacement of the above mentioned intrusives caused hydrothermal alteration of the host rocks they intruded. Supergene-enriched deposits formed from ground water percolation and subsequent dissemination of porphyry copper (Barnes, 1997).

Eruptions continued into the Tertiary with several episodes of dacite intrusion. Dacite deposits occur west of Webster Lake and in the northern part of the basin. Biotite is a major mineral present in all igneous intrusive rocks in the Pinal Creek area, but is particularly abundant in Tertiary age dacite. Peterson (1962) describes the dacite as having books of biotite, 0.3 to 1.5 millimeters across, altered to a reddish brown. A sample of the dacite, collected near *Old Dominion* Mine, was reported by Ransome (1903) as containing 0.03 weight percent Cl.

Pinal Creek basin deposits are composed of the Gila Conglomerate a thick, (more than 1,200 meters near Bloody Tanks Wash; Peterson, 1962) and well-cemented deposit of Tertiary to Quaternary age, overlain by a surficial deposit of unconsolidated Quaternary alluvium. The Gila Conglomerate is composed of rock debris deposited along two coalescing alluvial fans, one spreading out northeasterly from the Pinal Mountains and spreading out westward from the Apache Peaks. The conglomerate contains boulder to gravel size grains cemented in a carbonate matrix. The overlying unconsolidated alluvium is a thin (up to 50 meters thick) layer of Quaternary age stream deposits occurring along basin drainage features. Alluvial sediment, which is poorly sorted with grain sizes ranging from gravel and sand to fine lenticular clays.

Hydrogeology

The unconsolidated alluvium comprises an alluvial aquifer 50 meters thick, 300 to 800 meters wide, and 23 kilometers in length. Ground water flows through the aquifer at a rate of 4.2 to 5.6 meters per day (m/d) along a gradient of 10 meters per kilometer (m/km; Brown, 1996). The hydraulic conductivity of the aquifer is estimated to be between 150 and 260 m/d, with an effective porosity of 30 percent. The alluvial aquifer is underlain by a thick deposit of basin fill (the Gila Conglomerate), which creates a lower confining boundary for alluvial aquifer ground water due to its well-cemented rock matrix. The alluvium and basin fill form the basin's regional aquifer system. Basin deposits are thickest (1200 meters) in the southern part of the basin and taper to the north where it is truncated just beyond site 700 (Brown and Eychaner, 1996).

Surface-water drainage in the basin flows north-easterly from the flanks of the Pinal Mountains and westward from the Apache Peaks. Surface-water flow in drainage features is primarily intermittent, with streams carrying water only during storm events. The exception to this is a perennial reach of Pinal Creek beyond ground water well nest 500, where aquifer constriction forces ground-water flow to the surface, contributing perennial flow to Pinal Creek which flows north into the Salt River.

Regional ground water flow in the basin is from south-east to north-west, with deep flow systems in the basin originating from high elevation recharge areas in the Pinal Mountains (Crilley and Glynn, 1999). The contaminated ground-water plume flows under Webster Gulch, and merges with regional ground water flow proceeding north-westerly under Miami Wash and Pinal Creek.

Ground-water Geochemistry

Ground water from Pinal Creek can be divided into four distinct types: uncontaminated, acidified-contaminated, transitional, and neutralized-contaminated (see Figure 3). Background water composition in the basin is a calcium-magnesium-bicarbonate type (Glynn and Brown, 1996). Acid-contaminated ground water in the basin is primarily confined to the unconsolidated alluvium, but has penetrated into the upper portion of the basin fill. Besides being acidic, the contaminated ground waters are sulfidic and enriched in metal ions including Fe, manganese (Mn), aluminum (Al), and copper (Cu; Table 2). As the acid plume migrates down gradient, the pH is neutralized by reaction with carbonate sediments. Contaminated ground water along Miami Wash has a pH of 2 to 3 which increases the pH to about 5 to 6 in wells along Pinal Creek. The sample of alluvium analyzed in 1985 contained 0.34 percent calcite (Eychaner and Stollenwerk, 1985), while the basin fill contained about 1.5 percent calcite (Eychaner, 1989).

Major ion chemistry and pH for selected wells sampled in June 1988-90 are shown in Table 2. The analyses given are for wells used by Glynn and Brown (1996). Figure 6 shows a cross-section of Cl concentrations measured in ground water sampled at various depths in the alluvium and basin fill. Elevated concentrations of Cl (*i.e.* 120-280 mg/L Cl) measured in the alluvium and basin fill, compared to uncontaminated deeper basin fill (7.6-9.4 mg/L Cl) is due to contamination from Webster Lake (350 mg/L Cl).

Table 2. Ion concentrations in Pinal Creek basin ground water for wells used in modeling by Glynn and Brown (1996). [ft, feet; °C, degrees Celsius; $\mu\text{S}/\text{cm}$, microsiemens per centimeter; mg/L, milligrams per liter; <, less than; --, not determined; NA, not applicable; data from Brown, 1990 as cited in Glynn and Brown, 1996]

| Constituent | Webster Lake | Acidic Contaminated | Basinfill Background | Neutralized Contaminated |
|--------------------------------|-------------------------------|-----------------------------|--------------------------------|------------------------------|
| | Basin fill Well 504 2/01/1988 | Alluvium Well 402 1/12/1989 | Basin fill Well 504 11/22/1991 | Alluvium Well 503 11/22/1991 |
| Well depth (ft) | NA | 20.8 | 69.2 | 25 |
| Screen interval (ft) | NA | 19.8-20.7 | 67.6-68.6 | 23.4-24.3 |
| Water Temp (°C) | 11.0 | 18 | 20.5 | 18.2 |
| SC ($\mu\text{S}/\text{cm}$) | 13800 | 4600 | 393 | 3800 |
| DO (mg/L) | -- | 0.3 | 6.64 | <0.1 |
| pH field | 2.7 | 4.13 | 7.05 | 5.59 |
| Ca (mg/L) | 510 | 502 | 44.6 | 634 |
| Alkalinity | -- | -- | 227 | 66 |
| Mg (mg/L) | 730 | 161 | 15.6 | 200 |
| Na (mg/L) | 240 | 121 | 19.8 | 86 |
| K (mg/L) | -- | ^{1/7} | 2.1 | ^{1/5} |
| Cl (mg/L) | 350 | 140 | 9.7 | 112 |
| F (mg/L) | -- | ^{1/10} | 0.3 | ^{1/1.5} |
| SO ₄ (mg/L) | 20000 | 3260 | 14.2 | 2350 |
| SiO ₂ (mg/L) | -- | 85.6 | 27 | 91.8 |
| Fe (mg/L) | 5970 | 591 | 0.004 | <0.1 |
| Mn (mg/L) | 100 | 71.6 | <0.001 | 116 |
| Al (mg/L) | 850 | 18.4 | <0.01 | ^{1/2.3} |
| Cu (mg/L) | 210 | 3.6 | <0.01 | 0.1 |

^{1/} Values that have been estimated from concentrations in previous and later years

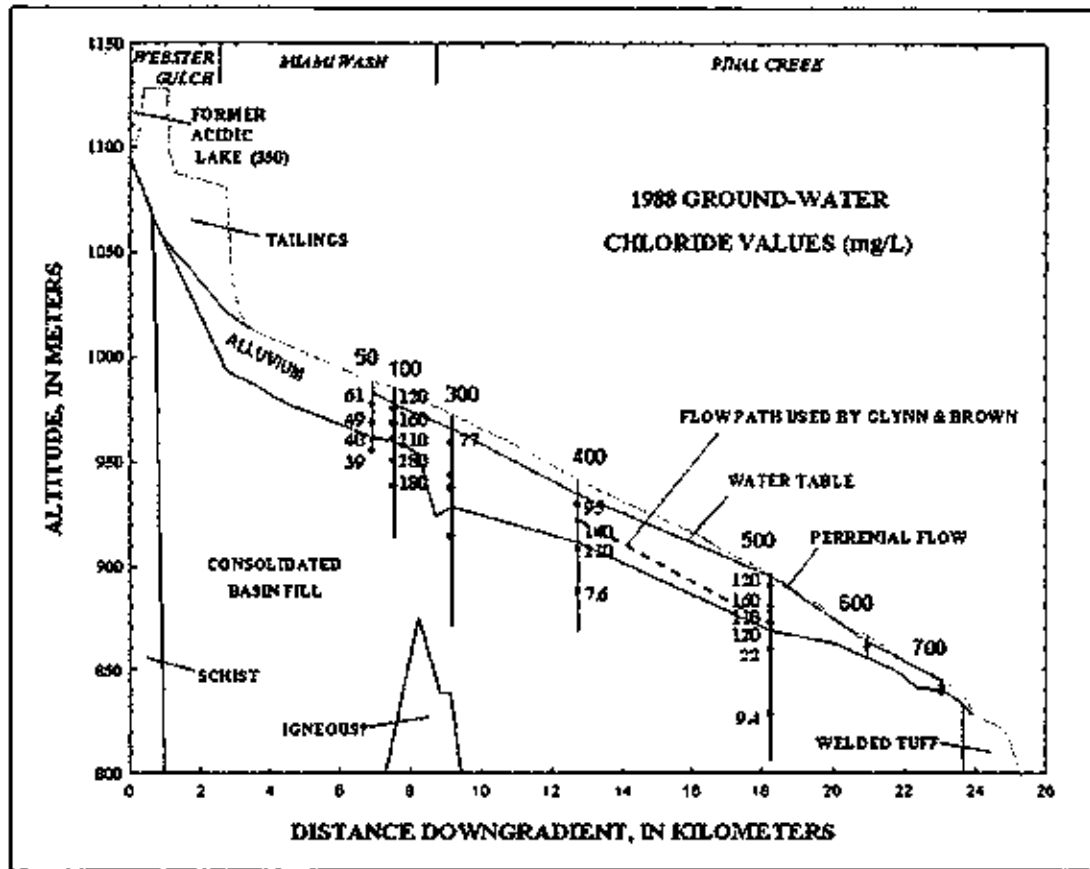


Figure 6. Cross-section of ground water chloride values. A cross-section showing variation in 1988-90 chloride values with depth in the alluvium and basin fill. Dotted line shows the flowpath used for modeling by Glynn and Brown (1996; figure modified from Brown and Eychaner, 1996, and data from Brown, 1990).

BIOTITE CRYSTAL STRUCTURE AND COMPOSITION

Biotite is a trioctahedral sheet structure or phyllosilicate, having the ideal composition $K_2(Mg, Fe)_6^{VI}(Al_2Si_6)^{IV}O_{20}(OH, F, Cl)_4$, based on a formula containing $O_{20}(OH)_4$ where *VI* indicates octahedral sites (O, see below) and *IV* indicates tetrahedral sites (T, see below). Magnesium (Mg) and ferrous iron (Fe^{2+}) are contained in octahedral sites in the layer marked O in Figure 7, whereas Al and silica (Si) are contained in tetrahedral layers, marked T. Interlayer cations, primarily potassium (K) and Na, with lesser amounts of calcium (Ca) and lithium (Li), are between repeating tetrahedral layers. Hydroxyl (OH), (Cl) fluoride (F), bromide (Br) and other, largely monovalent anions occupy non-bridging oxygen sites on the octahedral layer. A trioctahedral biotite is one in which the divalent cations (Mg^{2+} and Fe^{2+}) fill all available octahedral spaces. End member varieties of biotite include iron-rich annite, $KFe_3AlSi_3O_{10}(OH)_2$, and magnesium-rich phlogopite, $KMg_3AlSi_3O_{10}(OH)_2$.

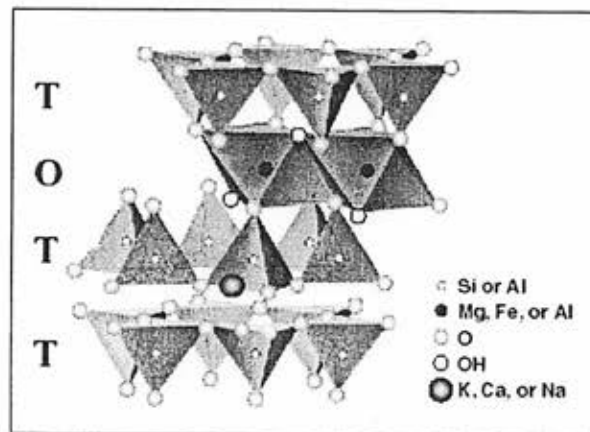


Figure 7. Structure of biotite (modified from Lang, 2003).

Biotite Dissolution

Biotite dissolution releases ions into the ground water providing soil nutrients, influencing oxidation-reduction potentials and aiding in the acid neutralization of ground water, especially in regions of low carbonate content. As little as 5 weight percent of biotite in the bulk composition of a soil can be a significant source of soil nutrients (Jeong, 2000). Secondary clays formed from the weathering of biotite are important contributors to soil cation exchange capacity (CEC), and include clay minerals such as vermiculite, kaolinite, illite and montmorillonite, as well as chlorite, ferric oxides and hydroxides (for a recent review, see Appelo and Postma, 1996). Biotite alteration occurs through intermediate steps described by Feldman *et al.* (1991) as:

biotite → hydrobiotite → randomly interstratified vermiculite → vermiculite →
montmorillonite/hydroxy interlayered vermiculite → kaolinite

Vermiculite, $(\text{Mg,Fe,Al})_3 (\text{Al,Si})_4 \text{O}_{10} (\text{OH})_2 \cdot 4\text{H}_2\text{O}$, is formed within the biotite structure. The formation of kaolinite indicates a more advanced stage of biotite weathering (*i.e.*, vermiculite), with gibbsite and other Fe and Al oxides forming under more extreme weathering conditions. Determining the stage of biotite weathering, either optically or by x-ray diffraction (XRD), is difficult due to the interstratified formation of kaolinite within biotite. Newman and Brown (1966) describe the steps involved in the alteration sequence of trioctahedral biotite as:

- 1) Exchange of interlayer cations (K^+) along mineral edges with solution cations
- 2) Interlayer openings allow OH^- release into solution causing layer expansion.

- 3) Expansion allows more interlayer cation exchange creating even more expansion.
- 4) Fe^{2+} in the mineral is oxidized by O_2 in solution and structural OH^- .
- 5) Octahedral cations are released due to the loss of structural OH^- .

Chloride Occurrence in Biotite

Cl-rich biotite results from halogen substitution, where halogen elements, primarily fluorine and chlorine, substitute for the hydroxyl group (OH) within the mineral structure. High concentrations of chloride in biotite (1 to 7 wt. % composition) have been observed in the porphyry copper deposits of Ray, Arizona and Santa Rita, New Mexico, as well as in other porphyritic deposits (Banks, 1976; Jacobs and Parry, 1979; Zhu and Sverjensky, 1992; and Zhu *et al.*, 1994). Halogenation is associated with hydrothermal metal-enrichment in porphyritic deposits and areas of supergene enrichment, as described in Barnes (1997).

In trioctahedral biotites, the orientation of the hydroxyl places the proton closer to the interlayer cation, which weakens the interlayer bond and slightly collapses the layers (Munoz, 1984, Hoda and Hood, 1972). When F and Cl substitute for the hydroxyl group, there is no proton to weaken the interlayer bond strength, making the structure more resistant to weathering (Munoz and Swenson, 1981, Hoda and Hood, 1972). However, the larger ionic radii of the Cl ion, in comparison with OH (Table 3), may strain the crystal lattice, promoting dissolution. The size effect may offset the proton effect; however, it is not known which effect dominates. Microprobe examinations of halogenated biotite have found Cl to be in homogeneously distributed, suggesting that

digestion of a bulk sample is more useful than a single point analysis in assessing the chloride content of biotite (Zhu *et al.*, 1994).

Table 3. Ionic radii for selected anions [nm, nanometers; values from Shannon (1976)].

| Ion | Charge | Coordination | Ionic Radius |
|-----|--------|--------------|--------------|
| Cl | -1 | VI | 0.181 nm |
| F | -1 | VI | 0.133 nm |
| OH | -1 | VI | 0.137 nm |

PREVIOUS PHYLLOSILICATE DISSOLUTION STUDIES

Biotite dissolution studies can provide insight into dissolution mechanisms, ion release rates, ion-ion interaction, and secondary mineral formation. This section examines methods and results for previous laboratory and field studies of biotite and phlogopite dissolution.

Laboratory Dissolution Studies

Biotite dissolution studies conducted in the laboratory under various controlled conditions are useful in determining the effect of time, temperature, and pH on the mineral dissolution rate. Previous laboratory dissolution studies of biotite and phlogopite (Table 5) include those by Lin and Clemency (1981b), Acker and Bricker (1992), Swoboda-Colberg and Drever (1993), Suarez and Wood (1996), Kalinowski and Schweda (1996), Malmstrom and Banwart (1997), and Taylor *et al.* (2000).

Biotite samples used in previous studies come from various formations, and the analysis varies depending on the analytical techniques employed by the investigators. The chemical composition of Bancroft biotite from Ontario, Canada used by Acker and Bricker (1992; Table 4) does not include MnO₂, TiO₂ and F, which has accounted for more than 5.5 wt. % of biotite from the same location analyzed in other studies (Turpault and Trotignon, 1994). Although F can occur in biotite, the concentration of F is not commonly analyzed. Previous biotite dissolution studies have not included Cl in their mineral analysis, thus the effect of halogen concentrations on dissolution rate is not known.

Table 4. Summary of previous laboratory studies of phyllosilicate dissolution [log R, log dissolution rate (moles/m²s) based on a formula containing O₂₀OH₄; μm, micrometers; FTC, flow-through column; FTF, flow-through film; FTDC, flow-through-dialysis cell; FB, fluidized bed; phlog, phlogopite]

| Author | Experimental Conditions | pH | Log R Basis | Log R | Sample Type | Sample Origin | Sample Formula |
|-----------------------------------|--|-----|----------------------------------|-------|-------------|----------------------------|---|
| Taylor <i>et al.</i> (2000) | Crushed sample (43-110 μm) in a FTC reacted with an HCl solution | 3.0 | K release | -11.6 | biotite | Adirondacks NY, USA | K _{1.86} (Mg _{4.62} , Fe ²⁺ _{0.36} , Fe ³⁺ _{0.76} , Al _{0.66}) (Si _{5.74} , Al _{2.20} , O ₂₀ (OH) ₄) |
| | | | | -11.2 | phlog | Adirondacks NY, USA | K _{1.60} Mg _{0.04} (Al _{1.76} , Si _{6.26} , O ₂₀ (OH) ₄) |
| Malmstrom and Banwart (1997) | Powdered sample (75-125 μm) in a FTF reacted by HClO ₄ in NaClO ₄ | 3.1 | Si release | -10.6 | biotite | Arendal, Norway | K _{1.58} (Mg _{1.66} , Fe ²⁺ _{2.06} , Fe ³⁺ _{0.38} , Al _{1.16}) (Si _{6.34} , Al _{1.34} , O ₂₀ (OH) ₄) |
| Kalinowski and Schweda (1996) | Ground sample (10-20 μm) in a FTDC reacted with a H ₂ SO ₄ or HCl solution | 3.0 | ^{1/2} total ion release | -11.8 | biotite | Norway (Moen) | (Ca _{0.02} , Na _{0.04} , K _{1.92}) (Mn _{0.01} , Mg _{2.70} , Fe ²⁺ _{1.71} , Fe ³⁺ _{0.82} , Al _{0.33}) (Si _{5.80} , Al _{2.20} , O ₂₀ (OH) _{3.97} , F _{0.03}) |
| | | | | -11.5 | phlog | Ontario, Canada (Burgess) | (Ca _{0.01} , Na _{0.09} , K _{1.92}) (Mn _{0.01} , Mg _{5.62} , Fe ²⁺ _{0.10} , Fe ³⁺ _{0.13} , Al _{0.12}) (Si _{5.77} , Al _{2.27} , O ₂₀ (OH) _{3.61} , F _{0.39}) |
| Suarez and Wood (1996) | Field sample (10-100 μm) reacted with DI H ₂ O | 5.0 | Mg release | -13.9 | biotite | CA, USA (Pachappa) | K ₂ (Mg ₃ , Fe ₃) (Si _{6.00} , Al _{2.00} , O ₂₀ (OH) ₄) |
| Swoboda-Colberg and Drever (1993) | Ground sample (75-150 μm) in a FB reacted with an HCl solution | 4.0 | ^{2/3} total ion release | -10.2 | biotite | Lead Mountain ME, USA | K ₂ (Mg _{0.6} , Fe _{1.4}) (Si _{6.00} , Al _{2.00} , O ₂₀ (OH) ₄) |
| Acker and Bricker (1992) | Broken sample (149-420 μm) in a FB reacted with a H ₂ SO ₄ soln | 3.0 | Mg release | -11.0 | biotite | Ontario, Canada (Bancroft) | (Ca _{0.01} , Na _{0.14} , K _{1.83}) (Mg _{3.17} , Fe ²⁺ _{2.19} , Fe ³⁺ _{0.05} , Al _{0.38}) (Si _{6.00} , Al _{2.00} , O ₂₀ (OH) ₄) |
| Lin and Clemency (1981b) | Ground sample (<400 μm) in a reaction cell with DI H ₂ O | 3.8 | Si release | -12.4 | phlog | Madagascar | (Ca _{0.01} , Na _{0.10} , K _{1.81}) (Mn _{0.02} , Mg _{5.15} , Fe ²⁺ _{0.24} , Fe ³⁺ _{0.14} , Al _{0.39} , Ti _{0.82}) (Si _{5.57} , Al _{2.43} , O ₂₀ (OH) _{2.86} , F _{0.91}) |

^{1/2}Weighted by ion abundance

^{2/3}Weighted by mineral abundance

The method of preparation employed in previous studies includes crushed, ground, hand broken, or unaltered samples. Crushing or grinding of the mineral is known to increase the surface area of the mineral, which can affect dissolution rates. A study of sample preparation by Acker and Bricker (1992) found that the dissolution rate of a ground sample was 2.5 times greater than a hand broken sample under similar conditions.

The types of experimental reactors employed in these studies include flow-through dialysis cells, flow-through columns, and flow-through dialysis cells. Flow through dialysis cells are designed to keep the mineral sample separated from dissolved reaction products using a dialysis membrane, as in the reactor used by Kalinowski and Schweda (1996). An internal loop circulates the sample suspended in solution. An external loop pumps the eluent solution parallel to the sample, where a membrane between the two loops allows for ion exchange. This type of reactor is ideal for reacting small quantities of material (>1g), however, this generally requires the sample to be ground or crushed. The internal circulating loop may cause sample abrasion from the velocity of the solution necessary to keep the minerals in suspension. A flow-through column is designed to pump a solution through a sample where the rate of pumping controls the residence time of the solution in contact with the mineral. The length of flow-through reactors can be short, as in the thin film flow-through cell used by Malmstrom and Banwart (1997), or can be longer, as in the column used by Taylor *et al.* (2000). A fluidized bed reactor is designed so that the mineral being reacted is continuously kept suspended in a solution by the bubbling of gas through the reactor. This type of reactor allows pressure control for the reaction but the bubbling of gas causes sample agitation, potentially creating mineral surface abrasion. A comparison of

reactor types by Acker and Bricker (1992) determined that biotite reacted in a fluidized bed dissolved 3 times faster than a sample reacted in a flow-through column under similar conditions. This can be attributed to sample abrasion in fluidized-bed reactors, which can act to increase dissolution.

Dissolution rates reported in previous studies vary widely for experiments conducted at the same pH (Table 4). For example, at pH 3, reported rates of dissolution vary between 10^{-11} and $10^{-11.8}$, a six-fold difference in rates. The variations can be attributed to differences in experimental methodology and materials, which includes reactor type, sample preparation, and mineral composition. Lin and Clemency (1981b) found that dissolution was incongruent and the dissolution of the octahedral sheet (based on Mg release) was 2 times greater than dissolution of the tetrahedral sheet (based on Si release). Acker and Bricker (1992) also found a preferential release of octahedral cations and detected vermiculite formation.

Table 5. Summary of previous field studies of phyllosilicate dissolution [μm , micrometers; log R, log dissolution rate (moles/ m^2s) based on a formula containing O_{20}OH_4]

| Author | Experimental Conditions | pH | Log R Basis | Log R | Sample Type | Sample Origin | Sample Formula |
|-----------------------------------|---|---------|-----------------------|-------|-------------|--|---|
| Murphy <i>et al.</i> (1998) | Field study of saprolite (100 μm) altered by natural ground water | 4.5 | Mg release | -14.7 | biotite | Luquillo Mountains Puerto Rico | $\text{K}_{1.58}(\text{Mg}_{2.50}, \text{Fe}^{2+}_{2.60}, \text{Fe}^{3+}_{0.10}, \text{Al}_{0.20}, \text{Ti}_{0.40})(\text{Si}_{5.60}, \text{Al}_{2.40}, \text{O}_{20}(\text{OH})_4)$ |
| Velbel (1985) | Field study of saprolite (100 μm) altered by natural ground water | 5.0-6.0 | Mg release | -12.6 | biotite | Nantahala Mountains, NC, USA (Coweeta) | $(\text{K}_{1.70}, \text{Na}_{0.12})(\text{Mg}_{2.40}, \text{Fe}^{2+}_{2.60}, \text{Al}_{0.90})(\text{Si}_{5.60}, \text{Al}_{2.40}, \text{O}_{20}(\text{OH})_4)$ |
| Swoboda-Colberg and Drever (1993) | Field study of saprolite (75-150 μm) altered by irrigation of an HCl solution | 4.0 | ^{29}Si flux | -13.6 | biotite | Lead Mountain ME, USA | $\text{K}_2(\text{Mg}_3, \text{Fe}_3)(\text{Si}_6, \text{Al}_2, \text{O}_{20}(\text{OH})_4)$ |

¹Weighted by mineral abundance

Field Dissolution Studies

Previous field studies have examined biotite dissolution *in-situ* (Velbel, 1985; Swoboda-Colberg and Drever, 1993; and Murphy *et al.*, 1998; Table 5). Swoboda-Colberg and Drever (1993) compared the dissolution of biotite in a saprolite profile irrigated with a hydrochloric (HCl) solution (pH 4.5). Their results determined laboratory rates to be 3.4 orders of magnitude faster than field rates. Field derived weathering rates for biotite (~100 μm) in saprolite profiles, are on average 1 to 3 orders of magnitude slower than laboratory derived rates, which has been attributed to the complexity of factors and unknowns inherent in the natural environment such as surface coatings, microbial activity, and uncertainties in hydrologic conditions, surface area, and temperature (Velbel, 1985; Suarez and Wood, 1996). These uncertainties are due to difficulties in estimating field values of mineral reactive surface area and wetted surface area, the degree of soil saturation, and connectivity of pore flow (Swoboda-Colberg and Drever, 1993). A detailed discussion of the uncertainties in field dissolution studies is beyond the scope of this paper, but can be found in Velbel (1993) and Schooner (1990).

Applications to This Study

Sample abrasion from reactors, as well as sample grinding, can increase the dissolution rate of minerals in laboratory studies. These stresses on the mineral can also promote the release of Cl from strained lattice sites. Since quantifying Cl release is the focus of this study, experimental design and sample preparation techniques were chosen appropriate to minimize the affect of these on Cl release in biotite. The most appropriate reactor appeared to be a flow-through column, as fluidized-bed reactors and flow-through

dialysis cells can cause sample abrasion. Specific design information and sample preparation techniques used in this study are discussed in detail the following section.

MATERIALS AND METHODS

Sample Collection and Separation

Seventy-five kilograms of unconsolidated stream alluvium was collected from the land surface near well site 700 down-gradient from the acidic ground-water plume (see Figure 2 for location). Previous column experiments by Stollenwerk and Eychaner, (1987), Lind and Stollenwerk (1993), and Stollenwerk (1994) demonstrated that the acid-neutralizing capacity of Pinal Creek alluvium does not vary with depth in the aquifer. Therefore, the surficial sample of alluvium used in this study was thought to be representative of the bulk alluvial material. The alluvial sediment was separated into size fractions using copper mesh ASTM (American Society for Testing and Materials) sieves placed in a Rototap shaker for 30-40 minute intervals. The sieves were scrubbed with a soft brush, washed with deionized water, rinsed with ethanol, and oven-dried prior to use. The 150-250 micrometer (μm) size fraction was retained and sieved three additional times to remove any finer-grained sediment. The 150-250 μm size fraction constituted 9 percent (%) of the original bulk sediment (Table 6) with optical examination showing quartz, feldspar and magnetite as the most abundant minerals present.

Biotite was isolated from the 150-250 μm size fraction using magnetic separation (Rosenblum, 1958; Deer *et al.*, 1962) and asymmetrical vibration techniques using a Faul Table². Heavy liquids were not employed due to their carcinogenic properties, and the potential for residual coating on the mineral surface interfering with dissolution. A FrantzTM Isodynamic Magnetic Separator was used to isolate biotite from the sediment using the magnetic susceptibility range of 0.2-0.5 amperes with a 20 degrees horizontal

² see Vrije Univ., Dept of Earth Science website at <http://www.geo.vu.nl/faculteit/fac/lms/faul-en.html>

tilt, and 15 degrees lateral tilt. Optical examination of this magnetic fraction showed the minerals biotite, chlorite, hematite, and pyroxene, with small amounts of magnetite all occurring as separate grains. Biotite was further isolated using a Faul Table, a vibrating mirrored surface with a horizontal tilt of approximately 30 degrees, provided by John Jackson of the U.S. Geological Survey, Reston, Virginia. The vibration and tilt of the plate separates minerals based on their shape. The platy cleavage of biotite made this method successful in attracting the biotite, which was electrostatically attracted to the mirrored surface while rounded minerals rolled off.

Table 6. Size fraction distribution of stream alluvium from Site 700 in Pinal Creek basin, Arizona [μm , micrometers; >, greater than; <l, less than]

| Percent of Bulk Alluvium | Sieve Size Fraction (μm) |
|--------------------------|---------------------------------------|
| 0.5 | <106 |
| 1.6 | 106-124 |
| 1.6 | 124-150 |
| 9.2 | ^h 150-250 |
| 22.9 | 250-500 |
| 30.1 | 500-900 |
| 22.9 | 900-2000 |
| 5.8 | 2000-4700 |
| 5.4 | >4700 |

^h size fraction used in this study

Approximately 35 grams of biotite were separated from the original 75 kilograms of alluvium collected. Optical inspection indicated that the sample was over 95 % biotite with small amounts of contamination from quartz, magnetite, feldspar, chlorite, and hematite. Pinal Creek biotite is reddish brown with zonation in color visible in some

flakes. Textural distinctions, such as recrystallized edges, are not always a reliable diagnostic tool in differentiating between igneous and hydrothermal biotite (Jacobs and Parry, 1979). Therefore, the percentage of Pinal Creek biotite that is halogenated could not be assessed from optical examination.

Table 7. Ion concentrations and pH of the biotite sample washing solutions measured at intervals during three consecutive washing events [ET, elapsed time; hrs, hours; nd, not detected]

| | Wash Solution 1 | | | Wash Solution 2 | | | Wash Solution 3 | | |
|------------------------|-----------------|------|------|-----------------|------|------|-----------------|------|------|
| ET (hrs) | 1.0 | 2.0 | 3.0 | 3.5 | 4.5 | 6.0 | 7.0 | 9.0 | 12.0 |
| pH | 3.34 | 3.85 | 4.55 | 3.25 | 4.88 | 5.81 | 5.62 | 5.34 | 5.16 |
| Cl (mg/L) | 0.15 | nd | nd | 0.09 | nd | nd | nd | nd | 0.05 |
| Na (mg/L) | 0.16 | 0.16 | 0.03 | 0.22 | 0.31 | 0.08 | 1.03 | 0.11 | 0.19 |
| NH ₄ (mg/L) | 1.97 | 0.19 | 0.05 | 0.82 | 0.16 | 0.04 | 0.26 | 0.09 | 0.05 |
| K (mg/L) | 2.17 | 0.62 | nd | 0.98 | 0.45 | nd | 1.17 | 0.09 | nd |
| Mg (mg/L) | 2.99 | 0.72 | 0.10 | 1.90 | 0.17 | 0.05 | 0.14 | nd | 0.03 |
| Ca (mg/L) | 11.47 | 2.59 | 0.25 | 10.7 | 0.57 | 0.25 | 0.47 | 0.04 | 0.03 |
| F (mg/L) | 1.39 | nd | nd | 0.09 | 0.21 | 2.94 | 0.15 | 0.12 | 0.02 |
| SO ₄ (mg/L) | 1.00 | nd | 0.27 | nd | nd | 1.27 | 0.89 | 1.05 | nd |

The biotite collected was ultrasonically cleaned and washed repeatedly in a weak 0.001M nitric acid solution to remove any sediment coatings, in particular carbonates, as well as fine particles adhering to the mineral surface. Between washings, the acid solution was decanted and the sample was rinsed three times with double deionized water. The pH and ion concentrations of the wash solution were measured at intervals during the three cleanings and are reported in Table 7. The sample was considered cleaned after 7.5 hours of acid reaction when calcium concentrations in the wash solution

decreased to 0.03 mg/L and the input pH no longer was increased by carbonate dissolution (Figures 8 and 9).

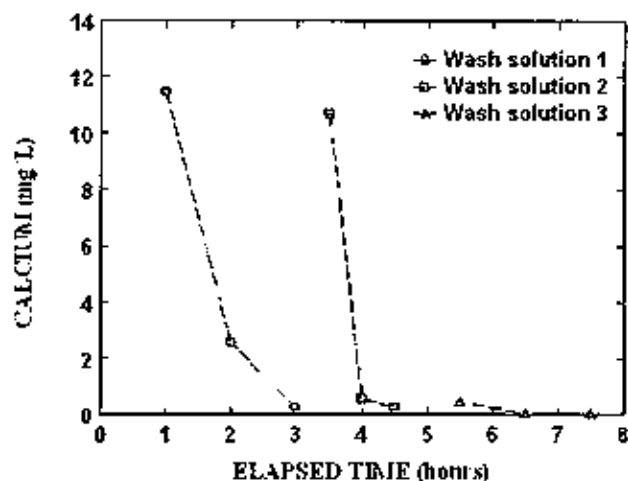


Figure 8. Concentration of calcium in biotite wash solutions. Solutions were measured at various time intervals during three consecutive washing events.

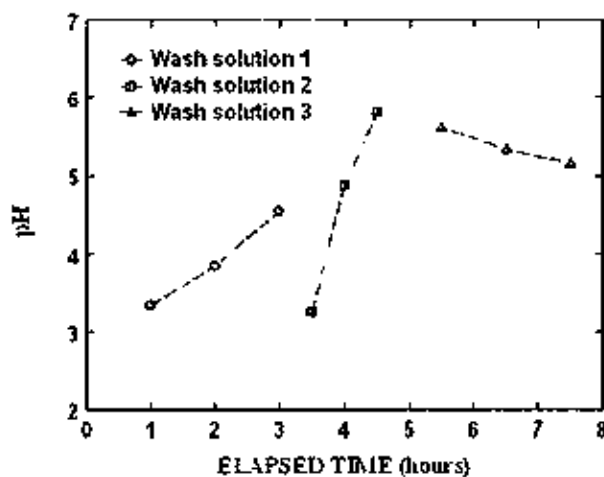


Figure 9. pH of biotite wash solutions. Solutions were measured at various time intervals during three consecutive washing events.

Sample Characterization and Composition

A sample of the Pinal Creek biotite was ground to a powder using an agate mortar and pestle and randomly mounted onto a frosted glass slide using Duco™ and acetone resin. The mounted sample was analyzed using a Rigaku D/Max-B x-ray diffractometer (XRD) and a conventional copper target x-ray tube set to 45 kilovolts (kV) and 30 milliamps (mA) at Temple University in Philadelphia, Pennsylvania with help from Dr. George Myer and Dr. Dennis Terry. XRD patterns (Figure 10) indicated that the sample was a 2M₁ trioctahedral biotite. The diffractogram revealed only biotite peaks, indicating that the sample was predominately (>95%) biotite.

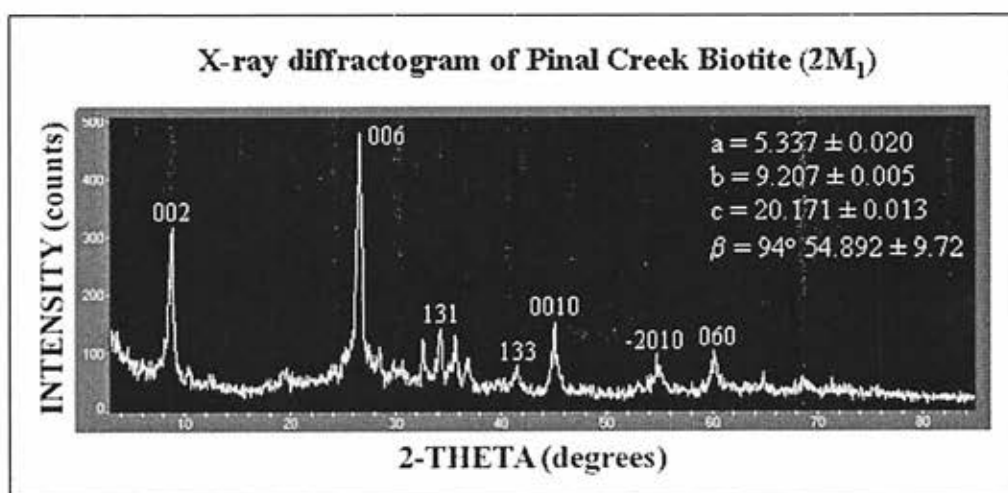


Figure 10. XRD pattern for randomly mounted Pinal Creek biotite (150-250 μm).

SEM analysis of the mineral surface was conducted at the Georgia State University Department of Biology³ in Atlanta, Georgia, using a LEO 1450vp SEM (LaB₆ kV imaging) and a LEO 906e transmission electron microscope (TEM), with help

³ http://biology.gsu.edu/research/facilities/imaging/elec_microscopy.html.

from Dr. Robert Simmons. For a before and after acid reaction comparison of biotite see SEM pictographs in the results section.

The specific surface area of the biotite was determined using a single point BET (after Brunauer *et al.*, 1938) Quantachrome Monosorb MS-12 analyzer (analytical uncertainty 5 %) with 75% N₂ and 25% He gas. The average sample surface area was 6.42 ± 0.22 meters squares per gram (m^2g^{-1}) based on replicate analysis (Table 8).

Table 8. Pinal Creek biotite BET surface area calculations [m^2/g , meters squared per gram; \pm , plus or minus]

| Analysis | Adsorption (m^2/g) | Desorption (m^2/g) |
|----------|------------------------|------------------------|
| 1 | 6.59 | 6.75 |
| 2 | 6.40 | 6.52 |
| 3 | 6.20 | 6.62 |
| 4 | 6.05 | 6.25 |
| Average | 6.31 ± 0.24 | 6.54 ± 0.21 |
| | 6.42 ± 0.22 | |

The chemical composition of the biotite was determined by x-ray fluorescence (XRF) analysis using a Phillips 2404 XRF vacuum spectrometer at Franklin and Marshall College Laboratories in Lancaster, Pennsylvania, with help from Dr. Stan Mertzman and Steve Sylvester. Analytical uncertainty in XRF analysis ranges from 1 to 5% for error associated with sample preparation, as well as instrument error (Rousseau, 2001). The XRF analysis for the biotite in Table 9 was averaged from three split analyses and the sediment analysis is for a single sample. A detailed description of analytical methodology

used in the XRF analysis can be found on the Franklin and Marshall Department of Earth and Environmental Science website⁴.

Table 9. Weight percent composition of stream alluvium and biotite from Pinal Creek basin, Arizona [wt%, weight percent; --, no data; ±, plus or minus]

| Component wt% | ¹ Biotite | ¹ Bulk Alluvium |
|--------------------------------|----------------------|----------------------------|
| SiO ₂ | 35.88 ± 1.01 | 36.07 |
| TiO ₂ | 6.45 ± 0.20 | 10.08 |
| Al ₂ O ₃ | 14.72 ± 0.40 | 6.87 |
| Fe ₂ O ₃ | 18.91 ± 0.39 | 32.41 |
| MnO | 0.47 ± 0.01 | 0.456 |
| MgO | 10.17 ± 0.35 | 1.621 |
| CaO | 1.63 ± 0.40 | 2.323 |
| Na ₂ O | 0.26 ± 0.01 | 1.012 |
| K ₂ O | 5.65 ± 0.14 | 1.488 |
| F | ² 0.5 | -- |
| Cl | ² 0.35 | -- |
| H ₂ O+ | 5.14 ± 0 | 0.481 |
| Total | 98.59 ± 2.55 | 1577.01 |

¹ XRF Analysis, Franklin and Marshall College, Lancaster, PA

² Wet Chemical Analysis, Temple University, Philadelphia, PA

Cl and F concentrations in biotite were measured by wet chemical techniques (hydrofluoric acid mineral digestion) and ion chromatography analysis. A detailed description of wet chemical rock analysis using hydrofluoric acid digestion can be found on the Union College Department of Geology website⁵. The formulaic composition of the

⁴ <http://www.fandm.edu/departments/earthandenvironment/facilities/xrf>

⁵ http://www.union.edu/public/geodept/hollocher/icp-ms/low_p_acid.html

biotite, calculated using oxide weight percentages in Table 10 (See Appendix A, Table A4 for normalization calculations), and based on an ideal biotite containing $O_{20}(OH)_4$, is:

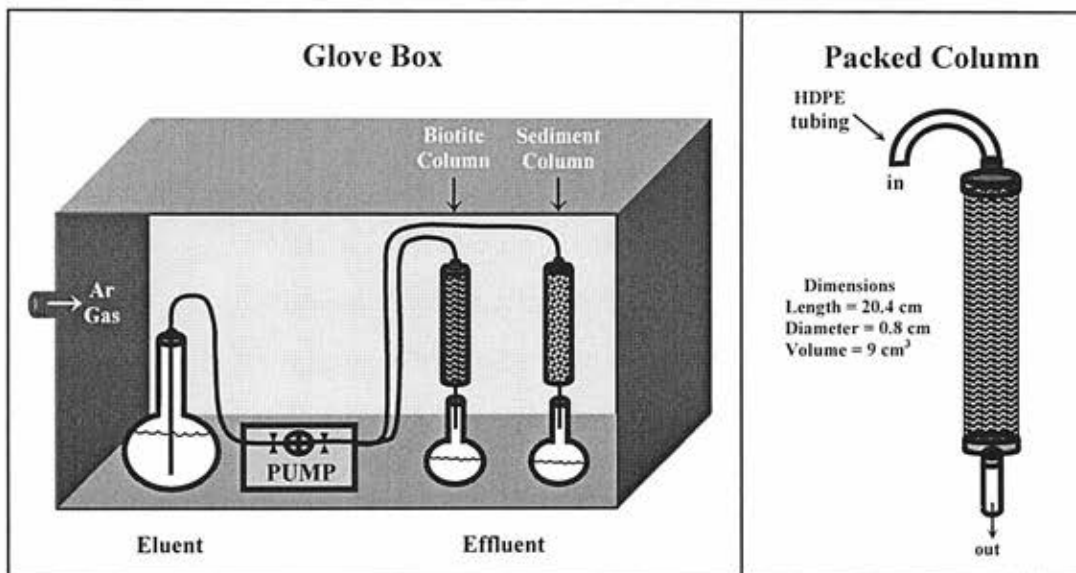
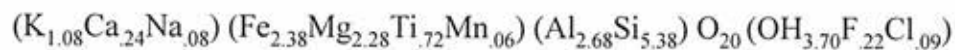


Figure 11. Schematic drawings of the flow-through column and glove-box housing.

Experimental Design

The flow-through column reactors used in this experiment were constructed from a 9 cubic centimeter polypropylene tubing 20.5 centimeter (cm) long and 0.8 cm in diameter (Figure 11). Both ends of the tube were capped with polypropylene luer tips and a 20 μ m polyethylene filter to prevent sample loss. A tube attached to the top delivered flow to the column, and a luer-lock valve at the bottom controlled flow from the column. Mineral samples loaded into the columns were weighed prior to and after the experiment

to measure any change in sample weight due to dissolution. The columns were housed in a glove box at 25 degrees Celsius and under low (<10 psi) flowing argon (Ar) gas.

Tubing

The use of Tygon™ or some other poly vinyl chloride (PVC) based tubing in the experiment raised some concerns that leaching of Cl from the tubing walls, due to the continuous feed of an acidic solution, would compromise the experimental results. For this reason, a high-density polyethylene (HDPE) material, Keltron™, was chosen as an alternative to PVC tubing. The HDPE tubing was compared with PVC tubing in an experiment to quantify chloride-release, if any. A H₂SO₄ acid solution of pH 2 was pumped through the tubing for 55 hours at a speed of 3 ml/hr. Effluent from both types of tubing was collected at intervals and analyzed for F and Cl. Experimental results show the PVC tubing had an initially high release of F and Cl, but concentrations decreased to below the detection limit after 47 hours (Figure 12). Release of F and Cl from the HDPE tubing was consistently below the analytical detection limit.

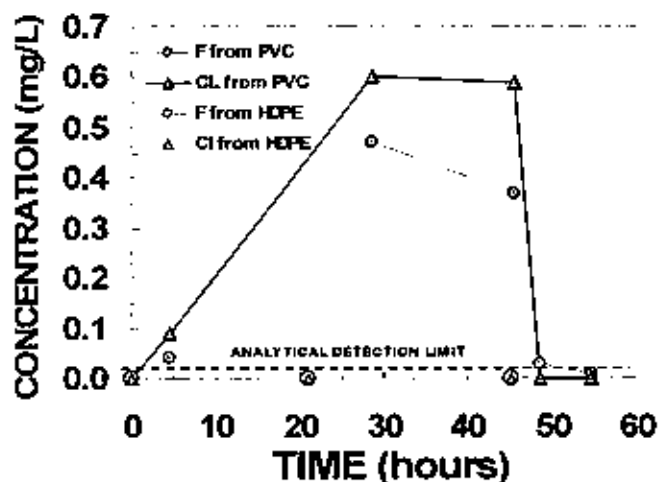


Figure 12. Comparison of fluoride and chloride release from PVC and HDPE tubing. Values are the difference between measured input and tubing output concentrations.

Experimental Procedure

A dilute sulfuric acid solution was used to mimic the acidic ground-water conditions in Pinal Creek Basin, (pH 4.13 and 3260 mg/L sulfate in January 1989, Brown, 1990). Acid solutions were prepared using trace-metal grade H_2SO_4 in 2000ml double de-ionized water and analyzed for pH and ion-content prior to use (Appendix Table A1). Periodic testing of the input acidic solution showed no detectable change in the concentration of cations, anions, or pH of the solution with storage time in the glove box.

Column effluent solutions were collected twice a day during the first 1000 hours of the experiment, then daily for the remainder of the experiment. Solutions were collected and stored in pre-weighed, acid-washed Pyrex volumetric flasks. Upon collection, the flasks were stoppered, weighed, and stored until analysis; typically within 1 to 5 days of collection. The temperature in the glove box, and pH of the aliquot samples were also recorded at the time of collection (Appendix Table A2). Over the course of the experiment, temperature in the glove box averaged 25 degrees Celsius (Figure 13). No preservatives were added to the solutions collected; however, the low pH of most samples precluded significant sorption or precipitation. The pH of a sample aliquot collected was measured over time, to determine the affect of storage on solution pH (Figure 14). Results showed that the pH of the stored sample solutions increased 0.04 pH units per day; indicating that, ideally, ion concentrations should be analyzed within 2 days of collection. The cation and anion concentrations in the output solutions were calculated by subtracting the ion concentrations of the acidic solutions from column aliquot sample analysis.

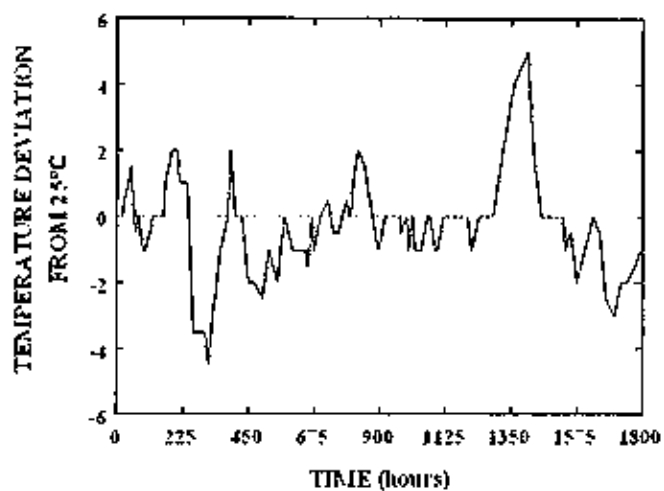


Figure 13. Temperature deviation from 25°C in the glove box during the experiment.

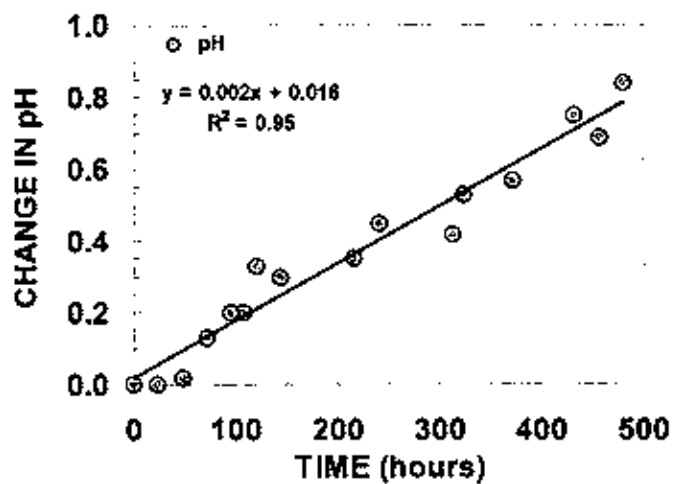


Figure 14. Change in pH of unpreserved output solutions with storage time. Analytical uncertainty is ± 0.005 pH units

Solution flow to the column was controlled using a peristaltic pump at an average flow rate of 3.1 milliliters per hour (ml/hr), and a solution residence time in the column of 103.5 minutes. Flow rates were determined from the volume of solution collected and the elapsed time, with solution residence time determined based on the calculated porosity and biotite density of 3.1 grams per cubic centimeter (g/cm^3). Normal stretching of tubing around the peristaltic pump head rollers caused tubing to degrade, therefore, tubing was replaced monthly during the experiment. The column was repacked after 1000 hours, due to a decrease in solution flow through the column, possibly due to secondary mineral precipitation in the column. The column was split apart and oven dried at 60 degrees Celsius for 24 hours. A spatula was used to gently disaggregate the individual grains and the same sample was repacked into a fresh column. To prevent further clogging, the pH was decreased from pH 3.4 to pH 2.9.

Analytical Methods

Sample aliquots were analyzed at Temple University for major dissolved species and pH. Major cation (K, Na, Mg, and Ca) and anion (F, Cl, and SO_4) concentrations were analyzed using a Dionex DX500 ion chromatograph (3 to 5 % analytical uncertainty). Since a sulfuric acid solution was used as the eluent, the SO_4^{2-} concentration of column effluent was determined as the difference in concentration between the two analyses. A Perkin-Elmer 3030 atomic adsorption (AA) spectrophotometer (3 to 5 % analytical uncertainty) was used to analyze the Al and Fe content of the effluent. Silica was analyzed using the molybdate blue method (APHA, 1992) at 410 nanometers with a Novaspec Spectronic-20 spectrophotometer (10 % analytical uncertainty). For a

discussion methods and techniques used in ion chromatography, atomic absorption spectrometry and colorimetry, see Fishman and Friedman (1989) or APHA (1992).

Calculations

Mineral dissolution rates used in this study were calculated based on Si release and reported in moles based on an $O_{20}(OH)_4$ formula unit per meter squared per second ($\text{mol m}^{-2} \text{s}^{-1}$) according to the equation:

$$r = \frac{(C_o - C_i) \times Q}{M \times SA}, \quad (2)$$

where

r = ion release rate ($\text{mol m}^{-2} \text{s}^{-1}$),

C_o = output solution ion concentration (mol mL^{-1}),

C_i = input solution ion concentration (mol mL^{-1}),

Q = flow rate (mL s^{-1}), M = sample mass (g), and

SA = BET surface area ($\text{m}^2 \text{g}^{-1}$).

Mineral dissolution rates used in this study were calculated based on Si release and reported in moles based on an $O_{20}(OH)_4$ formula unit per meter squared per second ($\text{mol m}^{-2} \text{s}^{-1}$) according to the equation:

$$R = \frac{r_i}{X_i}, \quad (3)$$

where

R = mineral dissolution rate ($\text{mol m}^{-2} \text{s}^{-1}$),

r = ion release rate ($\text{mol m}^{-2} \text{s}^{-1}$), and

X_i = stoichiometric number per formula unit.

The dissolution rate (R) can also be used to determine the order of the dissolution reaction with respect to the hydrogen ion (n), using the equation:

$$R = \frac{dC_i}{dt} = k_i^0 a_{H^+}^n, \quad (4)$$

where:

R = mineral dissolution rate ($\text{mol m}^{-2} \text{s}^{-1}$),

C_i = concentration of element i (mol mL^{-1}),

t = time, k_i = rate constant of the element,

a_{H^+} = the activity of the hydrogen ion, and

n = the order of the reaction.

The slope of $\log R$, plotted as a function of pH ($-\log a_{H^+}$), is equal to $-n$.

RESULTS

Specific data from the biotite column experiments, including concentrations of dissolved species and output pH, are given in Appendix A, Table A2. Graphical presentation and interpretation of the data are presented in this section.

A measure of the average flow rate is a necessary component in the calculation of the dissolution rate (Equation 3). The flow rate of acid solution through the biotite column was measured with time and is shown in Figure 15. Some variability in the flow rate is expected due to stretching of the tubes with time tubes around the rollers of the peristaltic pump. However, the large amount of variability in flow during the first 1000 hours of the experiment was possibly due to clogging from the precipitation of secondary minerals. The rate of solution flow through the column during the last 1000 hours of the experiment averaged 3.1 ml/hour, resulting in a solution residence time of 104 minutes.

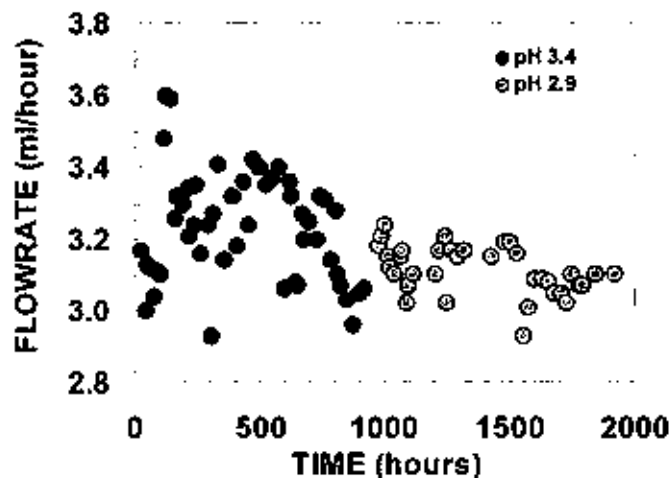


Figure 15. Flow rate of the acid solution through the biotite column. Values are shown for input solutions pH 3.4 and 2.9 over 2000 hours. Analytical uncertainty is 10%.

The concentrations of major ions released from the biotite column over a period of 2000 hours are shown in Figures 16, 17 and 18. During the first 1000 hours of the experiment, the input pH was 3.4. (Figure 16) To prevent column clogging, the input pH was then decreased to 2.9 for the remainder of the experiment. The output pH of the column was initially high (ca. pH 5.8) then stabilized near pH 3.4 after 1400 hours (813 pore volumes). The difference in input versus output pH is a measure of the rate of the reaction. After 1400 hours, the difference in input and output pH for the column had decreased to about 0.5 pH units, indicating that reaction rates had stabilized and that most calcite and fine grained phased had been removed. Therefore, concentrations and rates measured after 1400 hours are probably a result of biotite dissolution.

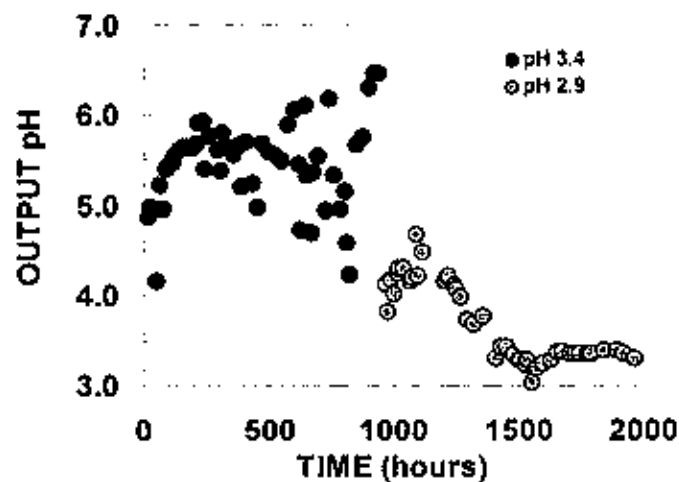


Figure 16. Output pH of biotite column effluent. Values are shown for input solutions pH 3.4 and 2.9 over 2000 hours. Analytical uncertainty is ± 0.05 pH units.

Concentrations of K and Ca released from the biotite were initially high, then decreased and stabilized after 1400 hours at an average of 0.50 mg/L, 1.14 mg/L, and 0.68 mg/L, respectively (Figure 17). The higher initial pH and high concentrations of K and Ca are attributed to the initially rapid dissolution of fine-grained mineral contaminants, such as calcite, and ion-exchange release from the biotite, and are not considered an artifact of sample preparation, since no grinding was used in this study.

Fe concentrations were below the analytical detection limit (0.002 mg/L) during the first 1000 hours, and then began to increase when the input solution pH was decreased to 2.9. Although most parameters became stable at 1400 hours, Fe-release was high, increasing to a peak of 5.5 mg/L, then decreased and stabilized to about 3.0 mg/L at 1600 hours. The peak in Fe concentration may be due to the rapid dissolution of colloiddally bound Fe. Like Fe, Al concentrations were also very low at input pH 3.4, but began to steadily increase after 1400 hours to about 1.7 by the end of the experiment. Because of the high initial pH, low concentrations of iron and aluminum in the first 1000 hours indicate that these ions were being removed from solution by the precipitation of secondary oxyhydroxide minerals. As calcite was removed from the column and the output pH decreased, these oxyhydroxides became undersaturated, releasing Fe and Al into solution. After that interval, *ca.* 1800 hours, concentrations of Fe and Al stabilized and became stoichiometric (see Stoichiometry). Si concentrations were initially high then decreased as some Si was precipitated as kaolinite (see Stoichiometry). As the kaolinite became undersaturated, Si concentrations increased and stabilized to about 2.3.

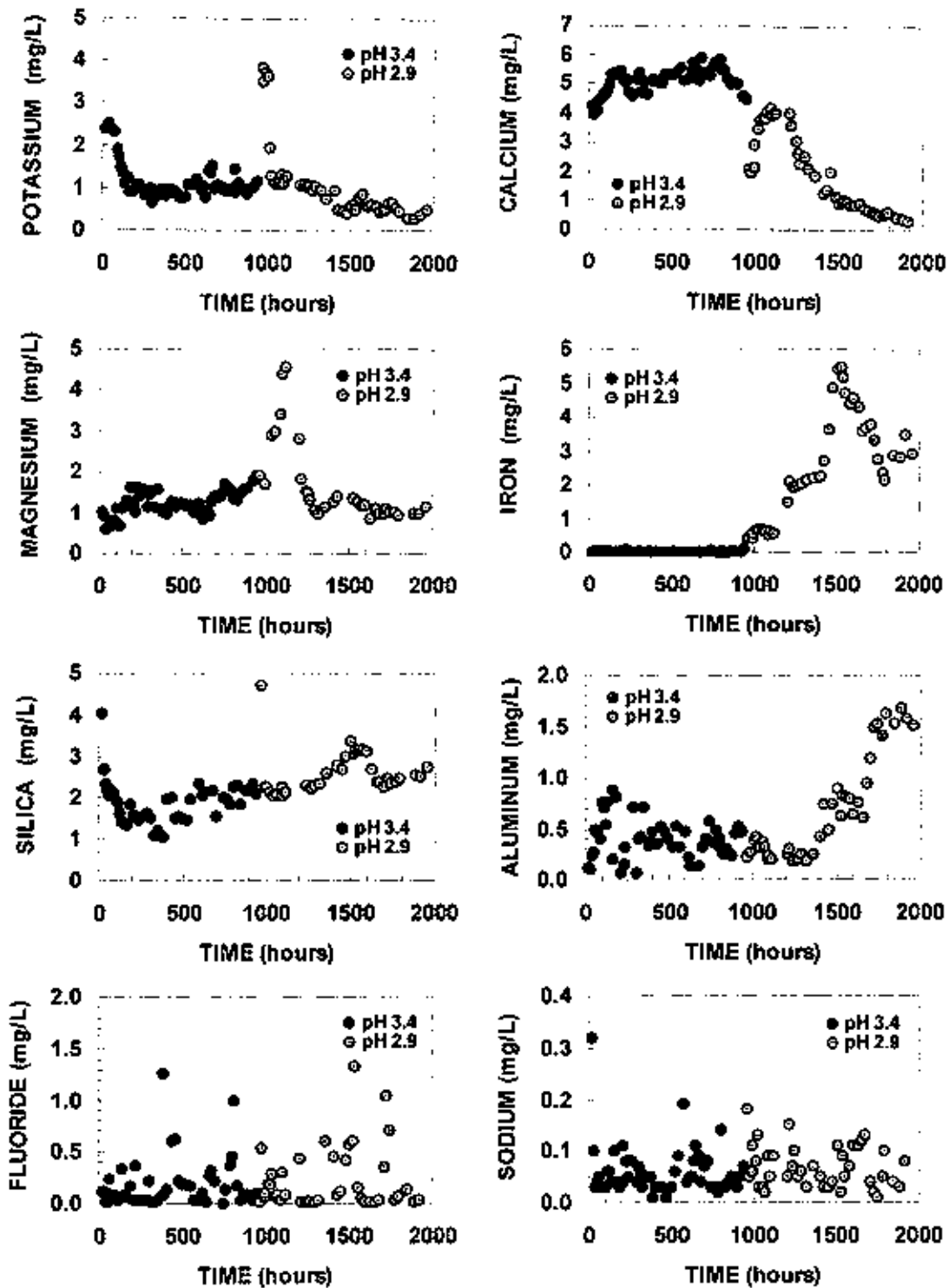


Figure 17 Concentration of major ions in biotite column output solutions. Values are shown for input solutions pH 3.4 and 2.9 over 2000 hours, with an analytical uncertainty of 5%. Values below the detection limit are plotted as zero.

Concentrations of F, Na (Figure 17), and Cl (Figure 18) were highly variable; many Cl values were below the analytical detection limit (0.01 mg/L), indicating an inhomogeneous distribution of these elements in the biotite. Such inhomogeneities have been observed by Munoz and Swenson (1981) in microprobe examination of hydrothermal biotites. Chloride may be contained along particular biotite growth zones or in inclusions in the biotite.

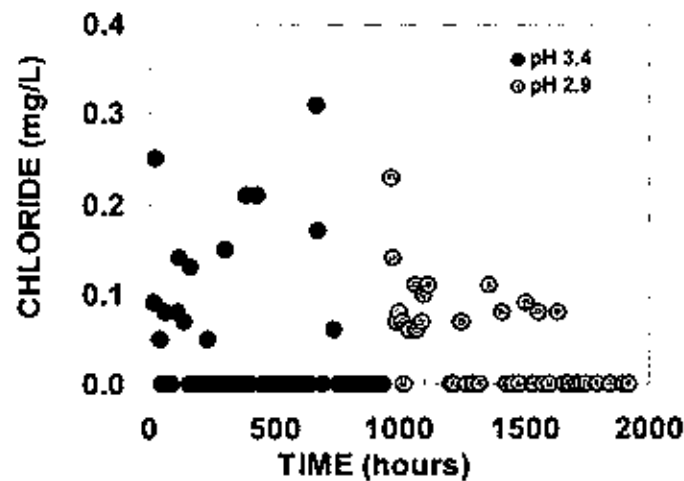


Figure 18. Concentration of chloride in biotite column output solutions. Values are shown for input solutions pH 3.4 and 2.9 over 2000 hours, with an analytical uncertainty of 5%. Values below the analytical detection limit (0.01 mg/L) are plotted as zero.

Ion Release Rates

The average rates of ions released (r) were calculated using equation 2 for concentrations sampled between 1400 and 2000 hours are shown in Table 10. Ion release rates varied with ion species where Cl was the slowest at $0.08 \text{ picomol m}^{-2} \text{ s}^{-1}$. The dissolution rate of

biotite (R) averaged for all the ions was similar to the dissolution rate calculated based on Si release, indicating that Si is a suitable ion to choose for calculation dissolution rate.

Table 10. Average ion release rates. Values are averaged between 1400 and 2000 hours [pmol m⁻² s⁻¹, picomoles per meters squared second]

| Ion | Average ion concentration (C in mg/L) | Average ion release rate (r in pmol m ⁻² s ⁻¹) | Average ion release rates normalized to biotite (R in pmol m ⁻² s ⁻¹) |
|----------------|---------------------------------------|---|--|
| K | 0.54 | 0.16 | 0.14 |
| Mg | 1.13 | 0.519 | 0.22 |
| Ca | 0.83 | 0.26 | 0.108 |
| Na | 0.063 | 0.031 | 0.38 |
| Cl | ^{1/} 0.025 | 0.0078 | 0.08 |
| F | 0.205 | 0.120 | 0.54 |
| Fe | 3.69 | 0.755 | 0.317 |
| Si | 2.80 | 1.11 | 0.216 |
| Al | 1.07 | 0.369 | 0.137 |
| Average | | | 0.277 |

^{1/} assumes values below the detection limit of 0.01 are zero

Stoichiometry

Initial dissolution was non-stoichiometric, with the ratio of major dissolved ions in column output solutions significantly different from ratios in the biotite. However, after 1400 to 1700 hours, ratios for dissolved species approached those for the bulk biotite sample composition,



Previous studies have found that phyllosilicate dissolution was initially non-stoichiometric, with preferential extraction of inter-layer cations and also preferential dissolution of the octahedral layer (e.g. Acker and Bricker, 1992, and Kalinowski and Schweda, 1996). The molar ratios of Mg/K, Al/Si, and Si/Mg observed for this study are discussed below.

The Mg/K molar ratio was initially high probably due to the dissolution of Mg-bearing carbonates or release of Mg in oxyhydroxides at the lower pH (Figure 19) As the concentration of Mg decreased the ratio of Mg/K approached the stoichiometric ratio of 2.11 after 1400 hours

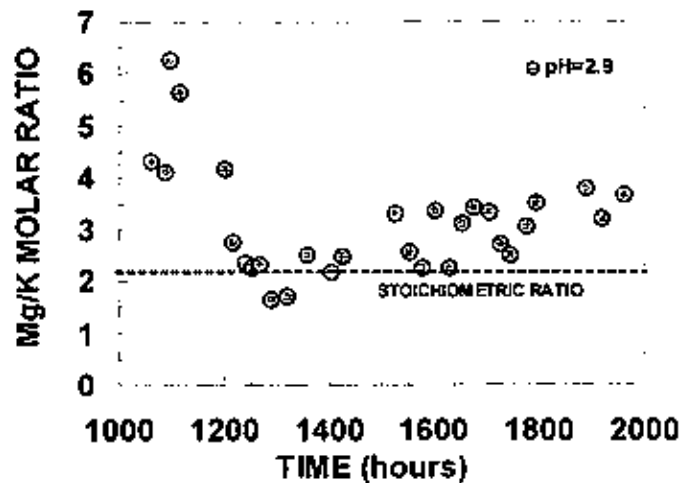


Figure 19. Mg/K molar ratios in biotite column output solutions. Ratios are plotted with respect to the stoichiometric ratio (2.11) of Mg to K in Pinal Creek biotite for the last 1000 hours of the experiment. Analytical uncertainty is 7%.

The Al/Si molar ratio was initially low, and did not approach stoichiometric conditions until 1700 hours into the experiment (Figure 20). This can be attributed to the precipitation of aluminosilicates during the initial part of the experiment at pH 3.4.

The Si/Mg molar ratio was initially much less than the stoichiometric ratio of 2.39 in the biotite (Figure 21), probably due to the precipitation of kaolinite during the first 1000 hours of the experiment. pH input due the dissolution of kaolinite. A stability diagram of Al and Si output concentrations indicates that initial reactions occurred in the kaolinite stability field, but when the input pH was changed to 2.9, concentrations migrated into the solution field (Figure 22).

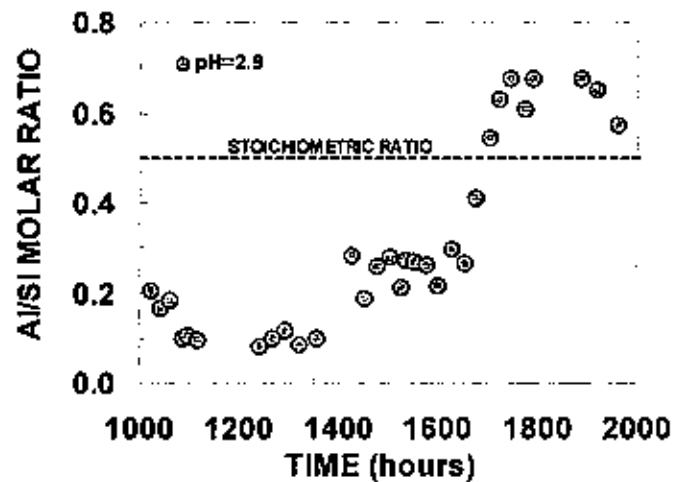


Figure 20. Al/Si molar ratios in biotite column output solutions. Ratios are plotted with respect to the stoichiometric ratio (2.36) of Al to Si in Pinal Creek biotite for the last 1000 hours of the experiment. Analytical uncertainty is 7%.

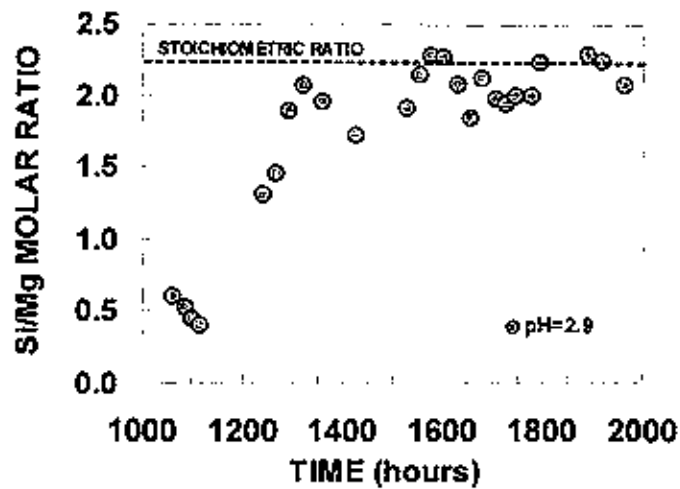


Figure 21. Si/Mg molar ratios in biotite column output solutions. Ratios are plotted with respect to the stoichiometric ratio (2.36) of Si to Mg in Pinal Creek biotite for the last 1000 hours of the experiment. Analytical uncertainty is 7%.

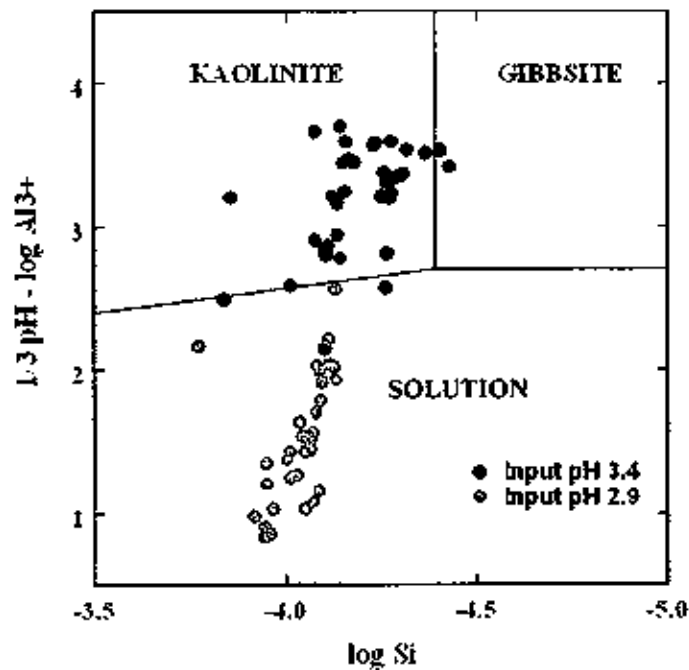


Figure 22. Stability of kaolinite in biotite column output solutions. Mineral stability diagram showing kaolinite stability in the column at input solution pH 3.4 and input solution pH 2.9.

Physical Alteration

The weight of the sample at the beginning of the experiment was 11.58 g, after 1000 hours of acid reaction at pH 3.4 it decreased to 11.52 g, and after another 1000 hours of acid reaction at pH 2.9 it decreased to 11.37 g. The amount of sample weight loss at pH 3.4 (6 g) was lower than at pH 2.9, probably due to lower dissolution rates at a slightly higher pH, or the loss due to dissolution was off set by an increase in weight from the precipitation of secondary minerals .

SEM was used to examine the surface of the biotite before and the experiment to assess physical alteration of the sample due to acid reaction. An image of the biotite before being reacted shows that the surface of the sample was covered with numerous etch pits resulting from previous *in-situ* weathering (Figure 23). The edges of the mineral plates exhibited slight curling, typically seen in weathered phyllosilicates (Figure 24).

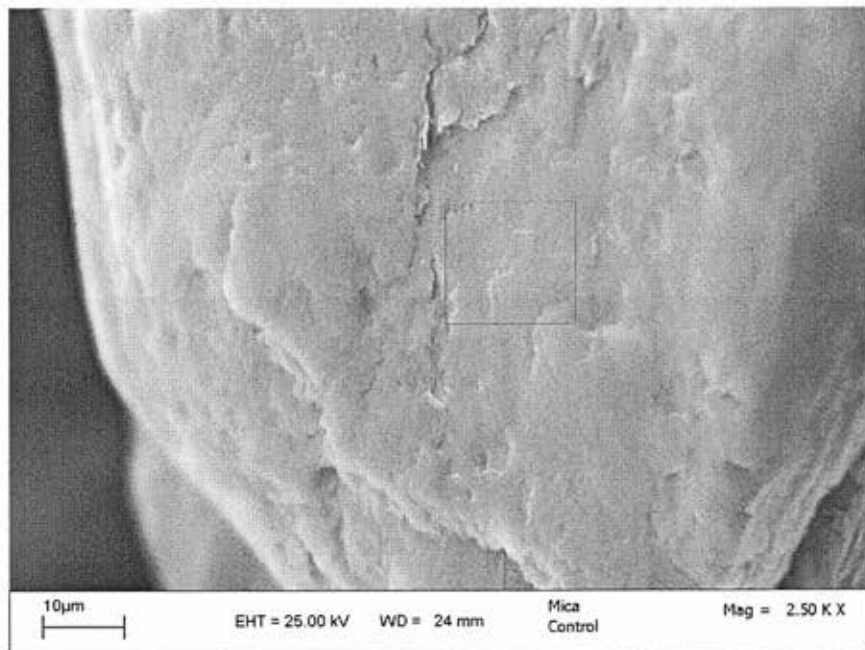


Figure 23. SEM pictograph of unwashed Pinal Creek biotite showing natural weathering of the basal surface prior to acid reaction. Scale bar = 10µm.

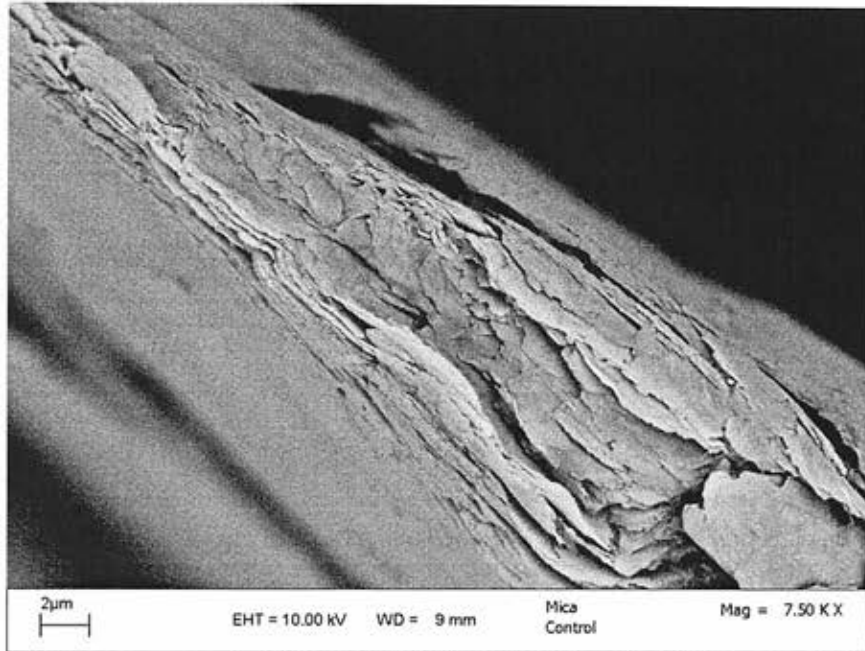


Figure 24. SEM pictograph of unwashed Pinal Creek biotite showing natural weathering of the mineral edge prior to acid reaction. Scale bar = 2 μ m.

Images of the post-reaction sample surface showed that etch pits observed in the unreacted biotite were not appreciably altered during these experiments (Figure 25). The mineral edges, however, were highly altered by the experiment, exhibiting opaque acicular crystals, possibly sepiolite, $Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$, or palygorskite (*a.k.a.* attapulgite, $Mg_5Si_8O_{20}(OH)_6 \cdot 4H_2O$; Figure 26; Dr. Owen Bricker, U.S. Geological Survey, personal communication, 2004). Figure 27 shows a SEM photomicrograph of an unidentified elongated bladed crystal, possibly hornblende, $Ca_2(Mg,Fe)_4AlSi_7AlO_{22}(OH)_2$, intermittently present throughout the SEM sample. This mineral was not observed in pre-reaction pictographs, indicating that it may have been an inclusion liberated from the biotite during the experiment. Iron coatings, which might have armored the biotite surface, were not observed in post-reaction SEM examination.

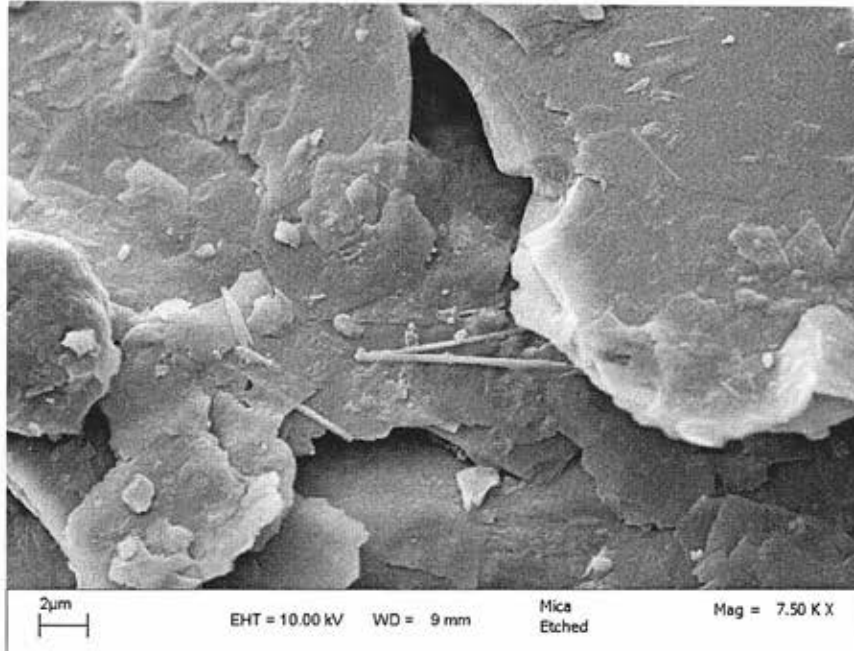


Figure 25. SEM pictograph of Pinal Creek biotite after 2000 hours of acid reaction showing basal weathering. Notice the formation of secondary clays on the basal surface. Scale bar = 2 μ m.

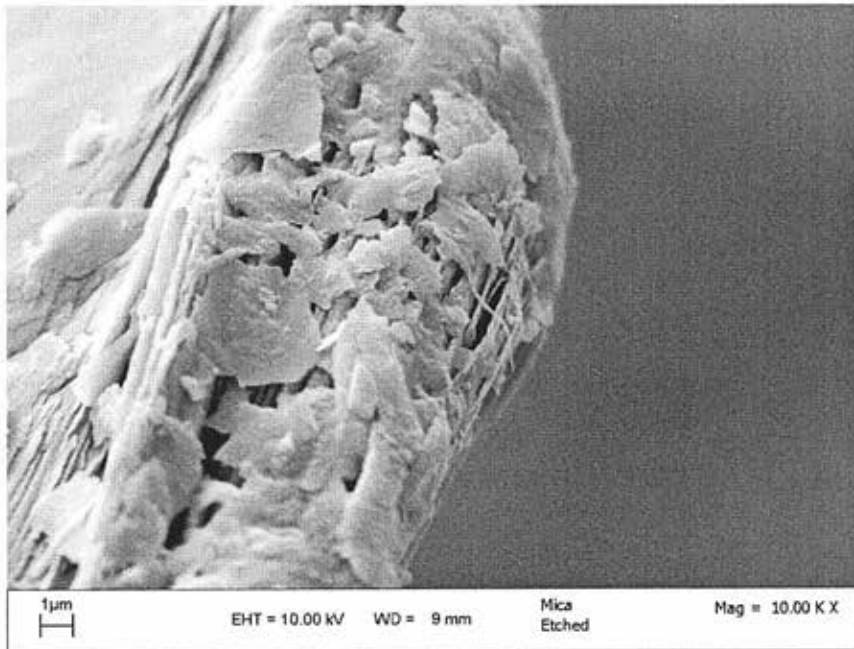


Figure 26. SEM pictograph of Pinal Creek biotite after 2000 hours of acid reaction showing edge weathering. Notice the formation of secondary clays, in particular acicular minerals, possibly attapulgite. Scale bar = 1 μ m.

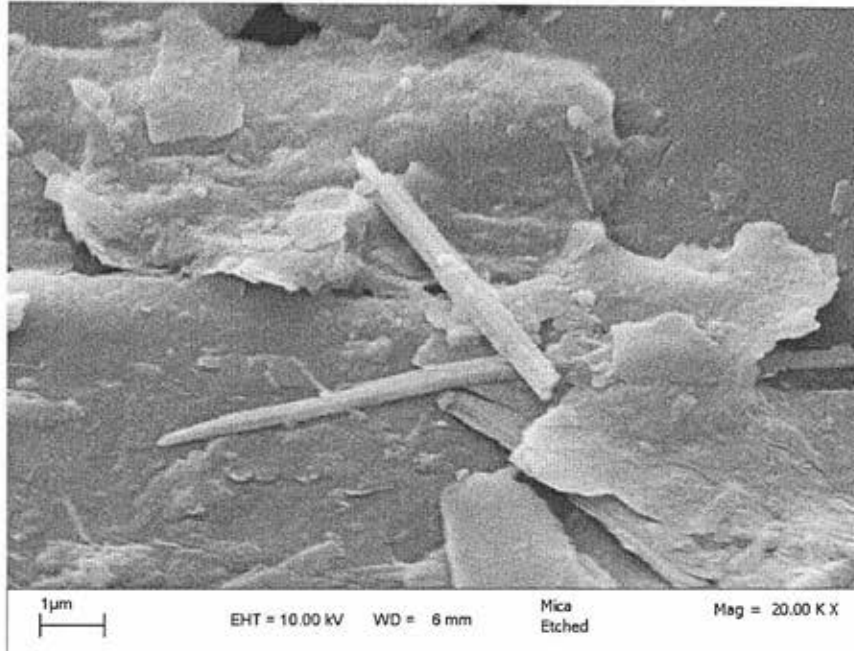


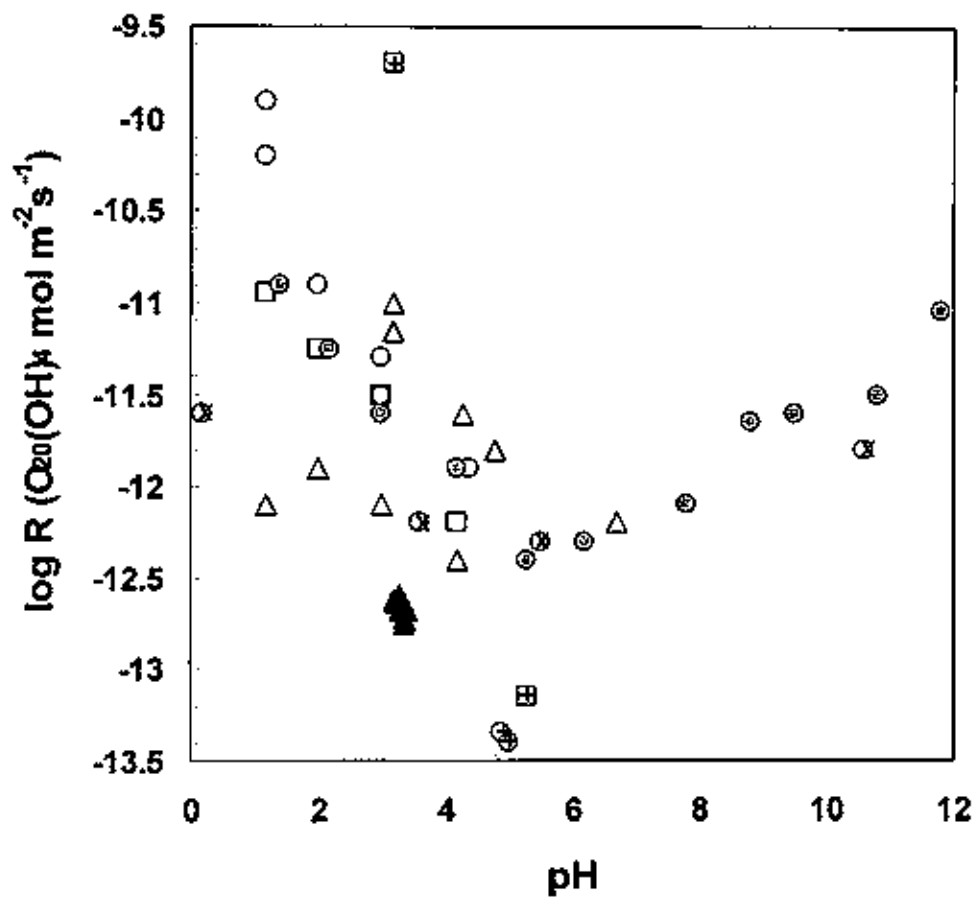
Figure 27. SEM pictograph of Pinal Creek biotite after 2000 hours of acid reaction. Notice the presence of a bladed mineral, possibly hornblende, shown in the center of the pictograph. Scale bar = 1 µm.

Dissolution Rate

Mineral dissolution rates were calculated using equation 3 and based on Si release after the pH had stabilized (about 1400 hours into the experiment). Si release was used as the dissolution rate determining ion since Si was the slowest ion released, and therefore exerted the greatest control over the dissolution rate. The dissolution rate measured in this study was $2.16 \times 10^{-13} \text{ mol m}^{-2} \text{ s}^{-1}$ based on a molar formula containing $\text{O}_{20}(\text{OH})_4$. This rate is somewhat slower than rates previously measured for ground hydroxylated biotite (*i.e.* Acker & Bricker 1992) and phlogopite (*i.e.* Kalinowski & Schweda 1996) in the same pH ranges (Figure 28). Differences in dissolution rates between these studies might result from experimental design, sample preparation, and/or mineral composition. Fluidized bed reactors that were used in some of the previous studies can produce sample abrasion and

commutation, resulting in more rapid dissolution rates. Grinding produces disordered surface layers which may also dissolve more rapidly. It is also possible that differences in halogen content in the mica samples could have affected the dissolution rates; however, Cl data are not available for biotites from previous studies.

The order of the reaction (n) with respect to hydrogen ion activity was 0.52 over the pH range 3.1 to 3.5 (Figure 29). This value was obtained from statistical regression ($y = 0.52x - 10.93$ and $r^2 = 0.46$) of $\text{Log } R$ as a function of output solution pH. Reaction orders (n) observed in trioctahedral micas from other studies are slightly less than the value determined in this study, (*i.e.*; 0.35-0.61 by Kalinowski and Schweda, 1996, and 0.34 by Acker and Bricker, 1992).



| Explanation | Phlogopite |
|---------------------------------|---|
| Muscovite | ⊞ Kalinowski and Schweda (1996) |
| ○ Kalinowski and Schweda (1996) | ⊞ Lin and Clemency (1981) – open system |
| ⊗ Knauss and Wolery (1989) | □ Lin and Clemency (1981) |
| ⊕ Lin and Clemency (1981) | Biotite |
| ⊗ Nickel (1973) | △ Kalinowski and Schweda (1996) |
| | △ Acker and Bricker (1992) |
| | ▲ This Study |

Figure 28. Comparison of dissolution rates from this study with results from previous studies (Modified from Kalinowski and Schweda, 1996). Only dissolution rates for the last 600 hours of this experiment at input pH 2.9 are plotted based on Si release.

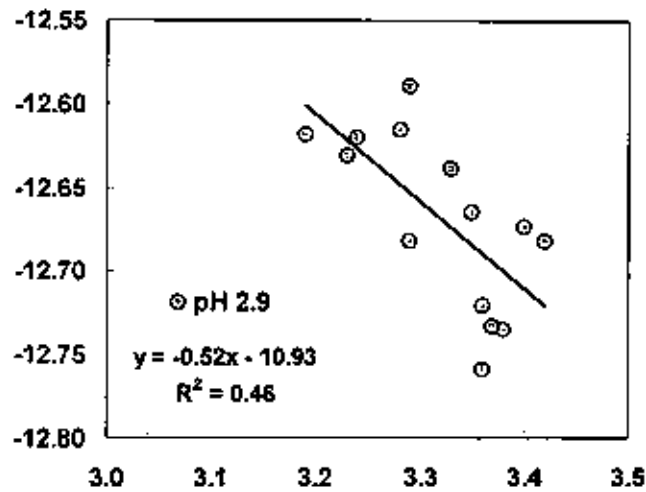


Figure 29. Biotite dissolution rate as a function of pH. The hydrogen ion dependence of Pinal Creek biotite dissolution is based on the measured release of Si in column outflow and a formula containing $O_{20}(OH)_4$.

Applications of Biotite Dissolution Rate to Pinal Creek

The dissolution rate (R_{Si}) and Cl content of Pinal Creek biotite (s) calculated in this study can be used to estimate the concentration of Cl in basin ground water (C_{Cl}) due to biotite dissolution. In particular, the concentration of Cl can be calculated for ground water along the flow path modeled by Glynn and Brown (1996) according to the equation:

$$C_{Cl} = R_{biot} \times X \times d \times \frac{1}{V} \times \rho_{rock} \times \frac{(1-\phi)}{\phi} \times M \times SA_{biot} \times mw_{Cl}, \quad (4)$$

where:

C_{Cl} is the concentration of Cl added to basin ground water from biotite dissolution

R_{biot} is the dissolution rate of biotite at pH 5 based on Si release and the hydrogen ion dependence ($2.8 \times 10^{-14} \text{ mol m}^{-2} \text{ s}^{-1}$),

X is the mol of Cl in a mol of biotite (0.09),

d is the distance between well group 400 and 500 (5600 m),

V is the flow rate of ground water (5.2 m d^{-1} , $6.02 \times 10^{-5} \text{ m s}^{-1}$),

δ is the density of alluvium derived from dacite in Pinal Creek, (2.28 g cm^{-3} ; Peterson, 1962),

ϕ is the porosity of Pinal Creek alluvium (0.3 cm^3),

M is the percent of biotite in Pinal Creek Shultz Granite (0.045; Peterson, 1962),

SA is the average BET surface area of the biotite ($6.4 \text{ m}^2 \text{ g}^{-1}$), and

mw_{Cl} is the molecular weight of chloride ($35.5 \times 10^6 \mu\text{g mol}^{-1}$).

Results of the calculation indicate that biotite dissolution could have contributed as much as 5.7 mg/L of Cl to basin ground water between wells 402 and 403. This equation makes the assumptions that; (1) 100% of Cl in the biotite structure is released into solution, and (2) the amount and chemical composition of biotite from this study is representative of sediment along the flow path modeled by Glynn and Brown (1996).

The error associated with this calculation is potentially large, due to uncertainties such as (1) analytical uncertainty in dissolution rate (R_{biot}) calculated (estimated as 20-50%), (2) uncertainty in mineral surface area (SA) which only accounts for biotite in the 100-250 μm fraction, and (3) uncertainty in Cl composition in biotite (X) from other size fractions. Despite these uncertainties, computations of this sort can be a useful tool for determining the contribution of Cl from halogenated biotite to basin ground water on a broad scale.

Sediment Column Experiment

A second experiment was conducted using a column packed with bulk alluvial sediment from Pinal Creek. Results from the sediment column experiment are discussed below and concentrations of dissolved species and pH for input and output solutions are given in Appendix A, Table A3. A general discussion of sediment column results is presented to give the reader an understanding of the geochemical conditions in which Pinal Creek biotite exists and determine whether any other Cl sources exist in the sediment.

The sediment was reacted for 2000 hours with the same acid solutions used with the biotite column. The average flow rate of the acid solution through the column packed with Pinal Creek alluvial sediment was 3.0 mg/L (Figure 30). Figures 31, 32 and 33 show concentrations of ions released from the sediment column. The output pH (Figure 31) was initially high (*ca.* pH 7) for the first 600 hours, before decreasing to *ca.* pH 3.5 during the latter part of the experiment.

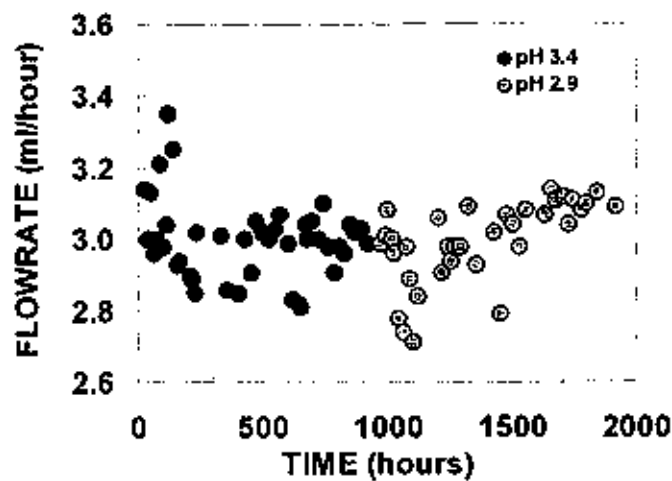


Figure 30. Flow rate of the acid solution through the sediment column. Values are shown for input solutions pH 3.4 and 2.9 over 2000 hours. Analytical uncertainty is 10%.

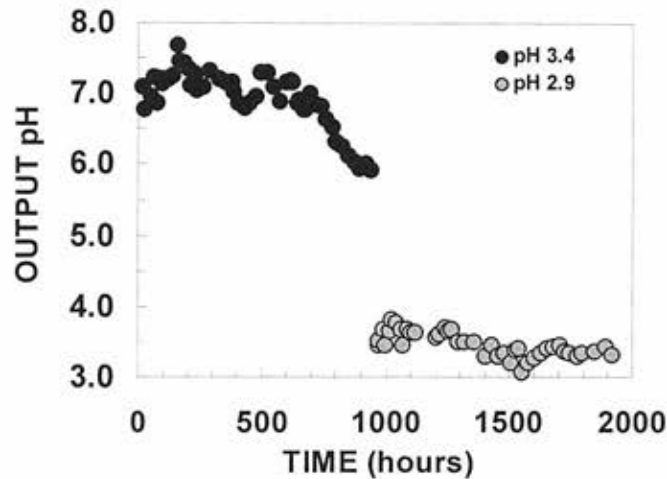


Figure 31. Output pH of the sediment column effluent. Values are shown for input solutions pH 3.4 and 2.9 over 2000 hours. Analytical uncertainty is ± 0.05 pH units.

The concentration of K was initially high then decreased and stabilized to 0.10 ± 0.04 mg/L at 1200 hours into the experiment (Figure 32). The release of Ca was initially high, about 10 mg/L, with values decreasing to about 1 mg/L after 600 hours. Mg was initially high then decreased and stabilized at around 0.6 mg/L before increasing to about 1.6 mg/L at 1450 hours. The higher initial pH and high concentrations of K, Ca and Mg are attributed to the rapid dissolution of fine-grained feldspar and calcite and ion-exchange release from phyllosilicates and clay minerals.

Fe concentrations were below the analytical detection limit (0.01 mg/L) during the first 1000 hours, because at higher pH any Fe released is precipitated in secondary minerals. When the pH of the input solution was increased to 2.9, Fe release was variable. Si had initial high release rate that decreased and stabilized between 300 and 600 hours to about 1.3 mg/L, but increased slightly to 2.1 mg/L at input pH 2.9.

Aluminum release was initially low, but steadily increased and stabilized at 1.32 ± 0.30 mg/L when the input pH was decreased to 2.9. Because of the higher initial pH, iron and aluminum were precipitated, along with silica and possibly magnesium, in formation of secondary clay and oxyhydroxide minerals. The concentrations of F, Na, and Cl (Figure 33) were low, with many Cl values below the analytical detection limit (0.01 mg/L).

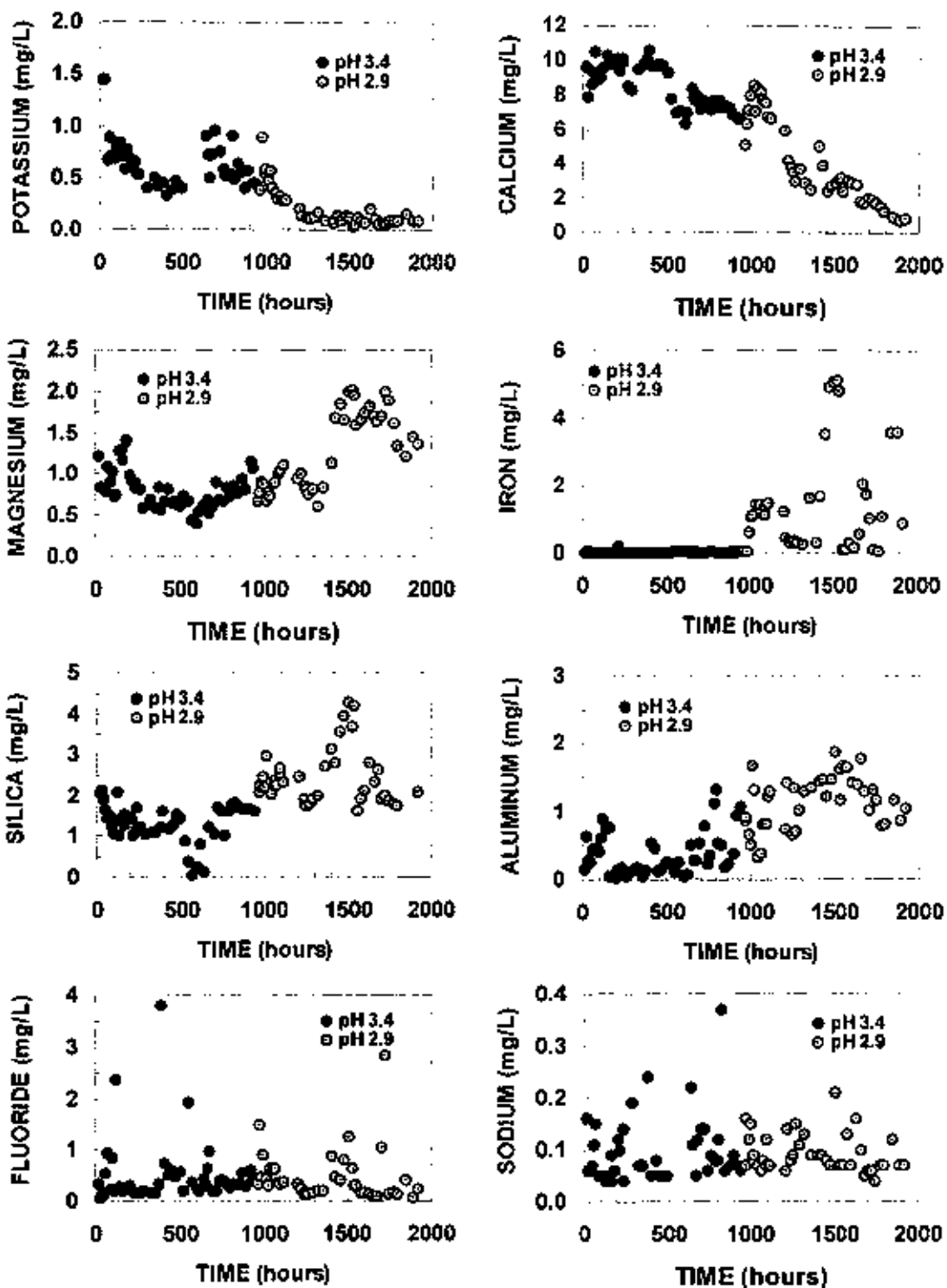


Figure 32. Concentration of major ions in sediment column output solutions. Values are shown for input solutions pH 3.4 and 2.9 over 2000 hours, with an analytical uncertainty of 5%. Values below the detection limit are plotted as zero.

CONCLUSIONS

Halogenated biotite isolated from Pinal Creek alluvium was reacted in a flow-through column for 2000 hours. The high initial concentrations of ions observed in column effluent can be attributed to the formation of residual layers, dissolution of fine-grained particulates, dissolution of rapidly-dissolving trace mineral impurities, such as calcite, and surface reactions, such as dissolution along etch pits (Wollast and Chou, 1985; Wieland *et al.*, 1988). The average release rate of Cl from the biotite was $0.08 \text{ picomol m}^{-2} \text{ s}^{-1}$. The release of Cl from the sediment column was low, indicating biotite is most likely the primary Cl-bearing mineral.

Some silica, aluminum, and iron were precipitated as gibbsite, $\text{Al}(\text{OH})_3$, kaolinite, and ferric hydroxides, determined from changes in ion concentration. SEM pictographs of the biotite after reaction showed significant edge weathering and presence of secondary clay minerals.

The order of the reaction (n) with respect to hydrogen ion activity was 0.52, over the pH range 3.1 to 3.5, which is consistent with data from previous studies. The rate of Pinal Creek biotite dissolution at pH 2.9, calculated from the dissolved silica concentration, is $R = 2.16 \times 10^{-13} \text{ mol m}^{-2} \text{ s}^{-1}$ based on a formula containing $\text{O}_{20}(\text{OH})_4$. This dissolution rate is slightly less than rates previous measured for ground biotite and phlogopite in the same pH ranges. Halogenation may have affected the dissolution rate by strengthening the biotite structure but is difficult to assess since Cl content of biotite is not reported for previous biotite dissolution experiments.

A model calculation of Cl inputs from biotite dissolution suggests that dissolution of halogenated biotite from alluvium in Pinal Creek basin can provide as much as 10

mg/L of Cl. The error associated with this calculation is potentially large, due to analytical uncertainties in the dissolution rate calculated in this study, and model assumptions made, such as assuming the biotite sample collected is representative of the alluvial aquifer in whole; *i.e.* the percentage of biotite in the sediment and/or its degree of halogenation does not vary spatially and/or with depth in the basin. Although the calculation has a large degree of error associated with it, it compares reasonably well with the imbalance of 18 mg/L Cl calculated for ground water used by Glynn and Brown (1996), a calculation which has its own associated error. This suggests that dissolution of Pinal Creek biotite could provide the Cl source suggested by Glynn & Brown (1996). More importantly, this study shows that Cl may not be a conservative tracer in modeling ground water in other porphyritic mining areas.

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APPENDIX A:

RAW DATA

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Table A1. Major ions and pH of column input acid solutions. Values below the analytical detection limit are reported as zero [mg/L, milligrams per liter; --, no data]

| Sample Number | Time (hours) | pH | Potassium (as mg/L K) | Magnesium (as mg/L Mg) | Calcium (as mg/L Ca) | Sodium (as mg/L Na) | Chloride (as mg/L Cl) | Fluoride (as mg/L F) | Iron (as mg/L Fe _{total}) | Silicon (as mg/L SiO ₂) | Aluminum (as mg/L Al) | Sulfate (as mg/L SO ₄) |
|---------------|--------------|------|-----------------------|------------------------|----------------------|---------------------|-----------------------|----------------------|-------------------------------------|-------------------------------------|-----------------------|------------------------------------|
| 0 | 0 | 3.39 | 0.09 | 0.03 | 0.01 | 0.04 | 0 | 0 | 0 | 0.25 | 0 | 19.22 |
| 4 | 50 | 3.39 | .10 | 0 | .01 | .04 | 0 | 0 | 0 | .16 | .11 | 18.78 |
| 12 | 160 | 3.40 | .05 | 0 | .12 | .02 | 0 | 0 | 0 | .21 | 0 | 18.13 |
| 24 | 355 | 3.40 | 0 | .04 | .02 | .02 | 0 | 0 | .025 | .17 | .12 | 18.02 |
| 37 | 625 | 3.40 | .09 | .02 | .11 | .10 | 0 | 0 | 0 | .17 | 0 | 18.06 |
| 45 | 760 | 2.93 | .09 | 0 | .02 | .04 | 0 | 0 | .011 | .12 | .13 | 38.88 |
| 55 | 968 | 2.93 | .07 | 0 | 0 | .03 | 0 | 0 | 0 | .01 | .01 | 38.36 |
| 67 | 1116 | 2.93 | 0 | 0 | 0 | .01 | 0 | 0 | 0 | -- | 0 | 38.57 |
| 78 | 1453 | 2.91 | .11 | 0 | 0 | .06 | 0 | 0 | .007 | -- | .01 | 36.42 |
| 86 | 1629 | 2.93 | 0 | 0 | 0 | .01 | 0 | 0 | 0 | -- | 0 | 38.92 |
| 96 | 1918 | 2.93 | 0 | 0 | .06 | .01 | 0 | 0 | 0 | -- | .07 | 38.61 |

Table A2. Major ions measured in biotite column effluent. Values below the analytical detection limit are reported as zero [mg/L, milligrams per liter; --, no data]

| Sample Number | Time (hours) | pH | Potassium (as mg/L K) | Magnesium (as mg/L Mg) | Calcium (as mg/L Ca) | Sodium (as mg/L Na) | Chloride (as mg/L Cl) | Fluoride (as mg/L F) | Iron (as mg/L Fe _{total}) | Silicon (as mg/L SiO ₂) | Aluminum (as mg/L Al) | Sulfate (as mg/L SO ₄) |
|---------------|--------------|------|-----------------------|------------------------|----------------------|---------------------|-----------------------|----------------------|-------------------------------------|-------------------------------------|-----------------------|------------------------------------|
| 1 | 20 | 4.86 | 2.38 | 1.02 | 4.25 | 0.32 | 0.09 | 0.11 | 0.020 | 4.04 | 0.12 | 18.51 |
| 2 | 28 | 4.97 | 2.45 | .92 | 3.95 | .10 | .25 | .11 | .020 | 2.71 | .11 | 19.02 |
| 3 | 42 | 4.96 | 2.53 | .60 | 4.14 | .03 | .05 | .02 | 0 | 2.34 | .24 | 19.12 |
| 4 | 50 | 4.16 | 2.39 | .66 | 4.05 | .04 | 0 | .02 | .010 | 2.20 | .27 | 22.03 |
| 5 | 66 | 5.22 | 2.37 | .68 | 4.44 | .05 | .08 | .24 | 0 | 2.04 | .49 | 23.52 |
| 6 | 74 | 4.95 | 2.31 | .70 | 4.46 | .03 | 0 | .09 | 0 | 2.19 | .47 | 19.24 |
| 7 | 91 | 5.40 | 1.92 | .82 | 4.69 | .03 | 0 | .09 | .010 | 2.11 | .41 | 18.79 |
| 8 | 100 | 5.45 | 1.72 | 1.09 | 4.65 | .03 | — | — | 0 | 1.94 | .76 | -- |
| 9 | 115 | 5.47 | 1.50 | .71 | 4.82 | .06 | .08 | .03 | 0 | 1.90 | .71 | 18.94 |
| 10 | 123 | 5.55 | 1.37 | .68 | 5.00 | .06 | .14 | — | .010 | 1.63 | .54 | 23.10 |
| 11 | 139 | 5.62 | 1.13 | 1.13 | 5.33 | .04 | .07 | .34 | 0 | 1.44 | .76 | 20.88 |
| 12 | 160 | 5.65 | 1.23 | 1.17 | 5.36 | .10 | 0 | .09 | 0 | 1.34 | .88 | 20.17 |
| 13 | 166 | 5.65 | .91 | 1.34 | 5.35 | .04 | .13 | .06 | .010 | 1.37 | .21 | 21.18 |
| 14 | 189 | 5.64 | .92 | 1.63 | 5.43 | .03 | 0 | .17 | .011 | 1.85 | .82 | 19.82 |
| 15 | 209 | 5.68 | 1.05 | 1.24 | 5.17 | .04 | 0 | .03 | .015 | 1.59 | -- | 19.79 |
| 16 | 215 | 5.91 | 1.06 | 1.03 | 5.07 | .11 | 0 | .37 | .027 | — | .06 | 22.19 |
| 17 | 233 | 5.93 | 1.05 | 1.64 | 5.12 | .08 | .05 | .03 | .029 | 1.48 | .33 | 19.31 |
| 18 | 240 | 5.40 | .99 | 1.43 | 4.75 | .05 | 0 | .03 | .029 | 1.49 | .16 | 17.21 |
| 19 | 262 | 5.77 | .82 | 1.59 | 4.60 | .08 | 0 | .03 | .011 | 1.55 | -- | 18.15 |
| 20 | 292 | 5.62 | .98 | 1.15 | 5.14 | .04 | 0 | .03 | 0 | 1.64 | .72 | 18.12 |
| 21 | 306 | 5.39 | .68 | 1.45 | 5.40 | .07 | .15 | .22 | .012 | 1.52 | .06 | 18.19 |
| 22 | 315 | 5.81 | .90 | 1.52 | 4.74 | .06 | 0 | .02 | .017 | -- | .40 | 18.14 |
| 23 | 330 | 5.65 | .83 | 1.15 | 5.08 | .03 | 0 | .02 | .005 | 1.10 | .42 | 18.12 |
| 24 | 355 | 5.56 | .94 | 1.60 | 4.66 | .05 | 0 | .04 | 0 | 1.20 | .72 | 19.03 |
| 25 | 379 | 5.66 | .97 | 1.10 | 5.14 | .05 | 0 | .08 | .002 | 1.04 | .34 | 19.04 |
| 26 | 388 | 5.21 | .84 | 1.03 | 5.11 | .01 | .21 | 1.26 | .010 | — | .37 | 18.64 |
| 27 | 406 | 5.70 | .97 | .99 | 5.09 | .03 | 0 | .14 | .013 | 1.96 | .48 | 18.97 |
| 28 | 430 | 5.24 | .94 | 1.27 | 5.04 | .03 | .21 | .60 | .020 | 2.01 | .35 | 17.79 |
| 29 | 453 | 4.98 | .87 | 1.16 | 5.32 | .03 | 0 | .63 | .020 | 1.53 | .53 | 19.00 |
| 30 | 473 | 5.68 | .77 | 1.22 | 5.32 | .01 | 0 | .22 | .020 | 1.54 | .48 | 18.96 |
| 31 | 498 | 5.60 | .77 | 1.22 | 5.34 | .03 | 0 | .19 | .020 | 1.52 | .41 | 18.55 |
| 32 | 522 | 5.56 | 1.08 | 1.18 | 5.37 | .06 | 0 | .18 | .010 | 1.48 | .32 | 18.64 |

Table A2. (continued) [mg/L, milligrams per liter; --, no data]

| Sample Number | Time (hours) | pH | Potassium (as mg/L K) | Magnesium (as mg/L Mg) | Calcium (as mg/L Ca) | Sodium (as mg/L Na) | Chloride (as mg/L Cl) | Fluoride (as mg/L F) | Iron (as mg/L Fe _{total}) | Silicon (as mg/L SiO ₂) | Aluminum (as mg/L Al) | Sulfate (as mg/L SO ₄) |
|---------------|--------------|------|-----------------------|------------------------|----------------------|---------------------|-----------------------|----------------------|-------------------------------------|-------------------------------------|-----------------------|------------------------------------|
| 33 | 549 | 5.48 | 1.09 | 1.19 | 5.59 | .09 | 0 | .17 | .010 | 1.96 | .52 | 18.76 |
| 34 | 571 | 5.90 | 1.19 | 1.02 | 5.13 | .19 | 0 | .03 | .002 | -- | .32 | 18.75 |
| 35 | 600 | 6.05 | .95 | 1.25 | 5.21 | .04 | 0 | .03 | .010 | 2.34 | .48 | 18.76 |
| 36 | 619 | 5.46 | 1.03 | .84 | 5.75 | .05 | 0 | .10 | .013 | 2.04 | .22 | 19.00 |
| 37 | 625 | 4.72 | .77 | 1.04 | 5.48 | .05 | 0 | -- | -- | 2.16 | .13 | 19.78 |
| 38 | 644 | 6.12 | 1.41 | .99 | 5.49 | .08 | 0 | .02 | .010 | -- | -- | 18.88 |
| 39 | 652 | 5.33 | 1.35 | 1.08 | 5.19 | .11 | -- | -- | .010 | -- | -- | -- |
| 40 | 668 | 4.69 | 1.52 | .95 | 5.15 | .09 | .31 | .27 | .012 | -- | -- | 21.76 |
| 41 | 677 | 5.36 | 1.00 | 1.30 | 5.91 | .04 | .17 | .32 | .021 | 2.20 | .13 | 20.32 |
| 42 | 697 | 5.55 | 1.06 | 1.40 | 5.39 | .07 | 0 | .22 | .010 | 1.56 | .33 | 18.57 |
| 43 | 723 | 4.94 | 1.03 | 1.42 | 5.33 | .08 | -- | -- | .010 | 3.88 | .41 | -- |
| 44 | 741 | 6.19 | .96 | 1.54 | 5.64 | .03 | .06 | .005 | .038 | 2.01 | .58 | 18.84 |
| 45 | 760 | 5.33 | .96 | 1.69 | 5.75 | .03 | 0 | .140 | .004 | 1.97 | .38 | 22.79 |
| 46 | 784 | 4.95 | .98 | 1.59 | 5.87 | .02 | 0 | .370 | .012 | 1.80 | .50 | 20.44 |
| 47 | 800 | 5.15 | .91 | 1.50 | 5.53 | .03 | 0 | .460 | .015 | 2.25 | 1.02 | 22.57 |
| 48 | 807 | 4.59 | 1.43 | 1.38 | 5.52 | .14 | 0 | .990 | .012 | -- | 1.08 | 22.96 |
| 49 | 824 | 4.22 | 1.11 | 1.34 | 5.23 | .03 | 0 | 0.17 | 0.019 | 2.30 | 0.25 | 22.76 |
| 50 | 847 | 5.66 | 1.01 | 1.50 | 5.02 | .04 | 0 | .03 | .001 | 1.83 | .30 | 22.50 |
| 51 | 872 | 5.75 | .87 | 1.57 | 5.09 | .05 | 0 | .08 | .026 | 2.20 | .24 | 23.29 |
| 52 | 896 | 6.31 | 1.00 | 1.61 | 5.04 | .03 | 0 | .08 | .025 | 2.22 | .45 | 22.09 |
| 53 | 918 | 6.47 | 1.02 | 1.81 | 4.60 | .05 | 0 | .03 | .021 | 2.34 | .93 | 22.40 |
| 54 | 938 | 6.46 | 1.14 | 1.93 | 4.51 | .07 | 0 | .10 | .081 | 2.12 | .47 | 22.29 |
| 55 | 968 | 4.12 | 3.86 | 1.94 | 2.11 | .18 | .23 | .01 | .398 | 4.70 | .23 | 38.86 |
| 56 | 973 | 3.81 | 3.52 | -- | 1.99 | .05 | .14 | .54 | .417 | -- | .22 | 42.50 |
| 57 | 990 | 4.18 | 3.71 | 1.71 | 2.17 | .06 | .07 | .07 | .430 | 2.28 | .27 | 37.89 |
| 58 | 997 | 4.02 | 3.62 | -- | 2.95 | .11 | .08 | .10 | .571 | 2.25 | -- | 41.09 |
| 59 | 1015 | 4.25 | 1.95 | -- | 3.50 | .08 | .07 | .18 | .653 | -- | .39 | 36.95 |
| 60 | 1022 | 4.30 | 1.28 | -- | 3.79 | .13 | 0 | .19 | .660 | 2.13 | .42 | 35.52 |
| 61 | 1041 | 4.29 | 1.12 | 2.90 | 3.85 | .03 | .06 | .29 | .687 | 2.06 | .33 | 36.92 |
| 62 | 1061 | 4.16 | 1.11 | 2.99 | 3.83 | .03 | .11 | .07 | .670 | 2.08 | .37 | 37.84 |
| 63 | 1071 | 4.19 | 1.15 | -- | 4.05 | .02 | .06 | .08 | .600 | -- | .32 | 38.33 |
| 64 | 1088 | 4.68 | 1.34 | 3.41 | 4.16 | .09 | .07 | .03 | .502 | 2.07 | .20 | 38.00 |

Table A2. (continued) [mg/L, milligrams per liter; --, no data]

| Sample Number | Time (hours) | pH | Potassium (as mg/L K) | Magnesium (as mg/L Mg) | Calcium (as mg/L Ca) | Sodium (as mg/L Na) | Chloride (as mg/L Cl) | Fluoride (as mg/L F) | Iron (as mg/L Fe _{total}) | Silicon (as mg/L SiO ₂) | Aluminum (as mg/L Al) | Sulfate (as mg/L SO ₄) |
|---------------|--------------|------|-----------------------|------------------------|----------------------|---------------------|-----------------------|----------------------|-------------------------------------|-------------------------------------|-----------------------|------------------------------------|
| 65 | 1098 | 4.20 | 1.13 | 4.40 | 3.96 | .05 | .10 | .30 | .599 | 2.26 | .23 | 48.75 |
| 66 | 1116 | 4.48 | 1.30 | 4.56 | 4.03 | .09 | .11 | .09 | .584 | 2.15 | .20 | 36.29 |
| 67 | 1202 | 4.15 | 1.09 | 2.83 | 5.00 | .05 | 0 | .43 | 1.465 | -- | .26 | 29.87 |
| 68 | 1216 | 4.20 | 1.09 | 1.85 | 3.60 | .15 | 0 | .02 | 2.093 | -- | .31 | 30.39 |
| 69 | 1240 | 4.10 | 1.05 | 1.53 | 3.03 | .07 | .07 | .02 | 1.933 | 2.31 | .18 | 26.20 |
| 70 | 1251 | 4.06 | 1.07 | 1.50 | 2.63 | .10 | .07 | .02 | 1.950 | -- | .19 | 26.00 |
| 71 | 1266 | 3.97 | .93 | 1.33 | 2.27 | .05 | 0 | .02 | 1.984 | 2.24 | .21 | 26.03 |
| 72 | 1290 | 3.72 | 1.05 | 1.06 | 2.49 | .06 | 0 | .02 | 2.061 | 2.32 | .26 | 25.94 |
| 73 | 1320 | 3.68 | .94 | 0.99 | 2.09 | .03 | 0 | .03 | 2.156 | 2.37 | .19 | 26.29 |
| 74 | 1357 | 3.77 | .74 | 1.15 | 1.83 | .07 | .11 | .61 | 2.228 | 2.61 | .25 | 26.51 |
| 75 | 1405 | 3.30 | .96 | 1.28 | 1.28 | .05 | .08 | .46 | 2.269 | -- | .42 | 37.85 |
| 76 | 1426 | 3.43 | .50 | 1.39 | 1.40 | .03 | 0 | .08 | 2.695 | 2.77 | .75 | 39.21 |
| 77 | 1453 | 3.42 | .44 | -- | 1.98 | .03 | 0 | .12 | 3.663 | 2.71 | .49 | 48.06 |
| 78 | 1479 | 3.33 | .40 | -- | 1.15 | .04 | 0 | .42 | 4.892 | 3.00 | .74 | 48.23 |
| 79 | 1503 | 3.29 | .56 | -- | .90 | .11 | .09 | .57 | 5.451 | 3.36 | .90 | 49.67 |
| 80 | 1527 | 3.23 | .67 | 1.38 | .93 | .02 | 0 | .61 | 5.467 | 3.05 | .62 | 49.27 |
| 81 | 1535 | 3.28 | .48 | -- | 1.01 | .09 | 0 | 1.33 | 5.166 | 3.16 | .83 | 47.06 |
| 82 | 1552 | 3.04 | .80 | 1.27 | .98 | .05 | .08 | .15 | 4.700 | 3.16 | .82 | 48.40 |
| 83 | 1576 | 3.19 | .85 | 1.19 | .85 | .07 | 0 | .05 | 4.420 | 3.14 | .79 | 49.03 |
| 84 | 1600 | 3.24 | .57 | 1.19 | .85 | .11 | 0 | .02 | 4.580 | 3.13 | .65 | 48.71 |
| 85 | 1629 | 3.29 | .60 | 0.84 | .88 | .11 | .08 | .02 | 4.290 | 2.71 | .77 | 46.69 |
| 86 | 1655 | 3.38 | .58 | 1.12 | .70 | .12 | 0 | .02 | 3.570 | 2.40 | .61 | 39.46 |
| 87 | 1676 | 3.37 | .46 | 0.98 | .64 | .13 | 0 | .04 | 3.670 | 2.41 | .95 | 39.21 |
| 88 | 1706 | 3.36 | .48 | 0.99 | .58 | .04 | 0 | .35 | 3.770 | 2.27 | 1.19 | 39.92 |
| 89 | 1725 | 3.36 | .65 | 1.10 | .54 | .02 | 0 | 1.04 | 3.350 | 2.48 | 1.50 | 40.42 |
| 90 | 1746 | 3.35 | .66 | 1.02 | .45 | .01 | 0 | .70 | 2.780 | 2.36 | 1.53 | 39.52 |
| 91 | 1775 | 3.35 | .55 | 1.04 | .53 | .05 | -- | .03 | 2.380 | 2.41 | 1.41 | 39.46 |
| 92 | 1792 | 3.36 | .44 | 0.96 | .58 | .10 | 0 | .07 | 2.130 | 2.49 | 1.62 | 38.92 |
| 93 | 1843 | 3.39 | .28 | -- | .43 | .04 | 0 | .14 | 2.860 | -- | 1.53 | 39.14 |
| 94 | 1889 | 3.39 | .27 | 0.97 | .38 | .03 | 0 | .02 | 3.820 | 2.57 | 1.67 | 39.73 |
| 95 | 1918 | 3.35 | .37 | 0.97 | .30 | .08 | 0 | .03 | 3.500 | 2.53 | 1.58 | 41.05 |

Table A3. Major ions measured in sediment column effluent. Values below the analytical detection limit are reported as zero [mg/L, milligrams per liter; --, no data]

| Sample Number | Time (hours) | pH | Potassium (as mg/L K) | Magnesium (as mg/L Mg) | Calcium (as mg/L Ca) | Sodium (as mg/L Na) | Chloride (as mg/L Cl) | Fluoride (as mg/L F) | Iron (as mg/L Fe _{total}) | Silicon (as mg/L SiO ₂) | Aluminum (as mg/L Al) | Sulfate (as mg/L SO ₄) |
|---------------|--------------|------|-----------------------|------------------------|----------------------|---------------------|-----------------------|----------------------|-------------------------------------|-------------------------------------|-----------------------|------------------------------------|
| 1 | 20 | 7.09 | 1.44 | 1.22 | 9.62 | 0.16 | 0.35 | 0.33 | 0.02 | 2.09 | 0.15 | 20.66 |
| 2 | 28 | 6.78 | 1.45 | .48 | 7.91 | .06 | .42 | .06 | .07 | 2.13 | .64 | 18.74 |
| 3 | 42 | -- | -- | -- | -- | -- | .05 | .14 | .03 | 1.90 | .29 | 22.74 |
| 4 | 50 | 6.97 | .67 | .84 | 8.56 | .07 | 0 | .14 | .02 | 1.67 | .26 | 21.32 |
| 5 | 66 | 7.22 | .89 | .80 | 9.24 | .11 | .88 | .55 | .02 | 1.44 | .44 | 21.14 |
| 6 | 74 | 6.86 | .71 | 1.09 | 10.49 | .15 | .06 | .93 | .02 | 1.52 | .47 | 18.94 |
| 7 | 91 | 7.21 | .69 | .90 | 8.91 | .05 | 0 | .22 | .02 | 1.23 | .47 | 18.15 |
| 8 | 100 | 7.14 | .80 | 1.02 | 8.96 | .05 | 0 | .83 | .01 | 1.06 | .41 | 25.49 |
| 9 | 115 | 7.20 | .74 | .73 | 9.43 | .05 | .06 | .21 | 0 | 1.40 | .61 | 19.24 |
| 10 | 123 | 7.20 | .84 | .76 | 9.62 | .05 | .11 | .34 | 0 | 2.07 | .89 | 19.67 |
| 11 | 139 | 7.25 | .70 | 1.28 | 10.28 | .04 | 0 | .28 | .02 | 1.03 | .74 | 18.88 |
| 12 | 160 | 7.68 | .58 | 1.17 | 9.78 | .04 | .07 | .25 | 0 | 1.54 | .76 | 19.58 |
| 13 | 166 | 7.45 | .77 | 1.30 | 9.89 | .09 | .08 | .20 | .02 | 1.26 | .06 | 38.12 |
| 14 | 189 | 7.44 | .69 | 1.41 | 9.85 | .06 | 0 | .22 | 0 | 1.46 | .05 | 18.88 |
| 15 | 209 | 7.35 | .58 | .99 | 10.07 | .12 | 0 | .29 | .01 | 1.44 | .02 | 19.28 |
| 16 | 215 | 7.11 | .65 | .93 | 9.40 | .10 | .06 | .19 | .20 | 1.01 | .14 | 23.05 |
| 17 | 233 | 7.27 | .53 | .91 | 9.89 | .04 | .06 | .16 | .03 | 1.19 | .19 | 19.00 |
| 18 | 240 | 7.04 | .54 | .85 | 10.12 | .14 | -- | -- | .01 | 1.70 | .10 | -- |
| 19 | 262 | 7.10 | -- | .82 | 8.46 | .58 | .41 | .16 | .02 | 1.22 | .06 | 17.30 |
| 20 | 292 | 7.31 | .41 | .59 | 8.31 | .19 | .10 | .21 | 0 | 1.06 | .13 | 18.48 |
| 21 | 306 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 22 | 315 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 23 | 330 | 7.21 | .51 | .69 | 9.44 | .07 | 0 | .17 | .02 | 1.08 | .17 | 18.48 |
| 24 | 355 | 7.17 | .42 | .59 | 9.76 | .07 | 0 | .17 | .01 | 1.10 | .04 | 18.64 |
| 25 | 379 | 7.17 | .45 | .84 | 10.05 | .24 | .06 | .34 | 0 | 1.21 | .13 | 18.65 |
| 26 | 388 | 7.02 | -- | .57 | 10.60 | .70 | 1.53 | 3.80 | -- | 1.61 | -- | 18.69 |
| 27 | 406 | 6.86 | .33 | .67 | 9.66 | .05 | .05 | .75 | .01 | -- | .53 | 18.85 |
| 28 | 430 | 6.80 | .38 | .82 | 9.71 | .08 | 0 | .49 | .01 | 1.20 | .46 | 19.19 |
| 29 | 453 | 6.86 | .47 | .66 | 9.79 | .05 | .08 | .62 | .01 | 1.29 | .13 | 20.10 |
| 30 | 473 | 6.95 | .43 | .67 | 9.72 | .05 | 0 | .47 | .01 | 1.52 | .15 | 18.89 |
| 31 | 498 | 7.29 | .41 | .60 | 9.30 | .05 | .05 | .57 | .01 | 1.44 | .26 | 19.86 |
| 32 | 522 | 7.30 | -- | .73 | 7.74 | .68 | 2.36 | .20 | .01 | 0.88 | .23 | 113.32 |

^F solution turned orange 24 hours after collection so 1 drop of HS was added to solution prior to analysis

Table A3. (continued) [mg/L, milligrams per liter; --, no data]

| Sample Number | Time (hours) | pH | Potassium (as mg/L K) | Magnesium (as mg/L Mg) | Calcium (as mg/L Ca) | Sodium (as mg/L Na) | Chloride (as mg/L Cl) | Fluoride (as mg/L F) | Iron (as mg/L Fe _{total}) | Silicon (as mg/L SiO ₂) | Aluminum (as mg/L Al) | Sulfate (as mg/L SO ₄) |
|---------------|--------------|------|-----------------------|------------------------|----------------------|---------------------|-----------------------|----------------------|-------------------------------------|-------------------------------------|-----------------------|------------------------------------|
| 33 | 549 | 7.10 | -- | 0.68 | 6.96 | 1.31 | 3.71 | 1.91 | 0.05 | 0.39 | 0.09 | U |
| 34 | 571 | 6.90 | -- | .44 | 7.01 | .81 | 1.02 | .38 | .04 | .06 | .25 | U |
| 35 | 600 | 7.17 | -- | .40 | 6.31 | .55 | 0 | .25 | .03 | .25 | .05 | 18.24 |
| 36 | 619 | 7.18 | -- | .55 | 6.93 | .55 | 0 | .20 | .03 | .82 | .07 | 18.45 |
| 37 | 625 | 7.17 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 38 | 644 | 6.88 | .90 | .64 | 8.33 | .22 | 0 | .45 | .06 | .14 | .50 | 18.81 |
| 39 | 652 | 6.91 | .72 | .57 | 7.90 | .11 | 0 | .31 | .01 | -- | -- | 18.64 |
| 40 | 668 | 6.78 | .51 | .69 | 7.68 | .05 | .06 | .64 | .02 | 1.25 | .28 | 21.76 |
| 41 | 677 | 6.78 | .72 | .53 | 7.94 | .12 | .87 | .98 | .03 | -- | .27 | 20.32 |
| 42 | 697 | 7.00 | .96 | .61 | 7.21 | .14 | .10 | .19 | .01 | 1.06 | .54 | 18.57 |
| 43 | 723 | 6.85 | .76 | .90 | 7.63 | .14 | 0 | .21 | .02 | 1.70 | .80 | -- |
| 44 | 741 | 6.83 | .59 | .70 | 7.54 | .06 | .04 | .40 | .03 | 1.59 | .23 | 18.84 |
| 45 | 760 | 6.64 | .52 | .68 | 7.18 | .09 | 0 | .40 | .03 | 1.01 | .35 | 22.79 |
| 46 | 784 | 6.54 | .54 | .84 | 7.70 | .08 | .20 | .32 | .03 | 1.61 | 1.12 | 20.44 |
| 47 | 800 | 6.33 | .90 | .74 | 7.53 | .12 | 0 | .26 | 0 | 1.80 | 1.32 | 22.57 |
| 48 | 807 | 6.30 | .49 | .82 | 7.62 | .08 | 0 | .31 | 0 | 1.78 | .53 | 22.48 |
| 49 | 824 | 6.25 | .64 | .86 | 7.31 | .37 | .13 | .32 | 0 | 1.83 | .51 | 22.72 |
| 50 | 847 | 6.13 | .56 | .77 | 7.34 | .06 | 0 | .32 | .01 | 1.70 | .19 | 22.55 |
| 51 | 872 | 6.04 | .41 | .95 | 7.22 | .07 | .07 | .54 | .01 | 1.66 | .23 | 23.30 |
| 52 | 896 | 5.93 | .57 | .81 | 6.87 | .09 | .05 | .29 | .03 | 1.66 | .38 | 22.32 |
| 53 | 918 | 6.01 | .46 | 1.15 | 6.69 | .07 | 0 | .60 | .02 | 1.65 | .94 | 22.34 |
| 54 | 938 | 5.92 | .43 | 1.08 | 6.61 | .06 | .06 | .45 | .03 | 1.59 | 1.07 | 22.27 |
| 55 | 968 | 3.45 | .39 | .68 | 5.17 | .07 | .10 | .33 | .06 | 2.09 | .86 | 38.76 |
| 56 | 973 | 3.52 | .89 | .78 | 6.33 | .16 | .10 | 1.48 | .06 | 2.26 | .92 | 37.32 |
| 57 | 990 | 3.67 | .53 | .91 | 7.16 | .12 | .11 | .48 | .05 | 2.46 | .65 | 37.21 |
| 58 | 997 | 3.45 | .59 | .89 | 7.94 | .15 | .09 | .92 | .63 | 2.21 | .52 | 42.23 |
| 59 | 1015 | 3.66 | .47 | .67 | 8.54 | .09 | .09 | .43 | 1.10 | 2.95 | 1.69 | 36.99 |
| 60 | 1022 | 3.82 | .57 | .77 | 7.08 | .09 | .10 | .30 | 1.15 | -- | 1.33 | 37.04 |
| 61 | 1041 | 3.76 | .41 | .74 | 8.42 | .07 | .07 | .63 | 1.42 | 2.03 | .32 | 36.80 |
| 62 | 1061 | 3.67 | .36 | .88 | 8.12 | .06 | .07 | .60 | 1.43 | 2.38 | .39 | 36.78 |
| 63 | 1071 | 3.45 | .31 | .91 | 7.72 | .08 | .08 | .63 | 1.24 | 2.25 | .82 | 43.83 |
| 64 | 1088 | 3.67 | .32 | 1.01 | 7.60 | .12 | .11 | .38 | 1.40 | 2.48 | .81 | 37.71 |

^U solution turned orange 24 hours after collection so 1 drop of HS was added to the solution prior to analysis

Table A3. (continued) [mg/L, milligrams per liter; --, no data]

| Sample Number | Time (hours) | pH | Potassium (as mg/L K) | Magnesium (as mg/L Mg) | Calcium (as mg/L Ca) | Sodium (as mg/L Na) | Chloride (as mg/L Cl) | Fluoride (as mg/L F) | Iron (as mg/L Fe _{total}) | Silicon (as mg/L SiO ₂) | Aluminum (as mg/L Al) | Sulfate (as mg/L SO ₄) |
|---------------|--------------|------|-----------------------|------------------------|----------------------|---------------------|-----------------------|----------------------|-------------------------------------|-------------------------------------|-----------------------|------------------------------------|
| 65 | 1098 | 3.63 | 0.29 | 1.04 | 6.75 | 0.07 | 0.12 | 0.35 | 1.13 | 2.67 | 1.21 | 37.57 |
| 66 | 1116 | 3.64 | .29 | 1.12 | 6.61 | .07 | .10 | .37 | 1.47 | 2.35 | 1.29 | 36.67 |
| 67 | 1202 | 3.57 | .21 | .95 | 5.92 | .06 | .07 | .35 | 1.25 | 2.46 | .73 | 36.61 |
| 68 | 1216 | 3.62 | .14 | 1.00 | 4.28 | .14 | .11 | .25 | .47 | -- | 1.43 | 31.34 |
| 69 | 1240 | 3.70 | .11 | .86 | 3.87 | .08 | 0 | .14 | .34 | 1.92 | .67 | 25.74 |
| 70 | 1251 | 3.66 | .11 | .81 | 3.48 | .09 | .07 | .18 | .30 | 1.73 | 1.34 | 26.11 |
| 71 | 1266 | 3.67 | .10 | .75 | 3.02 | .15 | 0 | .13 | .35 | 1.79 | .71 | 25.65 |
| 72 | 1290 | 3.50 | .12 | .81 | 3.71 | .11 | .06 | .16 | .29 | 1.90 | 1.01 | 25.60 |
| 73 | 1320 | 3.49 | .17 | .60 | 2.94 | .13 | 0 | .19 | .25 | 1.98 | 1.30 | 25.52 |
| 74 | 1357 | 3.50 | .08 | .85 | 2.50 | .09 | 0 | .20 | 1.64 | 2.71 | 1.35 | 26.71 |
| 75 | 1405 | 3.29 | .06 | 1.13 | 5.04 | .09 | 0 | .89 | .29 | 3.14 | 1.45 | 39.06 |
| 76 | 1426 | 3.46 | .13 | 1.68 | 3.89 | .09 | 0 | .48 | 1.70 | 2.81 | 1.47 | 38.24 |
| 77 | 1453 | 3.30 | .09 | 1.85 | 2.47 | .08 | 0 | .39 | 3.55 | 3.55 | 1.22 | 42.67 |
| 78 | 1479 | 3.35 | .13 | 1.67 | 2.68 | .07 | 0 | .79 | 4.94 | 3.94 | 1.47 | 46.98 |
| 79 | 1503 | 3.20 | .11 | 1.99 | 2.97 | .21 | 0 | 1.25 | 5.07 | 4.27 | 1.88 | 48.89 |
| 80 | 1527 | 3.39 | .04 | 2.02 | 3.17 | .07 | 0 | .64 | 5.11 | 3.67 | 1.16 | 48.44 |
| 81 | 1535 | 3.40 | .05 | 1.95 | 3.19 | .07 | 0 | .30 | 4.82 | 4.20 | 1.63 | 49.28 |
| 82 | 1552 | 3.07 | .11 | 1.59 | 2.43 | .07 | 0 | .29 | .12 | 1.62 | 1.69 | 47.85 |
| 83 | 1576 | 3.20 | .09 | 1.65 | 3.03 | .13 | .10 | .17 | .08 | 1.89 | 1.66 | 48.30 |
| 84 | 1600 | 3.27 | .06 | 1.75 | 2.94 | .07 | 0 | .16 | .32 | 2.13 | 1.42 | 48.46 |
| 85 | 1629 | 3.35 | .20 | 1.83 | 2.86 | .16 | 0 | .15 | .17 | 2.78 | 1.41 | 45.60 |
| 86 | 1655 | 3.41 | .10 | 1.70 | 1.83 | .10 | 0 | .11 | .55 | 2.34 | 1.79 | 39.52 |
| 87 | 1676 | 3.44 | .05 | 1.63 | 1.72 | .05 | 0 | .09 | 2.03 | 2.61 | 1.30 | 39.52 |
| 88 | 1706 | 3.45 | .06 | 1.70 | 1.98 | .06 | 0 | 1.03 | 1.74 | 1.90 | 1.01 | 39.57 |
| 89 | 1725 | 3.36 | .05 | 2.00 | 1.88 | .06 | 0 | 2.83 | 1.02 | 2.01 | 1.31 | 39.74 |
| 90 | 1746 | 3.33 | .09 | 1.90 | 1.69 | .04 | 0 | .13 | .08 | 1.86 | 1.18 | 38.67 |
| 91 | 1775 | 3.30 | .08 | 1.61 | 1.51 | .07 | 0 | .18 | .07 | 1.80 | .80 | 39.03 |
| 92 | 1792 | 3.33 | .08 | 1.35 | 1.26 | .07 | .06 | .15 | 1.07 | 1.73 | .82 | 38.48 |
| 93 | 1843 | 3.36 | .15 | 1.22 | .91 | .12 | 0 | .39 | 3.57 | -- | 1.18 | 39.96 |
| 94 | 1889 | 3.43 | .08 | 1.46 | .71 | .07 | 0 | .07 | 3.57 | -- | .86 | 39.92 |
| 95 | 1918 | 3.31 | .08 | 1.36 | .82 | .07 | 0 | .22 | .86 | 2.08 | 1.05 | 38.76 |

Table A4. Normalization of Pinal Creek biotite XRF mineral analysis [wt., weight; no., number]

| Oxide | Oxides | | | | Anions | | | Cations | | | |
|--------------------------------|---------------------------|---------------------------|----------------|---------------------------|-----------------|-----------------------------------|-------------------|----------------------------|------------------|---------------------------------|--------------------|
| | wt. % of oxide in biotite | Molecular weight of oxide | Moles of oxide | Number of oxygen in oxide | Moles of oxygen | Normalization Factor ¹ | Oxygen in formula | Number of cations in oxide | Moles of cations | Ratio of oxygen/cation in oxide | Cations in Formula |
| SiO ₂ | 35.88 | 60.08 | 0.60 | 2 | 1.19 | 9 | 10.77 | 1 | 0.60 | 2.0 | 5.38 |
| TiO ₂ | 6.45 | 79.90 | 0.08 | 2 | 0.16 | 9 | 1.46 | 1 | 0.08 | 2.0 | 0.73 |
| Al ₂ O ₃ | 14.72 | 102.00 | 0.14 | 3 | 0.43 | 9 | 3.90 | 2 | 0.29 | 1.5 | 2.60 |
| FeO | 18.91 | 71.85 | 0.26 | 1 | 0.26 | 9 | 2.37 | 1 | 0.26 | 1.0 | 2.37 |
| MnO | 0.47 | 70.94 | 0.01 | 1 | 0.01 | 9 | 0.06 | 2 | 0.01 | 0.5 | 0.12 |
| MgO | 10.17 | 40.30 | 0.25 | 1 | 0.25 | 9 | 2.28 | 1 | 0.25 | 1.0 | 2.28 |
| CaO | 1.63 | 56.08 | 0.03 | 1 | 0.03 | 9 | 0.26 | 1 | 0.03 | 1.0 | 0.26 |
| Na ₂ O | 0.26 | 62.00 | 0.00 | 1 | 0.00 | 9 | 0.04 | 1 | 0.00 | 1.0 | 0.04 |
| K ₂ O | 5.65 | 94.60 | 0.06 | 1 | 0.06 | 9 | 0.54 | 2 | 0.12 | 0.5 | 1.08 |
| F | 0.50 | 19.00 | 0.03 | 1 | 0.03 | 9 | 0.24 | 2 | 0.05 | 0.5 | 0.47 |
| Cl | 0.35 | 35.45 | 0.01 | 1 | 0.01 | 9 | 0.09 | 1 | 0.01 | 1.0 | 0.09 |

¹ calculated as the sum moles of oxygen divided by the total number of oxygen in biotite (22)

Table A5. Moles of ions measured in biotite column effluent. Values below the analytical detection limit are reported as zero [mg/L, milligrams per liter; --, no data]

| Sample Number | Time (hours) | Potassium (as mg/L K) | Magnesium (as mg/L Mg) | Calcium (as mg/L Ca) | Sodium (as mg/L Na) | Chloride (as mg/L Cl) | Fluoride (as mg/L F) | Iron (as mg/L Fe _{total}) | Silicon (as mg/L SiO ₂) | Aluminum (as mg/L Al) | Sulfate (as mg/L SO ₄) |
|---------------|--------------|-----------------------|------------------------|----------------------|---------------------|-----------------------|----------------------|-------------------------------------|-------------------------------------|-----------------------|------------------------------------|
| 1 | 20 | 2.38 | 1.02 | 4.25 | 0.32 | 0.09 | 0.11 | 0.020 | 4.040 | 0.12 | 20.51 |
| 2 | 28 | 2.45 | 0.92 | 3.95 | 0.10 | 0.25 | 0.11 | 0.020 | 2.710 | 0.11 | 21.02 |
| 3 | 42 | 2.53 | 0.60 | 4.14 | 0.03 | 0.05 | 0.02 | 0.00 | 2.340 | 0.24 | 21.12 |
| 4 | 50 | 2.39 | 0.66 | 4.05 | 0.04 | 0 | 0.02 | 0.010 | 2.200 | 0.27 | 24.03 |
| 5 | 66 | 2.37 | 0.68 | 4.44 | 0.05 | 0.08 | 0.24 | 0.00 | 2.040 | 0.49 | 25.52 |
| 6 | 74 | 2.31 | 0.70 | 4.46 | 0.03 | 0 | 0.09 | 0.00 | 2.190 | 0.47 | 21.24 |
| 7 | 91 | 1.92 | 0.82 | 4.69 | 0.03 | 0 | 0.09 | 0.010 | 2.110 | 0.41 | 20.79 |
| 8 | 100 | 1.72 | 1.09 | 4.65 | 0.03 | -- | -- | 0.00 | 1.940 | 0.76 | -- |
| 9 | 115 | 1.50 | 0.71 | 4.82 | 0.06 | 0.08 | 0.03 | 0.00 | 1.900 | 0.71 | 20.94 |
| 10 | 123 | 1.37 | 0.68 | 5.00 | 0.06 | 0.14 | 0.03 | 0.010 | 1.630 | 0.54 | 25.10 |
| 11 | 139 | 1.13 | 1.13 | 5.33 | 0.04 | 0.07 | 0.34 | 0.00 | 1.436 | 0.76 | 20.88 |
| 12 | 160 | 1.23 | 1.17 | 5.36 | 0.10 | 0 | 0.09 | 0.00 | 1.340 | 0.88 | 22.17 |
| 13 | 166 | 0.91 | 1.34 | 5.35 | 0.04 | 0.13 | 0.06 | 0.010 | 1.373 | 0.21 | 23.18 |
| 14 | 189 | 0.92 | 1.63 | 5.43 | 0.03 | 0 | 0.17 | 0.011 | 1.845 | 0.82 | 20.82 |
| 15 | 209 | 1.05 | 1.24 | 5.17 | 0.04 | 0 | 0.03 | 0.015 | 1.586 | -- | 20.79 |
| 16 | 215 | 1.06 | 1.03 | 5.07 | 0.11 | 0 | 0.37 | 0.027 | -- | 0.06 | 24.19 |
| 17 | 233 | 1.05 | 1.64 | 5.12 | 0.08 | 0.05 | 0.03 | 0.029 | 1.476 | 0.33 | 19.31 |
| 18 | 240 | 0.99 | 1.43 | 4.75 | 0.05 | 0 | 0.03 | 0.029 | 1.490 | 0.16 | 17.21 |
| 19 | 262 | 0.82 | 1.59 | 4.60 | 0.08 | 0 | 0.03 | 0.011 | 1.545 | -- | 18.15 |
| 20 | 292 | 0.98 | 1.15 | 5.14 | 0.04 | 0 | 0.03 | 0.00 | 1.640 | 0.72 | 18.12 |
| 21 | 306 | 0.68 | 1.45 | 5.40 | 0.07 | 0.15 | 0.22 | 0.012 | 1.517 | 0.06 | 18.19 |
| 22 | 315 | 0.90 | 1.52 | 4.74 | 0.06 | 0 | 0.02 | 0.017 | -- | 0.40 | 18.14 |
| 23 | 330 | 0.83 | 1.15 | 5.08 | 0.03 | 0 | 0.02 | 0.05 | 1.100 | 0.42 | 18.12 |
| 24 | 355 | 0.94 | 1.60 | 4.66 | 0.05 | 0 | 0.04 | 0.00 | 1.200 | 0.72 | 19.03 |
| 25 | 379 | 0.97 | 1.10 | 5.14 | 0.05 | 0 | 0.08 | 0.02 | 1.039 | 0.34 | 19.04 |
| 26 | 388 | 0.84 | 1.03 | 5.11 | 0.01 | 0.21 | 1.26 | 0.010 | -- | 0.37 | 18.64 |
| 27 | 406 | 0.97 | 0.99 | 5.09 | 0.03 | 0 | 0.14 | 0.013 | 1.968 | 0.48 | 18.97 |
| 28 | 430 | 0.94 | 1.27 | 5.04 | 0.03 | 0.21 | 0.60 | 0.020 | 2.010 | 0.35 | 17.79 |
| 29 | 453 | 0.87 | 1.16 | 5.32 | 0.03 | 0 | 0.63 | 0.020 | 1.530 | 0.53 | 19.00 |
| 30 | 473 | 0.77 | 1.22 | 5.32 | 0.01 | 0 | 0.22 | 0.020 | 1.540 | 0.48 | 18.96 |
| 31 | 498 | 0.77 | 1.22 | 5.34 | 0.03 | 0 | 0.19 | 0.020 | 1.517 | 0.41 | 18.55 |
| 32 | 522 | 1.08 | 1.18 | 5.37 | 0.06 | 0 | 0.18 | 0.010 | 1.480 | 0.32 | 18.64 |

Table A5. (continued) [mg/L, milligrams per liter; --, no data]

| Sample Number | Time (hours) | Potassium (as mg/L K) | Magnesium (as mg/L Mg) | Calcium (as mg/L Ca) | Sodium (as mg/L Na) | Chloride (as mg/L Cl) | Fluoride (as mg/L F) | Iron (as mg/L Fe _{total}) | Silicon (as mg/L SiO ₂) | Aluminum (as mg/L Al) | Sulfate (as mg/L SO ₄) |
|---------------|--------------|-----------------------|------------------------|----------------------|---------------------|-----------------------|----------------------|-------------------------------------|-------------------------------------|-----------------------|------------------------------------|
| 33 | 549 | 1.09 | 1.19 | 5.59 | 0.09 | 0 | 0.17 | 0.010 | 1.960 | 0.52 | 18.76 |
| 34 | 571 | 1.19 | 1.02 | 5.13 | 0.19 | 0 | 0.03 | 02 | -- | 0.32 | 18.75 |
| 35 | 600 | 0.95 | 1.25 | 5.21 | 0.04 | 0 | 0.03 | 0.010 | 2.340 | 0.48 | 18.76 |
| 36 | 619 | 1.03 | 0.84 | 5.75 | 0.05 | 0 | 0.10 | 0.013 | 2.040 | 0.22 | 19.00 |
| 37 | 625 | 0.77 | 1.04 | 5.48 | 0.05 | 0 | -- | -- | 2.159 | 0.13 | 19.78 |
| 38 | 644 | 1.41 | 0.99 | 5.49 | 0.08 | 0 | 0.02 | 0.010 | -- | -- | 18.88 |
| 39 | 652 | 1.35 | 1.08 | 5.19 | 0.11 | -- | -- | 0.010 | -- | -- | -- |
| 40 | 668 | 1.52 | 0.95 | 5.15 | 0.09 | 0.31 | 0.27 | 0.012 | -- | -- | 21.76 |
| 41 | 677 | 1.00 | 1.30 | 5.91 | 0.04 | 0.17 | 0.32 | 0.021 | 2.200 | 0.13 | 20.32 |
| 42 | 697 | 1.06 | 1.40 | 5.39 | 0.07 | 0 | 0.22 | 0.010 | 1.560 | 0.33 | 18.57 |
| 43 | 723 | 1.03 | 1.42 | 5.33 | 0.08 | -- | -- | 0.010 | 3.880 | 0.41 | -- |
| 44 | 741 | 0.96 | 1.54 | 5.64 | 0.03 | 0.06 | 05 | 0.038 | 2.010 | 0.58 | 18.84 |
| 45 | 760 | 0.96 | 1.69 | 5.75 | 0.03 | 0 | 0.140 | 04 | 1.970 | 0.38 | 22.79 |
| 46 | 784 | 0.98 | 1.59 | 5.87 | 0.02 | 0 | 0.370 | 0.012 | 1.860 | 0.50 | 20.44 |
| 47 | 800 | 0.91 | 1.50 | 5.53 | 0.03 | 0 | 0.460 | 0.015 | 2.250 | 1.02 | 22.57 |
| 48 | 807 | 1.43 | 1.38 | 5.52 | 0.14 | 0 | 0.990 | 0.012 | -- | 1.08 | 22.96 |
| 49 | 824 | 1.11 | 1.34 | 5.23 | 0.03 | 0 | 0.170 | 0.019 | 2.300 | 0.25 | 22.76 |
| 50 | 847 | 1.01 | 1.50 | 5.02 | 0.04 | 0 | 0.030 | 01 | 1.830 | 0.300 | 22.50 |
| 51 | 872 | 0.87 | 1.57 | 5.09 | 0.05 | 0 | 0.080 | 0.026 | 2.200 | 0.24 | 23.29 |
| 52 | 896 | 1.00 | 1.61 | 5.04 | 0.03 | 0 | 0.080 | 0.025 | 2.220 | 0.45 | 22.09 |
| 53 | 918 | 1.02 | 1.81 | 4.60 | 0.05 | 0 | 0.030 | 0.021 | 2.340 | 0.93 | 22.40 |
| 54 | 938 | 1.14 | 1.93 | 4.51 | 0.07 | 0 | 0.100 | 0.081 | 2.120 | 0.47 | 22.29 |
| 55 | 968 | 3.86 | 1.94 | 2.11 | 0.18 | 0.23 | 0.01 | 0.398 | 4.700 | 0.23 | 38.860 |
| 56 | 973 | 3.52 | -- | 1.99 | 0.05 | 0.14 | 0.54 | 0.417 | -- | 0.22 | 42.500 |
| 57 | 990 | 3.71 | 1.71 | 2.17 | 0.06 | 0.07 | 0.07 | 0.430 | 2.280 | 0.27 | 37.890 |
| 58 | 997 | 3.62 | -- | 2.95 | 0.11 | 0.08 | 0.10 | 0.571 | 2.250 | -- | 41.090 |
| 59 | 1015 | 1.95 | -- | 3.50 | 0.08 | 0.07 | 0.18 | 0.653 | -- | 0.39 | 36.950 |
| 60 | 1022 | 1.28 | -- | 3.79 | 0.13 | 0 | 0.19 | 0.660 | 2.130 | 0.42 | 35.520 |
| 61 | 1041 | 1.12 | 2.90 | 3.85 | 0.03 | 0.06 | 0.29 | 0.687 | 2.060 | 0.33 | 36.920 |
| 62 | 1061 | 1.11 | 2.99 | 3.83 | 0.03 | 0.11 | 0.07 | 0.670 | 2.080 | 0.37 | 37.840 |
| 63 | 1071 | 1.15 | -- | 4.05 | 0.02 | 0.06 | 0.08 | 0.600 | -- | 0.32 | 38.330 |
| 64 | 1088 | 1.34 | 3.41 | 4.16 | 0.09 | 0.07 | 0.03 | 0.502 | 2.070 | 0.20 | 38.000 |

Table A5. (continued) [mg/L, milligrams per liter; --, no data]

| Sample Number | Time (hours) | Potassium (as mg/L K) | Magnesium (as mg/L Mg) | Calcium (as mg/L Ca) | Sodium (as mg/L Na) | Chloride (as mg/L Cl) | Fluoride (as mg/L F) | Iron (as mg/L Fe _{total}) | Silicon (as mg/L SiO ₂) | Aluminum (as mg/L Al) | Sulfate (as mg/L SO ₄) |
|---------------|--------------|-----------------------|------------------------|----------------------|---------------------|-----------------------|----------------------|-------------------------------------|-------------------------------------|-----------------------|------------------------------------|
| 65 | 1098 | 1.13 | 4.40 | 3.96 | 0.05 | 0.10 | 0.30 | 0.599 | 2.260 | 0.23 | 48.750 |
| 66 | 1116 | 1.30 | 4.56 | 4.03 | 0.09 | 0.11 | 0.09 | 0.584 | 2.150 | 0.20 | 36.290 |
| 67 | 1202 | 1.09 | 2.83 | 5.00 | 0.05 | 0 | 0.43 | 1.465 | -- | 0.26 | 29.870 |
| 68 | 1216 | 1.09 | 1.85 | 3.60 | 0.15 | 0 | 0.02 | 2.093 | -- | 0.31 | 30.390 |
| 69 | 1240 | 1.05 | 1.53 | 3.03 | 0.07 | 0.07 | 0.02 | 1.933 | 2.310 | 0.18 | 26.200 |
| 70 | 1251 | 1.07 | 1.50 | 2.63 | 0.10 | 0.07 | 0.02 | 1.950 | -- | 0.19 | 26.000 |
| 71 | 1266 | 0.93 | 1.33 | 2.27 | 0.05 | 0 | 0.02 | 1.984 | 2.240 | 0.21 | 26.030 |
| 72 | 1290 | 1.05 | 1.06 | 2.49 | 0.06 | 0 | 0.02 | 2.061 | 2.320 | 0.26 | 25.940 |
| 73 | 1320 | 0.94 | 0.99 | 2.09 | 0.03 | 0 | 0.03 | 2.156 | 2.370 | 0.19 | 26.290 |
| 74 | 1357 | 0.74 | 1.15 | 1.83 | 0.07 | 0.11 | 0.61 | 2.228 | 2.610 | 0.25 | 26.510 |
| 75 | 1405 | 0.96 | 1.28 | 1.28 | 0.05 | 0.08 | 0.46 | 2.269 | -- | 0.42 | 37.850 |
| 76 | 1426 | 0.50 | 1.39 | 1.40 | 0.03 | 0 | 0.08 | 2.695 | 2.770 | 0.75 | 39.210 |
| 77 | 1453 | 0.44 | -- | 1.98 | 0.03 | 0 | 0.12 | 3.663 | 2.710 | 0.49 | 48.060 |
| 78 | 1479 | 0.40 | -- | 1.15 | 0.04 | 0 | 0.42 | 4.892 | 3.000 | 0.74 | 48.230 |
| 79 | 1503 | 0.56 | -- | 0.90 | 0.11 | 0.09 | 0.57 | 5.451 | 3.360 | 0.90 | 49.670 |
| 80 | 1527 | 0.67 | 1.38 | 0.93 | 0.02 | 0 | 0.61 | 5.467 | 3.050 | 0.62 | 49.270 |
| 81 | 1535 | 0.48 | -- | 1.01 | 0.09 | 0 | 1.33 | 5.166 | 3.160 | 0.83 | 47.060 |
| 82 | 1552 | 0.80 | 1.27 | 0.98 | 0.05 | 0.08 | 0.15 | 4.700 | 3.160 | 0.82 | 48.40 |
| 83 | 1576 | 0.85 | 1.19 | 0.85 | 0.07 | 0 | 0.05 | 4.420 | 3.140 | 0.79 | 49.03 |
| 84 | 1600 | 0.57 | 1.19 | 0.85 | 0.11 | 0 | 0.02 | 4.580 | 3.130 | 0.65 | 48.71 |
| 85 | 1629 | 0.60 | 0.84 | 0.88 | 0.11 | 0.08 | 0.02 | 4.290 | 2.710 | 0.77 | 46.69 |
| 86 | 1655 | 0.58 | 1.12 | 0.70 | 0.12 | 0 | 0.02 | 3.570 | 2.400 | 0.61 | 39.46 |
| 87 | 1676 | 0.46 | 0.98 | 0.64 | 0.13 | 0 | 0.04 | 3.670 | 2.410 | 0.95 | 39.21 |
| 88 | 1706 | 0.48 | 0.99 | 0.58 | 0.04 | 0 | 0.35 | 3.770 | 2.270 | 1.19 | 39.92 |
| 89 | 1725 | 0.65 | 1.10 | 0.54 | 0.02 | 0 | 1.04 | 3.350 | 2.480 | 1.50 | 40.42 |
| 90 | 1746 | 0.66 | 1.02 | 0.45 | 0.01 | 0 | 0.70 | 2.780 | 2.360 | 1.53 | 39.52 |
| 91 | 1775 | 0.55 | 1.04 | 0.53 | 0.05 | -- | 0.03 | 2.380 | 2.410 | 1.41 | 39.46 |
| 92 | 1792 | 0.44 | 0.96 | 0.58 | 0.10 | 0 | 0.07 | 2.130 | 2.490 | 1.62 | 38.92 |
| 93 | 1843 | 0.28 | -- | 0.43 | 0.04 | 0 | 0.14 | 2.860 | -- | 1.53 | 39.14 |
| 94 | 1889 | 0.27 | 0.97 | 0.38 | 0.03 | 0 | 0.02 | 3.820 | 2.570 | 1.67 | 39.73 |
| 95 | 1918 | 0.37 | 0.97 | 0.30 | 0.08 | 0 | 0.03 | 3.500 | 2.530 | 1.58 | 41.05 |

Table A6. Calculated values for ion molar ratios plotted in Figures 19, 20 and 21 [--, no data]

| Sample Number | K/Mg | Al/Si | Si/Mg | Sample Number | K/Mg | Al/Si | Si/Mg |
|---------------|------|-------|-------|---------------|------|-------|-------|
| 1 | 1.45 | 0.03 | 3.43 | 49 | 0.52 | 0.11 | 1.49 |
| 2 | 1.66 | 0.04 | 2.55 | 50 | 0.42 | 0.17 | 1.06 |
| 3 | 2.62 | 0.11 | 3.38 | 51 | 0.34 | 0.11 | 1.21 |
| 4 | 2.25 | 0.13 | 2.88 | 52 | 0.39 | 0.21 | 1.19 |
| 5 | 2.17 | 0.25 | 2.60 | 53 | 0.35 | 0.41 | 1.12 |
| 6 | 2.05 | 0.22 | 2.71 | 54 | 0.37 | 0.23 | 0.95 |
| 7 | 1.46 | 0.20 | 2.23 | 55 | 1.24 | 0.05 | 2.10 |
| 8 | 0.98 | 0.41 | 1.54 | 57 | 1.35 | 0.12 | 1.15 |
| 9 | 1.31 | 0.39 | 2.32 | 60 | -- | 0.21 | -- |
| 10 | 1.25 | 0.34 | 2.07 | 61 | 0.24 | 0.17 | 0.61 |
| 11 | 0.62 | 0.55 | 1.10 | 62 | 0.23 | 0.19 | 0.60 |
| 12 | 0.65 | 0.68 | 0.99 | 64 | 0.24 | 0.10 | 0.53 |
| 13 | 0.42 | 0.16 | 0.89 | 65 | 0.16 | 0.11 | 0.44 |
| 14 | 0.35 | 0.46 | 0.98 | 66 | 0.18 | 0.10 | 0.41 |
| 15 | 0.53 | -- | 1.11 | 67 | 0.24 | -- | -- |
| 16 | 0.64 | -- | -- | 68 | 0.37 | -- | -- |
| 17 | 0.40 | 0.23 | 0.78 | 69 | 0.43 | 0.08 | 1.31 |
| 18 | 0.43 | 0.11 | 0.90 | 70 | 0.44 | -- | -- |
| 19 | 0.32 | | 0.84 | 71 | 0.43 | 0.10 | 1.46 |
| 20 | 0.53 | 0.46 | 1.23 | 72 | 0.62 | 0.12 | 1.89 |
| 21 | 0.29 | 0.04 | 0.91 | 73 | 0.59 | 0.08 | 2.07 |
| 22 | 0.37 | -- | -- | 74 | 0.40 | 0.10 | 1.96 |
| 23 | 0.45 | 0.40 | 0.83 | 75 | 0.47 | -- | -- |
| 24 | 0.37 | 0.62 | 0.65 | 76 | 0.22 | 0.28 | 1.72 |
| 25 | 0.55 | 0.34 | 0.82 | 77 | -- | 0.19 | -- |
| 26 | 0.51 | -- | -- | 78 | -- | 0.26 | -- |
| 27 | 0.61 | 0.25 | 1.72 | 79 | -- | 0.28 | -- |
| 28 | 0.46 | 0.18 | 1.37 | 80 | 0.30 | 0.21 | 1.91 |
| 29 | 0.47 | 0.36 | 1.14 | 81 | -- | 0.27 | -- |
| 30 | 0.39 | 0.32 | 1.09 | 82 | 0.39 | 0.27 | 2.15 |
| 31 | 0.39 | 0.28 | 1.08 | 83 | 0.44 | 0.26 | 2.28 |
| 32 | 0.57 | 0.23 | 1.09 | 84 | 0.30 | 0.22 | 2.28 |
| 33 | 0.57 | 0.28 | 1.43 | 85 | 0.44 | 0.30 | 2.79 |
| 34 | 0.73 | -- | -- | 86 | 0.32 | 0.26 | 1.85 |
| 35 | 0.47 | 0.21 | 1.62 | 87 | 0.29 | 0.41 | 2.13 |
| 36 | 0.76 | 0.11 | 2.10 | 88 | 0.30 | 0.55 | 1.98 |
| 37 | 0.46 | 0.06 | 1.80 | 89 | 0.37 | 0.63 | 1.95 |
| 38 | 0.89 | -- | -- | 90 | 0.40 | 0.67 | 2.00 |
| 39 | 0.78 | -- | -- | 91 | 0.33 | 0.61 | 2.01 |
| 40 | 0.99 | -- | -- | 92 | 0.28 | 0.68 | 2.24 |
| 41 | 0.48 | 0.06 | 1.46 | 94 | 0.17 | 0.68 | 2.29 |
| 42 | 0.47 | 0.22 | 0.96 | 95 | 0.24 | 0.65 | 2.26 |
| 43 | 0.45 | 0.11 | 2.36 | -- | -- | -- | -- |
| 44 | 0.39 | 0.30 | 1.13 | -- | -- | -- | -- |

Table A7. Calculated values for log Si and pH + ½Al³⁺ plotted in Figure 22 phase diagram [mg/L, milligrams per liter, --, no data]

| Sample Number | Al ³⁺ (mg/L) | pH+ ½ log Al ³⁺ | Log Si | Sample Number | Al ³⁺ (mg/L) | pH+ ½ log Al ³⁺ | Log Si |
|---------------|-------------------------|----------------------------|--------|---------------|-------------------------|----------------------------|--------|
| 1 | 4.86 | -7.13 | 2.49 | 49 | 5.66 | -7.10 | 3.30 |
| 2 | 4.97 | -7.17 | 2.58 | 50 | 5.75 | -6.70 | 3.52 |
| 3 | 4.96 | -6.17 | 2.91 | 51 | 6.31 | -8.29 | 3.55 |
| 4 | 4.16 | -6.07 | 2.14 | 52 | 6.47 | -8.58 | 3.61 |
| 5 | 5.22 | -6.86 | 2.94 | 53 | 6.46 | -8.23 | 3.72 |
| 6 | 4.95 | -6.46 | 2.80 | 54 | 4.12 | -6.49 | 1.96 |
| 7 | 5.4 | -6.57 | 3.21 | 55 | 3.81 | -5.87 | 1.85 |
| 8 | 5.45 | -5.58 | 3.59 | 56 | 4.18 | -7.54 | 1.67 |
| 9 | 5.47 | -6.02 | 3.47 | 57 | 4.02 | -6.58 | 1.83 |
| 10 | 5.55 | -5.90 | 3.59 | 59 | 4.3 | -6.82 | 2.03 |
| 11 | 5.62 | -6.85 | 3.34 | 60 | 4.29 | -6.81 | 2.02 |
| 12 | 5.65 | -6.34 | 3.54 | 61 | 4.16 | -7.10 | 1.80 |
| 13 | 5.65 | -6.86 | 3.37 | 62 | 4.19 | -6.44 | 2.04 |
| 14 | 5.64 | -6.57 | 3.45 | 63 | 4.68 | -6.57 | 2.49 |
| 16 | 5.91 | -8.12 | 3.21 | 64 | 4.2 | -6.36 | 2.08 |
| 17 | 5.93 | -7.01 | 3.59 | 65 | 4.48 | -7.27 | 2.06 |
| 18 | 5.4 | -6.62 | 3.20 | 66 | 4.15 | -6.82 | 1.88 |
| 18 | 5.4 | -6.62 | 3.20 | 67 | 4.2 | -7.37 | 1.74 |
| 20 | 5.62 | -6.15 | 3.57 | 68 | 4.1 | -6.01 | 2.10 |
| 21 | 5.39 | -7.75 | 2.81 | 69 | 4.06 | -6.24 | 1.98 |
| 22 | 5.81 | -6.65 | 3.60 | 70 | 3.97 | -6.22 | 1.90 |
| 23 | 5.65 | -6.35 | 3.53 | 71 | 3.72 | -6.17 | 1.66 |
| 24 | 5.56 | -6.15 | 3.51 | 72 | 3.68 | -6.08 | 1.66 |
| 25 | 5.66 | -6.73 | 3.42 | 73 | 3.77 | -6.38 | 1.65 |
| 26 | 5.21 | -7.69 | 2.65 | 74 | 3.3 | -7.54 | 0.79 |
| 27 | 5.7 | -6.77 | 3.45 | 75 | 3.43 | -7.19 | 1.03 |
| 28 | 5.24 | -7.39 | 2.78 | 76 | 3.42 | -6.19 | 1.36 |
| 29 | 4.98 | -7.23 | 2.57 | 77 | 3.33 | -6.55 | 1.15 |
| 30 | 5.68 | -6.91 | 3.38 | 78 | 3.29 | -6.91 | 0.99 |
| 31 | 5.6 | -6.90 | 3.30 | 79 | 3.23 | -6.96 | 0.91 |
| 32 | 5.56 | -6.97 | 3.24 | 80 | 3.28 | -7.15 | 0.90 |
| 33 | 5.48 | -6.72 | 3.24 | 81 | 3.04 | -7.36 | 0.59 |
| 34 | 5.9 | -6.96 | 3.58 | 82 | 3.19 | -6.42 | 1.05 |
| 35 | 6.05 | -7.16 | 3.67 | 83 | 3.24 | -5.97 | 1.25 |
| 36 | 5.46 | -6.89 | 3.16 | 84 | 3.29 | -5.68 | 1.40 |
| 37 | 4.72 | -5.56 | 2.87 | 85 | 3.24 | -5.97 | 1.25 |
| 41 | 5.36 | -7.56 | 2.84 | 86 | 3.29 | -5.68 | 1.40 |
| 42 | 5.55 | -7.03 | 3.21 | 87 | 3.36 | -5.80 | 1.43 |
| 43 | 4.94 | -5.21 | 3.20 | 88 | 3.36 | -6.62 | 1.15 |
| 44 | 6.19 | -7.49 | 3.70 | 89 | 3.35 | -6.99 | 1.02 |
| 45 | 5.33 | -6.76 | 3.08 | 90 | 3.35 | -6.81 | 1.08 |
| 46 | 4.95 | -7.03 | 2.61 | 91 | 3.36 | -5.51 | 1.53 |
| 47 | 5.15 | -6.81 | 2.88 | 92 | 3.39 | -5.80 | 1.46 |
| 48 | 4.59 | -7.12 | 2.22 | 95 | 3.35 | -5.46 | 1.53 |