Sericite and Chlorite Dissolution Rates from Humidity Cell Testing of Greenstone Rock

Kim Lapakko[1]

[1]Minnesota Department of Natural Resources, Division of Lands and Minerals, St. Paul, MN, USA, kim.lapakko@state.mn.us

ABSTRACT

Fourteen samples of pyrite-bearing Archean greenstone rock ($d < 6.35$ mm, $0.08 \leq FeS_2 \leq 2.25$ wt. %) were characterized and subjected to laboratory dissolution testing for durations of 154 or 204 weeks. Effluent pH varied among samples and over time, reflecting the balance of acid production by pyrite oxidation and acid neutralization largely by sericite, chlorite, and siderite dissolution. Rates of sericite and chlorite dissolution were determined based on the observed rates potassium and magnesium release during four or five time periods. The ranges of base 10 logarithms for calculated rates (mol m^{-2} s^{-1}) of sericite and chlorite dissolution were -14 to -12.5 and -14 to -12.2, respectively, for the pH range of 3.5 to 7.3. Relative to published values, sericite rates were in good agreement and chlorite rates were roughly an order of magnitude lower. Potential factors contributing to lower chlorite rates include overestimation of surface area and inherent variability of dissolution rates as a function of chlorite composition.

Key Words: kinetics, kinetic tests, mine waste drainage, drainage quality prediction, acid neutralization

INTRODUCTION

Laboratory kinetic tests are commonly conducted to aid prediction of mine waste drainage quality. Leachate chemistry and rates of chemical release are typically reported for these tests, but rates of mineral dissolution are rarely reported. Mineral dissolution rates have been measured for many different minerals, but these measurements are commonly determined for a one-mineral system (eg White and Brantley 1995). Kinetic testing of individual rock types is needed to determine mineral dissolution rates for specific rock matrix. Distinct to each rock type are the chemistry, grain size, surface morphology, and extent of exposure (extent to which a mineral grain is exposed to gaseous and aqueous phase reactants) of the individual minerals. Within each rock type the interaction with other minerals and their dissolution products will also be unique. Consequently, it is unknown how well mineral dissolution rates determined from laboratory studies on individual, isolated minerals will approximate rates occurring during mine waste dissolution in the laboratory or field.

Mineral dissolution rates can be helpful when interpreting kinetic test data and in extrapolating predictive test results to full-scale operations. Furthermore, determination of these rates allows dissolution test results from different mineral assemblages to be compiled and compared. This will provide a source of data for a wide variety of mineral assemblages, provide greater insight into factors controlling mine waste weathering, and add a greater degree of confidence to interpretation and extrapolation of kinetic test results. On a practical level, this will reduce uncertainty in mine waste drainage quality predictions.

Greenstones are a mineral exploration target in Minnesota and are host to numerous gold and base metal deposits. Although the exact mineralogy and petrology can vary within and among formations, sericite and chlorite are minerals that commonly occur in these rocks. Their dissolution can neutralize acid produced by pyrite present in mineralized zones. This paper calculates sericite and chlorite dissolution rates in kinetic tests on greenstone rock from northeastern Minnesota and compares them to rates reported in the literature. Previous work found that the rates of pyrite oxidation in this experiment compared favorably with published rates (Lapakko and Antonson 2006).

SERICITE AND CHLORITE DISSOLUTION RATES

Some or all of the acid generated as a result of iron sulfide oxidation may be neutralized by dissolution of other minerals present in a mine waste. Mine waste drainage will acidify if the rate of acid production exceeds that of acid neutralization. Calcium and magnesium carbonates are the most effective of these neutralizing minerals and may be associated with greenstone ore deposits. Calcite ($CaCO_3$) is the most reactive carbonate, with a reported dissolution rate of approximately 2.4 x 10^{-3} mol m^{-2} s^{-1} at pH 6 (p_{CO2} = 0.1 atm, 25 ^{o}C; Busenberg and Plummer 1986). Relative to calcite dissolution at pH 6, siderite dissolution under anoxic conditions is about three orders of magnitude slower (Greenberg and Tomson 1992). Dissolution of silicate minerals will also neutralize acid, but this dissolution is much slower than that of calcium and magnesium carbonates.

Chlorite and sericite are silicate minerals that commonly occur in greenstones. Chlorite is a complex magnesium, aluminum, iron silicate [$(Mg, Fe)_3(Si, Al)_4O_{10}(OH)_2$•$(Mg,Fe)_3(OH)_6$], with a specific gravity of 2.6-3.3, a hardness of 2-2.5 (Klein and Hurlbutt 1985) and a reported surface roughness factor of 64 (Sverdrup 1990). It is commonly associated with greenstones, forming as a result of low-temperature metamorphism (Klein and Hurlbutt 1985), and is one of the minerals that lend the color for which greenstones are named (Bayly 1968).

Sverdrup (1990) presented the following reactions to represent a possible stoichiometry for the initial protonation of the chlorite surface and the reaction of the partially protonated surface.

$$Mg_3Fe_3AlSi_3O_{10}(OH)_7 + 11.2\ H^+ \rightarrow 3\ Mg^{2+} + 2.6\ Fe^{2+} + H_{11.2}Fe_{0.4}AlSi_3O_{10}(OH)_7 \qquad (1)$$

$$H_{11.2}Fe_{0.4}AlSi_3O_{10}(OH)_7 + 2.8H^+ \rightarrow Al^{3+} + 0.4Fe^{2+} + 7H_2O•H_7Si_3O_{10} \qquad (2)$$

A chlorite dissolution rate of 7.6 x 10^{-13} mol m^{-2} s^{-1} (25 ^{o}C, pH 5) was calculated using the chlorite composition and rate of cation release reported by Sverdrup (1990). May et al. (1995) reported a chlorite dissolution rate of 3.0 x 10^{-13} mol m^{-2} s^{-1} based on silica release for the same reaction conditions. They noted that this rate was one to three orders of magnitude slower than those reported for chlorites of higher iron content. Malmström et al. (1996) used magnesium release to determine a rate of 5.8 x 10^{-13} mol m^{-2} s^{-1} after about 25 days of dissolution at 25 ^{o}C and pH 8.2. The rate after three days of dissolution was about 2.8 times this value. The order of the rate with respect to [H^+] over the approximate pH range of 3 to 5 was reported as approximately 0.5 by May et al. (1995) and 0.7 by Sverdrup (1990). Palandri and Kharaka (2004) listed log k_a = -11.11 and n = 0.500 for the acid mechanism and a log k_n value of -12.52 for the neutral mechanism for clinochlore. These values are used to describe mineral dissolution rates based on the equation:

$$\log R = \log k_a - npH + \log k_n \qquad \text{(Equation 1)}$$

Lowson et al. (2005, 2007) reported on the dissolution of iron-rich chlorite with the following stoichiometry: $(Mg_{2.76}Fe^{2+}_{1.90}Fe^{3+}_{0.07}Al_{0.97})[Si_{2.48}Al_{1.52}O_{10}](OH)_8$). They provided the following expression for dissolution rate as a function of H^+ activity and presented a model for chlorite dissolution.

$$R = 10^{-9.79}a_H^{0.49} + 10^{-13.00} + 10^{-16.79}/a_H^{0.43} \qquad \text{(Equation 2)}$$

Sericite is a fine-grained muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$), which has a specific gravity of 2.76 to 2.88, a hardness of 2 to 2.5 (Klein and Hurlbutt 1985) and a reported surface roughness factor of 71 (Nickel 1973). One possible expression of its dissolution stoichiometry is as follows.

$$KAl_2(AlSi_3O_{10})(OH)_2 + H^+ + 9H_2O = K^+ + 3Al(OH)_3 + 3H_4SiO_4 \qquad (3)$$

Rates of dissolution have been reported based on observed release of its component elements. Reported rates (pH 5 - 5.6, 22-25°C) range from 1.2 x 10^{-14} to 1.7 x 10^{-12} mol m^{-2} sec^{-1}, with four of the six values ranging from 1 x 10^{-13} to 2.4 x 10^{-13} mol m^{-2} sec^{-1} (Nickel 1973; Lin and Clemency 1981; Stumm et al. 1987; Kalinowski and Schweda 1996). The dependence of the rate on pH was reported as 0.1 by Nickel (1973, pH 0.2-5.5), 0.08 by Stumm et al. (1987, pH 3-5), and 0.2 by Kalinowski and Schweda (1996, pH 1-4). Palandri and Kharaka (2004) listed log k_a = -11.85 and n = 0.370 for the acid mechanism and log k values of -13.55 and -13.00 for the neutral mechanism (Equation 1).

METHODS

MATERIALS

As part of a project unrelated to mining, the University of Minnesota Department of Physics constructed a cavern at a depth of 730 m in a greenstone formation near Soudan, MN. The goal of the project was to enlarge an underground physics laboratory at the Soudan Mine, and resulted in excavation of approximately 22,000 cubic yards of greenstone rock. Prior to excavation a 6.35-cm drill hole was bored through the center of the proposed cavern to characterize geotechnical properties of the rock. Because there were also concerns regarding disposal of the rock, drill core intervals were analyzed for sulfur content using a LECO furnace.

Fourteen samples spanning a range of sulfur contents were collected from the core for laboratory dissolution testing. Five-foot intervals of quarter core were stage-crushed to minus 0.64-cm to limit generation of fines. The three crushing steps were a large jaw crusher set at 1.92 cm, a small jaw crusher set at 0.95 cm, and a roll crusher set at 0.64 cm. After each step the minus 0.64 cm fraction was retained and the plus 0.64 cm fraction was subjected to the next step. Particle size distribution for the laboratory samples was determined using method ASTM E-276-93 (ASTM 2000) by Lerch Brothers Inc. All samples were dry-sieved and two samples were also wet-sieved.

The rock samples, as well as their size fractions, were analyzed for sulfur, sulfate (sulfide was determined by difference), and evolved carbon dioxide by ACTLABS in Tucson, AZ using ASTM E-1915-97 (ASTM, 2000). A 10 % HCl solution was used to decompose the carbonate minerals, and the carbonate present was quantified as the difference between total carbon in the initial sample and that in the residue. The remaining solid-phase constituents of the bulk samples were determined by ACTLABS in Ancaster, ON. Whole rock constituents were determined using a lithium tetraborate fusion modified from ASTM E-886-94 (ASTM, 2000) and analysis by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a Thermo Jarrell-Ash ENVIRO II ICP.

Mineral content was determined by Louis Mattson (Mineralogical Consulting Service, Pengilly, MN) using sample chemistry, optical microscopy, and previous x-ray diffraction data on drill core samples. Chemistry of siderite (present in two samples), sericite, and chlorite was determined by Jennifer Engstrom at Macalester College (St. Paul, MN) using scanning electron microscope (Zeiss DSM 960A) and electron dispersive spectrometry.

LABORATORY PROCEDURES

Fourteen samples of 6.35-cm diameter drill core were stage crushed and subjected to laboratory dissolution testing for 204 (or 154) weeks. The experimental apparatus was similar to that specified in ASTM Method 5744 (ASTM, 2000) and is described by Lapakko and White (2000). It had a 10.2-cm internal diameter and was approximately 19 cm tall. Each cell was charged with 1000 g of air-dried rock. A total of 18 cells were used for the fourteen drill core samples, four of which were run in duplicate. Prior to sample addition, the cells were washed with 10 % HNO_3, and then rinsed three times with distilled water.

Each cell and the contained 1000 g dry solids was weighed, and the solids were then rinsed daily with 500 mL of deionized water for three days (week 0) to remove oxidation products which accumulated prior to the beginning of the experiment. The outlet port was capped and 500 mL of deionized water was added slowly from a graduated cylinder to the cell. Ten minutes after all cells were filled, the outlets were uncapped and the cells drained. Subsequently the cells were rinsed weekly in a similar manner, with the exception that a single 500-mL volume of deionized water was slowly dripped into the cell from a separatory funnel. Dissolution tests on twelve solids continued for 204 weeks. The four replicates of these samples and two additional samples were terminated after 154 weeks of dissolution.

Between rinses, the cells were stored in a room in which temperature and humidity were controlled. Over the 204-week period of testing, temperature and relative humidity were measured three to four times per week, and average weekly values were determined. Temperature ranged from 22.2 ^{o}C to 27.5 ^{o}C and averaged 24.5 ^{o}C, with a standard deviation of 1.1 ^{o}C. Average weekly relative humidity ranged from 51.3% to 63.5% and averaged 57.9%, with a standard deviation of 2.4%.

Drainage samples were analyzed for specific conductance, pH, alkalinity, and acidity at the Minnesota Department of Natural Resources laboratory in Hibbing, MN. Specific conductance was determined using a Myron L conductivity meter. An Orion SA720 meter, equipped with a Ross combination pH electrode (8165), was used for pH determinations. Alkalinity (for pH > 6.3) and acidity were determined using standard titration techniques for endpoints of 4.5 and 8.3, respectively (American Public Health Association et al. 1992). Samples were filtered through a 0.45-micron filter and acidified for Ca, Mg, Na, and K determinations by the Minnesota Department of Agriculture (MDA, St. Paul, MN) using a Varian 400 SPECTRAA. Concentrations of other solutes were also determined, but those results are not immediately relevant to the present paper.

CALCULATIONS

Solute mass release was calculated as the product of the observed concentration and the volume of drainage. Rates of solute release were calculated by averaging the weekly rates for periods of 20-40, 40-60, 60-100, 100-154, and 154-204 weeks.

Rates of sericite and chlorite dissolution were calculated using 1) rates of potassium and magnesium release over specific time periods, 2) calculated mineral surface areas, and 3) individual mineral chemistries. Rates were not calculated for the period between weeks 0 and 20. For samples run in duplicate, rates were calculated only for the sample with the longer period of record.

Sericite and chlorite surface areas were determined using 1) the particle size distributions, 2) the geometrically calculated specific surface areas of each size fraction (determined using the geometric mean diameter), and 3) surface roughness coefficients (SR) reported for the individual minerals in the literature. Particle size analysis determined the rock masses present in the following fractions (μm): 4750-6300, 2000-4750, 850-2000, 600-850, 500-600, 300-500, 202-300, 150-212, 106-150, 75-106, and <75. The mineral mass in each size fraction was calculated as the product of the rock mass in the size fraction and the percent mineral present in the bulk sample divided by 100. This assumed that the mineral content did not vary substantially as a function of particle size, an assumption supported by chemical analyses of the individual size fractions.

The geometric specific surface area (area per unit mass) of a given mineral was calculated for each particle size fraction using the following equation.

$$A_S = 6/\rho d, \text{ where} \qquad \text{(Equation 3)}$$

A_S = specific surface area, in cm^{-2} g,

ρ = mineral density, g cm^{-3}, and
d = geometric mean diameter of particle size fraction, cm.

The respective densities used for sericite and chlorite were 2.82 and 3.0 g cm^{-3}.

The geometric mineral surface area in the individual size fractions was calculated as the product of the specific surface area and the mineral mass in the size fraction. The mineral surface area in the individual size fractions was summed to determine the total geometric surface area present. The total geometric mineral surface area was multiplied by the surface roughness factor of the mineral to determine the mineral surface area. The respective surface roughness factors used for sericite and chlorite were 71 (Nickel 1973) and 26 (Brandt et al. 2001). The latter value was calculated based on BET analysis of grains ranging from 63 to 200 μm in diameter.

Rates of sericite and chlorite dissolution were estimated assuming that all potassium release was from sericite, all magnesium release was from sericite and chlorite, and that dissolution of these minerals was congruent. The rate of sericite dissolution was determined by dividing the rate of potassium release by the product of the number of moles of potassium per mole sericite and the sericite surface area. The rate of magnesium release from sericite was calculated as the ratio of magnesium to potassium in sericite times the rate of potassium release. The rate of magnesium release from chlorite was calculated as the difference between the observed magnesium release rate and the calculated magnesium release from sericite. The rate of chlorite dissolution was determined by dividing this rate by the product of the number of moles of magnesium per mole chlorite and the chlorite surface area.

RESULTS

The applied objective of the laboratory experiment is to determine the variations of drainage pH with the sulfur content of the rock because these variations will inform decisions regarding the extent of mitigation required for mine wastes in the field. The major water quality concern regarding mine wastes is generation of acidic drainage. Consequently samples were classified based on their drainage pH during the first 204 weeks of experimentation. This classification must be viewed as provisional since laboratory testing of other low-carbonate mine wastes indicated that drainage pH decreases with time (Lapakko and Antonson 1994). The pH variation also provides a perspective for evaluating rates of sericite and chlorite dissolution, both of which are reported to be dependent on pH.

The 14 greenstone samples were analyzed for particle size distribution, chemistry, and mineralogy. Solids were crushed to finer than 6400 μm. Approximately 23 to 35 percent of the particles were finer than 850 μm, 9 to 14 percent finer than 212 μm, and 5 to 8 percent finer than 75 μm (Lapakko and Antonson 2006). Sulfur contents of the 14 samples ranged from 0.04 to 1.22 percent, and the sulfate-sulfur content exceeded 0.016% in only one sample (Table 1). Evolved carbon dioxide contents exceeded 0.05 percent in only the 0.50% S and 0.72% S samples (1.76 and 6.85 percent CO_2, respectively). The major whole rock chemical components were SiO_2 (49.4-84.8%), Al_2O_3 (7.4-21.2%), and FeO (3.5-14.8%), with lesser amounts of MgO (1.1-6.4%) and K_2O (0.55-4.48%). Contents of CaO (0.03-0.68%) and Na_2O (0.07-0.97%) were low.

Whole rock chemistry was determined on 11 size fractions of each sample to assess the variability of mineral content as a function of particle size. For each sample, the average and standard deviations for potassium and magnesium contents of the size fractions were calculated. The ratio of standard deviation to the average was used as an indicator of variability. For samples with sulfur contents of 0.16 % and lower, this ratio for potassium did not exceed 0.10, but for samples of higher sulfur content the ratio

Table1. Summary of sample compositions. Values in weight percent.

%S	%SO_4-S	CO_2	Pyrite	Quartz	Chlorite	Sericite	Siderite
0.04	<0.016	<0.05	0.1	29	55	12	<0.1
0.05a	<0.016	<0.05	0.1	24	30	42	<0.1
0.05b	<0.016	<0.05	0.1	24	39	32	<0.1
0.10	<0.016	<0.05	0.2	56	26	13	<0.1
0.12	<0.016	<0.05	0.2	28	41	28	<0.1
0.16a	<0.016	<0.05	0.3	48	31	13	<0.1
0.16b	<0.016	<0.05	0.3	42	35	19	<0.1
0.20	<0.016	0.05	0.4	72	14	12	0.1
0.26	<0.016	<0.05	0.5	68	14	8	<0.1
0.39	0.016	<0.05	0.7	59	21	16	<0.1
0.50	0.033	1.76	0.9	59	12	21	4.6
0.59	<0.016	<0.05	1.1	77	10	5	<0.1
0.72	<0.016	6.85	1.4	51	12	14	17.9
1.22	0.016	<0.05	2.2	48	33	13	<0.1

typically ranged from 0.13 to 0.24, with one value of 0.30. For the latter set of samples, the potassium content tended to increase as particle size decreased, and the potassium content in the -200 mesh fraction ranged from 1.13 to 1.33 times the average for the size fractions. Because the finer fractions have a relatively high specific surface area, this suggests that the assumption of a constant sericite content for all size fractions might have contributed to underestimation of the sericite surface area for these samples. The magnesium content was comparatively constant with respect to particle size. For all samples the standard deviation was less than or equal to nine percent of the average, indicating that chlorite content did not vary substantially with particle size.

Quartz (24-77%), chlorite (10-55%), and sericite (5-42%) contributed 90 to 98 weight percent of the mineral content in 13 of the 14 samples (Table 1). The exception was the 0.72%-S sample, in which the contribution of these three minerals was 77 percent and siderite ($Fe_{1.79}Mn_{0.15}Mg_{0.13}Ca_{0.003}Na_{0.07}(CO_3)_2$) content was 17.9 percent. Appreciable siderite ($Fe_{1.74}Mn_{0.13}Mg_{0.18}Ca_{0.004}Na_{0.06}(CO_3)_2$) was also present in the 0.50%-S sample, contributing 4.6 weight percent of the sample mass. The compositional range for sericite compositions of the fourteen samples is expressed by the following stoichiometric coefficients: $(K_{1.33\text{-}1.77}Na_{0.16\text{-}0.56}Ca_{0\text{-}0.02})(Al_{3.48\text{-}3.76}Mg_{0.05\text{-}0.24}Fe_{0.10\text{-}0.42}Mn_{0\text{-}0.01}Ti_{0.01\text{-}0.04})[(Si_{6.07\text{-}6.47}Al_{1.62\text{-}1.84})O_{20}](OH)_4$. The corresponding compositional range for chlorite can be similarly expressed as follows: $(Mg_{1.77\text{-}4.87}\ Al_{2.68\text{-}3.28}Fe_{3.66\text{-}7.11}Mn_{0\text{-}0.09}\ Ca_{0\text{-}0.09})\ [(Si_{5.16\text{-}5.43}\ Al_{2.43\text{-}2.84})\ O_{20}]\ (OH)_{16}$

Mattson (2003) suggested the very fine grain size and intergrowth of the chlorite and sericite may have contributed to error in the mineral chemistries determined (Figure 1). He noted that although many of the chlorite chemistries indicated the presence of small amounts of sodium and potassium, the chlorite structure cannot accommodate these large cations. He further noted that the sericite analyses indicated the iron content often exceeded the magnesium content, and this is contrary to most compositions reported in the literature. Consequently, Mattson (2003) determined alternative mineral contents using calculated chlorite chemistries. The alternative sericite contents deviated by more than three percent in

three of the 14 samples and this degree of deviation in chlorite content occurred in only one sample. Due

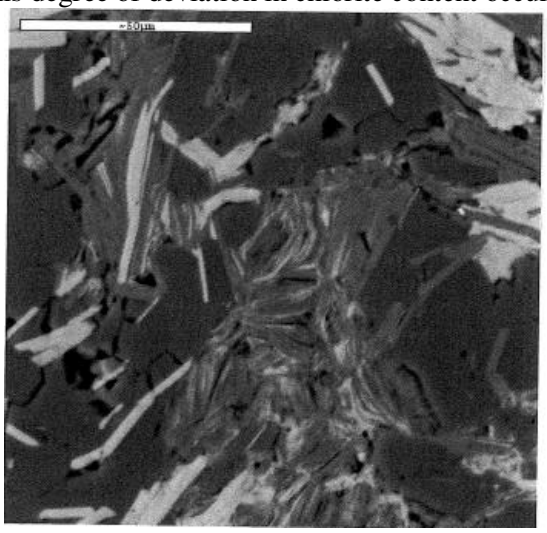


Figure 1. Typical SEM field of view for 0.016 %S (b). View shows fine-grained intimately intergrown chlorite (lightest gray) and sericite (medium gray) in relatively coarser-grained quartz (darkest gray). Black areas are voids in the polished thin section. Note the 50 μm scale bar at the top of the photo (Mattson 2003).

to the relatively small differences, the original values were used in calculations. The alternative calculations did indicate a degree of uncertainty in both mineral content and chemistry. The largest difference in sericite content was 20 percent vs 13 percent in the original analysis and correspondingly for the same sample, 24 vs 31 percent for chlorite.

Rates of potassium and magnesium release were calculated for five time periods for 12 samples with 204-week periods of record and four time periods for six samples with 154-week periods of record (Table 2). Rates of sericite and chlorite dissolution were calculated using these data (excepting the four replicated samples with 154-week periods of record) along with calculated mineral surface areas and individual mineral chemistries determined by EDS analyses. This yielded a total of 68 rate calculations for each mineral over the pH range of 3.5 to 7.3. The period from 0 to 20 weeks was omitted because potassium concentrations were highly variable, generally declining by about an order of magnitude during this period. This likely represented an ion exchange phase commonly associated with silicate mineral dissolution (Nagy 1995).

The dominant mechanism of silicate mineral dissolution typically varies with pH and, consequently, the magnitude of pH dependence varies with pH. In general, the dissolution rate for circumneutral pH is relatively independent of pH and rates tend to increase as pH decreases in the acidic range. Given this relationship, the base 10 logarithm of rates of sericite and chlorite dissolution calculated were plotted vs pH along with the rates determined from the equation provided by Palandri and Kharaka (2004). Additional lines were presented to represent one-third and three times the literature rates. This interval was arbitrarily selected to provide a “zone of agreement”, that acknowledges that exact accord between the observed rates and those published would be unlikely. For example, Blum and Stillings (1995) noted that feldspar rate determinations based on dissolution of individual minerals in a given laboratory generally varied by 50% and were “almost always within a factor of two”. They further noted that rates determined in different laboratories using similar conditions were “generally within a factor of 5". Thus, even under highly controlled conditions variability can be substantial, and the factor of three was selected as a reasonable representation of agreement.

Table 2. Median pH and average rates of potassium and magnesium release (μmol (kg rock*wk)$^{-1}$) for different time periods.

%S	Week 20-40			Week 40-60			Week 60-100			Week 100-154			Week 154-204		
	pH	K	Mg	pH	K	Mg	pH	K	Mg	pH	K	Mg	pH	K	Mg
0.04	7.19	20.8	9.58	7.28	13.9	10.9	7.04	12.4	9.68	7.12	8.31	7.73	7.01	5.22	5.59
0.05a	7.13	13.8	6.50	7.09	7.00	7.47	6.88	5.63	5.97	6.69	3.86	4.30	6.58	2.09	3.01
0.05b	7.13	15.3	5.73	7.07	9.01	6.77	6.87	5.70	5.91	6.72	3.00	4.42	6.54	2.42	2.91
0.10	6.89	5.69	9.87	6.72	3.72	8.69	6.37	3.62	6.86	6.00	1.84	3.89	5.89	1.15	2.01
0.10	6.83	4.92	9.96	6.63	3.25	8.67	6.31	2.39	6.76	6.06	1.46	4.00	n/a	n/a	n/a
0.12	6.81	8.25	11.1	6.61	3.99	10.2	6.33	2.98	7.63	6.18	1.88	5.07	6.00	1.94	3.67
0.16a	6.81	10.6	9.65	6.67	5.23	10.2	6.34	4.10	9.58	6.15	2.64	7.73	5.89	2.16	6.22
0.16b	6.56	12.9	8.48	6.36	5.86	8.33	6.06	4.11	7.18	5.78	2.64	5.71	5.63	2.13	4.64
0.16b	6.57	12.8	8.78	6.41	6.62	8.31	5.99	4.06	7.40	5.82	3.85	5.68	n/a	n/a	n/a
0.20	4.87	8.01	26.8	4.33	4.61	11.6	4.15	3.35	6.83	4.13	2.25	7.72	4.10	1.52	8.62
0.26	4.99	10.9	28.3	4.41	6.28	18.7	3.95	4.45	6.85	3.87	2.34	7.50	n/a	n/a	n/a
0.39	4.59	10.6	42.4	4.12	6.33	22.6	3.97	4.51	18.0	3.96	3.19	13.9	n/a	n/a	n/a
0.50	4.82	6.32	90.1	5.19	3.20	75.6	5.63	2.19	72.6	6.47	2.16	79.2	6.87	1.41	75.7
0.59	3.35	6.15	50.7	3.33	2.63	49.5	3.29	1.91	45.4	3.36	1.66	38.7	3.45	1.65	26.4
0.59	3.34	5.55	46.3	3.28	3.00	58.6	3.27	1.88	48.1	3.35	1.21	40.3	n/a	n/a	n/a
0.72	6.74	6.69	97.6	7.43	4.99	143	7.68	3.67	241	7.84	2.81	321	7.81	1.60	301
1.22	3.84	5.45	38.9	3.62	4.39	49.2	3.51	2.16	62.4	3.55	1.77	61.8	n/a	n/a	n/a
1.22	3.79	5.74	42.8	3.56	3.63	55.5	3.47	2.13	64.0	3.50	1.55	59.6	3.50	1.35	54.2

n/a: not applicable because cells were terminated after 154 weeks

The calculated rates of sericite dissolution were in good agreement with those presented by Palandri and Kharaka (2004). Of the 68 rates calculated, 56 (82 %) were within the boundaries established (Figure 2). Nine of the "anomalous" rates were above the upper boundary, with associated pH values of 6.6 to 7.3. The rates ranged from very near to about half an order of magnitude above the boundary. Closer examination of the data indicated that four of the anomalous points were from the 0.04 %S sample, suggesting that the sericite surface area for this sample might have been underestimated. The remaining five were from the 20 to 40 week rate period, and were associated with five different samples. This suggests that potassium release at this time might have been elevated, perhaps still affected by some of the initial, more rapid ion exchange. One additional rate was above the boundary at pH 5, but it is in close agreement with those presented by Kalinowski and Schweda (1996) and Stumm et al. (1987). Two of the rates were lower than the zone presented but were very close to the lower bound (Figure 2).

Samples with sulfur contents of 0.50 and 0.72 percent were omitted from chlorite rate calculations because of their elevated siderite contents. Release of magnesium from the magnesian siderite would interfere with the calculation of magnesium release resulting from chlorite dissolution. For the remaining 12 samples, the calculated chlorite dissolution rates were in reasonable agreement with those of Palandri and Kharaka (2004) when pH was below 5 (Figure 3). In the circumneutral pH range, the calculated rates of chlorite dissolution were lower than those presented by Palandri and Kharaka (2004), as well as those presented by Lowson et al. (2005) (Figure 3). To describe the observed data, the rate equation of Palandri and Kharaka (2004) was modified by changing the log k_n from -12.52 to -13.12. The boundaries associated with this equation (log rate ± 0.5) encompassed all but one data point for pH > 5, which suggests that the calculated rates were roughly one-fourth of the Palandri and Kharaka (2004) rates in the circumneutral pH range.

It is possible that the discrepancy in the circumneutral pH range was a result of the wide variation in chlorite chemistry, which can be written in general form as $A_{5\text{-}6}Z_4O_{10}(OH)_2$, where A = Al, Fe^{2+}, Fe^{3+}, Li,

Mg, Mn, Ni, and Z = Al, Si, Fe^{3+} (Klein and Hurlbutt 1985). May et al. (1995) attributed discrepancies among rates to differences in chemistry, indicating dissolution rate increased with increasing iron content.

Figure 2. Log d sericite/dt vs pH. All data. Solid line from Palandri and Kharaka 2004. Dashed lines are 1/3 and 3 times those values.

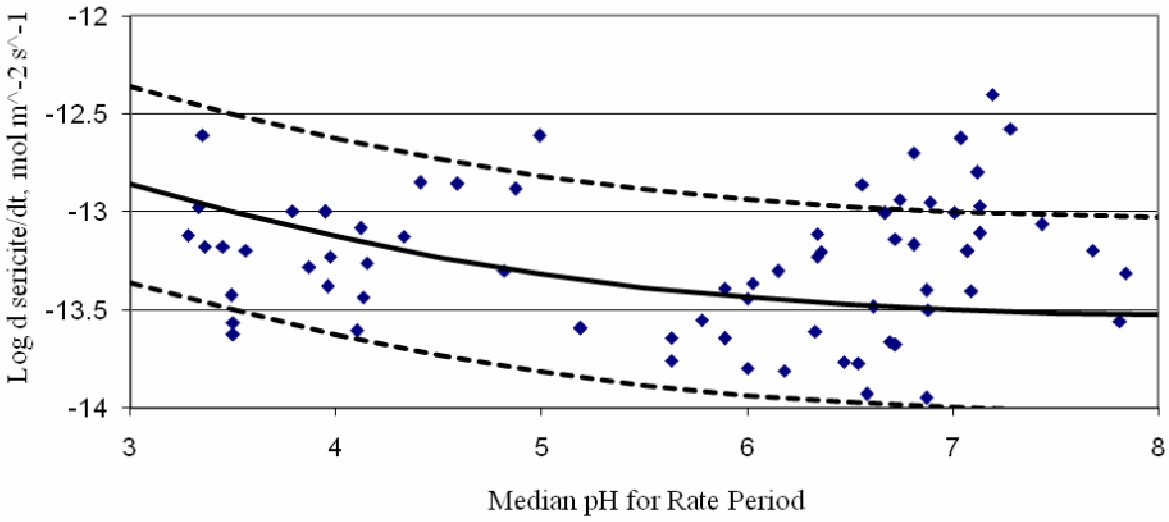
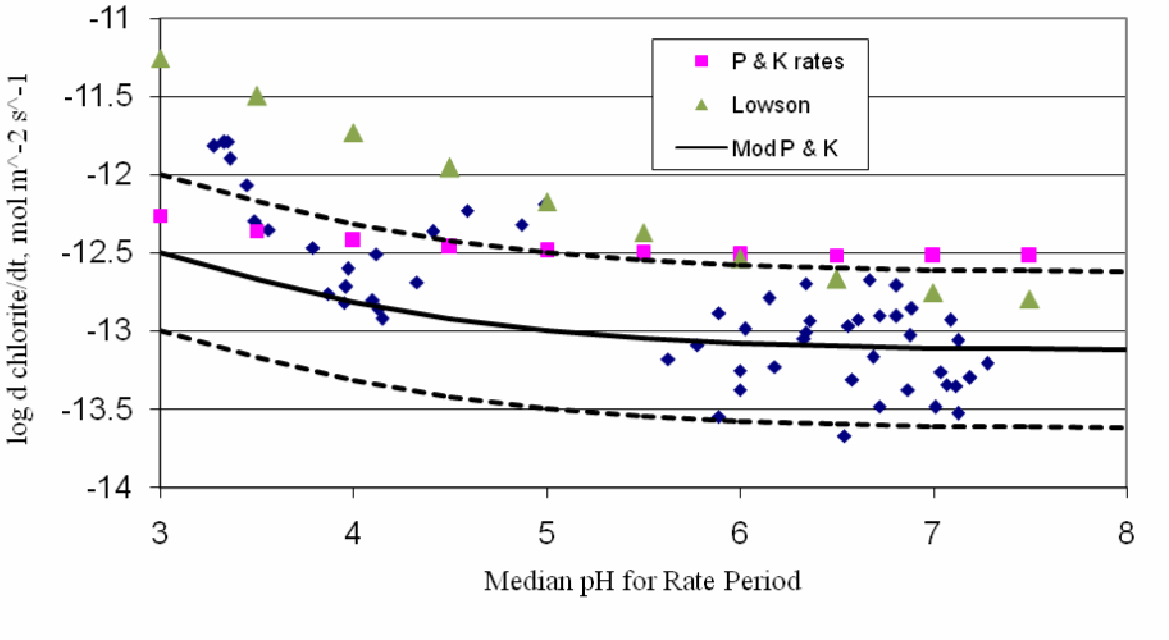


Figure 3. Log d chlorite/dt vs pH. All data from noncarbonate samples included. Modified Palandri and Kharaka (2004) uses -13.12 for log k_n rather than -12.52.



This, however, seems to be at odds with their identification of the brucitic interlayer as the most susceptible to weathering. The latter is more consistent with slower rates for the chlorite in the present set of samples for which concentrations of iron and aluminum were high and magnesium concentrations low relative to those presented by May et al. (1995) and Lowson et al. (2005, 2007). The magnesium:iron

ratios for the chlorite in the samples ranged from 0.25 to 1.05, with only three of the fourteen values exceeding 0.73 (Mattson 2000). The lower magnesium concentrations in the chlorite suggest a lesser degree of brucite, the most reactive layer, in the sample. If so, the lower magnesium content of the present samples might explain why calculated chlorite dissolution rates were lower than those predicted based on literature equations.

It is also possible that intergrown nature of the minerals present inhibited chlorite dissolution in the circumneutral pH range (Figure 1). Chlorite dissolution is reported to occur preferentially along the edges as opposed to the basal surfaces (Brandt et al. 2001). If the mode of chlorite occurrence preferentially limited exposure of the edges, a decrease in dissolution rates in the circumneutral pH range might occur. This seems unlikely because such an occurrence would be expected to result in lower rates at lower pH, and this was not the case.

SUMMARY AND CONCLUSIONS

Sericite and chlorite dissolution rates from greenstone rock were calculated over the pH range of 3.5 to 7.3 for four or five time periods in kinetic tests of 154- or 204-week duration. Agreement between calculated rates and rates based on equations presented by Palandri and Kharaka (2004) was deemed reasonable if calculated rates were within one-third to three times the published rates. Over 80 percent of the sericite rates were in reasonable agreement, with most disparate rates associated with a single sample or the initial period for rate calculation. Calculated chlorite dissolution rates were in reasonable agreement with published rates for pH values below 5 and were on average one-fourth of the published rates for higher pH values. These results, in conjunction with those determined earlier for pyrite oxidation rates (Lapakko and Antonson 2006) suggest that published mineral dissolution rates can provide a basis for interpreting and predicting solute release from mine wastes. They also suggest, that for silicate mineral dissolution rates 1) a factor of three around a predicted central tendency appears to be a reasonable range (ie scatter) to expect and 2) some dissolution testing is necessary to calibrate rates to specific rock types.

ACKNOWLEDGMENTS

Funding for this project was provided by the US BLM Utah State office, the US BLM Applications of Science program, the Minnesota Environmental Cooperative Research (ECR) program, and the Minnesota Minerals Coordinating Committee. Rick Ruhanen (MN DNR) provided geological expertise on Minnesota greenstone terranes and provided input on sample selection for the laboratory and field tests. Anne Jagunich and Patrick Geiselman assisted John Folman in conducting the experiment. Sue Saban provided data input. Erin Phillips, Bryn Milne, and Jennifer Engstrom analyzed the samples by XRD and SEM-EDS under the guidance of Karl Wirth and Jeff Thole at Macalester College. Louis Mattson also conducted mineralogical analyses and provided the ultimate interpretation of all mineralogic measurements.

REFERENCES

ASTM (2000) Annual Book of ASTM Standards, 11.04. American Society for Testing and Materials, West Conschohocken, PA.

American Public Health Association (APHA), American Water Works Association, Water Environment Federation. (1992) Standard Methods for the Examination of Water and Wastewater, 18th edition. American Public Health Association, Washington, D.C.

Bayly, B. (1968) Introduction to Petrology. Prentice-Hall, Inc., Englewood Cliffs, New Jersey. 371 p.

Blum, A. E. (1994) Feldspars in weathering. *Feldspars and their Reactions*, I. Parson, ed., Kluwer Academic Publishers, pp. 595-630.

Blum, A.E., Stillings, L.L. (1995) Feldspar dissolution kinetics. *Chemical Weathering Rates of Silicate Minerals, Mineral. Soc. Am., Vol 31.* White, A.F., Brantley, S.L. eds, Mineral. Soc. Am., Washington, D.C. pp. 291-352.

Brandt, F., Bosbach, D., Krawczyk-Baersch, Arnold, T. (2001) Weathering of chlorite in dilute solutions: a combined macroscopic and microscopic approach. Abstract in Eleventh Annual V.M Golschmidt Conference.

Busenberg, E., Plummer, L.N. (1986) A comparative study of the dissolution and crystal growth kinetics of calcite and aragonite. F.A. Mumpton, ed., Studies in Diagenesis, U.S. Geological Survey Bulletin 1578. pp. 139-168.

Chou, L. (1985) Study of the kinetics and mechanisms of dissolution of albite at room temperature and pressure. Doctoral Thesis, Northwestern University, Evanston, IL. 320 pp.

Chou, L., Wollast, R. (1985) Steady state kinetics and dissolution mechanisms of albite. American Journal of Science, 285. pp. 963-993.

Eary, E.L., Schramke, J.A. (1990) Rates of inorganic oxidation reactions involving dissolved oxygen. In Chemical Modeling of Aqueous Systems II, Melchior, D.C. and Basset, R.L. eds. ACS Symposium series 416, American Chemical Society, Washington, D.C. pp. 379-396.

Greenberg, J., Tomson, M. (1992) Precipitation and dissolution kinetics and equilibria of aqueous ferrous carbonate vs temperature. Applied Geochemistry, 7 (2), pp. 185-190.

Kalinowski, B.E., Schweda, P. (1996) Kinetics of muscovite, phlogopite, and biotite dissolution and alteration at pH 1-4, room temperature. Geochimica et Cosmochimica Acta , 60, 3. pp. 367-385.

Klein, C., Hurlbut, C.S. (1985) Manual of Mineralogy. John Wiley & Sons, New York. 596 pp.

Lapakko, K. A., Antonson, D. A. (1994) Oxidation of sulfide minerals present in Duluth Complex rock: A laboratory study. In Environmental Geochemistry of Sulfide Oxidation; ACS Symposium Series 550; American Chemical Society: Washington, DC, 1993. pp. 593-607.

Lapakko, K.A., Antonson, D.A. (2006) Pyrite oxidation rates from humidity cell testing of greenstone rock. In Proc. 2006, 7th ICARD, March 26-30, 2006, St. Louis MO. Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502. pp. 1007-1025.

Lapakko, K.A., White, W.W. III. (2000) Modification of the ASTM D5744-96 kinetic test. In Proc. from the Fifth International Conference on Acid Rock Drainage. SME, Littleton, CO. pp. 631-639.

Lin, F.C., Clemency, C.V. (1981) The kinetics of dissolution of muscovites and 25°C and 1 atm CO_2 partial pressure. Geochimica et Cosmochimica Acta, 43. pp. 571-576.

Lowson, R.T., Cormarmond, M-C.J., Rajaratnam, G., Brown, P.L. (2005) The kinetics of the dissolution of chlorite as a function of pH and at 25 °C. Geochim. Cosmochim. Acta, Vol. 69, No. 7, pp. 1687-1699.

Lowson, R.T., Brown, P.L., Cormarmond, M-C.J., Rajaratnam, G., (2007) The kinetics of the chlorite dissolution. Geochimica Et Cosmochimica Acta, Vol. 71, No. 6, pp. 1431-1447.

Malmström, M., Banwart, S., Lewenhagen, J., Duro, L., Bruno, J. (1996) The dissolution of biotite and chlorite at 25°C in the near-neutral pH region. J. Contaminant Hydrology, 21. pp. 201-213.

Mattson, L.A. 2000. Soudan mine cavern sample mineralogy. Report to Minnesota Department of Natural Resources from Louis A. Mattson, Mineralogical Consulting Service, Pengilly, MN. 27 September 2000. 6 pp.

Mattson, L.A. (2003) Re: Greenstone Mineralogy. Report to Minnesota Department of Natural Resources from Louis A. Mattson, Mineralogical Consulting Service, Pengilly, MN. 31 January 2003. 12 pp.

May, H.M., Acker, J.G., Smyth, J.R., Bricker, O.P., Dyar, M.D. (1995) Aqueous dissolution of low-iron chlorite in dilute acid solutions at 25°C. Clay Minerals Soc. Prog Abstr., 32, 88.

Nagy, K.L. (1995) Dissolution and precipitation kinetics of sheet silicates. *Reviews in Mineralogy, Vol. 31. Chemical weathering rates of silicate minerals.* White, A.F., Brantley, S.L. eds, Mineralogical Society of America, Washington, D.C. pp. 173-233.

Nickel, E. (1973) Experimental dissolution of light and heavy minerals in comparison with weathering and intrastratal solution. Contrib Sedimentology, 1. pp. 1-68.

Palandri, J.L., Kharaka, Y.K. (2004) A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modeling. U.S. Geological Survey Open File Report 2004-1068. U.S. Geological Survey in cooperation with the National Energy Technology Laboratory - United States Department of Energy. 70 pp.

Stumm, W., Wehrli, B., Wieland, E. (1987) Surface complexation and its impact on geochemical kinetics. Croatica Chemica Acta, 60, 3. pp. 429-456.

Sverdrup, H.U. (1990) The kinetics of base cation release due to chemical weathering. Lund University Press. Lund, Sweden. 246 pp.

White, A.F., Brantley, S.F. (1995) Reviews in Mineralogy, Volume 31 - Chemical weathering rates of silicate minerals. Mineralogical Society of America, 583 pp.

www.hep.umn.edu/minos. (2001) Webpage for University of Minnesota Department of Physics, High Energy Physics, MINOS project.