



PII S0016-7037(99)00248-3

AQUATIC CYCLES AT THE EARTH'S SURFACE

Weathering and Geochemical Cycles

The effect of microbial glucose metabolism on bytownite feldspar dissolution rates between 5° and 35°C

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(Received October 15, 1998; accepted in revised form April 29, 1999)

Abstract—The rate of Si release from dissolving bytownite feldspar in abiotic batch reactors increased as temperatures increased from 5° to 35°C. Metabolically inert subsurface bacteria (bacteria in solution with no organic substrate) had no apparent effect on dissolution rates over this temperature range. When glucose was added to the microbial cultures, the bacteria responded by producing gluconic acid, which catalyzed the dissolution reaction by both proton- and ligand-promoted mechanisms. The metabolic production, excretion, and consumption of gluconic acid in the course of glucose oxidation, and therefore, the degree of microbial enhancement of mineral dissolution, depend on temperature. There was little accumulation of gluconic acid and therefore, no significant enhancement of mineral dissolution rates at 35°C compared to the abiotic controls. At 20°C, gluconate accumulated in the experimental solutions only at the beginning of the experiment and led to a twofold increase in dissolved Si release compared to the controls, primarily by the ligand-promoted dissolution mechanism. There was significant accumulation of gluconic acid in the 5°C experiment, which is reflected in a significant reduction in pH, leading to 20-fold increase in Si release, primarily attributable to the proton-promoted dissolution mechanism. These results indicate that bacteria and microbial metabolism can affect mineral dissolution rates in organic-rich, nutrient-poor environments; the impact of microbial metabolism on aluminum silicate dissolution rates may be greater at lower rather than at higher temperatures due to the metabolic accumulation of dissolution-enhancing protons and ligands in solution. *Copyright © 1999 Elsevier Science Ltd*

1. INTRODUCTION

Bacteria are ubiquitous in soils, sediments, and subsurface environments with concentrations ranging from 10^5 to 10^9 cells/cm³ (Hicks and Fredrickson, 1989; Kampfer et al., 1991; Albrechtsen and Winding, 1992; Edwards et al., 1998). Natural consortia of bacteria are diverse, viable, metabolically active, and able to grow on a large number of carbon substrates (Balkwill, 1989; Frederickson et al., 1989; Madsen and Bollag, 1989; Sinclair and Ghiorse, 1989; Hazen et al., 1991; Phelps et al., 1989). Although some of these organisms are free-living (“planktonic”) in solution, most of these bacteria are attached to mineral surfaces (Hazen et al., 1991; Holm et al., 1992) where they can impact water–rock interaction, mineral surface chemistry, dissolution and precipitation of minerals, the evolution of groundwater geochemistry, and soil formation (e.g., Chapelle et al., 1987; Chapelle and Lovely 1990; Hiebert and Bennett, 1992; McMahon et al., 1992; Barker and Banfield, 1996; 1998; Barker et al., 1997). The interaction between microbes and mineral substrata can involve the oxidation or reduction of mineral constituents from which the organism derives energy for growth and reproduction (Ehrlich, 1990; Herring and

Stumm, 1990; Nealson and Stahl, 1997). However, other types of interactions are also possible and these may have impact on the diagenesis of a wider range of minerals including the abundant classes of silicate and aluminum–silicate minerals (Berthelin, 1983; 1986).

Microbes can enhance mineral dissolution rates by producing and excreting metabolic by-products that interact with the mineral surface. Complete microbial respiration and degradation of particulate and dissolved organic carbon can elevate carbonic acid concentration at mineral surfaces, in soils, and in groundwater (Chapelle et al., 1987; Barker et al., 1998), which can lead to an increase in the rates of mineral weathering by a proton-promoted dissolution mechanism. Soil pCO₂ concentrations as high as 1–5% have been measured, corresponding to solution pH of approximately 4.5–5.5 (Keller and Wood 1993; Drever, 1994). Increasing acidity below a pH of approximately 5 results in increased dissolution rate of many silicate and aluminum silicate minerals (see Welch and Ullman, 1996 and references therein).

In addition to carbonic acid, microbes can produce and excrete organic ligands by a variety of processes such as fermentation and degradation of organic macromolecules, or as a response to nutrient stress (Neijsssel and Tempest, 1975; Berthelin, 1983; Gottschalk, 1986; McMahon and Chapelle, 1991; Tempest and Neijsssel, 1992; Paris et al., 1996). These

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ligands can indirectly increase the rates of mineral weathering by forming stable soluble metal–organic complexes in solution, thereby increasing the apparent solubility of the mineral (Bennett et al., 1988). However, ligands can also directly increase mineral dissolution rates by a ligand-promoted mechanism involving the formation of stable and soluble metal–organic complexes at the mineral surface, the weakening of the metal–oxygen bonds, and thereby the catalysis of the dissolution reaction (Amrhein and Suarez, 1988; Wieland et al., 1988). In addition to low molecular weight compounds, microbes also produce high molecular weight compounds, such as microbial extracellular polysaccharides, that can enhance mineral dissolution by complexing with ions in solution, or inhibit dissolution by irreversibly binding to reactive sites on the mineral surface (Welch and Vandevivere, 1995; Barker et al., 1998; Welch et al., 1999). Microbial polymers can also serve as nucleation sites for secondary mineral phases (Ferris et al., 1988; 1989; Konhauser et al., 1994; Barker and Banfield, 1996; 1998).

The rates of both microbial metabolism and mineral dissolution reactions depend on temperature. The apparent activation energy of dissolution (E_a) for most silicate minerals ranges from 10 to 20 kcal/mol, which corresponds to a doubling in dissolution rate with a 13–6°C increase in temperature from 25°C (Lasaga et al., 1994 and references therein). The temperature dependence of Ca–Mg silicate mineral weathering is an important geochemical parameter controlling the feedback between atmospheric CO₂ concentrations and global climate. The weathering of Ca- and Mg-containing silicate and aluminum–silicate minerals, the transport of weathering products to the ocean, and the subsequent formation and burial of marine Ca–Mg carbonates is thought to be the major sink for atmospheric CO₂ over geologic time (Walker et al., 1981; Berner et al., 1983; Volk, 1987; Brady, 1991; 1997; Velbel, 1993; Gwizda and Broecker, 1994). Under abiotic conditions and at higher temperatures (brought on by higher levels of atmospheric CO₂), it is thought that silicate minerals should weather more rapidly, leading to an increase in the removal of CO₂ from the atmosphere (ultimately as Ca–Mg carbonates), and lower temperatures. The magnitude of this negative feedback between silicate mineral weathering and climate depends on the magnitude of the apparent activation energy of the primary Ca- and Mg–silicate dissolution (Brady, 1991; Velbel, 1993; Brady and Carroll, 1994).

The temperature dependence of mineral dissolution may not be the only process affecting mineral weathering in nature and CO₂ drawdown. The production and excretion of microbial products (including both the products of partial and complete respiration) are also temperature dependent (Kondo et al., 1993; Alvarez et al., 1995; MacDonald et al., 1995; Pöhhacker and Zech, 1995). Therefore, the temperature dependence of at least two processes (and perhaps more) must be considered to predict the overall impact of temperature on atmospheric CO₂ and global climate: (1) the effects of temperature on microbial metabolic rates; and (2) the effects of temperature on the metabolite-mediated rates of silicate weathering.

Several laboratory studies have shown that microbes can increase the dissolution rate of silicate and aluminum–silicate

minerals in laboratory batch experiments, primarily by generating organic and inorganic acids (for a review, see Barker et al., 1997). Several strains of bacteria also enhanced dissolution at neutral pH in a buffered glucose media by producing organic ligands, primarily gluconate (Vandevivere et al., 1994). However, most of these experiments were performed in concentrated solutions of complex media under poorly buffered conditions and therefore, it is difficult to separate the proton- and ligand-promoted effects on silicate mineral dissolution or to extrapolate these results to the more oligotrophic conditions found in most field environments.

There is, however, extensive evidence that microorganisms and microbial metabolites do have an effect on silicate weathering under nutrient availability much lower than that used in most laboratory experiments where the organisms are attached to surfaces. For example, microbial and fungal production of acidic mucopolysaccharides associated with lichens enhanced the weathering of the primary rock surfaces and also served as a nucleating surface for the formation of secondary phases (Barker and Banfield, 1996; 1998). Immediately below microbial cells and microbially produced extracellular polymers alteration of rock was enhanced, presumably because of the transport of soluble microbial metabolites through the pore spaces. Thorseth et al. (1992) reported etched structures on palagonite surfaces that were the size and shape of the cyanobacteria found on the mineral surface. In situ microcosm studies in an aquifer contaminated by an oil spill (Hiebert and Bennett, 1992; Bennett et al., 1996) show that feldspar and quartz weathering was increased when bacteria colonized mineral surfaces. Many of the etch pits on mineral surfaces were approximately the same size and shape as the bacteria. They hypothesized that attached bacteria create a microreaction zone where organic acids and other metabolites were concentrated at the mineral surface, thus locally increasing the mineral dissolution rate, a conclusion also supported by the recent work of Barker et al. (1998). More recent work suggests that these attached bacteria may be mobilizing particulate nutrients to support their metabolic requirements from the mineral substrata (Bennett et al., 1998; Taunton et al., 1998).

The purpose of our work is to determine whether a naturally occurring strain of bacteria could enhance mineral dissolution rates under conditions similar to those in soils and oligotrophic aquifers, the mechanism of enhancement if observed, and whether this enhancement is temperature dependent. As temperatures increase, microbial metabolic activity and production of organic acids should increase as well. Hypothetically, the increased production of dissolution-enhancing compounds with increasing temperature should greatly enhance mineral weathering rates at higher temperatures. Our experiments, however, demonstrate that microbially driven feldspar dissolution rates may not have such a simple temperature dependence. Our experiments suggest that biologically mediated silicate–mineral weathering may be much more intensive and extensive in cold environments than previously suspected. These results may have implications for predicting variations in biologically mediated mineral weathering as seasons change, in different climate regimes, and perhaps as global climate changes over geologic time scales.

2. METHODS

2.1. Minerals

Bulk bytownite feldspar (Crystal Bay, Minnesota) was purchased from Wards Scientific Establishment (Rochester, NY) for these experiments. The composition of this mineral was determined for previous mineral dissolution experiments in our laboratory and is approximately $\text{Na}_{0.25}\text{Ca}_{0.75}\text{Al}_{1.75}\text{Si}_{2.25}\text{O}_8$ (Welch and Ullman, 1993; 1996). Minerals were crushed, ground, and sieved and the 125–250 μm size fraction was collected for these experiments. The feldspar sand was rinsed with deionized water in an ultrasonic bath ≈ 50 times to remove fine particles. A magnet and a Frantz Isodynamic Magnetic Separator were used to remove magnetic minerals and iron filings produced during the crushing procedure. The feldspar sand was further washed with 0.1 mM HCl for several hours to remove fines and very reactive material from the mineral surface. This treatment should not significantly alter the mineral surface chemistry as the dissolution of the framework ions Si and Al is approximately stoichiometric at this pH (Welch and Ullman, 1993). Fresh feldspar sand was used for each experiment. The feldspar used in the longer dissolution experiments was prepared more than a year before its use; the feldspar used in the short duration experiments was prepared from the same bulk rock, but was crushed several months before use. The surface area of both bytownite samples was determined by single point Kr gas adsorption and was 0.08 m^2/g (Lowell and Shields, 1991).

2.2. Solutions

All solutions were prepared by dissolving reagent-grade chemicals in deionized water. Chemicals were purchased from Fisher Scientific and Sigma Chemical Company. Autoclaving or filtration was used to sterilize solutions, as necessary.

2.3. Bacteria

A strain of bacteria, B0665, was obtained from the Department of Energy Subsurface Microbial Culture Collection (Dr. David Balkwill, Florida State University) for these experiments. On the basis of molecular sequences this strain has been identified as a β -proteobacteria, closely related to *Burkholderia solanecorum* (S. A. Welch, unpublished data). It was isolated from the Middendorf formation at a depth of 259 m near the Savannah River Reservation. B0665 was initially grown for these experiments in a sterilized peptone–yeast–glucose media for 2–3 days and then harvested by centrifugation at 5000 rpm. The cultures were then resuspended and rinsed several times with deionized water to remove any remaining culture medium. This is a naturally occurring strain of bacteria that has been used in previous experiments in our laboratory, and is known to produce gluconate when cultured in buffered and nutrient-limited glucose solutions (Vandevivere et al., 1994).

2.4. Experimental

Dissolution experiments were performed in batch reactors. Two grams of clean feldspar sand were added to 100 mL of solution in each reactor. There were three experimental treatments, each run at three temperatures with three replicates for each treatment. The treatments consisted of an inorganic abiotic control (CON) in 100 μM KNO_3 solution; a treatment with bacteria (BAC) that was the control treatment with 10^8 cells/mL of B0665 added; and a treatment with bacteria and glucose (BG) that was the BAC treatment with 1 mM glucose added. Samples were placed on a rotary shaker and stirred at 100 rpm. This rate was chosen to mix and oxygenate the overlying solution but to limit physical mixing and abrasion of the feldspar sand along the base of the reactor. Dissolution experiments were run at three temperatures 5°, 20°, and 35°C to determine the effect of temperature on microbial reactions and mineral dissolution. Experiments were initially run for 15 days with samples of the overlying solution taken daily for the first 3 days and then every other day. On the basis of the results of the initial BG treatments at 5° and 20°C, which showed that much of the gluconate production and bytownite dissolution takes place within the first

few days, the experiments were repeated for a shorter time period, 3 days, with samples taken at 0, 1, 3, 6, 24, 48, and 72 hr.

Samples were analyzed for pH, Si, Al, organic acids, and in some cases, glucose concentration and microbial cell numbers. Samples were filtered through a 0.2 μm Acrodisc filter before analysis of dissolved constituents. The pH was measured potentiometrically. Dissolved Si was measured with a Perstorp Analytical Flo Solution analyzer using the silicomolybdate blue method. Dissolved Al was determined by cation exchange ion chromatography using a Dionex CS-2 column, a sodium acetate buffer (pH 4.5), lumogallion as a postcolumn reagent, and fluorescence detection. This method is based on the Al separation method developed by Bertsch and Anderson (1989) and the Al detection method of Hydes and Liss (1976). This procedure can separate and distinguish between free (or weakly complexed) and strongly complexed Al in solution. Organic acids were determined by anion exchange ion chromatography using a sodium hydroxide gradient and suppressed conductivity detection. Glucose was measured using a Stanbio enzymatic glucose test kit (Fisher Scientific) and a UV-Vis spectrometer. Microbial cells were counted using acridine orange stain and epifluorescence microscopy.

3. RESULTS

The release of dissolved Si to solution is taken as an overall indicator of feldspar dissolution in these experiments. Feldspar dissolution was not stoichiometric in these experiments and, with a few significant exceptions, Al concentrations were below the detection limit of the ion chromatographic method ($<0.3 \mu\text{M}$). Nonstoichiometric dissolution is commonly observed in short dissolution experiments and may be the result of the slow formation of leached layers on the mineral surface (Chou and Wollast, 1984) or the rapid precipitation of secondary phases, most likely amorphous Al hydroxides or gibbsite, as the feldspar reacted.

3.1. Long (15 Day) Experiments

In the inorganic control (CON) experiments, Si concentration from the dissolving feldspars increased rapidly in the first few days of the experiment, a common feature of batch dissolution experiments (Holdren and Berner, 1979). From day 5 through 15, however, the rate of Si release was slower and approximately linear with time at all three temperatures (Fig. 1a). Si concentration at the end of the experiments approximately doubled with each temperature increase of 15°C. There was no dissolved Al detected in these experiments. Solution pH was variable but remained between 5.7 and 7, the pH region often called the “dissolution plateau” where feldspar dissolution rates are at their minimum and independent of pH (e.g., Chou and Wollast, 1985; Blum and Lasaga, 1988; Welch and Ullman, 1993). Si concentrations were very reproducible in replicated experiments. Net Si release rates, ≈ 0.1 – $0.6 \mu\text{mol Si}/\text{m}^2/\text{d}$, were estimated from the linear increase in Si concentration corrected for the volume of overlying solution removed and normalized to initial mineral surface with time (Welch and Ullman, 1999). Rates increased systematically with temperature from 5–35°C. On the basis of the linear release of Si in these experiments and equilibrium calculations reported in Table 1, the solutions were apparently undersaturated with respect to both the dissolving and potential secondary Si-containing phases. At 35°C, however, solutions may have been slightly supersaturated with respect to kaolinite by the end of the experiment (Table 1).

The results of the dissolution experiments with added bac-

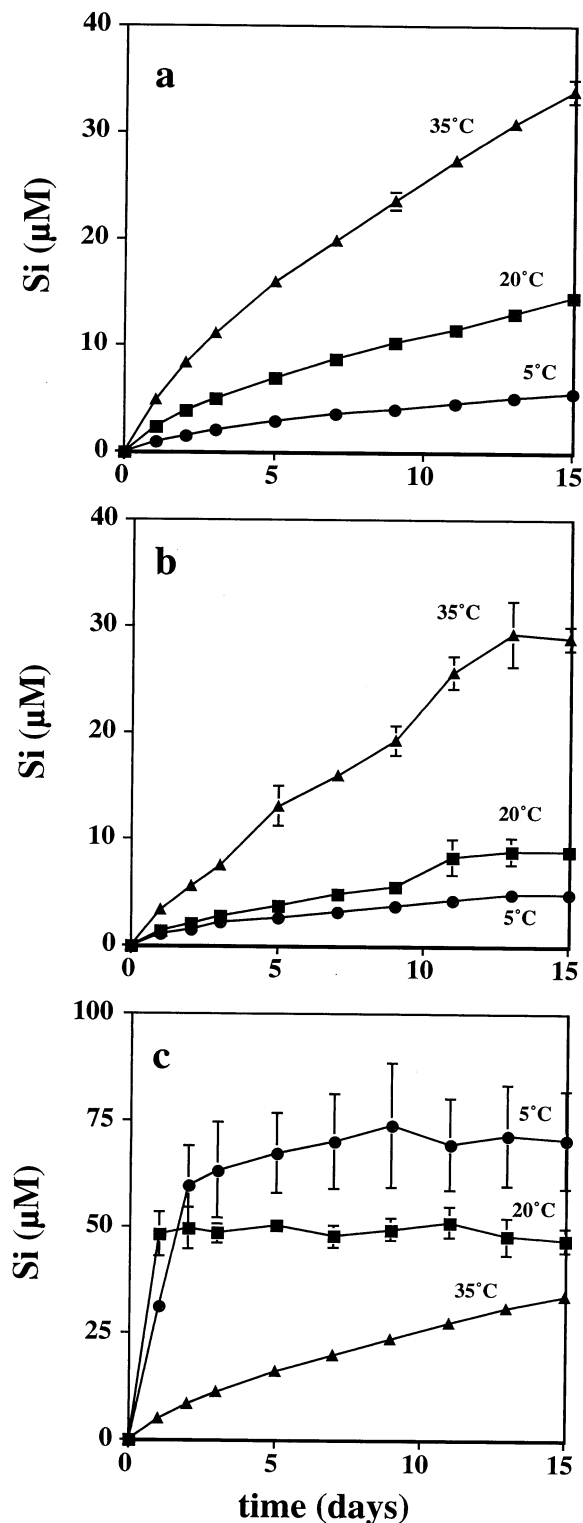


Fig. 1. Si concentrations vs. time in the long (15 day) experiments. (a) The CON treatments in $100 \mu\text{M KNO}_3$; (b) the BAC treatment with 108 cells/mL of BO665; and (c) the BG treatment with bacteria and 1 mM glucose at 5°C (●), 20°C (■), and 35°C (▲). Here and in subsequent figures, the error bars indicate the mean and standard deviation for three replicate treatments. Where the error bars are not shown, the standard deviation is encompassed within the symbol.

teria (BAC) were very similar to the abiotic control (CON), although there was somewhat more variability among replicated experiments (Fig. 1b). There was no significant increase in silica release in the BAC treatment compared to CON. However, mean Si concentration at the end of the experiment in the 20°C bacteria experiment was slightly lower than in CON. In these experiments there was no dissolved Al detected, no detectable organic acids excreted by the bacteria, and solution pH remained within the dissolution plateau.

In comparison to the CON and BAC experiments, there was substantial enhancement of Si release in the bacteria + glucose (BG) treatment at the two lower temperatures (Fig. 1c) and the pattern of Si release with time differs significantly. At 5°C , Si concentration increased rapidly in the first two days of the experiment, to $50\text{--}90 \mu\text{M}$ (compared to $\approx 2 \mu\text{M}$ in the controls), and then remained fairly constant for the remainder of the experiment (Fig. 1c). Si concentrations in the replicated experiments were also quite variable. Despite the variability, the pattern of rapid initial Si release followed by constant concentration was reproduced in all three replicate experiments. Solutions were supersaturated with respect to kaolinite by approximately an order of magnitude ($\log Q/K \approx 1$; Table 1) in all three replicates once Si concentration reached its maximum value. The bacteria produced and excreted several hundred micromolar of gluconate, a dissolution-enhancing ligand (Vandevivere et al., 1994), from glucose in the first day of the experiment although no gluconate was detected after day seven (Fig. 2). Traces of other organic acids, such as acetate and formate, were detected as well, although these should have negligible impact on mineral dissolution (Welch and Ullman, 1993). There was no dissolved Al detected in the 5°C experiments. However, samples for Al analysis were stored for many weeks before analysis and the lack of Al detection may be an artifact of sample storage as Al can precipitate as secondary mineral phases.

The pattern of silica release at 20°C in the BG experiments was similar to that at 5°C , but with a lower final dissolved Si concentration ($40\text{--}50 \mu\text{M}$) and less variability (see Fig. 1c). Dissolved Al concentrations were low, $<3.0 \mu\text{M}$, and extremely variable with time and among the replicate experiments. Solutions were supersaturated with respect to both gibbsite and kaolinite. Several tens of micromolar of gluconate were detected after the first day of the experiment; no gluconate was detected after that time (Fig. 2).

Although Si release and final concentration in the BG treatment was enhanced substantially compared to the CON and BAC treatments at the two lower temperatures, there was no significant difference between the BG treatment and CON at the highest temperature, 35°C (see Fig. 1a, c). There were no organic acids and no dissolved Al detected and no significant change in pH at 35°C .

In both the CON and BAC treatments, average silica concentrations increased continuously over the 15 day experimental duration, and feldspar dissolution rate increased with increasing temperature. However, in the BG treatment, silica release followed a different pattern and the integrated release of dissolved Si actually decreased with increasing temperature. At the lower two temperatures in the BG treatment, Si concentration increases rapidly in the first two days of the experiment and then reaches an apparent steady state. To further investigate

Table 1. Representative mineral saturation indices (log Q/K) for the primary bytownite and possible secondary phases, gibbsite and kaolinite for dissolution experiments calculated using PHREEQC (Parkhurst, 1995; update to Version 1.6, 20 May 1998) and metal organic stability constants from Smith and Martell (1993).

Experiment	Log Q/K		
	Gibbsite	Kaolinite	Bytownite
Long (15-d) experiments			
CON 5°C final	^a	-1.16	-15.02
BAC 5°C final	^a	-1.29	-15.09
BG 5°C (day 5 to final)	^a	0.99-1.07	-11.43--11.39
CON 20°C final	^a	-0.76	-12.76
BAC 20°C final	^a	-1.18	-13.59
BG 20°C initial	-1.41	-2.53	-12.56
BG 20°C (day 5 to final)	1.44-2.2	3.10-4.72	-7.81--5.83
CON 35°C final	^a	0.39	-12.41
BAC 35°C final	^a	0.25	-12.65
BG 35°C final	^a	0.03	-12.58
Short (3-d) experiments			
CON 5°C final	^a	-1.08	-14.84
BAC 5°C final	^a	-1.09	-14.97
BG 5°C (hour 3 to final)	-2.53--0.35	-7.25-0.75	-22.79--12.2
CON 20°C final	^a	-0.93	-13.11
BAC 20°C final	^a	-0.96	-13.15
BG 20°C (day 3 to final)	-0.39-0	-2.47--0.36	-15.14--12.37
CON 35°C final	^a	-0.51	-11.08

^a No Al detected. Equilibrium with gibbsite assumed for the purpose of estimating Al concentrations.

the kinetic controls of mineral dissolution in the presence of bacteria, these experimental treatments were repeated, over a shorter time interval, to examine the initial feldspar dissolution behavior in more detail.

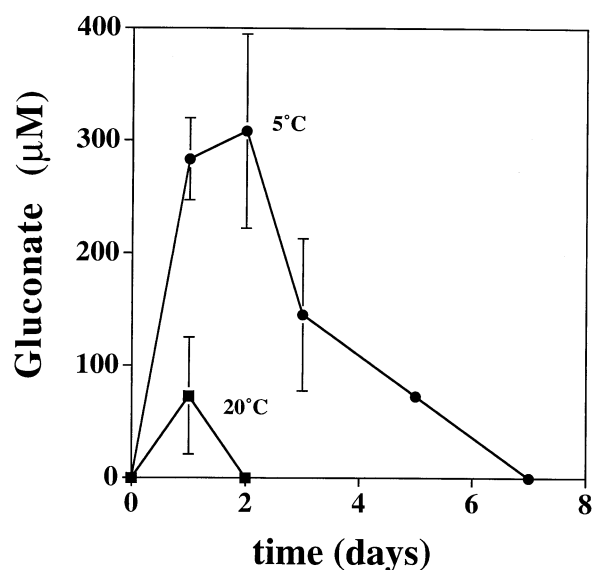


Fig. 2. Gluconate concentration in the long (15 day) bacteria plus glucose (BG) experiments at 5 (●) and 20°C (■). Gluconate was not detected in the 35°C experiment.

3.2. Short (3 Day) Experiments

Dissolved Si in the CON and BAC treatments in the 3 day experiments are very similar to the results of the longer experiments. Si-release rates and Si concentrations are higher in these experiments than in the longer experiments, reflecting the different aging history of the mineral samples used (Eggleston et al., 1989). In all of these experiments, Si concentration increased rapidly in the first few hours of the experiment followed by an approximately linear increase in dissolved Si with time for the next three days (Fig. 3a, b). Si concentration at the end of the experiment and the apparent rate of release approximately doubles with each 15°C increase in temperature. Dissolved Al is undetectable in the control experiments at all three temperatures. Solutions are undersaturated with respect to the dissolving mineral and possible Si-bearing secondary phases (Table 1). Net silica release rates from feldspar increased from 0.03 to 0.16 $\mu\text{mol}/\text{m}^2/\text{h}$ as temperatures increased from 5–35°C. There is no significant difference between the CON and BAC treatments at any of the three temperatures, no detectable Al or organic acids, and no significant change in solution pH.

The 3 day BG experiments replicate in more detail the results of the 15 day experiments (Fig. 3c). As in the 15 day experiment, the mean Si concentrations in the BG treatment at 35°C is not significantly different from that of the CON treatments (Fig. 4). As in the 15 day experiment, there was somewhat greater variability among the replicates in the BG treatments (see Fig. 3b) than in the CON or BAC treatments (see Fig. 3a, b).

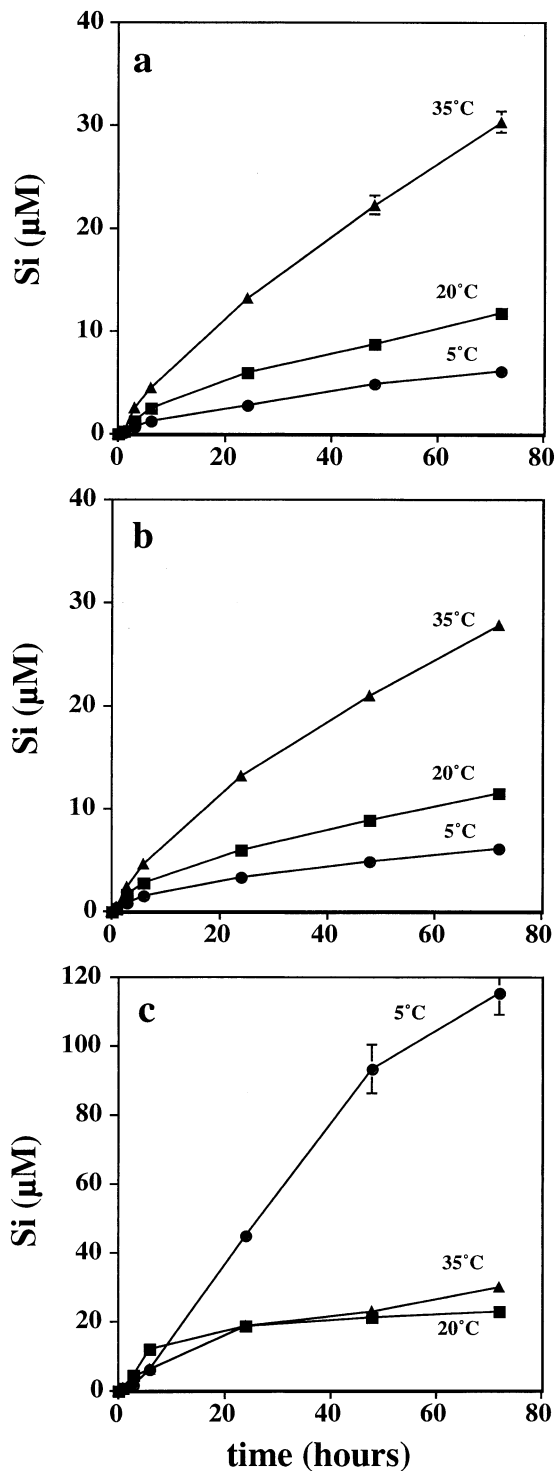


Fig. 3. Si concentrations vs. time in the short (3 day) experiments. (a) The CON treatments in $100 \mu\text{M KNO}_3$; (b) the BAC treatment with 108 cells/mL of BO665; and (c) the BG treatment with bacteria and 1 mM glucose at 5°C (●), 20°C (■), and 35°C (▲).

At 20°C , Si concentration in the BG treatment increased much more rapidly in the first 6 hr of the experiment than did the control (to $\approx 12 \mu\text{M}$ compared to the control $\approx 3 \mu\text{M}$;

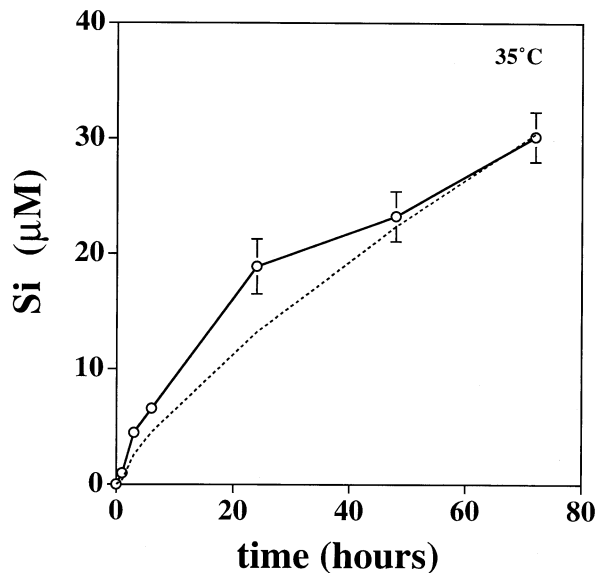


Fig. 4. The comparison of Si concentrations in the short (3 day) bacteria plus glucose (BG, ○) and control (CON, dashed line) experiments at 35°C . There is no significant difference between Si release rates of these experiments.

Fig. 5), followed by a much slower and approximately linear increase in Si concentration with time. There was also a corresponding rapid increase in both Al and gluconate concentration in this experiment. However, after 6 hr neither gluconate nor Al were detected in solution (Fig. 5). The mean concentration of Si at the end of the experiment is twice as high as in the control, although most of this enhancement is due to the

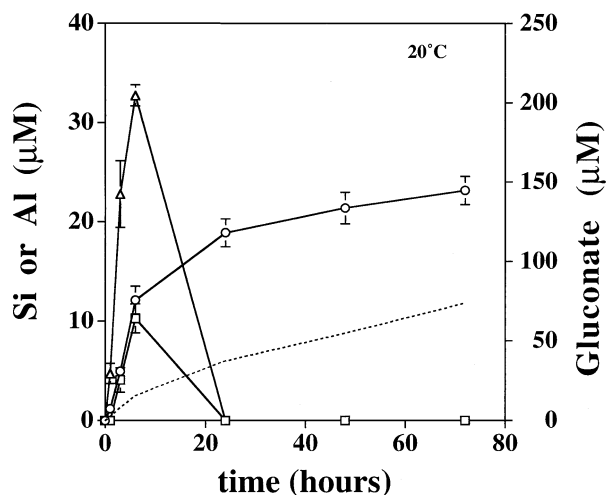


Fig. 5. The evolution of Si concentration (○), Al concentration (□), and gluconate concentration (Δ) in the short (3 day) bacteria plus glucose (BG) experiments with a comparison with Si concentration in the abiotic control (CON, dashed line) experiments at 20°C . The rapid increase in Si concentration in the BG experiment corresponds to the interval of gluconate production by the bacteria and Al release from the mineral surface. These results are indicative of a gluconate-promoted dissolution mechanism. After gluconate is depleted, the rate of Si release returns to that found in the control experiment.

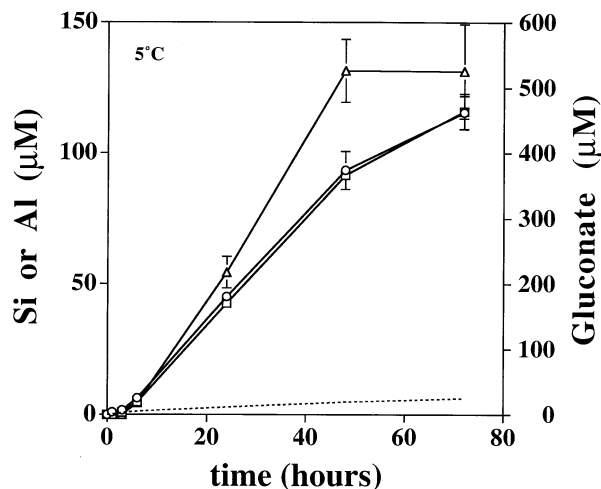


Fig. 6. The evolution of Si concentration (○), Al concentration (□), and gluconate concentration (△) in the short (3 day) bacteria plus glucose (BG) with a comparison with the Si concentration in the abiotic control (CON, dashed line) experiments at 5°C. In this experiment, unlike the 20°C experiment, the rate of Si and Al release appears to be independent of gluconate concentration. Also, there is an initial lag period before gluconic acid production begins during which Si release rate is similar to that of the controls.

initial Si release; after the first 24 hr the Si release was similar in the BG treatment to that of the CON treatment.

In contrast to the BG experiments at the higher temperatures, there is evidence that the initial (0–3 hr) rate of Si release at 5°C is slow and similar to the controls and then, after 3 hr,

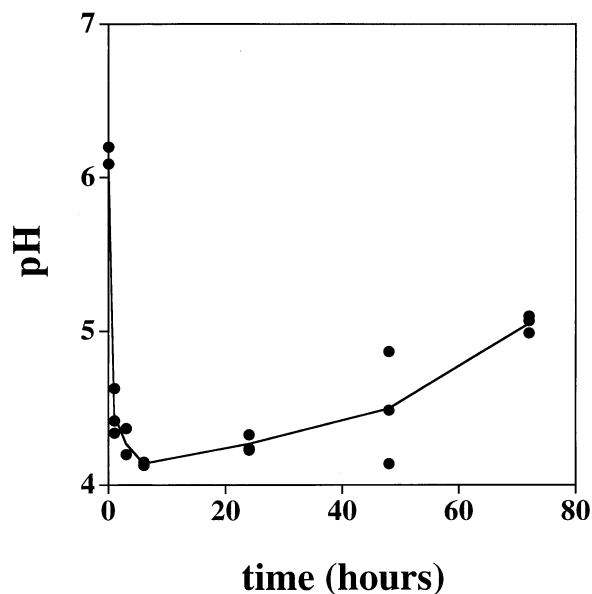


Fig. 7. The evolution of solution pH in the bacteria plus glucose (BG) experiment at 5°C. The initial high rate of acid production by reactions 2 and 3 and slow rate of acid consumption by reaction 4, lead to an initial depression of solution pH into a region (pH < 5) where proton-promoted dissolution predominates over the ligand-promoted mechanism.

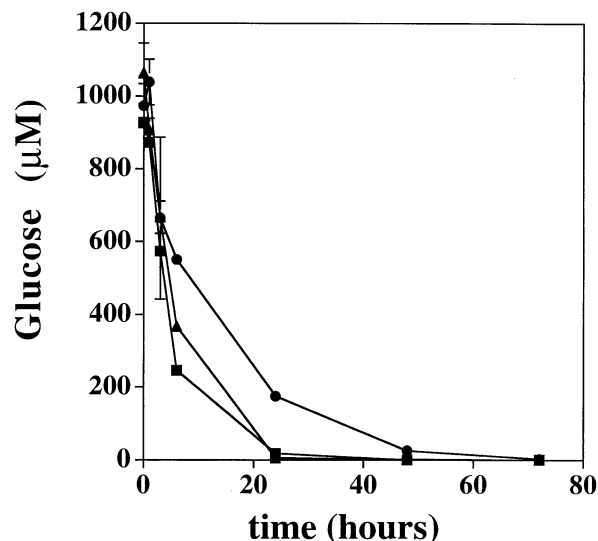


Fig. 8. Glucose concentrations vs. time in the short (3 day) bacteria plus glucose (BG) experiments at 5 (●), 20 (■), and 35°C (▲). Glucose consumption rate increases with increasing temperature.

increases rapidly with time (Fig. 6). During the period when Si concentration increased rapidly there was a corresponding increase in gluconate and Al concentrations and a decrease in solution pH to approximately 4–5 (Fig. 7). These results with an initial lag period, followed by a rapid increase in Si release corresponding to an increase in gluconate production, are very similar to the previous results of Vandevivere et al. (1994) with the same bacterial strain at 25°C.

The mean concentration of Si at the end of the experiment in the BG treatment at 5°C is ≈ 20 times greater than in the control. Mean glucose concentrations in the shorter time interval experiments decreased exponentially at all three temperatures (Fig. 8). Mean glucose concentration at 6 hr decreases with increasing temperature indicating that the rate of glucose uptake by the bacteria increases with temperature. The bacteria essentially metabolized all of the glucose within 24 hr, at 20°C and 35°C, and 48 hr, at 5°C.

As in the previous experiments with B0665 (Vandevivere et al., 1994), mineral surfaces were only sparsely colonized by the bacterial cells in both the BAC and BG experiments at all three temperatures; the bulk of the microbial population remained in suspension throughout these experiments.

4. DISCUSSION

Our experiments clearly indicate that there is a predictable pattern of silica release in the abiotic (CON) and metabolically inert biotic (BAC) experiments with Si-release rate increasing with temperature as previously found by a number of investigators (Brady and Carroll, 1994; Hellmann 1994; Lasaga et al., 1994; and references therein). However, the experiments with metabolically active bacteria (BG) show an unexpected result, with unexpectedly high rates of silica release at the lowest temperature (5°C) greatly exceeding the rates at 20° and 35°C. These observations suggest that the impact of bacteria on aluminum silicate weathering rates in nature may not be a

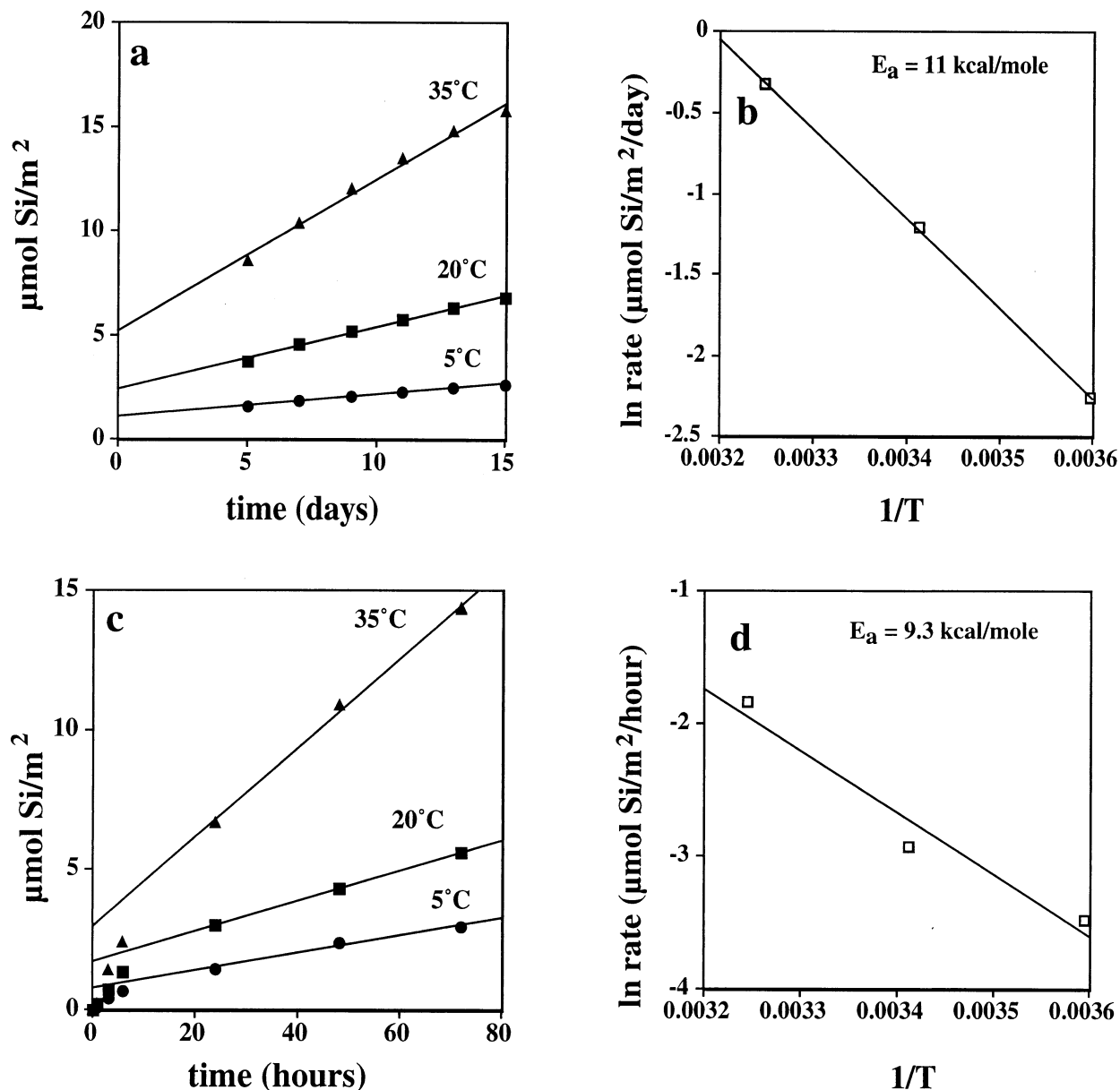


Fig. 9. Si release rates are calculated from Si concentration (Figs. 1 and 3) in the control (CON) experiments after correction for the volume of solution removed from each reactor and after normalization to the initial surface area of the mineral reactants. (a) Si release vs. time at 5 (●), 20 (■), and 35°C (▲) and (b) Arrhenius plot of Si release rate (based on a linear fit to the data from days 5–15) in the long (15-d) abiotic control experiments. (c) Si release vs. time at 5 (●), 20 (■), and 35°C (▲) and (d) Arrhenius plot of Si release rate for the short (3-d) abiotic control experiments. Si release rate was calculated from a linear fit of the data from hours 24–72.

simple monotonic function of temperature, and that microbially mediated mineral weathering at low temperature might be more important than previously thought.

4.1. Abiotic Feldspar Dissolution

In these experiments, the net Si release from feldspar increased, as expected, with increasing temperature in the abiotic controls (CON) and in the metabolically inactive biotic experiments (BAC). Net Si-release rates in the long experiments

ranged from ≈ 0.1 – $0.6 \mu\text{mol Si/m}^2/\text{d}$ or 1.2 – $7 \times 10^{-12} \text{ mol Si/m}^2/\text{s}$, as temperatures increased from 5° to 35°C. Net Si-release rates in the short experiments were somewhat higher, ≈ 0.9 – $5 \times 10^{-11} \text{ mol Si/m}^2/\text{s}$. Experimentally determined feldspar dissolution rates at near neutral pH reported in the literature typically range from $\approx 10^{-12}$ to $10^{-11} \text{ mol Si/m}^2/\text{s}$, although rates vary somewhat depending on mineral composition and experimental conditions (Stillings et al., 1996; Welch and Ullman, 1996; and references therein).

The temperature dependence of geochemical reactions may often be described using the Arrhenius relationship:

$$k = Ae^{-\left(\frac{E_a}{RT}\right)} \quad (1)$$

where k is the reaction rate constant, A is a preexponential factor, E_a is the apparent activation energy, R is the gas constant, and T is absolute temperature. In the CON treatments (both short and long) it was assumed (based on the low concentrations of Si found and the linearity of Si release with time after the first few days or hours) that the rate of Si release is directly proportional to the rate constant. The application of the Arrhenius relationship to these results yields an E_a of ≈ 9 – 11 kcal/mol (Fig. 9). All of these values of the apparent activation energy of Si release are consistent with other estimates of the temperature dependence of feldspar dissolution under similar experimental conditions (Knauss and Wolery, 1986; Brady and Carroll, 1994).

In principal, the Arrhenius relationship should be used only to describe the temperature dependence of single elementary reactions and feldspar dissolution certainly results from a series of elementary processes, each with its own temperature dependence. However, the good fit of the Arrhenius equation to the results of these and previous experiments is consistent with a single rate-determining step in the dissolution process, although it is not clear which step this is (Welch and Ullman, 1999). The activation energies determined here are the apparent activation energies of silica release only, one step, an important step, in the feldspar dissolution process. The activation energies reported here are not necessarily the apparent activation energies for overall feldspar dissolution, as stoichiometric dissolution was not achieved in these experiments.

4.2. Biotic Feldspar Dissolution

It is not surprising that there was no significant effect on mineral dissolution rates or on the temperature dependence of dissolution in the experiments (BAC) with metabolically inert bacteria. These bacteria were not producing any metabolites (except possibly a small amount of CO_2 from stored carbon reserves) that may affect dissolution rates. Some of these bacteria may be dying during the experiments. Our results, however, are somewhat at odds with field studies that have demonstrated microbial enhancement of mineral dissolution under even relatively oligotrophic conditions (Thorseth et al., 1992; 1995). The discrepancy between the laboratory and field-based observations can be attributed to the limited extent of microbial attachment to mineral surfaces, the limited contact time between microbes and minerals, or to the accelerated mineral dissolution rates found under laboratory conditions.

In soils and aquifers, most bacteria are attached to surfaces (Hazen et al., 1991; Holm et al., 1992); therefore, any dissolution enhancing metabolites (protons, ligands, oxidants, reductants) that are produced are most concentrated at or near the mineral surface where dissolution occurs. In our laboratory experiments, the bacteria are primarily in suspension ("planktonic") and any metabolites produced by the bacteria are diluted by the bulk solution. Under field conditions, the length of contact time between the mineral, microbe, and solution is also

much greater than we can maintain in the laboratory with live bacterial cultures.

In natural environments, surface reactivity, as measured by overall mineral dissolution rates, is at least one to three orders of magnitude lower than in those determined in the laboratory (Velbel, 1986; Swoboda-Colberg and Drever, 1992). These differences have been attributed to differences in solution saturation state, temperature, fluid flow and contact time with mineral surfaces, and differences in reactivity between freshly prepared laboratory mineral surfaces and natural weathered surfaces. Because of the enhanced reactivity of minerals in laboratory experiments, microbially mediated dissolution rates must also be significantly enhanced above the natural rates to be observed. To determine the possible effect of microbial metabolism on mineral dissolution, either the intrinsic reactivity of experimental minerals needs to be decreased to the natural level or the rates of microbial metabolism need to be significantly enhanced by increasing cell numbers or adding additional nutrients or organic carbon. Our BG experiments are of the latter type.

It is not solely the presence of bacteria that is necessary for mineral dissolution enhancement, as bacteria that are not metabolizing carbon in the BAC treatment had no apparent effect. Previous laboratory experiments with killed bacteria also had no detectable effect on mineral dissolution (Vandevivere et al., 1994) although extracellular microbial polymers may cause a small, but significant, enhancement of dissolution rates even in inert cultures, as microbial cell surfaces and extracellular polymers contain sites that can complex with metal ions released from minerals cultures (Welch and Vandevivere, 1995; Barker and Banfield, 1996). For a significant enhancement of dissolution to occur and to be observed under laboratory conditions, the microorganisms need a carbon source, need to be viable, and need to be metabolically active.

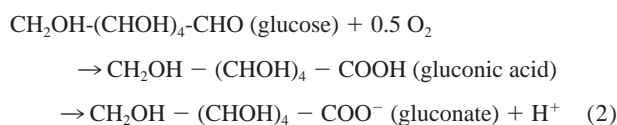
In the BG treatments with live and metabolically active bacteria, Si release from feldspar was significantly enhanced at the lower temperatures (5° and 20°C) by the production and excretion of gluconic acid. In the longer duration experiments in the presence of gluconic acid (Figs. 1 and 2), there was an acceleration in dissolution rate compared to the controls, as has been observed in previous experiments (Vandevivere et al., 1994). However, after gluconate was depleted there was no further increase in dissolved Si concentration, indicating that solution had reached steady state, possibly due to saturation with respect to some secondary phase or phases. If Si release was controlled solely by the abiotic dissolution of the primary mineral and the precipitation and solubility of secondary phases (such as kaolinite and gibbsite), the final Si concentration in the experiments should have increased with increasing temperature, as the solubilities of these secondary minerals increase with increasing temperature over this range (Welch and Ullman, 1999). The opposite trend was observed here, indicating that the bacteria and their extracellular polymers may be affecting the kinetics of the dissolution/precipitation reactions or the apparent solubility of these minerals by forming complexes with both Al and Si on the cell surfaces or serving as nucleation sites for possible secondary phases (Ferris et al., 1988; 1989; Konhauser et al., 1994; Barker and Banfield, 1996; 1998; Daughney et al., 1998; Fein et al., 1998; Welch et al., 1999).

The shorter duration experiments at the lower temperature

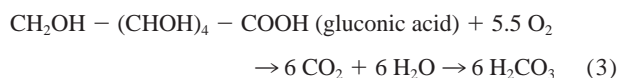
yielded similar results to the longer experiments; the rapid increase in both Si and Al concentrations corresponded to the production of gluconate from glucose (Figs. 5 and 6). However, Si release from the feldspar in these shorter experiments did not follow the identical trends observed in the first 3 days of the longer duration experiments. In the 20°C BG experiment, there was a rapid initial increase in Si and Al concentration corresponding to the interval of gluconate production. After gluconate was depleted, however, Si concentration continues to increase, but at a much slower rate, similar to the rate observed in the abiotic CON treatment. Al concentration was very low or undetectable in the absence of gluconate, indicating that the Al that was complexed by gluconate early in the experiment was either reprecipitated as the bacteria metabolized the gluconate or was metabolized by the bacteria together with the gluconate. In the 5°C BG experiment, both Si and Al increased for the duration of the experiment due to the presence of gluconate and the decrease in solution pH. The mean Si concentration at the end of the short experiment, 120 μM , is higher than the steady-state concentration in the longer duration experiments at this temperature, 50–80 μM . The results from the shorter experiments indicate that microbial production of gluconic acid catalyzed the dissolution reaction by increasing the rate of Al release from the mineral surface, thereby increasing Si release rate, but that the catalytic mechanism may not be identical at both temperatures where significant enhancement was observed.

4.3. Mechanism of Biotic Dissolution Enhancement

The results of these experiments may be interpreted as the result of two sequential acid-producing metabolic reactions and an acid-consuming feldspar dissolution reaction, each with the expected temperature dependence described by a positive E_a . The first metabolic step involves the partial oxidation of glucose to gluconate by the experimental bacteria:

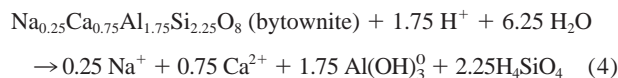


This is a common metabolic reaction in some bacteria, although under most conditions, the oxidation continues beyond the glucose intermediate (Gottschalk, 1986). Under stress conditions, gluconic acid accumulates in cultures of a wider range of bacteria. It is clear, based on the rates of glucose depletion (Fig. 8), that the rates of this reaction are lower at 5°C than at the higher temperatures, although the confounding effects of glucose exhaustion make it difficult to determine the relative rates at 20° and 35°C. This reaction proceeds until the glucose is largely exhausted, at which point the gluconate is further respired, in a number of metabolic steps, to CO_2 :



Some of the CO_2 produced by this reaction is lost to the atmosphere and therefore, a complete stoichiometric balance based on protons is not possible. The experimental evidence, however, indicates that these reactions proceed in sequence with the reactions having positive but different apparent acti-

vation energies. Equations 2 and 3 produce protons and Eqn. 2 produces gluconate. Both gluconate and protons catalyze the acid-consuming bytownite dissolution reaction:



The CON experiments, among others, demonstrate that this reaction also has normal temperature dependence with a positive E_a .

There is evidence that both protons and gluconate can catalyze the feldspar dissolution process (Eqn. 4). Proton-promoted dissolution of silicates and aluminum silicates has been demonstrated by a number of researchers under a wide range of experimental conditions (Welch and Ullman, 1996 and references therein). At constant pH, Vandevivere et al. (1994) found bytownite dissolution rate to be linearly related to gluconate concentration. Similar linear dependence on ligand concentration has been reported by other investigators as well (Welch and Ullman, 1992; Stillings et al., 1996; and references therein). The evidence, however, also suggests that the relative importance of the two catalytic mechanisms is dependent on the relative concentrations of the catalysts, with proton-promoted dissolution predominating at acid pH and gluconate-promoted (or generally ligand-promoted) dissolution predominating at neutral pH when the effect of protons is minimal (Ullman and Welch, 1998). Thus, the overall rate of metabolically enhanced dissolution will be dependent on the relative concentrations of the catalysts and on the relative rates of the three temperature-dependent reactions describing metabolic acid and gluconate production (Eqns. 2 and 3) and of the acid-consuming dissolution reaction (Eqn. 4).

At 5°C, the first metabolic reaction (Eqn. 2) is relatively more rapid than the second (Eqn. 3) leading to the accumulation of gluconic acid in solution. As the rate of the abiotic dissolution reaction (Eqn. 4) is very slow at this temperature, the pH of the solution is depressed by the microbial metabolism and the dissolution proceeds predominantly by the proton-promoted catalytic mechanism. This is seen by the lack of dependence of the rate of silica (and aluminum) release on the concentration of gluconate at this temperature (Fig. 6) as has been previously observed for gluconate-promoted dissolution (Vandevivere et al., 1994). As glucose becomes exhausted, gluconic acid concentrations are reduced (Eqn. 3 and Fig. 2) and protons are consumed by reaction (Eqn. 4) or lost as a consequence of CO_2 degassing from the culture (Fig. 7). At 20°C, the rates of all reactions are more rapid than at 5°C leading to a lower accumulation of gluconic acid and a kinetic buffering of pH. During the period when gluconate is present, Si release rates from Eqn. 4 are higher than the controls due to the gluconate-promoted dissolution mechanism until the gluconate is metabolized by Eqn. 3. At this point the rate of Si release returns to that of the controls (CON and BAC; Figs. 3 and 5). At 35°C, the rate of Eqn. 3 is sufficiently rapid to prevent the accumulation of gluconic acid in solution and the rate of Eqn. 4 is sufficiently rapid to maintain solution pH within the range in which feldspar dissolution rates are independent of pH. In this experiment, the rates of Si release are, as a result, indistinguishable from those of the controls (Figs. 3 and 6).

The results of the BG treatments show an increase in Si concentration in solution and therefore, an apparent increase in

feldspar dissolution rate, with decreasing temperature. In contrast to our hypothesis, the apparent activation energy for microbially mediated feldspar dissolution has an unexpected negative value. This result is due to the change in actual and relative rates of the three sequential reactions each with normal positive Arrhenius behavior. It appears, from these experiments, that ligand-promoted enhancement of feldspar dissolution predominates at 20°C, proton-promoted dissolution predominates at 5°C, and that neither mechanism is important at the higher metabolic and dissolution rates observed at 35°C.

Although these results are contrary to our initial hypothesis, they are consistent with other studies on the temperature dependence of microbial processes and on microbially mediated silicate mineral weathering. These results could have important implications for biologically mediated seasonal weathering cycles and for weathering at low temperatures.

4.4. Implications for Natural Weathering

Several studies have demonstrated that naturally occurring soil and groundwater microbes increase CO₂ production as temperatures increase (Kondo et al., 1993; Alvarez et al., 1995; MacDonald et al., 1995; Pöhhacker and Zech, 1995). However, there is little information on microbial production of organic acids in natural sediments at different temperatures. Kondo et al. (1993) measured the production of low molecular weight fatty acids, formate, acetate, lactate, propionate, and butyrate, from glucose in anoxic sediments. In their study, organic acids were produced primarily by fermentation, not by metabolic overproduction as in our experiments (Tempest and Neijssel, 1992). The production rate of organic acids in the Kondo et al. (1993) experiment increased with increasing temperature from 10–30°C. However, the consumption of these compounds also increased with increasing temperature. As in our experiments, organic acids accumulated in solution and, in general, bulk solution concentrations were higher and organic acids persisted for longer times at lower rather than at the highest temperature. Similar results were obtained from a study of soil organic carbon and CO₂ production (Kirschbaum, 1995). Soil organic carbon content decreased, and CO₂ production increased with increasing temperature, which implies a lower residence time for intermediate organic products at higher temperatures. Consistent with our observations, these results suggest that organic acids could potentially have a larger effect on natural mineral dissolution rates at the lower temperatures or colder climates than at the higher temperatures or warmer climates. This expectation would be due to an increased concentration of dissolution-enhancing compounds in soils and sediments, a longer residence time for these compounds to react with surfaces, and increased surface complexation at the lower temperatures.

Biologically mediated silicate weathering varies as a function of temperature, and there is substantial field evidence that biologically mediated weathering is important at low temperatures. Brady (1997) examined lichen-mediated and abiotically weathered Hawaiian basalts as a function of temperature (elevation) and rainfall. Lichens greatly accelerated (by a factor of 2–20 times) feldspar and olivine weathering compared to uncolonized surfaces, although there was a relatively larger effect at low temperatures, leading to a decrease in the apparent

activation energy for biologically (≈ 11 – 13 kcal/mol) vs. abiotic (≈ 21 – 23 kcal/mol) silicate mineral weathering.

In situ microcosm studies by Hiebert and Bennett (1992) and Bennett et al., (1996) in an aquifer contaminated by an oil spill have also demonstrated enhanced mineral dissolution due to bacteria at low temperatures ($< 10^\circ\text{C}$). Rates of mineral dissolution up-gradient of the oil pool are very low. However, under the oil pool, concentrations of dissolved mineral constituents increase significantly. Minerals suspended in wells in this zone show dissolution features associated with bacteria on the mineral surfaces, even when the bulk solutions were apparently supersaturated with respect to the dissolving phases. These researchers hypothesized that the very rapid rates of mineral dissolution under the oil spill were due to microbial production of organic acids in microreaction zones on the mineral surface. Our experiments are consistent with their hypothesis; the reaction conditions and results of this field experiment are comparable to the 5°C bacteria + glucose experiment where nearly all of the observed mineral dissolution was due to microbial production of organic acids.

Perhaps one of the most striking examples of the importance of biologically mediated weathering at low temperature is found in Antarctica (Weed and Norton, 1991; Johnston and Vestal, 1993). In this extremely cold environment, endolithic microorganisms (bacteria, cyanobacteria, alga, and fungi) produce oxalate, which rapidly mobilized Si, Al, and Fe, rapidly producing secondary siliceous crusts and iron staining. In these environments, the rates of biological processes are comparable to the abiotic rates.

These observations are generally consistent with soil profiles in different climatic regimes (Schlesinger, 1997). In temperate climates, soils tend to be more organic rich and enriched in Si compared to Fe and Al. The relatively high organic content is due to slow rates of microbial decomposition of organic material, and this high organic content increases the mobility of Fe and Al. In tropical environments, soils tend to be thinner, organic poor, and generally enriched in Al and Fe compared to Si. Large-scale watershed studies demonstrate that overall weathering rates increase with increasing temperature with an apparent activation energy of ≈ 15 kcal/mol (White and Blum, 1995). In general, the fastest mineral weathering rates occur in the tropics, areas of high temperature and rainfall, despite of the low organic content of the soils. However, in these types of watershed studies, it is difficult to decouple biological vs. inorganic or abiotic effects. Although it is clear that rates of both inorganic and biologically mediated mineral weathering increase with temperature, it may be that these processes have a different response to changing temperature. The E_a of 15 kcal/mol reflects the sum of both inorganic and biological effects. The results of our laboratory experiments (which represent an extreme case) together with field observations by other investigators suggests that the impact of bacteria on weathering rates is greater at lower temperature as a result of the longer residence time of dissolution-enhancing metabolic products. Although stepwise reaction rates are slower at these temperatures, the net impact of microbial metabolism is enhanced by these compounds due to temperature-dependent changes in relative rates.

5. CONCLUSIONS

In abiotic experiments, mineral dissolution rates increased with increasing temperature. Rates approximately doubled with each 15°C increase in temperature, which corresponds to an apparent activation energy of 9–11 kcal/mol for Si release from feldspar. In spite of the abundant field evidence for microbial enhancement of mineral dissolution in oligotrophic environments, metabolically inert bacteria alone had no apparent enhancement effect on mineral dissolution in the laboratory. Microbial enhancement of dissolution rate could not be detected over the accelerated abiotic mineral dissolution rates found in the laboratory. When glucose was added to the cultures, however, bacteria enhanced dissolution rates by producing gluconic acid, which catalyzed the dissolution reaction by both a proton- and gluconate-promoted mechanism. Organic acid production and, therefore, the microbial enhancement of mineral dissolution, increased with decreasing temperatures. For this particular organism under these laboratory conditions there is a positive feedback between the microbial enhancement of weathering and temperature. However, this is attributable in part to a relative increase in the rate of gluconate consumption at higher temperatures.

Acknowledgments—Much of our work was motivated and inspired by the research of Professor Werner Stumm, his students and colleagues who developed an appreciation for the complex interactions between natural surfaces and solutes and the impact of these interactions on the rates of mineral–water exchange. At an early stage of this work we received personal encouragement from Professor Stumm for which we have been and continue to be grateful. This paper benefited from critical reviews by P. V. Brady and two anonymous reviewers. This research on microbially mediated aspects of mineral water exchange is supported by a grant to WJU from the U.S. Department of Energy Subsurface Science Program (Dr. F. Wobber, Program Director).

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