

MOBILITY OF MAJOR AND TRACE ELEMENTS DURING BIOLOGICALLY MEDIATED WEATHERING OF GRANITE

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INTRODUCTION

Microorganisms can dramatically modify the rates and products of mineral dissolution reactions by controlling mineral solubility and surface reactivity (e.g., dissolution rates). This has great environmental importance because it leads to new patterns of mineral distribution and redistribution of elements in the environment. Because elemental uptake, redox reactions, and microbial products (primarily organic ligands) can exert significant control on mineral weathering rates, organisms can affect the larger-scale geochemical cycles of both major (Si, Al, Fe, Ca, K, Na) and trace (Ge, Ga, P, REE, etc.) elements in minerals

It is well known that biologically mediated reactions can affect both the rate and stoichiometry of mineral weathering compared to predominately inorganic/abiotic processes. Microbes affect mineral dissolution-weathering as a reaction as a by-product of their metabolism (see reviews by Barker *et al.* 1997). However, it is often not clear if mineral alteration is simply a consequence of microbial metabolic processes, or if microbes are able to actively attack minerals for trace nutrients such as P and Fe (Taunton *et al.* 1998, 1999, 2000a, b, Rogers *et al.* 1998). Organisms can have a direct chemical effect on mineral weathering-dissolution rates and mechanisms by changing solution pH, especially in microenvironments where they are attached, by producing organic ligands which complex with ions released from minerals or on the mineral surface, or by changing redox conditions. All organisms produce organic ligands that can affect silicate mineral weathering reactions both due to their acidity and to their complexing ability (Figures 1-5). Low molecular weight organic acids, in particular oxalic, are most often cited as the main component in biogeochemical weathering of silicate minerals. Microbes produce and excrete low molecular weight organic acids such as fermentation products (e.g., lactate, formate) and Krebs cycle compounds (citrate, succinate, α -ketoglutarate, oxalacetate, pyruvate) that can have profound effects on mineral weathering reactions. These compounds have been detected in soils and natural waters. In addition to these direct chemical effects, organisms can have indirect effects on mineral weathering reactions as well, such as by taking up ions released from minerals, retaining water at the mineral surface.

Previous experimental work has demonstrated that complexing organic compounds can significantly increase Al release to solution from aluminosilicate minerals (see below) compared to inorganic conditions. The purpose of this work is to determine if microorganisms or microbial processes can similarly fractionate Ge from Si, or Ga from Al, during weathering/dissolution reactions. It is expected that for inorganic abiotic conditions, in the early stages of the weathering (essentially dissolution) reaction, the geochemical behaviour of Ge will be similar to Si, and Ga will be similar Al. However, for biologically or organically mediated reactions in the presence of complexing organic ligands, it is expected that Ge will be preferentially leached from the solid phase compared to Si due to the formation of Ge-organic complexes. Similarly, Al will be preferentially removed compared to Ga and Si due to the formation of Al-organic complexes, leading to significant redistribution of elements in both the primary and secondary mineral phases and in solution.

PREVIOUS EXPERIMENTAL RESULTS

Experimental studies with feldspars and common low molecular weight organic acids showed that these compounds increased mineral dissolution rates (based on Si release) by factors of between 2 and 10 (Welch & Ullman 1993, 1996, Ullman *et al.* 1996 [Figure 1]). Organic acids catalyzed the reaction by forming complexes with Al, either at the mineral surface (which weakens metal-oxygen bonds), or in solution (which lowers solution saturation state). Difunctional organic ligands—those that form bidentate complexes with Al—had a much larger effect than monofunctional ligands such as acetate or formate. Several laboratory studies have demonstrated a positive correlation between microbial production of low molecular

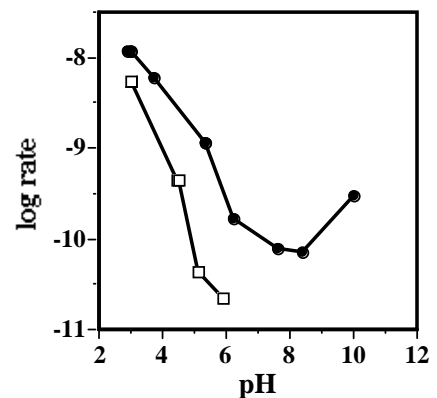


Figure 1: Feldspar dissolution rate mol Si/cm²s versus pH in 1 mM oxalate (λ) and in inorganic solutions (θ). Data from Welch & Ullman (1993).

weight organic acids and mineral dissolution rate (e.g., Vandevivere *et al.* 1994, Welch & Ullman 1999, Barker *et al.* 1998). Vandevivere *et al.* (1994) measured a 200-fold increase in Si release rate from a Ca-rich plagioclase in an organic acid producing bacterial culture compared to an abiotic control.

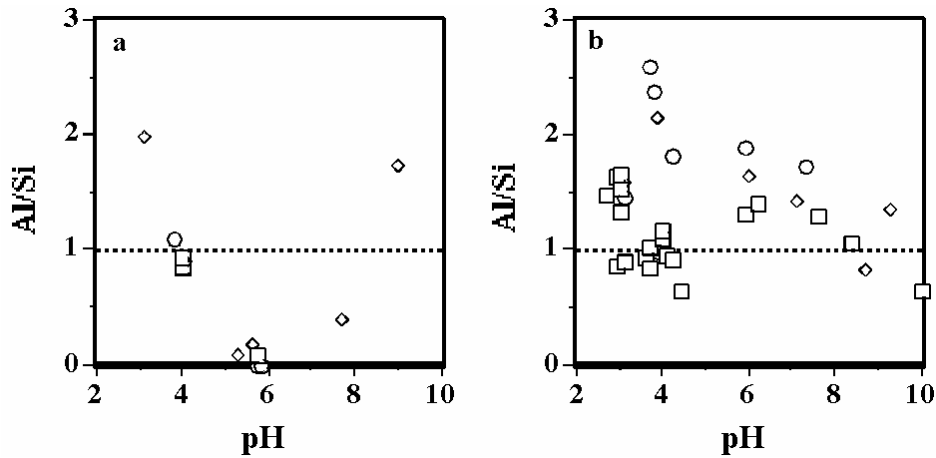


Figure 2: Stoichiometry of Al/Si release (normalized to Al/Si in the mineral) from plagioclase feldspars (bytownite θ , and two labradorite feldspars $\mu\Gamma$) dissolved in (a) inorganic and (b) 1 mM organic acids solutions over a range of pH. Data from Welch & Ullman (1993).

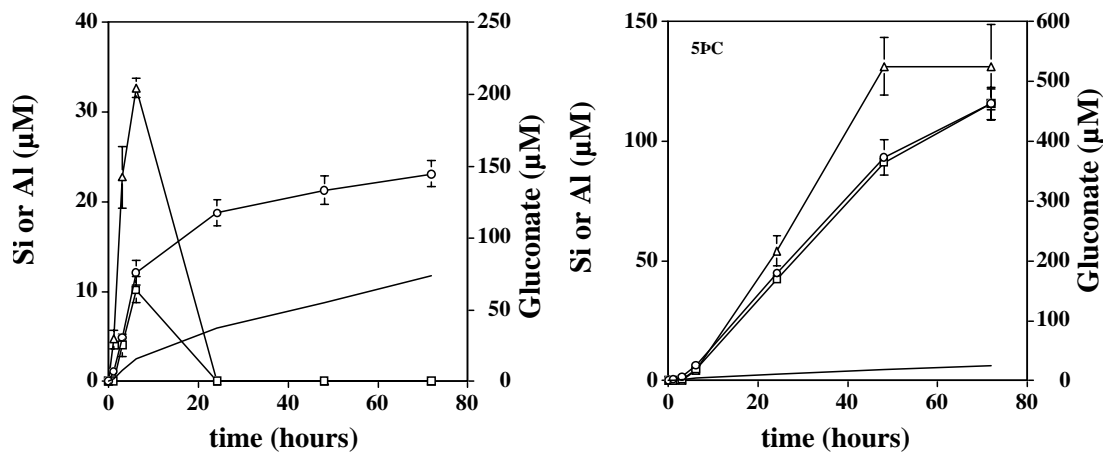


Figure 3: Si(θ), Al(μ) and gluconate (Δ) concentration in batch mineral dissolution experiments at 20°C and 5°C. The dashed line is Si concentration in the abiotic controls. Al release to solution is correlated with organic acid production, which correlates with increase in Si release to solution. Data from Welch & Ullman (1999).

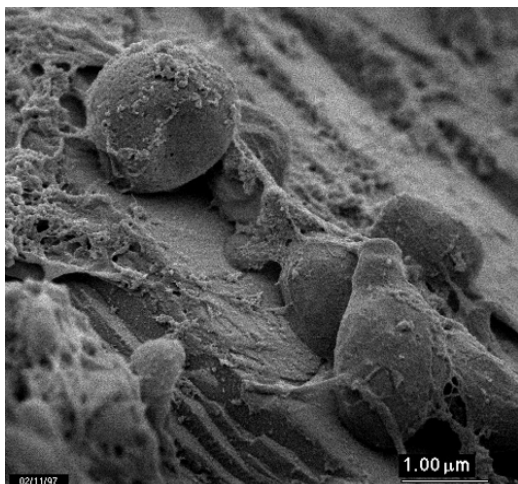


Figure 4: Extra-cellular polymer producing bacteria attached to an etched mineral surface. The microbial slime covers a much larger area of the mineral surface than the cells themselves.

In addition to producing low molecular weight organic acids, microorganisms can also produce extracellular polymers (predominantly acid-polysaccharides). These can affect mineral weathering reactions directly by forming complexes with metal ions (either at the mineral surface or metals released to solution), serving as a template for the formation of secondary mineral phases, or indirectly by keeping the mineral surface hydrated. Experimental studies have shown that under mildly acid conditions, acid-polysaccharide gels can increase mineral dissolution by a factor of 100 compared to the inorganic controls at the same pH (Welch *et al.* 1999)

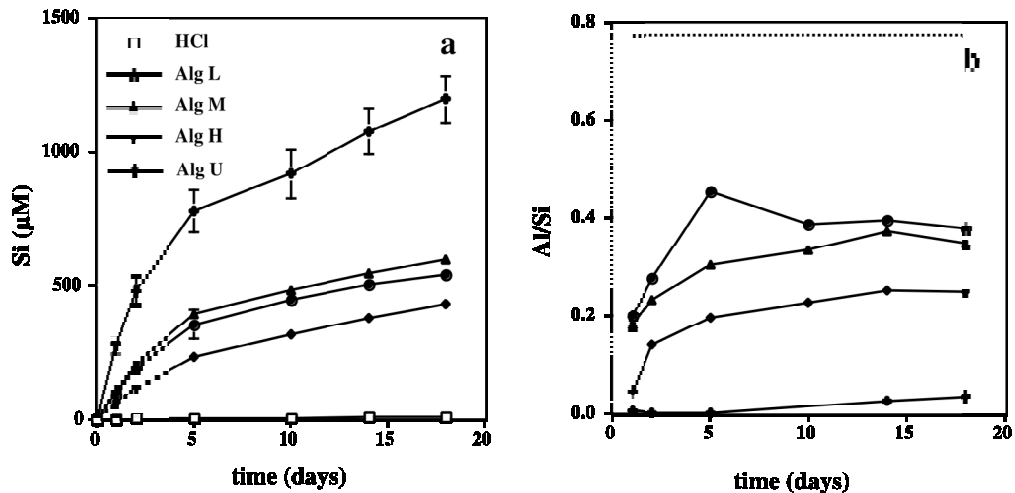


Figure 5: Batch feldspar dissolution experiment in alginate polymers and an inorganic control at $\text{pH} \cong 4$. Si and Al release to solution is ca. 100 times greater in the acid polysaccharides compared to the inorganic control. Data from Welch *et al.* (1999).

FIELD STUDIES

Samples have been collected from a series of granite weathering profiles on the Bemboka Granite, New South Wales. Rock samples will be analysed for bulk rock geochemistry, microbial populations and organic content. Fine scale variability in chemical composition will be measured using laser ablation ICP-MS (LA-ICP-MS). Previous work on this site has shown a significant difference between rock weathering in the biologically impacted versus inorganic weathering zones (Welch *et al.* 1998, 1999b, Taunton *et al.* 1998, Taunton *et al.* 2000a, b, Green & Banfield 2003). In the upper part of the profile (the biologically impacted zone) K, Mg, Mn and Ti are lost much faster than the average rate estimated for the weathering profiles due to the biologically induced weathering of biotite. Compared to samples collected lower in the weathering profile, samples collected in the soil show evidence of increased mobility of Al and Fe.

Current research at this site focuses on determining small scale variability of trace elements with respect to major elements from naturally weathered granite. Preliminary analyses of mineral grains by LA-ICP-MS shows that Ge and Ga concentrations seem to be relatively constant along transects taken across any given mineral grain, although relative abundance depends on chemical composition and mineralogy. For example, Ge and Ga concentrations are lower in quartz and higher in feldspar and biotite. Both Ge and Ga are significantly elevated in Al- and Fe-rich secondary mineral phases. Although Ga concentration is elevated in these secondary mineral phases, the Ga to Al ratio is lower in these secondary mineral phases compared to adjacent minerals, indicating that Ga is preferentially mobilized compared to Al (Figure 6).

In addition to Ge and Ga, most of the other trace elements analysed are significantly enriched in the secondary Al-Fe sesquioxide that forms as a result of weathering. The REE are enriched by a factor of ca. 10 to 1000 (in the case of Ce) in Fe-Al rich secondary phases compared to the primary phase. Other trace elements (P, V, Sc, Ti, Rb, Cs, Pb, U) are enriched by a factor of ca. 2 to 100 compared to adjacent mineral phases. The one notable exception is Ba, which is depleted in the Fe-Al rich secondary mineral phases compared to the primary phases.

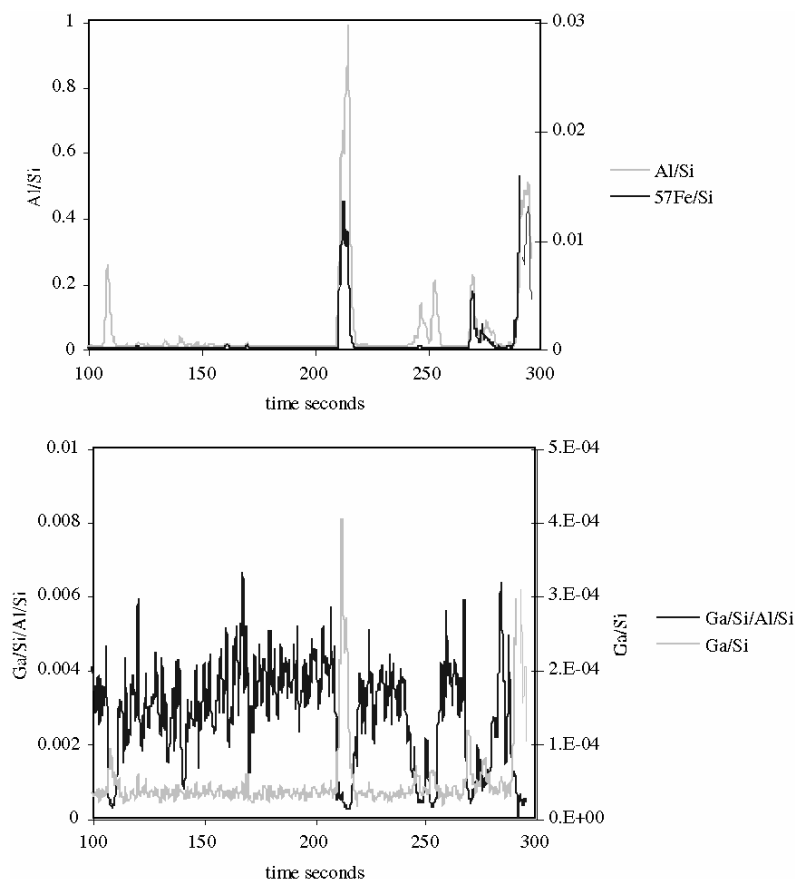


Figure 6: a) Al/Si and Fe/Si, and b) Ga/Si and Ga/Si/Al/Si (essentially Ga/Al) ratios (based on counts/sec) from a transect across a quartz grain. The peaks in Ga/Si signal correspond to peaks in peaks Al/Si and Fe/Si.

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