## Microbial destruction of feldspars

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It now seems clear that feldspar weathering dynamics in natural systems is not well modelled by the typical inorganic and abiotic laboratory experiment. In particular, the role of micro-organisms in feldspar weathering has only recently been directly examined or documented. Mounting evidence, however suggests that bacteria attached to feldspar surfaces can greatly accelerate the rate of feldspar dissolution, but two important questions remain – why, and how. Here we report the results of field experiments combined with parallel laboratory experiments that help constrain the question of how, and suggests a hypothesis for why; microorganisms may destroy feldspars to gain access to trace or limiting nutrients, primarily by the production of organic ligands.

## Methods

For this study we used parallel field- and laboratorybased methods. Field microcosms of selected mineral chips were placed in different areas of a microbiologically active petroleum-contaminated aquifer for periods up to 12 months (e.g. Hiebert and Bennett 1992). In the aquifer the mineral chips were exposed to the native microbial population, and after recovery the pattern of colonization and the extent of reaction of the surface was characterized using SEM and related techniques. At the time of microcosm placement and recovery, the ground water chemistry and microbiology were characterized and compared to over 15 years of record established for this site (e.g. Bennett *et al.* 1993).

Using the same mineral specimens, we also examined some of the fundamental controls on feldspar dissolution kinetics within the context of a limited experimental question – how can a microorganism accelerate the dissolution rate of a feldspar orders of magnitude over the rate of an uncolonized surface? Specimens of Bancroft albite and a microcline were ground to a uniform size fraction, cleaned, and dissolved in an all-Teflon mixed flow reactor system. Dissolution rate was examined as a function of pH, ionic strength, and the concentration of 3 target organic compounds: citrate, dihydroxy benzoate, and tropolone. These organic acids were chosen as representative of the class of compounds known as siderophores, microbiallyproduced iron chelating ligands. The effect of these variables was monitored by measuring the change in absolute dissolution rate and *apparent* activation energy (the observed relationship between dissolution rate and temperature not corrected for the enthalpy of proton adsorption, e.g. Casey and Sposito, 1992).

## Field observations and experimental findings

In the most organic-rich area of this aquifer, the ground water is extremely reducing, with iron reduction and methanogenesis the primary microbial processes (e.g. Bennett *et al.* 1993). Dissolved ferrous iron increases along the principle flow path due to dissimilatory iron reduction, while pH decreases from ~7.8 to ~6.5. Dissolved silica increases from 0.3 mmole  $l^{-1}$  to > 1 mmole  $l^{-1}$  due to the greatly accelerated dissolution of quartz and feldspars (Bennett *et al.* 1993).

The field microcosms experiments show there is significant variability in colonization pattern colonization density, and etch-pit depth on different silicates allowed to react for periods up to 12 months. Colonization of feldspars is only observed in the very anaerobic zone, and those feldspars that are colonized all show evidence of rapid and extensive dissolution. Other feldspars reacted in the same location, in contrast, are uncolonized and unweathered. The apparent rate of dissolution of the colonized surfaces, based on etch pit depth is *at least* a factor of 100 greater than the uncolonized surfaces (Bennett *et al.*, 1996).

We found that the feldspars that are colonized in this environment all contain minor phosphorus, while virtually identical feldspars without phosphorus are uncolonized and unweathered (Rogers *et al.*, 1998). The P is present as apatite inclusions, and should be available to the microorganisms.

The weathering pattern on the colonized feldspars suggest that the microorganisms are dissolving the feldspar matrix in addition to the exposed apatite inclusion. This is reasonable considering the exposed surface area of silicate vs. the surface area of exposed apatite inclusion. Assuming the organism is colonizing these surfaces to gain access to limiting P (and no other systematic difference has been identified to date) feldspar matrix must eventually be removed to expose new P. There are, however, a limited number of mechanisms available to accelerate silicate dissolution (e.g. Brady and Walther, 1989). Principally this can accomplished by perturbing temperature, pH or ionic strength, or by the production of metal chelating ligands.

In the laboratory experiments, we examined the dissolution dynamics of one feldspar that consistently is colonized and weathered (microcline) and one feldspar that consistently is uncolonized and unweathered (albite). The results of our experiments were then compared to other published results using similar material to try and identify possible mechanisms for the microbial acceleration of weathering. We found that the dissolution rate of both feldspars is almost independent of proton activity between pH 6.5 (the ground water pH) and pH 4.5, while the rate of dissolution only increases by a factor of ~3.3 between pH 4.5 and 3.0 for the microcline. Dissolution rate decreases with increasing ionic strength (using LiCl as an ionic strength buffer) by 50-75% up to I = 0.05 molar, with a larger effect found at lower temperature. These results suggest that ionic strength is not a factor, and the pH around the attached microorganism would have to be substantially less than 3.0 to achieve the observed field rate of microcline dissolution, an unreasonable expectation.

The dissolution rate of both the albite and microcline increased with even low (0.5-2.0 millimolar) concentrations of the siderophores, while the apparent activation energy is substantially lower

(decreasing from 50 kJ/mol to 32 kJ/mol for microcline). The increase in rate, and decrease in the apparent activation energy suggests that these organic ligands can substantially increase feldspar weathering rate, particularly at low temperature or under a biofilm layer where ligand concentration could be quite high.

We propose that microorganisms attached to feldspars in this environment are producing ironchelating ligands to scavenge scarce ferric iron for metabolic processes, and the concentration of the ligand is highest near the organism. The result of this ligand excretion is the accelerated weathering of the feldspar, and in some cases, the release of a limiting nutrient. The presence of a limiting nutrient will act as a positive feedback for further metabolism, and possibly, additional colonization. The end result of this interaction is the selective weathering of only those feldspars that provide a nutritive advantage to the microorganism, while almost identical feldspars without nutritive benefit will be left untouched, and presumably preserved in the rock record.

## References

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