Biochemical release of a limiting nutrient from feldspars

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Phosphorus and nitrogen are essential nutrients needed for the survival of virtually all living organisms. In subsurface aqueous environments these nutrients can be scarce, and tightly cycled within the community, limiting the growth of indigenous microbial populations (Ghirorse and Wilson, 1988). Some microorganisms can extract phosphorus from insoluble mineral sources such as apatite, variscite, strengite and vivianite, by using organic acidity or chelators. However, these detrital phosphates are rarely abundant in the subsurface.

While phosphate minerals are not widely distributed, phosphorus is a trace or minor constituent in many rocks. Pegmatitic feldspars can contain up to 2000 ppm phosphorus in the crystal matrix, while many igneous feldspars contain apatite as inclusions. Feldspars can also contain nitrogen, typically as ammonium, with the mineral buddingtonite as the endmember ammonia feldpar with ~8% $(NH_4)_2O$ (Erd *et al.*, 1964). While these feldspar-bound nutrients have not previously been considered a viable source of phosphorus and nitrogen, in very nutrient-limited environments colonizing microorganisms may have few other choices.

We propose that microorganisms extract phosphorus from apatite inclusions in feldspars, scavenging the nutrient while destroying the silicate matrix. We have observed this in carbon-rich, but phosphorus-poor, anaerobic groundwater.

Methods

Using *in situ* field microcosms (Hiebert and Bennett, 1992) we examined silicate sources for phosphorus by characterizing the microbial colonization and weathering of a variety of feldspars. The microcosms were left in aerobic and anaerobic ground water in a petroleum-contaminated aquifer near Bemidji, Minnesota for periods up to one year. The anaerobic water has a pH of ~6.4, with very high DOC, ferrous iron and silica, while the aerobic region has a slightly higher pH, 6.8, and is characterized by the dissolution carbonates, with less DOC, little silica and no ferrous iron. The native microbial population in the anaerobic ground water consists of iron reducers, fermenters and methanogens, with as many as 10^6 per gram of soil, and methanogens 10-50% of that number (Essaid *et al.*, 1995), while the aerobic groundwater is host to a variety of aerobes. Approximately 95% of the microorganisms are sessile, but the planktonic distribution is a good representation of the sessile population (Bekins, pers. com.).

After microcosm removal the biological tissue was fixed using a field critical point drying method (Nation, 1983; Vandevivere and Bevaye, 1993). Scanning electron microscopy was then used to characterize the types of microorganisms present, colonization patterns and weathering on the feldspar surfaces.

Feldspar chemistry

In this study five different feldspars were exposed to the microbially active ground water environment. It is assumed that these feldspars had similar starting surface charge and surface character, but with differing compositions. The reaction of these feldspars varied with differential colonization and weathering observed. Only those feldspars which contain phosphorus, however, were colonized, only colonized feldspars were weathered, and this only occurred in the anaerobic groundwater, and not the aerobic.

Whole rock, trace element, microprobe and light microscope analysis of all feldspars were used to determine compositional and mineralogical variations. The plagioclase (~Ab_{60}) is a mixture of plagioclase, albite, and muscovite, with no detectable phosphorus, while oligoclase (~Ab_{75}) had trace phosphorus, and some iron of unknown redox state. The Ontario microcline was homogeneous with no detectable phosphorus, but some iron. There was no detectable ammonia in any of these minerals. The South Dakota microcline is more heterogeneous, with less iron than the Ontario microcline, but with 0.28%

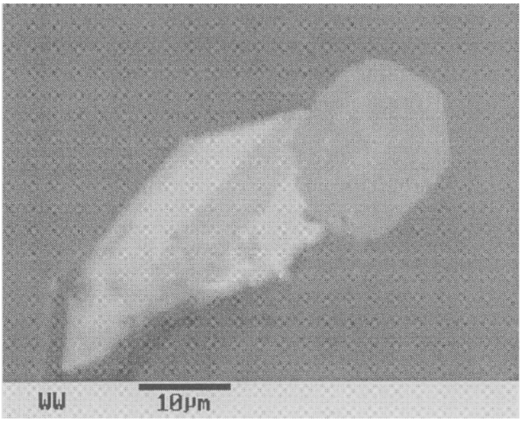

FIG. 1. Electron microprobe image of anorthoclase showing apatite intergrown with iron oxide.

P_2O_5, which occurs as small apatite inclusions, intergrown with albite. Ammonia was <1 umol/g. The anorthoclase is also very heterogeneous, with 0.24% P_2O_5 occurring as mixed phosphate mineral inclusions. Inclusions are typically pure apatite, but some yttrium and barium were detected. The anorthoclase also contained plagioclase, biotite and iron/titanium oxides throughout its matrix (Fig. 1). Trace ammonia was detected at ~1umol/g. The apatite in both the South Dakota microcline and the anorthoclase was extractable with a weak acid solution and should be available to microorganisms. The aquifer sediment had ~2.8 to 7 µmol/g total phosphorus of which only 0.03 to 0.12 µmol/g was available.

Surface character

SEM examination of mineral surfaces after reaction in the aquifer showed that the albite and the Ontario microcline had no etching and little or no colonization by microorganisms. The oligoclase had minor etching a few microorganisms were detected. In contrast the South Dakota microcline and the anorthoclase were both heavily colonized and etched.

There is little available phosphorus in the aquifer sediments, and no dissolved phosphorus in the aquifer water, and there is a strong correlation between colonization and phosphorus-content in these feldspars. This suggests that microorganisms can utilize phosphorus from feldspars and further that increased phosphorus availability results in microbial growth and additional surface colonization. Redox environment is an important factor in the etching of the feldspar surfaces. In the anaerobic groundwater at Bemidji iron-reducing bacteria use ferric iron oxides from sediment grain coatings as a terminal electron acceptor (TEA). In many near-neutral pH environments, where iron is in an insoluble form, native iron-reducing microorganisms will produce solubilizing ligands, or siderophores to scavenge iron. Some of these simple siderophores or iron chelators associated with low affinity uptake have been found in the Bemidji aquifer, and these ligands, effective chelators of aluminum and silicon, may be responsible for silicate weathering in the vicinity of microorganims (Bennett *et al.*, this vol.) It is not clear, however, why colonization and weathering is only observed under anaerobic conditions. Nutrient depletion may be more severe in these areas as the phosphorus-containing iron-oxide coatings here have been stripped, or the microbially produced ligands could be more stable in oxygen-depleted water, or these ligands may only be produced by anaerobes specifically for iron reduction utilities.

We hypothesize that phosphorus in feldspars is released secondary to microbial production of these ligands, which interact with the silicate matrix, dissolve it and expose the apatite inclusions in it. The release of phosphorus secondary to the silicate weathering provides a limiting nutrient to colonizing microorganisms, which promotes growth and in turn increases mineral weathering.

References

Bennett, P.C., Choi, W.J. and Rogers, J.R. (1998) *Mineral. Mag.*, this issue.

Erd, R.C., White, D.E., Fahey, J.J. and Lee, D.E. (1964) *Am. Min.* **49**, 831–50.

Ghirorse, W.C. and Wilson, J.L. (1988) *Adv. Appl. Microbio.*, **33**, 107–72.

Hiebert, F.K. and Bennett, P.C. (1992) *Science*, **258(5080)**, 278–81.

Nation, J.L. (1983) *Stain Tech.*, **58**, 347–51.

Vandivivere, P. and Bavaye, P. (1993) *J. of Microscopy*, **167**, 323–30.