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Feldspars as a source of nutrients for microorganisms

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ABSTRACT

Phosphorus and nitrogen are essential macronutrients necessary for the survival of virtually all living organisms. In groundwater systems, these nutrients can be quite scarce and can represent limiting elements for growth of subsurface microorganisms. In this study we examined silicate sources of these elements by characterizing the colonization and weathering of feldspars in situ using field microcosms. We found that in carbon-rich anoxic groundwaters where P and N are scarce, feldspars that contain inclusions of P-minerals such as apatite are preferentially colonized over similar feldspars without P. A microcline from S. Dakota, which contains 0.24% P_2O_5 but <1 μmol/ g NH_4^+, was heavily colonized and deeply weathered. A similar microcline from Ontario, which has no detectable P or NH_4^+, was barren of attached organisms and completely unweathered after one year. Anorthoclase (0.28% P_2O_5, ~1 μmol/g NH_4^+) was very heavily colonized and weathered, whereas plagioclase specimens (<0.01% P, <1 μmmol/g NH_4^+) were uncolonized and unweathered. In addition, the observed weathering rates are faster than expected based on laboratory rates. We propose that this system is particularly sensitive to the availability of P, and the native subsurface microorganisms have developed biochemical strategies to aggressively scavenge P (or some other essential nutrient such as Fe^{3+}) from resistant feldspars. The result of this interaction is that only minerals containing P will be significantly colonized, and these feldspars will be preferentially destroyed, as the subsurface microbial community scavenges a limiting nutrient.

INTRODUCTION

Increasing attention is being directed toward finding and identifying subsurface microbial populations, and viable microorganisms have been found as deep as 1600 m (Fliermans et al. 1994) and at temperatures exceeding 100 °C (Ehrlich 1996). Little is known, however, about subsurface microbial ecology and nutrient availability, yet these issues are critical to understanding the viability of these organisms in the subsurface. In many groundwater environments, critical macronutrients such as nitrogen and phosphorus are scarce, and their availability can limit growth of the indigenous microbial community (e.g., Madigan et al. 1997). Even in oligotrophic environments, terminal electron acceptor and carbon availability are often sufficient for a larger population of microorganisms. Dissolved and extractable P and N, however, are just as often depleted, and these elements are tightly cycled within the microbial community, limiting cell growth and potentially metabolic efficiency (Ghiorse and Wilson 1988).

Microorganisms are known to extract P from cryptocrystalline Fe phosphates and Al phosphates, and from some crystalline phosphate minerals as well (Ehrlich 1996). Important primary mineral sources of P include apatite [$Ca_5(PO_4)_3$(F, Cl, OH)], variscite ($AlPO_4 \cdot 2H_2O$), strengite ($FePO_4 \cdot 2H_2O$) and vivianite [$Fe_3(PO_4)_2 \cdot 8H_2O$]. Total P in soils averages 26 μmol/g (805 ppm as P) (Bowen 1979), but the solubility of these minerals is extremely low, especially in water with high Ca concentrations. A groundwater at pH 7 in equilibrium with calcite and hydroxyapatite [$Ca_5(PO_4)_3$(OH), log Ksp = −116.4] would be expected to release <0.05 μmol/L each of HPO_4^{2-} and $H_2PO_4^-$ (Lindsay 1979). Many microorganisms therefore have developed biochemical strategies to enhance the P availability of these insoluble sources (Babu-Khan et al. 1995; Ehrlich 1996), including the production of mineral or organic acidity, or the production of Fe- or Al-chelating substances.

Although phosphorus is present in most rocks as a minor constituent, phosphate minerals are typically scarce, with the average P_2O_5 content of sandstones ~0.04% (Blatt et al. 1980). The P_2O_5 content of igneous rocks is much higher, however, ranging from 0.01 to 0.5% (Nash 1984), and as high as 2.0% in alkaline, low-silica rocks. The actual solubility of P in silicates is quite low and P in primary feldspars is reported to range from only 6 to ~2000 ppm in alkali feldspars (Mason 1982; Smith 1983). Feldspars containing high concentrations of P in solid solution are rare, and typically crystallize in pegmatitic environments after P has been concentrated in the residual melt (Nash 1984). However many feldspars, particularly those from igneous rocks, contain abundant apatite inclusions. In these minerals, the fraction of P can be substantial, and potentially biochemically significant.

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Feldspars can also contain a small amount of nitrogen, most commonly as ammonium, which can replace potassium in the feldspar structure (Smith and Brown 1988). Potassium feldspars have been found with ammonium concentrations ranging from 6 to 196 ppm (Honma and Itihara 1981), and the mineral buddingtonite (Barker 1964) is an end-member ammonia feldspar with up to ~8% $(NH_4)_2O$ (Erd et al. 1964). It is possible that in N-limited environments, colonizing microorganisms may benefit from ''fixed'' ammonia in feldspars; however, it is not known whether microorganisms can utilize ammonia directly from the feldspar lattice, or how the ammonia could be made available.

To date, the trace quantities of phosphorus found as inclusions in feldspars and replacement ammonium in feldspars have not been considered a viable source of nutrients, and there are no known references to microorganisms using feldspars as a source of P or N. Feldspars are probably not a desirable nutrient source if other sources are present, such as dissolved or organic nitrogen species, diagenetic or detrital phosphate minerals, or organic P. In many aquifer systems, however, detrital phosphate minerals in particular are scarce, and the aqueous solubility of these minerals is very low. In the absence of soluble mineral phases, the subsurface microbial consortia will be required to find other sources of P, and possibly N.

We propose that subsurface microorganisms extract inorganic P from apatite inclusions in feldspars, aggressively scavenging this nutrient while destroying the silicate matrix (Bennett et al. 1996). We have observed this interaction in an extremely anaerobic groundwater system where there is abundant carbon substrate, but apparently insufficient P for metabolism and growth. The nutrient requirements of the organism therefore control mineral surface colonization, and the subsequent feldspar weathering.

Experimental methods

This study uses field microcosms to study microbial identity, abundance, and colonization pattern on feldspars, and the relationship between colonization, phosphate content, and feldspar weathering. The weathering features observed on mineral specimens from the field microcosms were then compared to those observed on minerals from laboratory dissolution experiments to distinguish macro- from microbial micro-environment effects.

Bemidji research site

The Bemidji Research Site of the U.S. Geological Survey (USGS) is a hydrocarbon-contaminated aquifer located in northern Minnesota near the town of Bemidji. At present there is a pool of free-phase petroleum ~1 m thick floating on the water table, and a plume of dissolved organic carbon (DOC) compounds extending down-gradient from the source (Baedecker et al. 1993; Bennett et al. 1993). The aquifer is a glacial sand and gravel outwash dominated by quartz (48–57%), plagioclase feldspar (17–21%), and alkali feldspar (11–17%), with minor calcite, dolomite, hematite, magnetite, and biotite. In the uncontaminated aquifer, most of the sand surfaces are coated with ferric oxyhydroxide.

Beneath the floating oil, the groundwater is anoxic, and a small population of iron-reducers, fermenters, and methanogens actively degrade the soluble aromatic components of the oil (Baedecker et al. 1993; Cozzarelli et al. 1990; Eganhouse et al. 1993; Essaid et al. 1995). Iron-reducing bacteria dominate in most areas, where they oxidize aromatic hydrocarbons by using Fe^{3+} in oxyhydroxide grain-coatings as the terminal electron acceptor (Lovely et al. 1989). Total viable iron reducers are as high as 10^6 per gram of soil, with methanogens typically 10–50% of that number, although the organism distribution is spatially variable (Essaid et al. 1995). There are few aerobes and sulfate reducers. Approximately 95% of the viable organisms are found on the surfaces of mineral grains in the sediment, except in some locations where as many as 50% of the iron reducers are planktonic (B. Bekins, USGS, Menlo Park, California, personal communication).

Mineral colonization experiments

In situ field microcosm experiments (e.g., Hiebert and Bennett 1992) were performed for periods of three to twelve months to permit colonization by microorganisms. The microcosms were constructed of 8 mL Nalgene bottles that were punctured to permit flow-through of water and planktonic microorganisms. Specimens of a white microcline (South Dakota), a pink microcline (Ontario), plagioclase (Ontario), anorthoclase (Norway), and oligoclase (various) were obtained from Wards Scientific. These minerals were crushed in a shatterbox using a tungsten carbide grinding vessel and sieved to 5–10 mm size fraction. Selected crystals were cleaned ultrasonically for 4×15 s periods to remove adhering fine grains, and then dry-sterilized for approximately 2 h at 150 °C (this procedure was chosen to avoid alteration of the surface during conventional steam sterilization). Mineral chips were then placed into microcosm bottles, and suspended in the screened flow-through portion of the wells in background and contaminated locations, and the wells sealed. Aseptic procedures were used at all times, and at the time of emplacement and recovery water samples were taken from the wells to monitor the water chemistry of the aquifer. One microcosm was reserved as a reference.

Microcosms were recovered aseptically and anaerobically, and processed for scanning electron microscope (SEM) examination. The well was first purged from the bottom up with oxygen-free argon [d_{air} = 1.38 (density relative to air)] by running the gas outlet tube down to the water table. After purging, the microcosm set was pulled up through the purging argon stream into a purged storage tube, and sealed. This tube was then transferred to an argon-purged glove box for processing.

In the anaerobic glove box, several chips of each mineral type were transferred to serum bottles containing

PRAS (pre-reduced and anaerobically sterile) prepared media for culturing fermenters, iron reducers, and methanogens (e.g., Essaid et al. 1995). These bottles were then sealed while in the argon-purged atmosphere, and brought back to the laboratory where the iron-reducer and methanogen bottles were charged to 1 atm (gauge pressure) with a 70:30 H_2:CO_2 gas mixture. The fermenter bottles were graded for visible growth after one week at room temperature. The iron-reducer bottles were graded for metabolic activity after 6 weeks by colorimetric analysis of dissolved Fe^{2+} using the bipyridine method measured at 520 nm (Skougstad et al. 1979). The methanogen bottles were graded for metabolic activity after 6 weeks and 10 weeks by analysis of headspace methane using a gas-solid chromatography separation of a 250 μL direct injection of headspace gas and detection by flame ionization detector.

Groundwater chemistry

Groundwater pH, dissolved oxygen, temperature, and specific conductance were measured in the field using a down-hole electrode package (Perstorp Scientific). Measurements were taken with the electrodes positioned in the screened interval of the well while pumping the well using a small down-hole pump placed immediately above the data sonde. Specific conductance, pH, and temperature were also measured using standard methods at the surface using a flow-cell. Alkalinity was determined in the field on a filtered sample by standard titration methods (pH 4.3 end point), and again in the laboratory by end point seeking autotitration.

Several unstable constituents were measured immediately in the field by colorimetric methods using a field Spectronics 20 spectrophotometer (Milton Roy). Dissolved oxygen was measured at the surface by the Rhodazine D method (CHEMetrics, Inc.), with a detection limit of ~0.1 μmol/L. Dissolved P was screened in the field by the stannous chloride/molybdenum blue method (CHEMetrics, Inc.). Dissolved Fe^{2+} and Fe^{2+} + Fe^{3+} were measured by colorimetry in the field by the bypridine method (Skougstad et al. 1979) and again in the laboratory using a Perkin Elmer Lambda 6 spectrophotometer (performance testing of the method has shown that the color is stable for several days).

Groundwater samples were collected for determination of dissolved anions, nutrients, major cations, metals, carbon, and organic acids. All samples were filtered to at least 0.2 μm (0.1 μm for the trace metals), and stored at <4 °C until analysis. Samples for metals analysis were preserved by acidification to pH <2 using trace-metal grade nitric acid. Anions and nitrogen species were determined from a filtered unpreserved sample by single-column ion chromatography (IC) with detection by conductance and UV absorbance at 210 nm. Major cations, silica, and metals were determined on the filtered acidified sample by Inductively Coupled Plasma Emission Spectrometer (ICPES). Phosphate was determined on a filtered sample preserved with mercuric chloride using the stannous chloride-molybdenum blue method (Greenberg et al. 1992).

Inorganic carbon was determined on a filtered sample by acidification and measurement of the evolved carbon dioxide using a non-dispersive IR spectrometer on a Dohrman DC-180 carbon analyzer. Purgeable carbon was determined by acidification and sparging of a filtered unacidified sample followed by wet-oxidation of the volatile carbon and measurement of the evolved carbon dioxide. Non-purgeable organic carbon was determined on a filtered sparged acidified sample by wet-oxidation. Organic acids were characterized by HPLC (high-performance liquid chromatography) and UV detection at 210 nm.

Scanning electron microscopy

Biological material on the mineral chips was fixed under a nitrogen atmosphere immediately in the field using a chemical critical point drying method (Nation 1983; Vandevivere and Bevaye 1993). Mineral chips were then inspected using conventional scanning electron microscopy (C-SEM) and environmental SEM (E-SEM). Minerals imaged by C-SEM were stub-mounted, and gold sputter coated for 2 × 25 s. Minerals imaged by E-SEM were done so without coating.

SEM images were examined for evidence of microbial attachment, the types of microorganisms present, the pattern and extent of microbial colonization, and changes in the mineral surface. Microorganisms were distinguished morphologically initially as either rods or cocci. If microorganisms were present, it was noted as to which types and how many of each occurred. Occurrence of colonies as opposed to singular microorganisms was noted. If etching of the mineral surface was observed, the relationship between the etch pits and attached microorganisms was noted as well as the types of microorganisms attached.

Mineral chemistry

Aquifer sediments were collected anaerobically and aseptically using a freezing-shoe piston core barrel (Murphy and Herkelrath 1996). A ~2 m core was recovered in a core tube, sealed at both ends, and then pressurized with oxygen-free nitrogen or argon. After extraction of the interstitial fluids, the gas-purged core was then sectioned, immediately sealed, and brought into a field anaerobic chamber purged with oxygen-free argon. For each core the outer few centimeters of material was assumed to be contaminated with oxygen, and was wasted before collection of a sample for SEM examination and chemical analysis.

Mineral specimens and aquifer material were characterized using light microscopy, SEM-EDS, X-ray diffraction (XRD), electron microprobe analysis, and whole-rock analysis. XRD analysis of rock samples was done using standard powder methods. Preliminary light microscopy examination was made at 200× and 400× of a ~35 μm thin section. For the microprobe analysis, the sections were imaged and probed for qualitative compositional information using an accelerating voltage of 15

TABLE 1. Compositions of feldspars and aquifer sediments

Element	Plag	Olig	O-Micr	SD-Micr	Anor	603	9705	DL
SiO_2	59.8	62.97	66.93	65.17	60.63	82.45	81.22	0.01
Al_2O_3	20.87	22.72	17.62	18.38	10.08	7.51	8.4	0.01
Fe_2O_3	1.07	1.3	1.78	0.9	4.41	1.36	1.8	0.01
MgO	0.08	0.03	0.04	0.01	0.93	0.48	0.59	0.01
CaO	2.37	4.51	0.14	0.15	3.04	3.08	2.88	0.01
Na_2O	6.69	8.16	2.41	2.18	6.62	2.17	2.2	0.01
K_2O	7.37	0.6	11.88	13.5	3.99	1.56	1.82	0.01
TiO_2	<0.01	<0.01	0.01	<0.01	0.93	0.05	0.1	0.01
P	<50	131.1	<50	1223.6	1048.8	87.4	218.5	50
Ba	438	51	102	36	1130	406	493	2
Zr	<2	<2	<2	<2	243	25	62	2
Cu	6	11	11	7	10	—	—	1
Pb	28	46	137	133	5	—	—	5
Zn	3	6	3	2	96	—	—	1
Ni	2	19	5	4	36	—	—	
Mn	57	106	85	48	841	—	—	1
Sr	399	230	40	73	612	233	249	1
V	2	2	2	2	42	<2	16	2
Y	2	2	2	2	35	3	5	2

Note. Major elements in weight percent oxide, trace elements in parts per million (μg/g). DL is detection limit, expressed in the unites of analysis for that analyte. Minerals analyzed are anorthoclase (Anor), South Dakota microcline (SD-Micr), Ontario microcline (O-Micr), plagioclase (Plag), and oligoclase (Olig). 603 is a background uncontaminated aquifer sediment, and 9705 is sediment from the contaminated zone of the aquifer.

kV and a sample current of 15 nA. Both the silicate host and the accessory minerals were examined to determine compositional differences. In addition, major element oxides were determined by XRF and trace element analysis was done using ICP-OES (Activation Laboratories, Ontario, Canada).

Silicate ammonia was determined on a whole-rock sample by HF-HCl dissolution followed by distillation of the ammonia using standard methods (Bremner 1965). Available P on aquifer sediments was determined by extraction into a solution of 0.05N HCl + 0.025N H_2SO_4, and analysis of P by the standard stannous chloride-molybdenum blue method (Olsen and Dean 1965). This analysis is specific for orthophosphate, and does not include organic P.

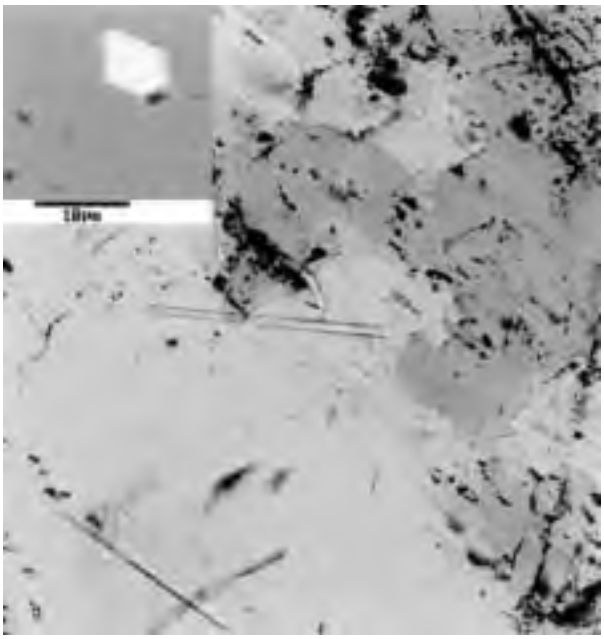

FIGURE 1. Transmitted light micrograph of South Dakota microcline showing abundant needles of apatite (magnification = 200×). Inset shows BSE image of apatite inclusion.

RESULTS

Mineral chemistry

XRD and electron microprobe analysis of the plagioclase specimen showed it to be a complex mixture of plagioclase (~Ab_{60}), albite, and muscovite, but without detectable P, while the oligoclase (~Ab_{75}) had only trace phosphorus, and some iron of undetermined redox state. The Ontario microcline was homogeneous, with no detectable P, but some iron replacement of Al (Table 1). There was no detectable NH_4^+ (detection limit = 1 μmol/g) in any of these minerals.

The S. Dakota microcline, in contrast, is somewhat heterogeneous, with less iron but a significant fraction of total inorganic phosphorus (Table 1). P is present as small apatite inclusions in intergrown albite (Fig. 1), and much of it is ''available'' P based on the weak acid extraction (the actual concentration of available P is a function of surface area and exposed surface apatite, and so is not specifically reported here). Ammonia in the S. Dakota microcline was <1 μmol/g.

The anorthoclase was also very heterogeneous, and had significant P as phosphate mineral inclusions. The mineral specimen contained intergrown plagioclase and several biotite inclusions with zoned iron and titanium oxides. Apatite inclusions occurred as hexagonal crystals (Fig. 2) and blades that were slightly larger than those found in the microcline, although the phosphates were not exclusively pure apatite, with some barium and yttrium detected. The phosphate mineral blades were ubiquitous in the feldspar matrix, and often were found adjacent to

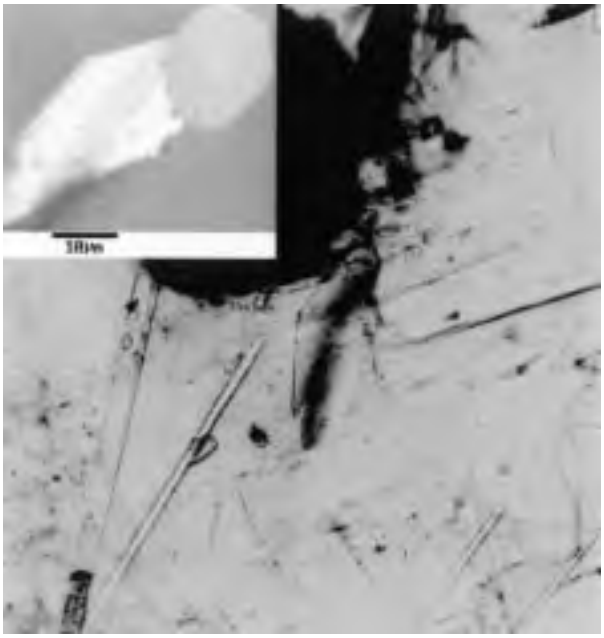

FIGURE 2. Transmitted light micrograph of anorthoclase showing abundant needles of apatite and oxide (magnification = 200×). Inset shows BSE image of apatite inclusion intergrown with Fe-Ti oxide.

inclusions of biotite and iron/titanium oxides (Fig. 2). Again, much of the total P present in the anorthoclase dissolved in weak acid, and would be considered ''available.'' There was a trace of NH_4^+ in the anorthoclase, ~1 μmol/g.

The whole-rock chemistry of a background and contaminated zone sediment sample is also summarized in Table 1. The aquifer sediments had 87.4–218.5 ppm total P, of which only 0.93 to 3.7 ppm was ''available.'' Extractable Fe^{3+} in the sediments is approximately 1116.9 ppm, with extractable Fe^{2+} ranging from 1116.9 to 2233.9 ppm (B. Bekins, USGS, Menlo Park, California, personal communication).

Water chemistry

A detailed description of the water chemistry at the site has been published elsewhere (Baedecker et al. 1993; Bennett et al. 1993; Cozzarelli et al. 1990), and is summarized in Table 2. The background uncontaminated groundwater is an oxic Ca-HCO_3 type water at pH 7.8 with dissolved oxygen >100 μmol/L, dissolved Fe^{2+} <0.1 μmol/L, and dissolved silica ~250 μmol/L. Background organic carbon is about 200 μmol/L, which is typical for a shallow unconfined aquifer. Groundwater temperature ranges from 8–10 °C.

In the contaminated zone examined here, dissolved non-purgeable organic carbon is >5000 μmol/L, with significant methane (up to 1500 μmol/L). The pH decreases to <6.5 in places, while dissolved Fe^{2+} increases to ~900 μmol/L as Fe-reducing microorganisms oxidize carbon and reduce oxidized Fe minerals. Dissolved Ca, Mg, Na, K, and DIC^- all increase as a result of the accelerated dissolution of carbonate and silicate minerals, and dissolved silica increases to >1000 μmol/L. There is no detectable dissolved orthophosphate at any location, and only traces of inorganic N species are present in the groundwater under the oil.

Microbiology

Culture experiments were all positive for the presence of fermenters, iron reducers and methanogens on all five feldspars. Based on the observed rate of growth, and the production of dissolved Fe, the anorthoclase specimen supported the largest population, whereas the oligoclase and Ontario microcline supported the smallest population. Other researchers at the site have identified two species of iron-reducing bacteria: Geobacter *metallireducens* and Geothrix (T. Anderson, University of Massachusetts, Amherst, personal communication), and we believe that both are present on the microcosm samples.

Extensive examination of the preserved mineral surfaces shows clear patterns of preferential colonization. The plagioclase (Fig. 3) and Ontario microcline specimens are almost completely barren of colonizing microorganisms, and are devoid of any evidence of chemical weathering. The surfaces had little evidence of biological material such as glycocalyx, and they were generally smooth and unaltered. Similar results were found with both the unfixed ESEM methodology and the field fixed followed by gold coating and examination by conventional SEM techniques. The oligoclase specimens had a few attached rod-shaped microorganisms, but no evidence of biofilm development.

The S. Dakota microcline and anorthoclase surfaces, in contrast, are colonized with various microorganisms. On the microcline the microbial population consisted of both rods and cocci. The anorthoclase surface had various rods

TABLE 2. Summary of groundwater chemistry

Well	pH	DOC	O_2	DIC	N	Ca	Mg	Na	K	Si	Fe
310	7.66	0.23	0.28	3.41	<0.001	1.27	0.58	0.084	0.01	0.29	<0.01
707	6.80	1.58	0.10	9.67	0.16*	3.55	1.58	0.099	0.01	0.33	0.01
1015	6.33	4.33	<0.01	16.4	0.003	4.10	1.14	0.15	0.16	1.08	0.90

Notes. Water analysis at a background location (310), at the upgradient edge of the oil (707), and in the contaminated zone under the oil (1015). Concentrations are in mmol/L. DOC is total dissolved organic C, equal to the sum of the nonvolatile and volatile fractions, expressed as mmol/L C. DIC is the dissolved inorganic carbon as mmol/L C. N is the sum of NO_2^-, NO_3^-, and NH_4^+. Fe is as Fe^{2+}.

* The relatively high N (present as nitrate) at this location is the result of the surface application of a fertilizer package by the pipeline company in 1986.

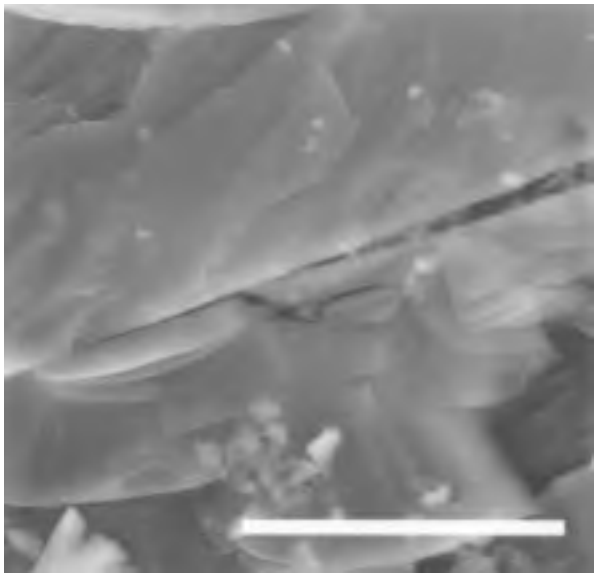

FIGURE 3. Scanning electron micrograph of a specimen of plagioclase after ~1 year in the contaminated region of the aquifer. No visible etching is observed on the surface, and no evidence of biological material or adhering microorganism. Bar scale = 15 μm.

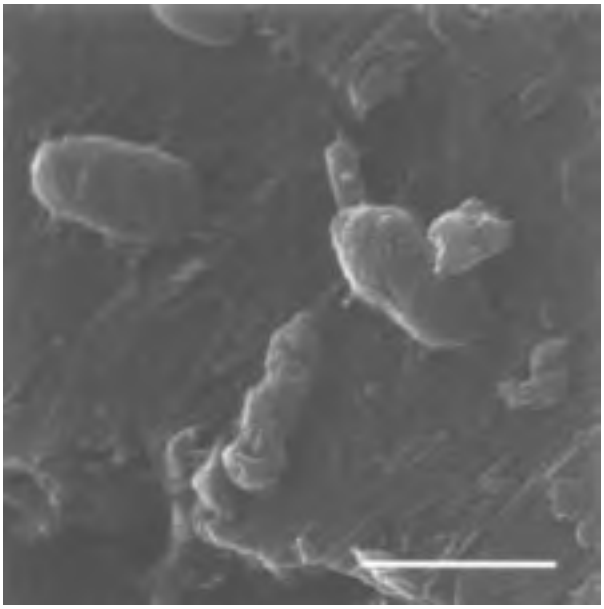

FIGURE 4. Scanning electron micrograph of anorthoclase left in situ for 4 months. Two types of microorganisms are present with a non-viable (dead) organism near the center of the image. Light etching of the mineral surface is visible. Bar scale = 2 μm.

and cocci (Fig. 4) on chips left in situ for four months, while with longer experiments (up to 14 months) the anorthoclase was populated almost exclusively by pairs of cocci resembling *diplococcus.* There is also evidence of biofilm development on the anorthoclase (Fig. 5), and extensive weathering of the feldspar surfaces, with deep etch pits in the vicinity of the attached microorganisms. Differences in the types of colonizing organisms may be attributed to the length of time the mineral remained in the aquifer, or it could reflect a change in the environment in the period separating the two experiments.

DISCUSSION

The change in groundwater chemistry from the background to the contaminated area shows the effects of microbial metabolism on geochemical processes. Addition of oil as a carbon substrate has stimulated the native microbial consortia, resulting in oxidation of petroleum and production of carbon dioxide, with the partial pressure of CO_2 >0.1 atm (Bennett et al. 1993). Once oxygen is depleted at the upgradient edge of the oil, Fe^{3+} in oxyhydroxide minerals act as the principle electron acceptor for carbon oxidation, with the release of dissolved Fe^{2+}, and the probable precipitation of magnetite and, possibly, iron carbonates.

The large increase in concentrations of dissolved cations not associated with the oil suggests that various minerals are dissolving, dominated by calcite, dolomite, and silicate minerals. There is no detectable P and little N in the groundwater, and extractable sediment P is less than 10% of what is considered adequate for plant growth (Thomas and Peaslee 1973). The system is substrate rich, but apparently nutrient limited.

The lack of detectable dissolved N or P, and the very limited availability of extractable P, is consistent with investigations of the rate of petroleum biodegradation (Essaid et al. 1995). The native microbial community, dom-

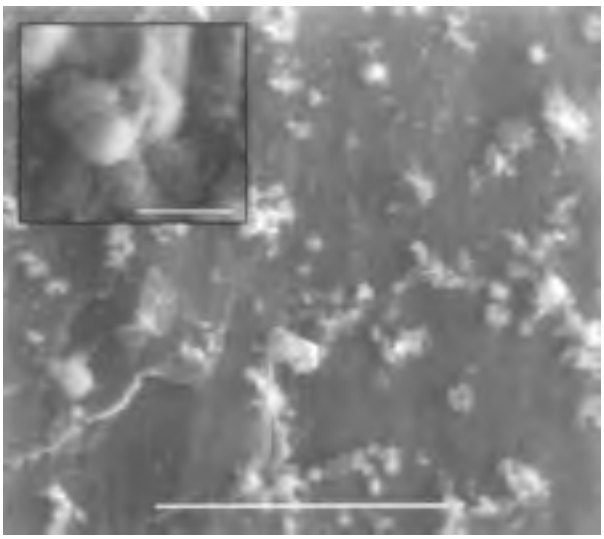

FIGURE 5. Scanning electron micrograph of many microorganisms on an anorthoclase surface left in situ for ~14 months. Bar scale = 45 μm. Inset is close-up of microorganism resembling *dipplococcus* with weathering visible around the attached body. Bar scale = 5 μm.

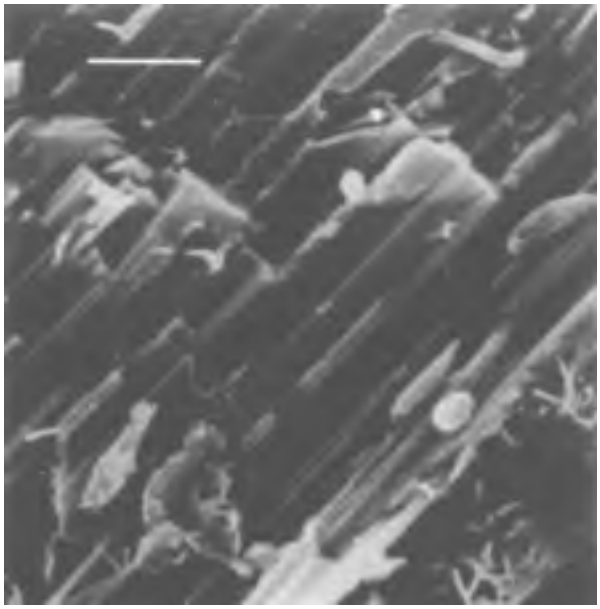

FIGURE 6. South Dakota microcline surface showing extensive weathering after ~1 year in the contaminated region of the aquifer, with several attached microorganisms visible. Bar scale = 2 μm.

inated by dissimilatory iron reducers, is not substrate limited, and the native population is efficiently transforming the petroleum. Little addition of biomass is detected, however, even when the available substrate should support a community several times that size, possibly due to nutrient limitation. Phosphorus is often a limiting macronutrient in groundwater systems (e.g., Chapelle 1993), and increasing availability of P can have a dramatic effect on microbial growth and viability (e.g., Madigan et al. 1997). In phosphorus-poor environments, such as the Bemidji aquifer, microorganisms are forced to scavenge P from resistant sources.

In this study, five different feldspars were exposed to this microbially active environment for periods of up to about a year. Although the starting surface charge and surface character of these minerals were very similar, only the feldspars containing phosphorus were significantly colonized, and only those feldspars were extensively weathered.

The oligoclase and Ontario microcline had no etching and typically little or no colonization by microorganisms. While an occasional microorganism was observed, the surfaces were not altered. Major and trace element analysis of these minerals show that they do not contain any potentially beneficial nutrients (Table 1), such as phosphorus; neither do they appear to contain high concentrations of potentially toxic elements, such as Pb. These minerals may act as sites for occasional attachment, but do not represent a significant positive or negative influence on growth.

Significant microbial colonization and etching are observed on both the South Dakota microcline (Fig. 6), and the anorthoclase (Figs. 4 and 5). Both these minerals have abundant P as apatite inclusions (Figs. 1 and 2), and the anorthoclase contains trace amounts of NH_4^+. There is little available P in the aquifer, and there is a strong correlation between colonization and P-content of the feldspars, but P-containing feldspars with and without NH_4^+ are equally colonized. This suggests that microorganisms can utilize the P in feldspars, and further, that the increased availability of P results in microbial growth and colonization on the surfaces.

While the mechanism of inorganic phosphate utilization is enzymatic (e.g., Ehrlich 1996), the etching of the mineral is apparently not specific to the apatite inclusions. SEM images show the entire mineral surface is weathering and retreating (Figs. 4–6), and the etching is not simply due to the preferential removal of apatite. Nor are the etch pits forming in the shape of the microorganism, with weathering restricted to the area under the attached organism or biofilm.

The observed weathering is also related directly to the colonization by microorganisms, and not simply secondary to macroscopic, aquifer-scale chemical dissolution. Comparison of the observed weathering features with the results of parallel abiotic dissolution experiments (Choi 1997) show that the plagioclase should dissolve very quickly, with distinctive etch features as soluble phases are removed (Fig. 7a). The S. Dakota microcline, in contrast, should dissolve much more slowly, without distinctive etch pits (Fig. 7b). These experiments were run using organic and inorganic acid solutions over an ~1 year period, and they arrived at the expected laboratory finding–that plagioclase dissolves faster than microcline. This does not account, however, for the influence of preferential colonization by microorganisms.

We hypothesize that the P in specific feldspars is released due to microbially produced acidity and chelating ligands in the vicinity of attached microorganisms. The P in the feldspars is apparently available, but only at surface-exposed apatite inclusions, so microorganisms benefit from the wide-scale weathering of feldspar and the progressive exposure of new apatite. The release of a limiting nutrient resulting from the silicate weathering promotes microbial growth, which in turn increases mineral weathering. It is also possible that sufficient P is released to attract planktonic organisms via chemotaxis (e.g., Madigan et al. 1997), resulting in additional colonization as well as growth. Only P-containing feldspars are colonized and therefore only the P-containing feldspars are weathered. Mineral weathering results in the general destruction of the feldspar and the precipitation of secondary clay minerals at rates orders of magnitude faster than predicted based on laboratory rates.

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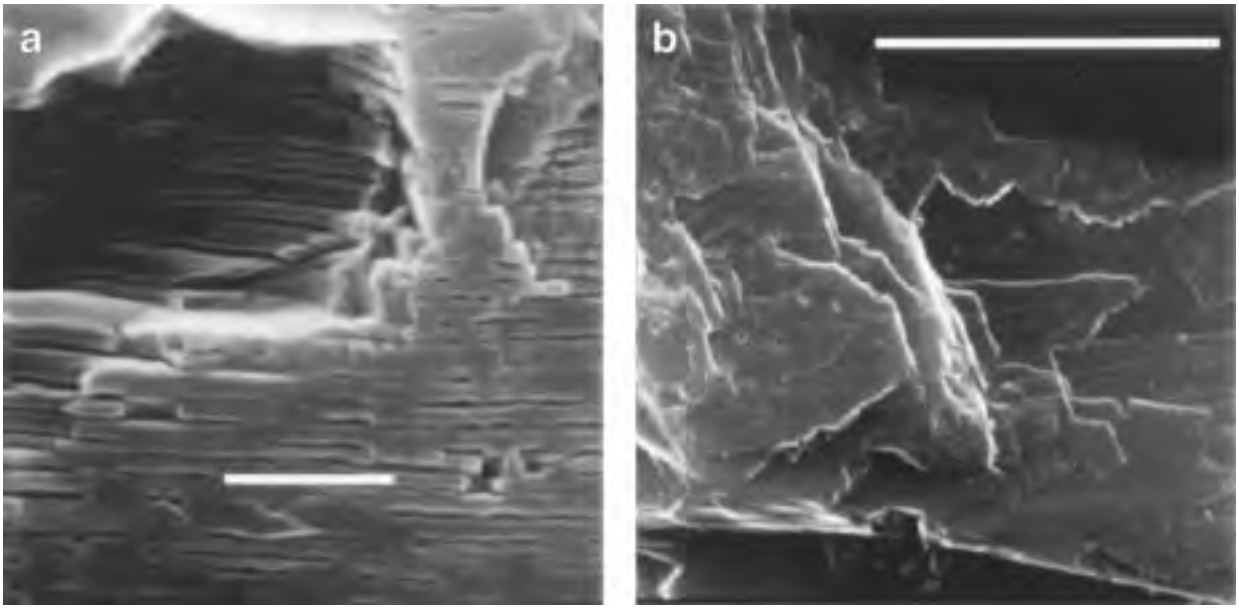

FIGURE 7. Scanning electron micrographs of mineral surfaces after ~1 year of abiotic reaction in a mixed flow reactor using inorganic and organic acids at pH 3 and pH 5, from Choi (1998). (**a**) Plagioclase specimen showing distinctive deep prismatic etch pits on the entire surface as the more easily weathered phases dissolved. Bar scale = 1.0 μm. (**b**) S. Dakota microcline with light surface-weathering visible without evidence of distinctive etch pits. Bar scale = 5.0 μm.

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