Biotic versus abiotic dissolution, alteration and precipitation of iron minerals

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Iron-rich sediments, including banded iron formations, contain both Fe(II) and Fe(III) in a variety of oxide, hydroxide and silicate minerals, where the oxidized and reduced forms are often in close proximity (Brown *et al.*, 1995). Our research has been the investigation of the microbial involvement in the weathering of iron containing minerals in granite, and the production of ferrous and ferric iron minerals in sediments.

Our interest in the different forms of iron in the subsurface was initiated by the formation of a biofilm in the Underground Research Laboratory (URL), excavated in the granitic Lac du Bonnet batholith by Atomic Energy of Canada Ltd. (AECL), Manitoba (Brown *et al.*, 1994). This biofilm had developed rapidly over several weeks, and was found to contain both oxidized and reduced iron as well as silicate minerals (Brown *et al.*, 1994). The Lac du Bonnet granite is commonly homogeneous and equigranular, containing 27% quartz, 34% K-feldspar, 32% plagioclase and 5% biotite, as well as small quantities of accessory minerals including zircon, apatite, monazite, allanite, magnetite and ilmenite.

Terrestrial groundwaters contain a variety of microorganisms that help determine the local ecosystem through their metabolic activities. Organisms that live in nutrient poor groundwaters form biofilms, where they preferentially live as a microbial consortium. The organisms are surrounded by a layer of slime that they have excreted, and which is made up of extracellular polymeric substances (EPS), often negatively charged polysaccharides. These biofilms are ubiquitous in the aqueous environment and generally form at rock/water interfaces. Individuals of the consortium are arranged within the slime layer so that the metabolism of each organism can contribute most effectively to the whole biofilm ecosystem.

Although iron is an essential element for all life, only trace amounts are actually needed. The biological accumulation of large amounts of iron is instead the result of biomineralization, which can be either direct or indirect. Direct reactions are metabolically mediated, and although this includes the assimilation for nutrition, a very much larger volume is involved in the production of energy for microbial growth by the utilization of ferric iron as an electron acceptor. Indirect reactions can be passive physiocochemical sorption of ions onto the negatively charged microbial and EPS surfaces, which can then form nucleation points for further precipitation, or they can affect the environmental pH and Eh through microbial influences on the local solution chemistry (McLean *et al.*, 1996).

Microbial culture

Microbial cultures for our experiments were enriched from the surficial Shield water that was used as mine water at the URL, as well as directly from a fracture zone within the granite. The cultures were maintained in a laboratory bioreactor that contained chips of granite, with a medium of 5.0 g ferric ammonium citrate, 0.5 g K_2HPO_4, 0.2 g $MgSO_4 \cdot 7H_2O$, and 0.01 g $CaCl_2 \cdot 2H_2O$ per litre of deionized water. The consortium consisted mainly of many different morphological types of bacteria, but as well, there was an active protozoan which grazed on the bacteria.

In our first attempt at growing a biofilm in the laboratory we slowly ran the bacterial containing medium over a large slab of Lac du Bonnet grey granite. Later we used plastic boxes, in which we placed small granite billets that were just covered with active media, which were gently rocked. In each experiment, sterile controls with the same media, were used to assess the effects of chemical versus biological activity.

Dissolution of iron from granite

A biofilm formed on polished thin sections of the granite only showed alteration of magnetite, where holes up to 100 mm in diameter, were formed in the grains. Sterile controls showed no visible change in the appearance of any of the granitic minerals, although there was an increase in the amount of iron in solution compared to that of the active cultures

(Brown *et al.*, 1998a). In flask experiments with magnetite, biotite, hematite and ilmenite, iron was removed from the minerals and transformed into a ferric gel in the media.

Alteration of iron minerals

The interaction of the bacterial consortium with magnetite was investigated further in flask experiments. Samples of crushed magnetite were incubated with bacterial cultures in an iron-free medium. Mössbauer spectrometry and in powder X-ray diffraction patterns showed the consortium was able to mediate the transformation of 11% of the iron in magnetite into hematite within three weeks. No hematite was found either in the original magnetite or in duplicate sterile controls (Brown and Sherriff, 1997). Previously research had found that magnetite is transformed abiotically to hematite (α-Fe_2O_3) via maghemite (γ-Fe_2O_3), usually by cation transfer in the solid state. However, we have not found maghemite in our bacterial alteration.

Precipitation of iron

Further reactions of this microbial consortium were studied in a series of flask experiments. The first observation was that the bacteria lowered the Eh to below -300 mV, and raised the pH to over 8.5. After three days the microbial culture precipitated iron from media containing ferric ammonium citrate. In the sterile controls it has proved impossible to precipitate iron, even when the pH and Eh were altered to match those of the incubated media.

The iron is initially chelated in solution by the citrate, but microbial activity causes the iron to be precipitated as a mixed ferric/ferrous gel. The relative amounts of Fe(II) and Fe(III) precipitated is determined by the initial ratio of carbon to iron in the media as this controls the metabolic activity of the consortium. Once the iron is precipitated, more iron is reduced to the ferrous state due to the metabolic activity, and it remains reduced so long as the organisms are active.

This biologically precipitated iron (both ferrous and ferric) were aged for 12 weeks under varying oxygenic conditions at 80 and at 4°C to simulate low temperature diagenesis; the gels and products were monitored using Mössbauer spectroscopy. The ferrous precipitate remained reduced except under air at 80°C when it formed fine-grained hematite. The more oxic precipitate formed ferrous hydroxide at 4°C and hematite at 80°C (Brown *et al.* 1998b).

Iron was precipitated chemically by neutralizing 0.4M $FeCl_3$ solution with NaOH. When consortium organisms were present during aging, fine-grained hematite was formed at both 80 and 4°C. However, when the chemically precipitated iron was aged without organisms under sterile conditions at 80°C, goethite was formed; this is the only time we have seen the formation of geothite.

Microscopic observation

We have investigated our iron-precipitating biofilm by a variety of light and electron microscopic techniques. No one microscopic method by itself was able to provide complete information, but the integration of complementary light and electron techniques give a more complete analysis than any one procedure alone. Observation of the active organisms in hydrated samples by light microscopy, particularly differential interference contrast episcopic Normarski microscopy (DIC), gave an insight into the dynamic biomineralization that occurs within the biofilm. SEM proved to be useful in viewing the detail of the initial bacterial attachment to the mineral surface before the biofilm extracellular polymeric substances (EPS) become established. Transmission electron microscopy (TEM) showed the iron precipitate to be disseminated throughout the EPS, as well as on the cell walls and extracellular layers of many of the bacteria. Some of the bacteria had cell walls that became coated with iron, which were visible from the light that was reflected by the iron using the DIC technique. Where the culture contained protozoa, these iron-coated bacteria were the preferential prey of the protozoa, who became encysted after ingesting these bacteria. The encysted protozoa are potentially sites for further iron mineral growth. Where no protozoa were present, the iron was precipitated in a similar manner, but the nucleation sites were on the bacteria that in some cases developed small crystallites.

Conclusion

Our results demonstrate that a microbial consortium is able to remove iron from minerals in granitic rock, change magnetite into hematite, as well as precipitating both ferrous and ferric iron from aqueous solution. The consortium readily produces a EPS-containing biofilm that controls the pH and Eh of the environment. They also appear to be involved in low temperature diagenesis of the precipitated iron. These reactions are all thermodynamically feasible so that in the natural environment the role of the bacteria appears to be an increase the rate of reaction.