Alteration of microbially precipitated iron oxides and hydroxides

D. Ann Brown,1 J. A. Sawicki,2 and Barbara L. Sherriff1,*

1Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada
2AECL, Chalk River Laboratories, Chalk River, Ontario K0J 1J0, Canada

ABSTRACT

Iron oxide and hydroxides can be precipitated from solution with both Fe2+ and Fe3+ states by a microbial consortium enriched from surface water draining a granitic batholith. The Fe2+/Fe3+ ratio of the microbial precipitate is determined by both the initial environment and subsequent diagenesis. To evaluate the thermal aspects of diagenesis, biological precipitates, either largely Fe2+ or equally divided between Fe2+ and Fe3+ states, were heated at 80 °C for 12 weeks, under various redox conditions and compared to samples maintained under the same conditions at 4 °C. Mössbauer spectroscopy showed the iron oxide and hydroxides precipitated as Fe2+ to be more stable than that as Fe3+. Only under air at 80 °C are the ferrous minerals altered to hematite, while the more labile ferric minerals are altered to Fe(OH)2 at 4 °C and to hematite at 80 °C. In contrast, chemically precipitated Fe compounds, when incubated with the consortium, only form Fe3+ compounds, mainly fine-grained hematite. When no microbes are present, goethite is formed during diagenesis. Fe speciation in sediments may reflect a combination of microbial mediation that causes the initial precipitation of iron oxides and hydroxides and the subsequent conditions of the diagenetic processes characteristic of that particular depositional environment.

INTRODUCTION

Microorganisms play an important role in the natural environment by determining the speciation of Fe; they can also cause considerable Fe accumulation through biomineralization. For heterotrophic bacteria to grow they must have access to organic matter, and even in oligotrophic waters containing few nutrients, some microbial oxidation of organic material will take place. Such organisms obtain their energy by electron transfer from a reduced species to an oxidized one. Oxygen is the preferential electron acceptor, but where it is not available, inorganic compounds are utilized instead (Stumm and Morgan 1981). The most common electron acceptor in the natural environment is Fe, and because of its widespread abundance, groundwaters are generally reduced due to the activity of the Fe-reducing bacteria.

Ehrenberg (1836) was the first to put forward the suggestion that biological processes were important in the deposition of Fe-rich sediments. In 1888, Winogradsky showed that a bacterium, Leptothrix, was only able to live and grow where Fe2+ was present in solution. Harder and Chamberlin (1915) suggested that, although the precipitation of FeOOH from solution during the deposition of Fe-formations could be purely chemical, it was much more likely to have been caused by “well-known iron bacteria.” However, Fe precipitation was regarded by most geologists as a chemical process, so at that time the idea that it could be due to biological processes was not generally accepted (Starkey and Halvorson 1927), and even when microorganisms were thought to be involved, their action was considered to be non-specific (Lovley 1995). It has never been demonstrated that the widespread reduction of Fe3+ to Fe2+ in nature could be mediated by chemical means alone. Indeed, Lovley (1991) has shown that actual contact with the bacterial cell is required for enzymatic reduction to occur. More importantly, it has become apparent that most, if not all, of the Fe reduction occurring in natural waters is microbially mediated (Schwertmann and Taylor 1989; Lovley 1991, 1995). Microbial metabolic reactions therefore have a widespread influence on the geochemistry of natural waters.

In oligotrophic terrestrial waters bacteria generally live as consortia that form biofilms preferentially at rock/water interfaces. A biofilm is a layer of slime that comprises extracellular polymeric substances (EPS), often polysaccharides, that are excreted by the consortium (Costerton et al. 1994). Individual species of the consortium are arranged so that each one can contribute most efficiently to the biofilm ecosystem and, as a result, few free-living microorganisms are found in oligotrophic waters. Both the cell walls and the EPS in the biofilm are negatively charged so that positively charged metal ions, such as Fe2+ and Fe3+, are adsorbed onto their surfaces. These metal ions may then act as nucleation sites for the deposition of further minerals from solution (Beveridge and Fyfe 1985).