Biomineralization associated with microbial reduction of Fe$^{3+}$ and oxidation of Fe$^{2+}$ in solid minerals

Gengxin Zhang,1,# Hailiang Dong,1† Hongchen Jiang,2 Ravi K. Kukkadapu,3 Jinwook Kim,4 Dennis Eberl,5 and Zhiqin Xu*  

1Department of Geology, Miami University, Oxford, Ohio 45056, U.S.A.  
2Geomicrobiology Laboratory, State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Beijing 100083, China  
3Pacific Northwest National Laboratory, MSIN K8-96, Richland, Washington 99352, U.S.A.  
4Department of Earth System Sciences, Yonsei University, Seoul, Korea  

*Chinese Academy of Geological Sciences, Institute of Geology, Beijing 10037, China

ABSTRACT

Iron-reducing and oxidizing microorganisms gain energy through reduction or oxidation of iron, and by doing so play an important role in the geochemical cycling of iron. This study was undertaken to investigate mineral transformations associated with microbial reduction of Fe$^{3+}$ and oxidation of Fe$^{2+}$ in solid minerals. A fluid sample from the 2450 m depth of the Chinese Continental Scientific Drilling project was collected, and Fe$^{3+}$-reducing and Fe$^{2+}$-oxidizing microorganisms were enriched. The enrichment cultures displayed reduction of Fe$^{3+}$ in nontronite and ferric citrate, and oxidation of Fe$^{2+}$ in vivianite, siderite, and monosulfide (FeS). Additional experiments verified that the iron reduction and oxidation was biological. Oxidation of FeS resulted in the formation of goethite, lepidocrocite, and ferricyanide as products. Although our molecular microbiological analyses detected Thermoanaerobacter ethanolicus as a predominant organism in the enrichment culture, Fe$^{3+}$ reduction and Fe$^{2+}$ oxidation may be accomplished by a consortia of organisms. Our results have important environmental and ecological implications for iron redox cycling in solid minerals in natural environments, where iron mineral transformations may be related to the mobility and solubility of inorganic and organic contaminants.

Keywords: CCSD, iron redox cycling, nontronite, subsurface, Thermoanaerobacter ethanolicus

INTRODUCTION

Iron is the fourth most abundant element and one of the most dominant redox active metals in the Earth’s crust. Depending on environmental conditions, iron can form stable minerals in both the divalent and trivalent state. Iron cycling depends on redox reactions that are driven by both abiotic and biotic factors, which often result in precipitation and dissolution of Fe-bearing minerals. Coupled with the carbon, nitrogen, phosphorous, and sulfur cycles (Petsch and Berner 1998; Berner et al. 2003), microbial activity can mediate the iron cycle (Fortin and Langley 2005; Kappler and Straub 2005; Lovley 2000a). Microorganisms can gain energy by reducing Fe$^{3+}$ with either organic acids or H$_2$ as electron donors (Lovley 1993; Nealson and Saffarini 1994) or oxidizing Fe$^{2+}$ with either O$_2$ (Kappler and Newman 2004; Kappler and Straub 2005; Neubauer et al. 2002) or nitrate (Benz et al. 1998; Kappler and Straub 2005) as electron acceptors. Numerous Fe$^{2+}$-reducing microorganisms have been isolated and characterized (Lovley 1993, 2000a). Whereas it is now well established that diverse microorganisms are capable of reducing both aqueous and solid Fe$^{3+}$ in near-surface and subsurface environments (Liu et al. 1997; Lovley and Chapelle 1995; Lovley et al. 1996; Roh et al. 2002; Zhang et al. 2007a, 2007b), the microbial role in Fe$^{2+}$ oxidation requires further investigation. Although aerobic oxidation of Fe$^{2+}$-bearing minerals by acidophiles has been recognized for many years (Ghirose 1984; Harrison 1984; Straub et al. 2001), nitrate-dependent, phototrophic Fe$^{2+}$ oxidation was discovered only recently (Kappler and Newman 2004; Kappler and Straub 2005). In those studies, certain phototropic and nitrate-reducing bacteria have been demonstrated to be capable of utilizing Fe$^{2+}$ as an electron donor coupled with reduction of CO$_2$ and nitrate, respectively. The role of anaerobic Fe$^{2+}$-oxidizing bacteria in iron cycling has recently become a subject of intense investigation (Fortin and Langley 2005; Kappler and Straub 2005; Roden et al. 2004; Straub et al. 2001, 2004; Weber et al. 2006). A recent study reported that a single bacterial species (Desulfotibacterium frappieri) was capable of both reducing Fe$^{3+}$ with H$_2$ as an electron donor and oxidizing Fe$^{2+}$ with nitrate as an electron acceptor (Shelobolina et al. 2003). Clearly, such microbially mediated iron cycling is