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Fe(II) oxidation processes at the surface of bacterially colonized iron deposits

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ABSTRACT

Fe(II) oxidation processes at the surfaces of bacterially colonized iron deposits are examined at three hot springs in Japan for which the chemical profiles of the pH, redox, and O_2 and Fe(II) concentrations at the water/deposit interface are measured via microelectrodes. The three hot springs share similar bulk chemistry with a weakly acidic pH of 5.7–6.3, a high iron concentration of 50–130 μM, and a high dissolved inorganic carbon concentration of 20–60 mM. At the Sambe and Shionoha hot springs where the bulk water O_2 concentration is ca. 80 μM, abiotic Fe(II) oxidation via autocatalysis prevails. At the Okuoku-hachikurou hot spring where the bulk water O_2 concentration is ca. 50 μM, autocatalytic Fe(II) oxidation is suppressed and biotic Fe(II) oxidation induced by cyanobacterial photosynthesis is effective. These observations indicate that an O_2 concentration of ca. 50 μM is the threshold of reversing the relative contribution of biotic and abiotic Fe(II) oxidation. Protons from Fe(II) oxidation are compensated by reactions among the dissolved inorganic carbon species, which sustain the pH condition and continuous Fe(II) oxidation at the deposit surface. The observations of this study provide implications for understanding the deposition of banded iron formations in the geological past.

1. Introduction

Banded iron formations (BIFs) were deposited 3.8–0.8 billion years ago (e.g., Klein and Beukes, 1992) and provide important information for understanding the evolution of early life and Earth environments. One of the primary minerals leading to BIF deposition is thought to be the hydrated amorphous Fe(III) phases (Klein, 2005), and several processes have been proposed for the oxidation of Fe(II) to Fe(III) (e.g., Chan et al., 2016a; Konhauser et al., 2007; Koehler et al., 2010; Posth et al., 2013; Trouwborst et al., 2007). Abiotic processes include photooxidation via ultraviolet light without using oxygen, while biotic processes include 1) indirect oxidation by oxygenic phototrophs (cyanobacteria), 2) direct oxidation by anoxygenic phototrophs (green and purple bacteria) without using oxygen, and 3) direct oxidation by chemolithoautotrophs (iron-oxidizing bacteria; FeOB) using oxygen. Although the actual oxidation process of indirect Fe(II) oxidation is abiotic (i.e., non-enzymatic Fe(II) oxidation using oxygen produced by cyanobacteria; Chan et al., 2016a; Swanner et al., 2015; Trouwborst et al., 2007), it can be regarded as a biotic process sensu lato in case that Fe(II) oxidation is caused by elevated oxygen concentration at the cyanobacterial vicinity.

Of these, Fe(II) oxidation processes via ultraviolet light and anoxygenic phototrophs are potentially important for depositing BIFs prior to the emergence of oxygenic phototrophs, even though the former process is thought to have been limited in ancient seawater settings (Kappler et al., 2005; Koehler et al., 2010; Konhauser et al., 2002, 2007; Posth et al., 2013). After the emergence of oxygenic phototrophs, it has been traditionally assumed that the indirect Fe(II) oxidation process via metabolically released oxygen was important for BIF deposition (Cloud, 1973; Klein and Beukes, 1989). However, significant contributions of direct microbial processes by chemolithoautotrophs inhabiting the microaerobic ocean (Chan et al., 2016a; Holm, 1989) and anoxygenic phototrophs inhabiting the anoxic niche (Kappler et al., 2005) have been suggested for Fe(II) oxidation in ancient oceans. Indeed, it has been suggested that most of the iron in BIFs is explained by their metabolic processes, even during the periods of maximum BIF deposition (Chan et al., 2016a; Kappler et al., 2005; Konhauser et al., 2002).

It is thought that most BIFs were deposited in the deeper parts of ocean basins (water depth of about > 200 m) because they commonly exhibit fine lamination (and/or microbanding) and lack detrital components (Klein, 2005; Posth et al., 2013). Biotic Fe(II) oxidation

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processes potentially involved in such BIFs were direct/indirect oxidation by planktonic bacteria: Fe(II) was mainly oxidized in the water column and the resulting Fe(III) minerals settled out uniformly on the basin scale (Koehler et al., 2010; Posth et al., 2013). Conversely, BIFs of about 2.2–1.8 Ga are thought to have been deposited in shallow oceans due to their granular textures (Klein, 2005). Biotic processes potentially involved in such BIFs were direct and indirect oxidation by benthic bacteria: Fe(II) was mainly oxidized at the surface of the deposits consisting of benthic bacteria and Fe(III) minerals (i.e., iron-depositing microbial mats). Indeed, Planavsky et al. (2009) investigated iron formations of about 1.9 Ga and suggested that FeOB prevailed in the benthic microbial communities in the Paleoproterozoic shallow oceans.

To verify the depositional models of shallow-ocean BIFs, information from modern analogs is essential. Although there are several studies about biotic Fe(II) oxidation processes by modern benthic bacteria (Druschel et al., 2008; Emerson and Revsbech, 1994b; Kikuchi et al., 2016; Roden et al., 2012; Trouwborst et al., 2007), many of them have focused on the microbial Fe redox cycle inside the sediments, which is potentially related to the early diagenesis of BIF. To understand the Fe (II) oxidation processes at deposit surface, it is particularly important to evaluate the influence of a diffusive boundary layer (DBL; Jørgensen and Revsbech, 1985) developing there, because 1) it potentially affects the Fe(II) oxidation processes by establishing chemical gradients within DBL and 2) the consumption/production of dissolved components including Fe(II) can be estimated using these gradients (Fig. 1; see also below). Therefore, this study investigates the Fe(II) oxidation processes at the water/deposit interface of bacterially colonized iron deposits developing at three hot springs in Japan (the Sambe, Shionoha, and Okuoku-hachikurou hot springs), for which chemical profiles of the pH, redox, and O_2 and Fe(II) concentrations within DBL were measured via microelectrodes. Because these deposits are developing under shallow and microaerobic conditions, they would provide insights especially into interpreting the shallow-water BIFs deposited during the ocean oxygenation.

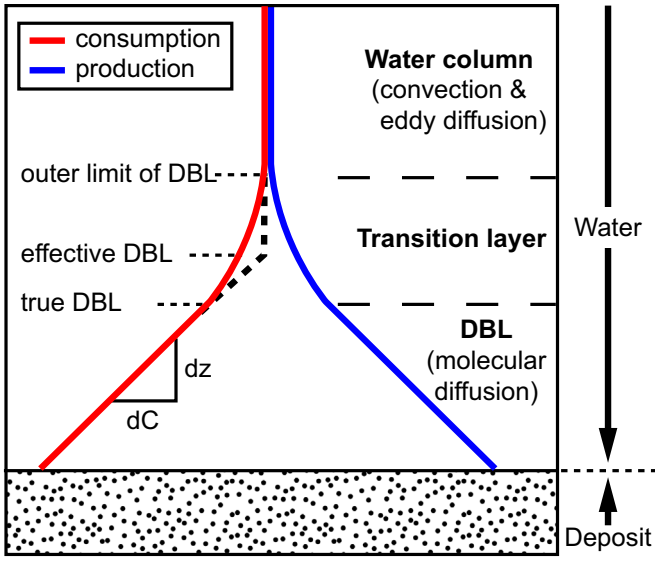

Fig. 1. Schematic figure showing the chemical gradients around the water/deposit interface. Red and blue lines represent consumption and production profiles, respectively. Consumption/production flux is calculated using the concentration gradient (dC/dz). Thickness of DBL primarily depends on the flow velocity, which was ca. 300 μm under the experimental conditions of this study. Modified after Jørgensen and Revsbech (1985). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Geological settings and study samples

2.1. The Sambe hot spring

The Sambe hot spring (35°7′ 18″ N, 132°37′ 36″ E; Fig. 2A) is located approximately 1 km SSE from the summit of Mt. Sambe, an active volcano. Iron- and manganese-rich hot water with trace amounts of dissolved oxygen discharge from dacitic volcaniclastic rocks (Ando, 1959). At the vent site, orange-colored deposits consisting primarily of ferrihydrite are developed on a cement construction (Fig. 2B) and are inhabited by a microbial community including FeOB (phylotypes related to *Gallionella* spp.) with a few cyanobacteria (Mitsunobu et al., 2012, 2013). These orange-colored deposits were selected as the study samples. The field investigation at this hot spring was conducted in November 2014.

2.2. The Shionoha hot spring

The Shionoha hot spring (34°15′ 43″ N, 136°2′ 27″ E; Fig. 2A) is located at the intersection of two faults, the Butsuzo Tectonic Line and the Shionoha fault. Iron- and calcium-rich hot water without detectable dissolved oxygen discharges from a borehole penetrating the Jurassic–Cretaceous accretionary complex, and the heat source of the water is assumed to be fluid dehydrated from the mantle (Umeda et al., 2004; Takashima and Kano, 2005). At the vent site, red-colored deposits consisting primarily of ferrihydrite and calcite are developed on a container (Fig. 2C) and are inhabited by a microbial community including FeOB (phylotypes related to *Sideroxydans* spp.; Takashima et al., 2008). Accompanying deposits exhibit green and light green colors reflecting the relative abundance of cyanobacteria. The red- (site A), green- (site B), and light green- (site C) colored deposits were selected as the study samples. The field investigation at this hot spring was conducted in July 2016.

2.3. The Okuoku-hachikurou hot spring

The Okuoku-hachikurou hot spring (40°24′ 26″ N, 140°45′ 22″ E; Fig. 2A) is located approximately 7 km WSW of Lake Towada, a caldera lake associated with an active volcano. Iron- and calcium-rich hot water without detectable dissolved oxygen discharges from a borehole penetrating rock related to a submarine volcano (basaltic–andesitic–dacitic lava layers with tuff and mudstone; Hirano et al., 2009; Takashima et al., 2011). At the vent site, red-colored deposits consisting primarily of ferrihydrite and aragonite are developed (Fig. 2D) and are inhabited by a microbial community including cyanobacteria (phylotype related to *Leptolyngbya* sp.), purple bacteria (phylotype related to *Rhodobacter* sp.), and FeOB (phylotypes related to *Sideroxydans* spp.; Takashima et al., 2011). These red-colored deposits were selected as the study samples. The field investigation at this hot spring was conducted in June 2015.

3. Methods

3.1. Characterization of iron deposits

To characterize the iron deposits investigated in this study, X-ray diffraction (XRD) analysis were conducted. The surface part (ca. 5 mm) of iron deposits were air-dried, powdered using a mortar and pestle, and analyzed using a powder X-ray diffractometer with CuKα radiation (40 kV, 40 mA) and a graphite monochromator (MultiFlex, Rigaku).

In addition, vertical sections of the iron deposit surfaces were observed using thin sections. Deposit samples were first fixed using phosphate-buffered saline (PBS) containing 3.7% formaldehyde for 2 days, after which the solution was replaced with 50% ethanol in PBS and the sample was stored at 4 °C until further processing. Thin sections were then prepared from resin-embedded samples, as described