Mineralogical characterization and formation of Fe-Si oxyhydroxide deposits from modern seafloor hydrothermal vents

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ABSTRACT
We have studied mineralogical characteristics of Fe-Si oxide precipitates from hydrothermal fields of the Valu Fa Ridge, Lau Basin, especially the role that the neutrophilic Fe-oxidizing bacteria played in their formation, using various analytical techniques (XRD, SEM, EPMA, TG/DTA, and FTIR). According to this examination, the Fe-Si oxide formation can be divided into two stages. At the initial stage, the Fe-oxidizing bacteria bound and oxidized Fe$^{2+}$ into Fe$^{3+}$ to fix CO$_2$, triggering precipitation of Fe-oxyhydroxide (ferrihydrite) and construction of a loose network of Fe-rich filaments. Subsequently, the decreased porosity of the network resulting from the gradual growth of the filaments led to a decline in the mixing between seawater and the hydrothermal fluids. Then the conductive cooling of the network resulted in saturation of the dissolved Si with respect to amorphous silica. As a result, significant precipitation of opal-A occurred through inorganic polymerization. However, part of the silica was immobilized by bonding to Fe-OH functional groups and yielded unpolymerized silica, which is characterized by Fe-O-Si bond. Owing to the incorporation of Si into the ferrihydrite structure and its adsorption on the ferrihydrite surface, the modern hydrothermal Fe-Si oxides are thermally stable. DSC measurements indicate the full segregation of cristobalite from hematite at about 800 °C in an O$_2$ atmosphere. These observations indicate that primary alternating Si- and Fe-rich layers may be absent in the Archean ocean and that alternating bands in BIFs represent a diagenetic process; our work thus provides a potential clue that can be used to unravel the precipitation and diagenetic mechanisms of Precambrian banded iron formations (BIF).

Keywords: Lau Basin, hydrothermal Fe-Si oxides, banded iron formations, neutrophilic Fe-oxidizing bacteria

INTRODUCTION
Fe-Si oxide/oxyhydroxide (hereafter referred to as Fe-Si oxide) is identified as a common constituent of modern seafloor hydrothermal vent systems. It occurs as chimneys, irregularly shaped edifices, mounds and interstitial precipitates filling cracks between lava flows (Hekinian et al. 1993). Following the discovery of modern hydrothermal vents in late 1970s (Corliss et al. 1979), Fe-Si oxide precipitates have been documented in hydrothermal systems globally. Previous studies have shown that Fe-Si oxide precipitates are favored by relatively low temperatures (<100 °C) in chimney structures and under diffuse flow conditions. This type of precipitate is probably comprised of amorphous silica and poorly crystalline phases of which ferrihydrite is the most pervasive. Sometimes crystalline iron-rich silicates such as nontronite are also found in these precipitates. Fe-Si oxide deposits are now considered to be a result of either hydrothermal plume fallout of Fe-Si oxyhydroxide precipitates or the mass wasting and erosion of primary submarine massive sulfides. Textural and molecular biological evidences also suggest that microorganisms (for instance iron-oxidizing bacteria) are essential in both these processes (e.g., Boyd and Scott 2001; Edwards 2004; Edwards et al. 2003, 2011; Little et al. 2004; Kato et al. 2009; Langley et al. 2009; Toner et al. 2009).

Three main neutrophilic Fe-oxidizing bacteria have been identified by molecular analysis from modern hydrothermal Fe-Si oxyhydroxide deposits (Emerson et al. 2007; Davis and Moyer 2008; Hodges and Olson 2009; Kato et al. 2009; Langley et al. 2009). Although abiotic mechanisms for Fe-Si filament formation have been proposed (Hopkinson et al. 1998) and similar structures of filaments have even formed under abiotic conditions (Garcia-Ruiz et al. 2002, 2003), several questions still remain unsolved. For example, abiotic mechanisms alone cannot explain the formation of hollow cylinders in the Fe oxides, the straight, twisted and branching morphologies of the filaments, the internal septate structures and the occurrence

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