Speciation of iron in natural and synthesized Bacteriogenic Iron Oxides (BIOS) using XAFS and μ-XRF-XAFS

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Speciation of Fe in natural and synthesized bacteriogenic iron oxides (BIOS) was studied using XAFS, μ-XRF-XAFS, SEM and EPMA. Natural BIOS were collected at 2 sampling sites: seafloor at Mariana trough and from groundwater stream discharged at Sambe Hot Spring in Shimane Prefecture. BIOS was synthesized using a diffusion cell which consists of two cells that are separated by a membrane. Anoxic and oxic conditions were created in each cell to simulate the appropriate condition to BIOS precipitation in natural environment. Chemoautotrophic iron-oxidizing bacterium (*Mariprofundus ferrooxydans* [1]) or heterotrophic iron-oxidizing bacterium (*Leptothrix discophora* [2]) were cultured in the oxic cell.

SEM and EPMA analysis suggested similar precipitation morphology to all samples where iron oxides precipitated around bacterial-induced organic materials. Although each natural BIOS were precipitated in different environment, the XAFS spectra exhibited similar structures. Synthesized BIOS also showed spectra similar to natural samples regardless of the species of iron oxidizing bacteria and the medium employed in culture. In addition, μ-XAFS spectra collected at several Fe-precipitated area within few micro scale in the stalk were approximately identical, which is consistent with our bulk XAFS results of natural and synthesized BIOS. These results suggest that minerals presented in BIOS were homogeniously distributed in micrometer scale. The liniar combination fitting suggested that ferrihydrite is one of the Fe species in BIOS. It is also implied that Fe-carboxylate complex or Fe (III)-phosphate is a second Fe species of BIOS. These results will provide better insights into understanding the role of BIOS in the migration of trace elements in natural waters.

[1] Emerson D. *et al*. (2007) *PLoS ONE* **2**,e667. [2] Plam C. *et al*. (1992) *Appl. Environ. Microbiol*. **58**, 450-454.

Origin of ultramafic rocks from Hero Fracture Zone, Antartic

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Serpentinites are rocks composed predominantly of the serpentine minerals, lizardite, chrysotile, or antigorite that form through hydrothermal alteration of peridotite. Substantial exposures of serpentinized peridotites are commonly found in fracture zones and in slow spreading mid-ocean ridge settings. Serpentinites from the Hero Fracture Zone, Drake Passage, Antarctica, contain serpentine, amphibole, talc, chlorite, and magnetite as well as relict olivine, pyroxene, and spinel from a spinel peridotite precursor. Two episodes of serpentinization are recognized. The initial serpentinization event resulted in material that contains relatively abundant relict minerals and small amount of lizardite and antigorite. This event resulted from seawater infiltration at about 178 - 283 °C seawater and a water/rock ratio less than 5. The second serpentinization event resulted in a material highly enriched in serpentine. This second event was caused by seawater infiltration at 170 - 298 °C and a water/rock ratio in excess of 5. The buoyant serpentinite ridge model is invoked to explain the ascent of serpentinite from the upper mantle to the surface. Increasing fracturing and seawater infiltration during the process resulted in increasing degrees of serpentinization and decreasing rock density. Buoyant uplift of serpentinite resulted from the contrast in density between serpentinite and surrounding mafic rocks. Some serpentinite rock fragments were detached from the serpentinite during ascent and embedded in oceanic sediment after exposure to the surface.