

## Redox Stability of Aged Biogenic Iron Oxides

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Biogenic iron oxides (BIOS) are defined as a mixture of poorly ordered nanometer aggregates of hydrous ferric oxides (HFO) and bacterial cells. Such small scale aggregates (2-500nm) display large surface area-to-mass ratios making BIOS an effective sorbent of various contaminants, such as heavy metals and radionuclides, in natural environments [1]. Depending on the environmental conditions, poorly ordered HFO (ex. ferrihydrite) tend to transform into more ordered iron oxides such as goethite and hematite. However, according to previous research, the presence of organic matter (ex. bacterial cells) retards the transformation of ferrihydrite into more crystalline iron oxides [2].

Accordingly, the long term stability of BIOS in the environment is unknown. This study examined the chemical and mineralogical composition of sterile BIOS samples collected from wetlands and deep sea vents that were stored in the dark at 4°C for 7 years to simulate early diagenesis. Furthermore, the redox stability of the aged BIOS in the presence of a well known iron reducing bacterium, *Shewanella putrefaciens* CN32, was examined.

Similar to the fresh BIOS, XRD, Fe K-edge EXAFS and chemical extractions indicated that aged BIOS were primarily composed of 2-line ferrihydrite with minor amounts of more crystalline iron oxides, lepidocrocite and goethite. SEM showed the occurrence of twisted stalks and sheaths similar to those of neutrophilic iron oxidizing bacteria *Gallionella* spp. and *Leptothrix* spp., similar to what was observed in the fresh BIOS. However, the reduction rates of aged BIOS were significantly lower than that of fresh BIOS ( $P < 0.05$ ). Further characterization with TEM showed the formation of large iron oxide aggregates in close association of microbial surfaces. Aggregation could have reduced the surface area of bioavailable iron oxides, consequently aggregation may lead to crystal growth and subsequent phase transition may affect the bioavailability of adsorbed contaminants [3].

- [1] Langely *et al* (2009) *Chem. Geol.* **262**, 218-228. [2] Kennedy & Ferris (2004) *Chem. Geol.* **212**, 269-277. [3] Banfield *et al* (2000) *Science* **289**, 751-754.