SPECTROSCOPIC CHARACTERISTICS OF NATURAL BIOGENIC IRON (OXYHYDR)OXIDES FROM FRESHWATER AND MARINE ENVIRONMENTS. Srishti Kashyap[1], Elizabeth Sklute[2], Laura Ross[2], David Emerson[3], Thomas J. Tague Jr.[4], Peng Wang[4], James F. Holden[1], and M. Darby Dyar[2], [1]Dept. of Microbiology, Univ. of Massachusetts Amherst, 639 N. Pleasant St., Amherst, MA 01003, skashyap@umass.edu. [2]Dept. of Astronomy, Mount Holyoke College, South Hadley, MA 01075. [3]Bigelow Laboratory for Ocean Sciences, East Boothbay, ME 04544. [4]Bruker Optics Inc., 19 Fortune Dr. Billerica, MA. 01821, USA.

Introduction: Bacteria are capable of oxidizing various reduced inorganic substrates as energy sources for growth. Among these is Fe(II), which is oxidized to Fe(III) (oxyhydr)oxides (FeOxs) using O_2 as the oxidizing agent [1]. At neutral pH, chemical oxidation of Fe(II) to Fe(III) occurs rapidly in the presence of O_2. To circumvent this problem, Fe(II) oxidizing bacteria (FeOB) require low pO_2 and sustained Fe(II) concentrations. This metabolism has received little attention in natural systems, but is increasingly found in marine and freshwater environments. Examples of these are high iron, low sulfide areas of hydrothermal venting at seamounts or crustal spreading centers and lacustrine environments. Substantial deposits of FeOxs often occur at these sites, and have been shown to contain tubular sheath casts or twisted stalks of iron-oxidizing bacteria. These deposits or mats are intricately organized and often recognized by their distinctive orange-rust colored FeOxs. Yet, very little is known about the spectral properties of the FeOxs produced by FeOB, especially those in natural environments [2].

This project uses several types of spectroscopy to characterize the mineralogy of natural biogenic FeOxs formed by FeOB in two marine iron mats from South Hiolo Ridge, Loihi Seamount and one freshwater iron mat from a water well filter (50 ft. deep). We also studied FeOxs formed by *Mariprofundus* sp. strain DIS-1, a common FeOB in microbial iron mats found at Loihi Seamount [3], for comparison with natural samples. Systematically characterizing Fe mineralogy using complementary spectroscopies in this manner will improve our fundamental understanding of biogenic FeOx precipitation and the influence of primary morphotype (sheath or stalk) on mineral formation. This work will eventually assist in interpreting Fe microfossils and biosignatures in the rock record.

Methods: Four samples (Table 1) were used in this study. A pure culture of *Mariprofundus* DIS-1 was obtained from growth of cells on zero-valent iron under microaerobic conditions as described in [4]. All samples were 'live' (not fixed) and stored as fluids at 4° C until preparation for spectroscopic analysis. Samples were vacuum-filtered just prior to spectral analyses. Raman analysis was performed at Bruker Optics Inc. on a Bruker Senterra Raman microscope using a 20× objective and 532 nm excitation laser powered to either 0.2 or 2 mW depending on the sensitivity of the samples to heat transformation. Fourier transform infrared (FTIR) attenuated total reflectance (ATR) spectra were acquired at Bruker Optics Inc. on a Bruker Vertex 70 FTIR using a diamond ATR accessory, ultra-wide range beamsplitter, and wide range DTGS detector. Visible and near infrared (VNIR) spectra were collected at Mount Holyoke College (MHC) on an ASD Fielspec 4 Max spectrometer with incidence and emission angles set to 30° and 0°, respectively. Mössbauer spectroscopy at MHC used a WEB Research Co. (now See Co.) W100 spectrometer (50–30 mCi ^{57}Co in Rh; referenced to α-Fe foil).

Table 1. Samples used for spectroscopy

Sample Name/Site	Mat Type
Freshwater iron mat, water well (50ft)	Sheath-rich
South Hiolo Ridge, Loihi Seamount (J2 675-SC6B)	Stalk-rich
South Hiolo Ridge, Loihi Seamount (J2 675-SS Yellow)	Sheath-rich
Mariprofundus sp. strain DIS-1	Stalk-rich

Results: FTIR spectra of J2 675-SS yellow and J2 675-SC6B (**Figure 1**) are similar in appearance to ferrihydrite below 500 cm^{-1} but the positions of the absorptions are shifted to higher wavenumbers. These two samples also show an absorption at ~600 cm^{-1} that is reminiscent of akaganéite, along with multiple absorptions in the 1600-900 cm^{-1} range that may be due to hydration, phosphate, amide, and carbonate groups [5]. The iron mat sample is a closer match to ferrihydrite and lacks the prominent absorption features of the J2 675 samples at ~950 cm^{-1}. DIS-1 is a complex mixture with clear evidence of lepidocrocite and features likely due to ferrihydrite and possibly hematite.

VNIR spectra (**Figure 2**) of J2 675 and iron mat samples are similar, with hydration features close in position and appearance to ferrihydrite, but with a VIS maximum and a $^6A_1 \rightarrow {}^4T_1$ Fe^{3+} spin-forbidden crystal field absorption much closer to those of goethite or akaganéite. DIS-1 has a slightly longer wavelength $^6A_1 \rightarrow {}^4T_1$ transition and also a $^6A_1 \rightarrow {}^4T_2$ similar to goethite, lepidocrocite, or hematite. No sample shows the characteristic akaganéite absorption at ~2.45 μm.

Raman spectra (**Figure 3**) show the poorly crystalline nature of the J2 675 and iron mat samples, all of which have one broad absorption similar to ferrihydrite. DIS-1, however, is a closer match to lepidocrocite.

Mössbauer spectra mirror and corroborate other results. The J2 675 and iron mat samples all resemble ferrihydrite. DIS-1 (**Figure 4**) is a complicated mixture of multiple phases, likely including unreacted zero-

valent iron, ferrihydrite, lepidocrocite, and perhaps akaganéite.

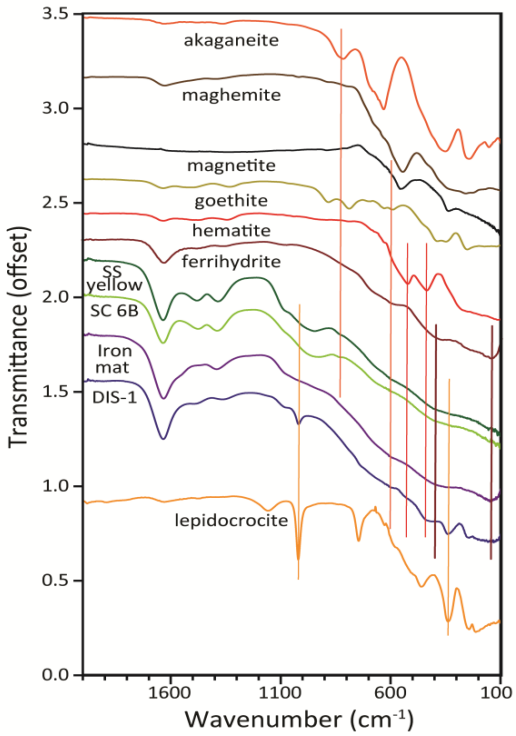

Figure 1. FTIR spectra of biogenic Fe(III) samples with nanophase FeOxs for reference. Vertical lines mark absorptions of references and are color-coded by mineral.

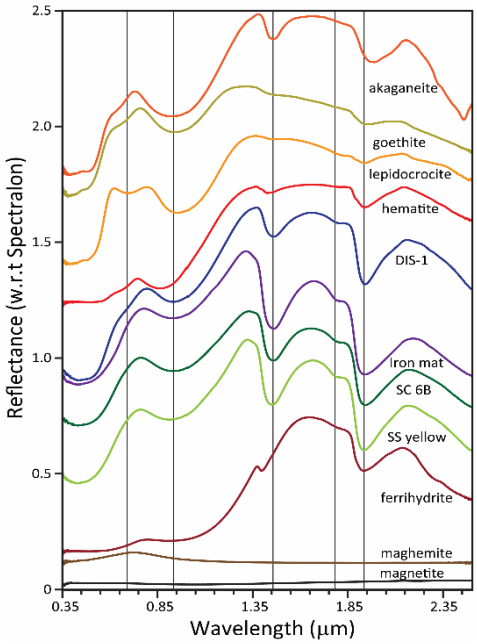

Figure 2. VNIR spectra of biogenic Fe(III) samples with nanophase FeOxs for reference. Vertical lines mark prominent absorptions for biogenic samples.

Implications: Bio-oxidized natural samples are spectrally distinct from synthetic nanophase iron (oxy-hydr)oxides. The differences can result from production of mixed phases and organic inclusions, which may be indicative of distinctive biosignatures. Ideally, multiple spectroscopic methods are needed to characterize bioreduced minerals associated with these iron-oxidizing microbes.

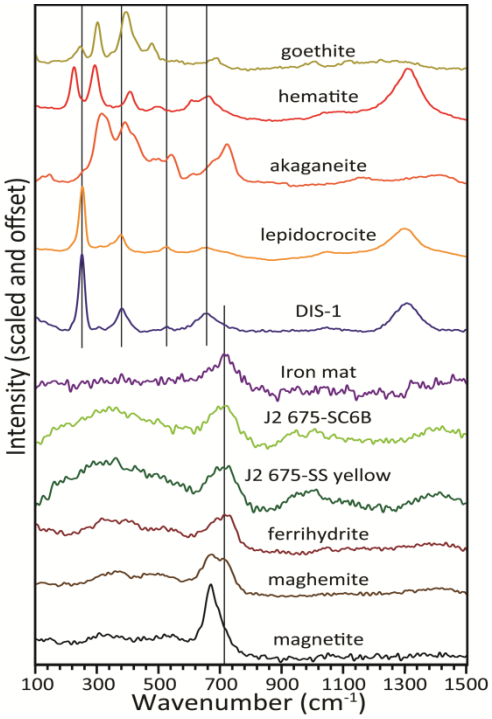

Figure 3. Raman spectra of biogenic Fe(III) samples with nanophase FeOxs for reference. Vertical lines mark prominent absorptions for biogenic samples.

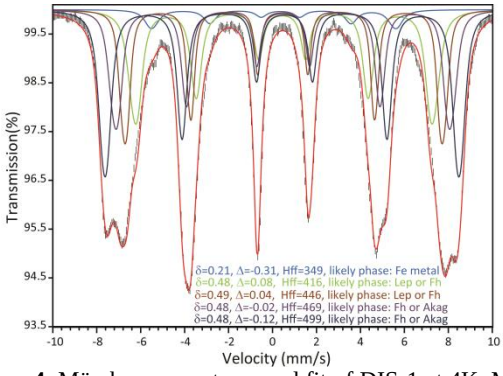

Figure 4. Mössbauer spectrum and fit of DIS-1 at 4K. Mössbauer fit parameters and likely phases color coded by distribution. Center shift (δ) and quadrupole splitting (Δ) are in mm/s and hyperfine field (Hff) is in kOe.

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