SPECTRAL EVOLUTION OF BIOREDUCED FERRIHYDRITE BY HYPERTHERMOPHILES. E. C. Sklute[1], S. Kashyap[2], J. F. Holden[2], and M. D. Dyar[1], [2]Mount Holyoke College, Dept. of Astronomy, South Hadley, MA, 01075, [2]University of Massachusetts, Amherst, Dept. of Microbiology, Amherst, MA. 01003, ecsklute@mtholyoke.edu.

Introduction: It is likely that any putative life on Mars, past or present, is microbial. Yet finding distinct evidence of that life is challenging because all organic signatures may have been lost. Thus, understanding mineralogy associated with microbial activity is important as it could reveal and identify extinct or extant life in extraterrestrial environments. Microorganisms that reduce Fe^{3+} oxide minerals to form other iron oxide minerals are among the more favorable organisms to study for microbial mineral transformations. Hyperthermophiles (T_{opt} >80°C) occupy the deepest and least evolved branches in the phylogenetic tree of life [1], and thus may represent extraterrestrial life elsewhere.

Most of what is known about microbial Fe^{3+} reduction has been established for mesophiles rather than the hyperthermophiles, and the analytical tools used are often incompatible with extraterrestrial capabilities. Here, we characterize biogenic minerals produced by hyperthermophilic Fe^{3+} reduction through a combination of instrumentation that could reasonably appear on remote or landed missions. We critically examine how sample preparation techniques influence end products of these transformations to enable understanding of how signatures on Mars may differ from laboratory spectra and how those signatures change with time.

Methods: Ferrihydrite was synthesized [2] and stored as a liquid suspension to maintain mineral-fluid surface properties. *Pyrodictium* sp. Su06 was grown [3] using four variations for each experiment to add controls to the study: 1) a sample with no cells added (but with growth medium and oxide) left at room temperature (RT); 2) a sample with no cells incubated at 90º C; 3) a sample with cells left at RT; and 4) a sample with cells incubated at 90 ºC. Growth and Fe^{2+} were determined [4] and transformed mineral products were characterized using mid-infrared attenuated total reflectance (Thermo Fisher Nicolet 6700 FTIR, 256 scans per spectrum), visible near infrared (ASD Fieldspec3 Max), and Raman (WiTec alpha300R confocal imaging system; 532 nm Nd YAG laser; 50X; 360 1-sec. integrations) spectroscopies as well as transmission electron microscopy (TEM; Philips CM 100, tungsten filament, 80KV). Mössbauer (See-Co.W100; 50-30 mCi ^{57}Co in Rh; referenced to α-Fe foil) spectra were acquired for both freeze-dried samples (initially frozen samples dehydrated under vacuum at RT) as well as frozen suspensions.

Results: In all cases, ferrozene assays showed that that Fe^{2+} resides in or on the mineral phase. Yet Mössbauer results show that the freeze-dried sample has >10% $Fe^{2+,}$ where the frozen sample has at least 23%.

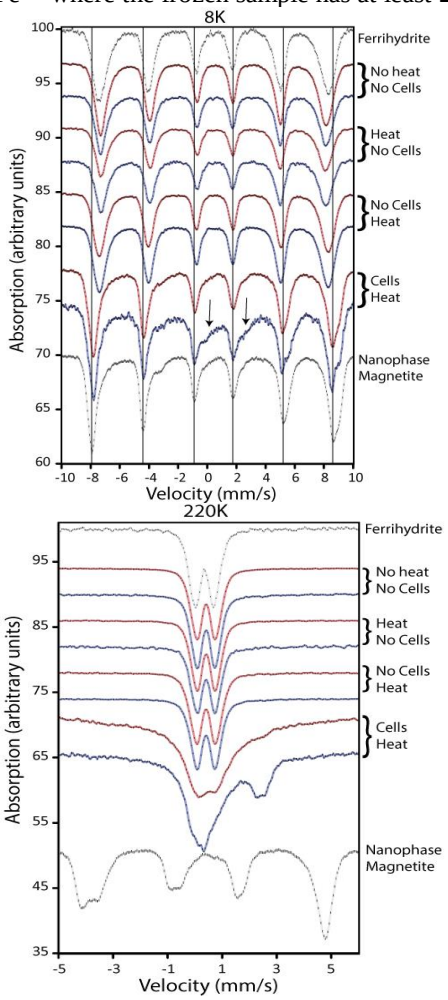

Figure 1. Mössbauer spectra of frozen (blue) and freeze dried (red) bioreduced samples and controls.

Conclusions: These results indicate that even under vacuum, bioreduced samples may oxidize during drying. Alternatively, the solutions phase may create an energetically different coordination environment for a percentage of the iron in these samples. These represent two possible spectral signatures of microbial life.

References: [1] Woese, C. R. *et al.* (1990) *Proc. Natl. Acad. Sci.* , *87*, 4576-4579. [2] Sklute, E. C. *et al.* (2016) *LPSC XXXXVII*, Abstract #2112. [3] Kashyap, S. *et al.* (2016) *LPSC XXXXVII*, Abstract #2192. [4]] Lin, T. J. *et al.* (2014) *Geobiol.*, *12*, 200-211.