In Search for Life Elsewhere in our Solar System: Characterizing Transformations of Iron Oxides by Hyperthermophiles. S. Kashyap[1], E. C. Sklute[2], M. D. Dyar[2], J. F. Holden[1], [1]Department of Microbiology, University of Massachusetts, Amherst, MA 01003 (Email: skashyap@umass.edu), [2]Department of Astronomy, Mount Holyoke College, South Hadley, MA 01075 USA.

Introduction: Fe(III) is a widely available electron acceptor in many mildly-reducing deep-sea hydrothermal vents and terrestrial hot springs. Dissimilatory iron reduction, or the extracellular reduction of Fe(III) to Fe(II), is an integral biogeochemical process at these sites. It may have also been an important process on early Earth and could potentially serve as means for supporting life elsewhere in the Solar System [1].

Most of what is known about microbial Fe(III) reduction, however, has been established for mesophiles rather than the hyperthermophiles that are found in hot environments. Hyperthermophilic archaea occupy the deepest and least evolved branches of the tree of life, and as a result are believed to be most closely related to the last universal common ancestor [2]. Here, we examine the rates and constraints of Fe(III) bioreduction by hyperthermophilic archaea to address the iron oxide minerals that are favored for growth, the kinetics of such reactions, and the mineral transformations that occur depending upon the electron acceptor. Evaluating the reactants and products of microbial iron reduction will shed light on the relevant geochemistry needed to sustain and detect life on Earth and elsewhere.

Bioavailability of Iron Oxides: Iron oxides are mineralogically diverse, and not much is known about the factors that constrain the reduction capacity of different iron oxides by hyperthermophiles. To begin addressing this gap, our study determined the types of environmentally-relevant nanophase iron oxides that favored growth of two model hyperthermophilic organisms – *Pyrodictium delaneyi* and *Pyrobaculum islandicum.* We synthesized six different nanophase iron oxides: 2-line ferrihydrite, lepidocrocite, akaganéite, goethite, hematite and maghemite [3]. We examined cell growth and Fe(II) production rates of *P. delaneyi* and *P. islandicum* on the different oxides at 90°C and 95°C, respectively. All oxides used in this study were kept in solution to maintain fluid-mineral surface properties.

Both organisms were able to utilize all six different iron oxides synthesized, albeit with varying success (**Table 1**). Results show that many oxides may be bioavailable to hyperthermophiles, and can contribute to a range of mineral transformations in the environment.

Characterizing Mineral Transformations: To further characterize the products of mineral transformation and possible variations with electron acceptor, we used a combination of transmission electron microscopy (TEM), visible near-infrared (VNIR), mid-infrared attenuated total reflectance (MIR ATR), Raman, and Mössbauer spectroscopies. Heat-treated controls were evaluated to distinguish abiotic from biotic transformations. We also critically examined how sample preparation techniques influenced end products of these transformations by comparing freeze-dried samples against those still in solution.

Table 1. Growth of Hyperthermophiles on Varying Iron Oxides

Microbe	Mineral	Max Fe(II) Produced	Max Cells/mL
P. delaneyi	ferrihydrite	18-20 mM	9×10^7
	lepidocrocite	2 mM	1×10^7
	akaganéite	2 mM	2×10^7
	maghemite	1 mM	1×10^7
	hematite	<1 mM	1×10^6
	goethite	<1 mM	2×10^6
P. islandicum	ferrihydrite	6 mM	5×10^7
	lepidocrocite	2-3 mM	2×10^7
	akaganéite	2 mM	2×10^7
	maghemite	1 mM	1×10^7
	goethite	<1 mM	1×10^7
	hematite	<1 mM	7×10^6

Spectroscopic data reveal subtle differences in mineral end products between the two hyperthermophilic microbes when grown on ferrihydrite. While *P. delaneyi* produces a product most similar to nanophase magnetite, *P. islandicum* yields a mixture of magnetite and maghemite. Heat-treated control samples are comparable to ferrihydrite in both cases. Subtle spectral differences resulted when samples prepared by freeze-drying or run in solution were compared. Differences showed that even under vacuum, mineral end-products may partially oxidize during the drying process; this is especially true for biogenic samples.

Our ongoing work is identifying these subtle differences, and spectral parameters in order to help distinguish and characterize the potential spectroscopic biosignatures that result from microbial bioreduction. With this body of research, we also hope to inform the combination of instrumentation, either on remote or landed missions, that could ideally be used to detect signs of life.

References: [1] Vargas, M. et al. (1998) *Nature, 395*:65-67. [2] Stetter, K. O. (1996) *FEMS Microbio Rev 18:*149-158. [3] Sklute E. C. et al. (submitted) *Amer. Mineral.*