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BIOREDUCTION OF NANOPHASE FERRIHYDRITE, AKAGANEITE, AND LEPIDOCROCITE BY THE AUTOTROPHIC THERMOPHILE *DESULFOTHERMOBACTER FERRIREDUCENS* AS SEEN THROUGH MÖSSBAUER SPECTROSCOPY.
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Introduction: Critical components in the effort to find evidence for past and present extraterrestrial life are the identification of biosignatures and development of life detection techniques. Iron (oxyhydr)oxides, which host a redox-active metal, are widely distributed in Earth and Martian soils [1]. Microbes that can respire iron using dissimilatory iron reduction (DIR) are of interest because Fe(III) was likely abundant on the early Earth and, therefore, DIR may be an ancient kind of metabolism [2]. As such, these microbes may also be indicators of extraterrestrial life. Improving our understanding of DIR microbe-mineral interactions and how they modify the environment can help to inform development of spacecraft-relevant instruments capable of identifying microbe-associated mineralogy.

Previous studies have focused on microbial DIR in mesophilic bacteria and hyperthermophilic archaea. Little is known about the mechanisms for DIR in autotrophic thermophilic bacteria. In this study, we examine and characterize biogenic minerals produced by an obligate autotrophic thermophile, *Desulfothermobacter ferrireducens* strain Ax17, using Mössbauer spectroscopy. *D. ferrireducens* was isolated from a deep-sea hydrothermal vent at Axial Seamount on the Juan de Fuca Ridge. *D. ferrireducens* uses sulfur compounds and nanophase iron (oxyhydr)oxides (FeNPOs) such as ferrihydrite, akagenéite, and lepidocrocite as terminal electron acceptors and H_2 as an electron donor.

Methods: *D. ferrireducens* (hereafter called Ax17) was grown at 55°C on modified DSM 981 mineral medium [3]. Nanophase ferrihydrite, akagenéite, and lepidocrocite were synthesized and suspended in double-deionized water as in [1] to preserve mineral-fluid surface properties. They were used separately as terminal electron acceptors at a concentration of 100 mmol/l with 2 atm of 80% H_2-20% CO_2 in the headspace as energy and carbon sources.

To separate mineral transformations associated with Ax17's growth from those that may occur abiotically through the interaction of the FeNPOs with growth medium and heat, each mineral was reacted using three experimental variations: 1) a sample with Ax17 cells incubated at 55°C, 2) a sample with FeNPO and growth medium incubated at 55°C without cells, and 3) a sample with FeNPO and growth medium incubated at room temperature without cells. Incubation time to late-logarithmic growth phase was five days as

determined by previous growth curve experiments. After incubation, samples were filtered onto a 0.02 μm pore size filter (Millipore) in an anoxic chamber. Samples were left to dry in the anoxic chamber after filtering for ~12 h before being anaerobically mixed with sugar and mounted into plastic washers confined with Kapton tape. The samples were transported in sealed, anoxic, airtight containers to Mount Holyoke College where they were mounted on a See Co. WT 302 Mössbauer spectrometer equipped with a Janis closed cycle He compressor. The sample tube was immiately vacuumed and backfilled with He. Spectra were aquired at 4, 80, 150, 220 and 295K using a ~40 mCi ^{57}Co source in Rh and referenced to α-Fe foil at 295K.

Results: Fourier transform infrared (FTIR) and visible near infrared (VNIR) spectra for these samples are described in [4]. Ferrihydrite bioreduced by Ax17 (Figure 1) resulted in a dark brown to black, magnetic end product, whereas controls varied only slightly in color from starting materials. The FTIR spectrum has
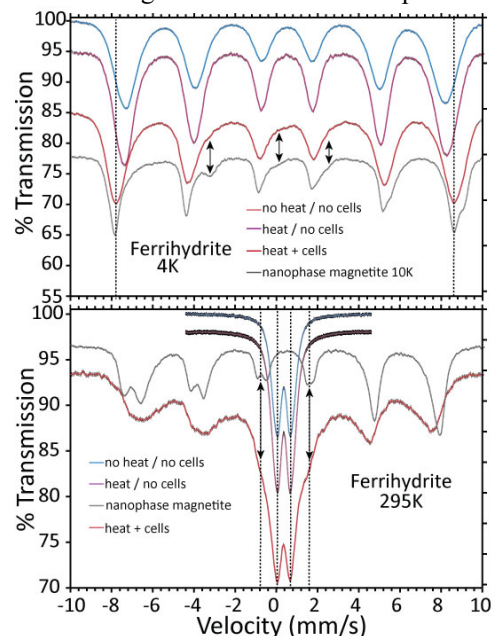

Figure 1. Mössbauer spectra of Ax17 grown on ferrihydrite, along with reference nanophase magnetite, at 295K and 4K.

clear magnetite absorptions. Mössbauer spectra of nanophase oxides can be more challenging to fit than their macroscopic counterparts [5], particularly for magnetite. Where a macroscopic and even most nano-

scopic samples would display a clear 2-sextet pattern at 295K that is easy to identify even in mixed spectra, decreasing grain size can lead the sample to be super-paramagnetic, i.e., to be a doublet at room temperature. However, a more likely reason for a doublet is that Fe is in the process of magnetic ordering. This can persist down below the Verwey temperature, where the magnetite spectrum becomes much more complicated and less distinct even for bulk sample [5].

This behavior is observed for the ferrihydrite bioreduced sample. The sample is magnetically ordering at 295K; the overlapping, broad sextets make it impossible to differentiate phases. By 4K, the spectrum is still broad but ordering is nearly complete. Although fit parameters are still equivocal due to overlap, comparison with a nanophase magnetite spectrum indicates that the sample is partially transformed to magnetite, maghemite, cation-deficient magnetite, or a mixture.

Akaganéite bioreduced by Ax17 produced a dark brown product with FTIR results pointing to the partial formation of green rust (although lack of vibrational spectra are a challenge to that identification). Mössbauer spectra (Figure 2) support the identification of green rust. While the 295K spectrum of bioreduced akaganéite is overwhelmed by a Fe(III) doublet likely due to unreacted akaganéite, magnetic ordering is observed below 220K, making the new phase easier to analyze. The 295K green rust spectrum is shown for comparison. In spite of slight peak shifts anticipated with the temperature difference, the match is good. At 4K (green rust spectrum at 15K), the match is less compelling. Perhaps this is due to the temperature difference; magnetic orientation of phases near 0K can lead to large changes over small temperature ranges. It could also be due to the fact that the reference is sulfate green rust and the medium in which Ax17 was grown makes chloride green rust (for which Mössbauer data are unavailable) more likely.

Lepidocrocite bioreduced by Ax17 resulted in a dark green to brown product. It is appreciably different from from the controls only in its VNIR spectra [4]. Mössbauer spectra (Figure 3) also show that both the heated control and the bioreacted sample have a small amount of goethite.

Conclusions: Mössbauer spectra of bioreduction products of Ax17 grown on nanophase ferrihydrite, akaganéite, and lepidocrocite show different reaction extent and different reaction products depending on terminal electron donor.

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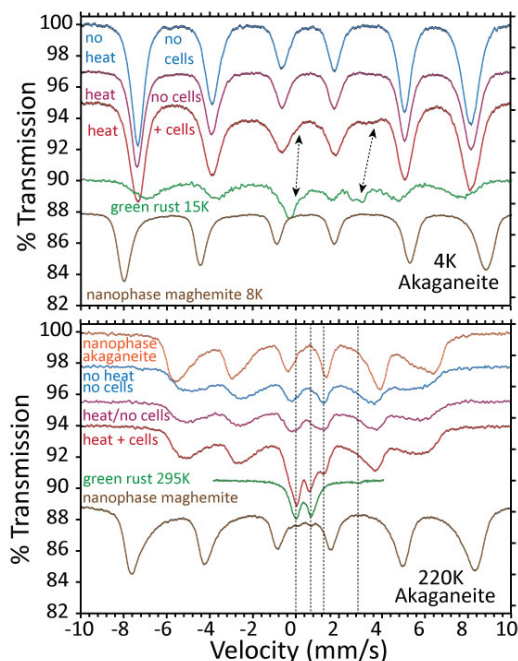

Figure 2. Mössbauer spectra of Ax17 grown on akagenéite at 220K and 4K. Reference sulfate green rust sample #5 [6] and maghemite are of closest available temperature.
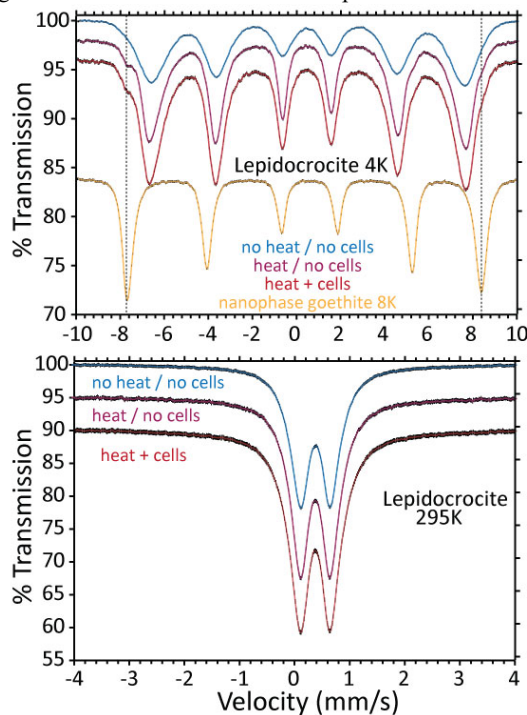

Figure 3. Mössbauer spectra of Ax17 grown on lepidocrocite.

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