Characterization of the Effects of Precursor Mineralogy on Hematite Spectra: Application to Martian Hematite Mineralization.

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Introduction. The Thermal Emission Spectrometer (TES) instrument aboard Mars Global Surveyor discovered several isolated deposits of gray, crystalline hematite in Sinus Meridiani, Aram Chaos, and Valles Marineris. A variety of formation mechanisms has been proposed for the martian hematite deposits [1-5], including aqueous and non-aqueous processes. Comparison of the average Sinus Meridiani hematite spectrum measured by TES to laboratory emissivity spectra for a variety of naturally occurring hematites shows small but potentially important differences. In particular, the emissivity minimum at 300 and 445 cm^{-1} in the Sinus Meridiani (SM) spectrum is displaced 10-25 cm^{-1} to lower frequencies compared to some natural hematite samples [6]. In addition, these bands in the TES data are narrower than the broad bands seen in many natural hematite spectra. These differences may imply that the natural variability of hematite spectra has not been fully characterized, especially with respect to the reaction pathway (precursor mineralogy and temperature of hematite formation) and crystal morphology. Here, we describe the thermal infrared spectral characteristics of several series of synthetic hematite samples derived by direct precipitation, dehydroxylation of fine-grained goethite and the oxidation of magnetite. Several natural hematite sample spectra are also presented for comparison. Transmission electron microscopy (TEM) and Mössbauer spectral analyses of selected samples were performed in order to help determine the causes of the changes seen in the infrared spectra.

Procedure. Several possible hematite precursor minerals, including fine-grained synthetic goethite, fine-grained synthetic magenetite, and coarse-grained natural magentite were used in this study. Samples were heated to a variety of temperatures, for either 24 hours or 1 week. The fine-grained samples were packed into small discs at 10,000 psi using a hydraulic press. This greatly increased the spectral contrast of the emissivity spectra of the samples, eliminating the poor spectral contrast problem commonly associated with fine-grained samples. Fine-grained samples shown in this work were first heated as powders, and then pressed into high-density discs to prevent excessive sintering. Some selected hematite powders were also used for TEM and Mössbauer analyses.

Results.

Infrared Analysis. There are some important differences between the magnetite-derived hematite sample spectra and the average SM hematite spectrum. First, the positions of the absolute minima of the 300 and 445 cm^{-1} fundamental absorptions are offset between 10 and 25 cm-1 to higher frequencies. In addition, the shapes of the 445 cm^{-1} absorption bands of the magnetite-derived hematite samples are broader and, the minimum is rounded off compared to the average SM hematite spectrum. Each magnetite-derived hematite spectrum also has an absorption near 390 cm^{-1}.

By contrast, the positions and shapes of the fundamental absorption bands of the goethite-derived samples match well with those of the martian spectrum. The goethite-derived hematites formed at 300 and 400 °C show no sign of an absorption at 390 cm^{-1}. As the goethite dehydroxylates to hematite with increasing temperature, the 390 cm^{-1} band appears, and becomes more pronounced. The closest match to the SM hematite spectrum is the goethite-derived hematite synthesized at 300°C. Figure 1 shows a comparison of the SM hematite spectrum with both magnetite and goethite-derived hematite spectra.

TEM Analysis. Three samples have been characterized with TEM so far. The goethite precursor heated at 300 °C appears as nearly perfect pseudomorphs of acicular goethite crystals (Figure 2). The flat crystals have an average length of about 0.5 μm and an average width of about 0.1 μm. When heated to 700 °C, the goethite-precursor hematite shows evidence of extensive recrystallization. Very small (< 0.1μm) plates dominate the field of view, with only a hint of the former goethite crystal morphology being present. Finally, the magnetite-precursor sample heated to 700 °C appears as clumps of roughly equant particles, possibly pseudomorphic after the magnetite, ranging from about 0.3 to 0.5 μm in diameter. Our results are consistent with those previously reported by Cornell and Schwertmann [7]

Mössbauer Analysis. Mössbauer spectra show that the goethite sextet has been completely replaced by the hematite sextet for the 300 °C experiments.

Discussion. The absorption at 390 cm^{-1} seen in some samples results from an a-axis contribution to the hematite spectra, and is not seen in the Mars sample spectrum. This led Lane et al. [3] to conclude that

martian hematite grains are platy in shape. Additionally, based on samples examined in this work and review of Lane et al.'s [3] spectra, the emissivity of the 540 cm^{-1} absorption bands decrease significantly as the 390 cm^{-1} absorptions become more prominent. This provides an additional diagnostic tool to assess the shape of the hematite particles. Lath-shaped hematite crystals, pseudomorphic after goethite, would easily align along their c axes, which point perpendicular to the flat face of the crystal [8]. Low-grade burial metamorphism or diagenesis could easily convert originally deposited goethite to gray hematite. By contrast, equant-shaped, magnetite-derived hematite particles would be difficult to align such that all of their c axes are pointing in the same direction. Complete recrystallization to microplaty hematite and alignment of the particles must occur to remove the 390 cm^{-1} absorptions from the spectra of these samples. This would require much greater burial depths and/or temperatures than would be needed for conversion of goethite [3].

Based solely on the laboratory spectra, the closest match to the SM hematite spectrum is a goethite-derived sample heated at 300°C. Review of the literature, however, points out that on Mars, goethite should be unstable relative to hematite under all geologic conditions [9-12]. Given appropriate time and pressure, the martian crystalline hematite deposits could have formed at temperatures as low as 40°C [13].

Conclusion and Future Work. No magnetite-derived hematite spectrum acquired to date provides an accurate fit for the martian SM hematite spectrum, but goethite-derived hematite spectra acquired at 300 and 400 °C provide good fits. Additional characterization of the martian hematite will be carried out by the Mini-TES instrument, if, as is likely, one of NASA's MER rovers is chosen to land at the Sinus Meridiani hematite region. Particularly important will be the shape and position of the 540 cm^{-1} band as seen from Mini-TES. While this band can be retrieved from TES spectra by factor analysis and target transformation, its close proximity to the 667 cm^{-1} CO_2 fundamental absorption decreases the accuracy of the method. Future laboratory work will focus on decoupling the spectral effects of axis orientation and precursor mineralogy on hematite spectra.
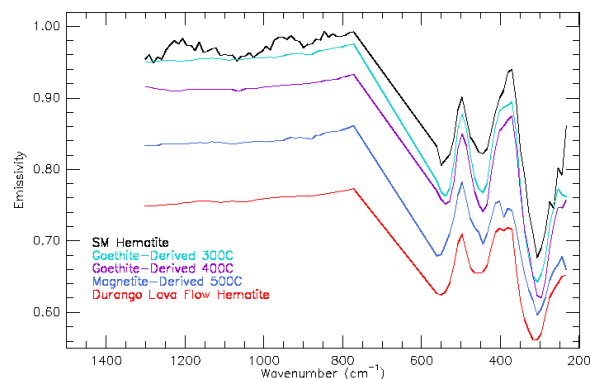

Figure 1. Comparison of some goethite-derived and magnetite-derived hematite spectra with the martian SM hematite spectrum. Magnetite-derived hematite spectra, including the Durango Lava Flow sample, provide poor fits for the SM hematite spectrum, while the goetite-derived spectra formed at 300 and 400 °C provide good fits.
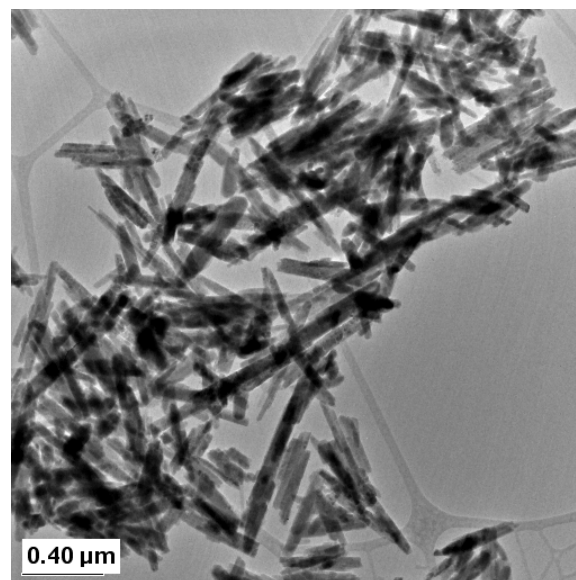

Figure 2. Hematite derived from goethite at 300 °C seen at high resolution. Crystals are pseudomorphs after goethite, and the c axes (perpendicular to the plane of the image) are easily aligned when pressed, resulting in the lack of a 390 cm^{-1} absorption band.

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