

Fine-grained Goethite as a Precursor for Martian Gray Hematite. T. D. Glotch¹, R. V. Morris², T. G. Sharp¹, P.R. Christensen¹, ¹Department of Geological Sciences, Arizona State University, Tempe, AZ 85287-6305, ²SR/NASA Johnson Space Center, Houston, TX 77058

Introduction: Several isolated deposits of gray, crystalline hematite on Mars were discovered using data returned from the Thermal Emission Spectrometer (TES) instrument aboard the Mars Global Surveyor spacecraft [1,2].

Christensen et al. [1] provided five testable hypotheses regarding the formation of crystalline hematite on Mars: 1) low-temperature precipitation of Fe oxides/hydroxides from standing, oxygenated, Fe-rich water, followed by subsequent alteration to gray hematite, 2) low-temperature leaching of iron-bearing silicates and other materials leaving a Fe-rich residue (laterite-style weathering) which is subsequently altered to gray hematite, 3) direct precipitation of gray hematite from Fe-rich circulating fluids of hydrothermal or other origin, 4) formation of gray hematitic surface coatings during weathering, and 5) thermal oxidation of magnetite-rich lavas.

Since this initial work, several authors have examined the hematite deposits to determine their formation mechanism. *Lane et al.* [3] cited the absence of a 390 cm⁻¹ absorption in the martian hematite spectrum as evidence for platy hematite grains. Their model for the formation of the deposits includes deposition of any of a variety of iron oxides or oxyhydroxides by aqueous or hydrothermal fluids, burial and metamorphism to gray platy hematite grains, and exhumation in recent times. Based on a detailed geomorphic examination of the Sinus Meridiani region, *Hynek et al.* [4] conclude that the most likely method of hematite formation was either emplacement by a hydrothermal fluid or oxidation of a magnetite-rich pyroclastic deposit. Similarly, *Arvidson et al.*, [5] favor a model involving the alteration of pyroclastic deposits by aqueous or hydrothermal fluids. Finally, based on geochemical modeling and an examination of Aram Chaos, *Catling and Moore* [6] favor emplacement by hydrothermal fluids with a minimum temperature of 100 °C.

Comparison of the average martian hematite spectrum measured by TES to hematite emissivity spectra for a variety of naturally occurring hematites shows small but potentially important differences [3]. In particular, band shapes, positions and relative band emissivities of hematite spectra vary over the range of samples. These differences imply that the natural variability of thermal infrared hematite spectra has not been fully characterized, especially with respect to the reaction pathway and crystal structure.

Objective: This work attempts to distinguish between the various proposed models of hematite formation by examining the spectral response of a series of synthetic and natural hematite samples with regards to precursor mineralogy, temperature of formation, and crystallinity. It is proposed that the hematite formations in Sinus Meridiani, Aram Chaos, and Valles Marineris were derived by the low-temperature dehydroxylation and compaction of fine-grained goethite. Goethite is a common mineral on Earth, forming in a variety of environments. It occurs as a weathering product of iron-bearing minerals, such as might be found in the basaltic rocks in the hematite-bearing regions of Mars. Goethite can also be directly precipitated (both inorganically and organically) in aqueous environments, and it is known to form gossan deposits on the surface of metalliferous veins. It is also proposed that the hematite does not occur as coarsely crystalline grains, but rather as a compressed, finely crystalline cement or coating.

The thermal infrared spectral characteristics of hematite samples derived by the dehydroxylation of goethite and the oxidation of magnetite are reported. In addition, the grain shape, size, and degree of post-hematite formation crystal growth are characterized by transmission electron microscopy (TEM). Finally, Mössbauer data are used to help characterize the crystallinity and purity of the hematite samples. Results are examined and used to explain TES spectra of martian crystalline hematite.

Procedure: A series of fine-grained synthetic magnetite and goethite powders were used as hematite precursors in this study. In addition several natural hematite samples from various geologic settings were also examined. The goethite and magnetite samples were heated to a temperatures between 300 and 700 °C for 24 hours. They were then 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 hematite powders were also selected for TEM and Mössbauer analyses.

The three natural gray hematite samples used in this study were selected based on the wide variety of

their geologic settings and their inferred formational mechanisms.

The first hematite sample is a thick gray-black hematite coating collected near Swansea, AZ that covers a quartz-rich fault breccia. A plausible method to form a coating of this nature would involve weathering of iron-rich minerals and later diagenesis that turned the coating black. Hydrothermal fluids have altered other rocks in the fault zone region, perhaps indicating alteration of the original coating at elevated temperatures. It is unlikely that the fluid directly deposited the coating because it is not of the coarse-grained variety commonly associated with deposition under hydrothermal conditions.

Two massive gray hematite samples were provided by Dr. Steven Reynolds. One sample is from the Cerro de Mercado iron deposits, part of the Mercado Iron Member of the Cacaria Formation near Durango, Mexico. Like much of the hematite in these iron deposits, this sample was derived by the oxidation of magnetite. The original iron deposits were emplaced during a break in the two major eruptive cycles of the 30 Mya Chupaderos caldera. The iron deposit was the result of an eruption of an iron magma which was also rich in fluorine, chlorine, carbon dioxide, and water. Iron oxides were originally in the form of magnetite. Later, large volumes of halogen-rich gases flowed through the iron deposits and oxidized the magnetite to hematite [7].

A second sample from the Olympic Dam ore in southern Australia was the result of emplacement by hydrothermal fluids [8,9]. The Olympic dam deposit is located in the mid-Proterozoic granite basement of South Australia. It is composed of steeply dipping breccia columns and dikes formed by mechanical brecciation and hydrothermal metasomatism of the host granite. Stable oxygen isotopes indicate that hematite was emplaced by fluids ($\delta^{18}\text{O} < 9\%$) at temperatures of 200–400 °C [8].

Results:

Infrared Analysis. There are some important differences between the magnetite-derived hematite sample spectra and the average martian hematite spectrum. Most noticeably, the shapes of the 300 cm^{-1} absorption bands of the magnetite-derived hematite samples are broader than that seen in the martian hematite spectrum. In addition the 445 cm^{-1} minimum is rounded off compared to the average martian hematite spectrum. Each magnetite-derived hematite spectrum also has an absorption near 390 cm^{-1} that is not present in the martian hematite spectrum.

By contrast, the positions and shapes of the fundamental absorption bands of the goethite-derived samples match well with those of the martian spectrum, although the fits become increasingly poor at

higher dehydroxylation temperatures. 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 at increasingly higher temperatures, 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 martian hematite spectrum with both magnetite and goethite-derived hematite spectra as well as the natural hematite samples.

The Durango and Olympic Dam samples provide poor fits to the martian hematite spectrum but the Swansea sample is a close match.

The Durango hematite sample spectrum has major absorptions at 552, 460, and 312 cm^{-1} with a local emissivity minimum at 394 cm^{-1} . A striking feature of this spectrum is the depth of the 552 cm^{-1} absorption. It has a much lower emissivity than the 460 cm^{-1} absorption, to a degree not seen in any of the synthetic hematite spectra.

The Olympic Dam hematite has absorption bands are located at 540, 477 and 296 cm^{-1} . The 477 cm^{-1} band is unique in its shape, sloping continuously from 477 to 434 cm^{-1} , and the 296 cm^{-1} band is much thinner than that of the martian hematite spectrum. A prominent 390 cm^{-1} band is present.

By contrast, the Swansea hematite coating spectrum is more similar to the lower temperature (300 to 400 °C) goethite-derived hematite spectra. It has major absorptions at 545, 444, and 308 cm^{-1} , with only a hint of a local emissivity minimum at 391 cm^{-1} .

TEM Analysis. Several synthetic samples were imaged at high resolution to assess whether the degree of crystallinity or crystal morphology could be responsible for the variations in the infrared spectra. The goethite precursor heated at 300 °C appears as nearly perfect pseudomorphs of acicular goethite crystals (Figure 2a). The flat crystals have an average length of about $0.5\text{ }\mu\text{m}$ and an average width of about $0.1\text{ }\mu\text{m}$. When heated to 700 °C, the goethite-precursor hematite shows evidence of extensive recrystallization (Figure 2b). Very small ($< 0.1\text{ }\mu\text{m}$) extensively sintered crystallites dominate the field of view, with only a hint of the former goethite crystal morphology being present. The magnetite-precursor sample heated to 700 °C appears as clumps of subangular crystals which display some characteristics of the original octahedral magnetite. They range from about 0.3 to $0.5\text{ }\mu\text{m}$ in diameter. Our results are consistent with those previously reported by Cornell and Schwertmann [10].

Mössbauer Analysis. Mössbauer spectra show that the hematite samples made at the highest tempera-

tures are the most crystalline. In every case, the precursor mineral was completely replaced by hematite.

Discussion: Qualitative estimates of the various hematite samples' fits to the martian hematite spectrum can be made by inspecting Figures 1 and 2. It is desirable, however, to quantify the various relationships between the hematite spectra to arrive at a more robust result. The minimum emissivity value of the 540, 450 and 300 cm^{-1} absorption bands and the widths of the 450 and 300 cm^{-1} absorption bands were measured for each hematite spectrum. The widths reported are the full widths at half the minimum band depth.

Figures 3 shows two of the measured spectral parameters plotted against each other. This plot shows a clear trend in the properties of hematite spectra based on their precursor mineralogy, temperature of formation, and indirectly, crystallinity. In general, there are large scatters for the goethite- and magnetite-derived samples. However, there are several goethite-derived samples and a single natural sample that plot close the Mars spectrum. The martian hematite plots in the region of the graphs dominated by the lower temperature (300-400 °C) goethite-derived samples. The natural sample is the gray hematite coating from Swansea, AZ. The spectra of these samples have band widths and relative band depths that are consistent with the martian hematite spectrum. Higher temperature (500-700 °C) goethite-derived samples plot increasingly farther away from the martian hematite. These sample spectra have 390 cm^{-1} absorptions and their relative band depths, shapes, and positions are often poor fits for the martian hematite spectrum.

In no case does a magnetite-derived sample plot closest to the martian hematite spectrum. Additionally, there is a large scatter in the positions of the magnetite-derived hematite samples. This corroborates the visual inspection of the magnetite-derived hematite spectra, which show a large variation in the shapes of the magnetite-derived spectra. This large variation is partly caused by the different magnetite precursors used in the study and partly by the drastic change in the shape of the hematite spectrum at 600 and 700 °C. The natural magnetite-derived sample (Durango) and the natural hydrothermal sample (Olympic Dam) plot far away from the martian hematite.

The absorption at 390 cm^{-1} seen in some sample spectra 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 [11]. Low-grade burial metamorphism or diagenesis could 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].

Implications for Mars. Several lines of evidence indicate that the hematite-rich units on Mars were deposited in a relatively low temperature aqueous environment and are in the form of a fine-grained cement or coating. In terms of band shapes, positions, and relative emissivities, infrared spectra of magnetite-derived hematite (both synthetic and natural) universally provide poor fits for the martian hematite spectrum. In addition, every magnetite-derived hematite sample spectrum has a strong 390 cm^{-1} absorption band. TEM diffraction patterns indicate that emission from these samples is not dominated by the c-crystallographic axis. These data strongly suggest that water-free thermal oxidation of a magnetite-rich ash or lava [1,4,5] is not a valid mechanism for the formation of the martian crystalline hematite deposits.

By contrast, the spectra of lower temperature goethite-derived hematite samples provide good fits for the martian hematite spectrum. Infrared spectra of the synthetic samples show that acicular hematite samples derived at 300 or 400 °C from goethite lack a 390 cm^{-1} absorption feature. As the temperature of dehydroxylation of goethite to hematite increases, the 390 cm^{-1} band appears and becomes deeper. TEM images show that the cause of this is growth of hematite crystals in random orientations. As sintering and crystal growth occurs, infrared emissions are no longer dominated by the c-crystallographic face, leading to the presence of the 390 cm^{-1} band.

TEM images also show that these higher temperature samples are composed of fine crystallites that have been heavily sintered together. Mössbauer spectra show that even though the individual crystallites can be much less than 1 μm in size, the effect of sintering make the sample act like a coarsely crystalline particulate. Since these are the samples that provide

the worst overall fits to the martian hematite spectrum, it appears unlikely that the martian crystalline hematite is coarsely crystalline. The alternative is that the original iron oxide was deposited as a finely crystalline coating or cement and was then compressed and dehydroxylated to hematite by burial.

In summary, based on the laboratory spectra, in conjunction with the TEM and Mössbauer analyses, the closest match to the martian hematite spectrum is the 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 [12-15]. Given appropriate time and pressure, the martian crystalline hematite deposits could have formed at temperatures as low as

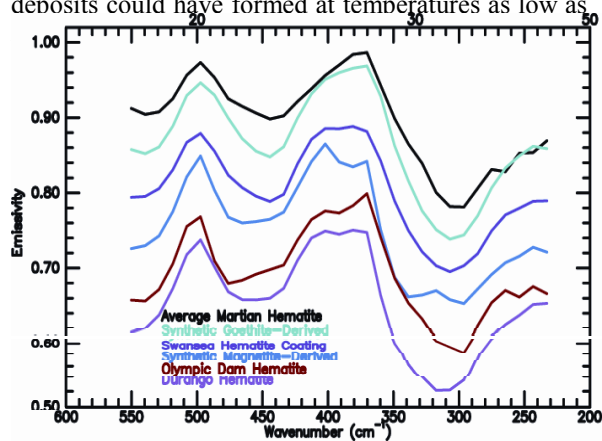


Figure 1. Goethite- and Magnetite-derived synthetic samples and the natural Swansea, Durango, and Olympic Dam hematite samples compared with an average martian TES hematite spectrum.

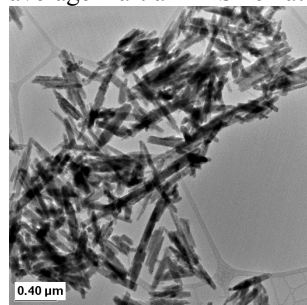


Figure 2a. Hematite derived from goethite at 300 °C, pseudomorphic after goethite

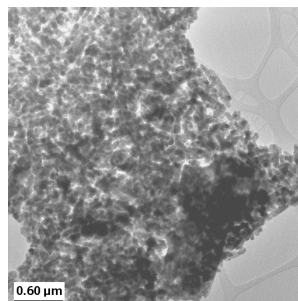


Figure 2b. Hematite derived from goethite at 700 °C. The sample is heavily recrystallized and sintered, and acts coarsely crystalline in IR and Mössbauer spectra.

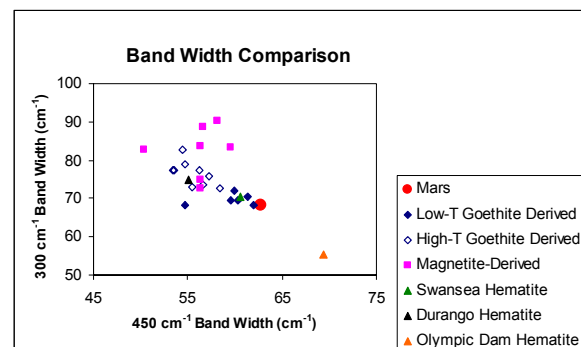


Figure 3. Plot of the 300/400 cm^{-1} band ratio vs the 450 cm^{-1} bandwidth. Mars plots in the region dominated by low temperature (300-400 °C) goethite-derived samples and the Swansea hematite coating.

References: [1] Christensen, P.R. et al. (2000) *JGR*, 105, 9623-9642 [2] Christensen, P.R. et al. (2001) *JGR*, 106, 28873-28886 [3] Lane, M et al. (2002) *JGR*, 107, 5126-5140 [4] Hynek, B.M et al. (2002) *JGR*, 107, E10, 18.1-18.14 [5] Arvidson, R. E. et al. (2003) *JGR*, in press [6] Catling, D.C. and Moore, J. M. (2003) *Icarus*, in press [7] Lyons, J. I. (1988) *Econ. Geol.*, 83, 1886-1906 [8] Oreskes, N., and Einaudi, M.T. (1992) *Econ. Geol.*, 87, 64-90 [9] Haynes, D.W. et al. (1995) *Econ. Geol.*, 90, 281-307 [10] Cornell, R. M., and U. Schwertmann (1996) *The Iron Oxides*, pp84, 369 [11] Morales, M. P. et al. (2002) *App. Spec.*, 56, 200-204 [12] Fish, F. Jr (1966) *JGR*, 71, 3063-3068 [13] O'Connor, J. (1968) *JGR*, 73, 5301-5311 [14] Berner, R. (1969) *Geochim. Cosmochim. Acta*, 33, 267-273 [15] Langmuir, D. (1971) *Am. J. Sci.*, 271, 147-156