

EVIDENCE FOR HEMATITE ON MARS: SPECTRAL PROPERTIES OF FERRIC IRON PHASES IN ANNEALED, Al-RICH PRECIPITATES OF Fe-Al SULFATE SALT SOLUTIONS. Richard V. Morris, Code SN4, NASA-JSC, Houston, TX 77058 and Howard V. Lauer, Jr., LEMSCO, Houston, TX 77058.

Introduction. Characteristics of the reflectance spectra of the martian bright regions generally attributed to ferric iron are a weak absorption edge extending from approximately 0.75 μm to 0.40 μm , a relative reflectance maximum at approximately 0.75 μm , and a shallow band minimum near 0.87 μm [e.g., 1]. Certain palagonites and other poorly crystalline materials containing ferric iron have similar spectral characteristics, suggesting that the dominant ferric-containing phases on Mars are also poorly crystallized [e.g., 2, 3]. The implication is that specific mineralogical assignments are not possible from either the martian or analogue spectral data. The 0.87 μm band minimum and the 0.75 μm relative reflectance maximum are consistent, but the weak absorption edge is not consistent, with spectra for crystalline hematite as they are known for fine hematite powders having mean particle diameters greater than approximately 0.1 μm [e.g., 4]. In this paper we discuss experimental evidence that indicates that the ferric spectral features in the martian and analogue spectral data are due to ultra-fine (i.e., x-ray amorphous) hematite particles. We produced such particles in annealed, Al-rich precipitates of Al-Fe sulfate salt solutions.

Methods. Coprecipitation from ferrous and aluminum sulfate salt solutions ($\text{Al/Fe} > 3$) was initiated by rapid addition of excess NaOH. The precipitates were washed by repeated decanting and adding of deionized water and then hydrolyzed by heating aqueous suspensions at 100°C. After drying in air, the precipitates were ground and annealed at 100, 500, and 920-1180°C to induce phase changes. NUV-VIS-NIR spectral reflectivity, Mossbauer, x-ray diffraction, and compositional data were obtained for the annealed precipitates.

Results and Discussion. The precipitates annealed at 100°C are amorphous to x-rays. The spectral data for these samples (not shown) show a weak band centered near 0.91 μm which is indicative of goethite [e.g., 4]. The Mossbauer spectra of these samples are a doublet ($\text{IS} = 0.34 \text{ mm/s}$; $\text{QS} = 0.75 \text{ mm/s}$); superparamagnetic doublets have been observed for goethite at sufficiently small particle size [e.g., 5]. It is likely that the 100°C samples contain "embryonic" goethite particles, perhaps incorporating some Al. We use the term "embryonic" to refer to very small and non-crystalline particles which have diffuse boundaries with their surroundings and are the precursors of somewhat larger particles which are a physical entity having definite crystal structure and sharp boundaries.

The precipitates annealed at 500°C are also amorphous to x-rays. Their reflectivity data are shown in Figure 1 for iron concentrations (on a water-free basis as Fe_2O_3) of 4.2, 7.4, and 13.5 wt. %. The bands near 1.4 and 1.9 μm are due to H_2O . With increasing iron content, the absorption edge shifts to longer wavelengths and the feature centered near 0.85 μm deepens progressively and changes in shape from a plateau to a shallow band. The shift in the absorption edge is probably due to deepening of bands both centered in the edge (the feature near 0.45 μm) and the intense oxide \rightarrow ferric charge transfer bands centered in the UV. The spectrum of the sample with 13.5 % Fe_2O_3 is particularly suggestive of hematite. The band minimum near 0.85 μm and the relative reflectivity maximum near 0.76 μm are characteristics of crystalline hematite. The absorption edge is, however, shallower. Rather than this implying that the absorbing phase is not hematite, we suggest that the relatively shallower edge is a characteristic of embryonic hematite. The

shift in the band minimum from 0.91 in the 1000°C samples to 0.85 μm in the 500°C samples is consistent with dehydration of embryonic goethite to embryonic hematite; crystalline goethite dehydrates by approximately 300°C [e.g., 6]. The Mossbauer spectra of the 500°C samples are doublets ($IS=0.34$ mm/s; $QS=1.2$ mm/s) which is consistent with superparamagnetic hematite [7].

The x-ray data show that the precipitates ($\text{Fe}_2\text{O}_3 < 13$ wt. %) heated between 920 and 1180°C are single phase-corundum. The diffractions lines are systematically broadened and shifted in position from pure corundum due to the iron substituted in the lattice. Such formation of solid solutions over our compositional range and annealing temperatures is consistent with phase equilibria studies [8]. The reflectivity spectra of three samples with Fe_2O_3 contents between 4.7 and 13.2 wt % are shown in Figure 2. The positions of the spectral features are consistent with those found for ferric iron in natural corundum sample having approximately 0.8 wt. % Fe_2O_3 [9]. Band assignments are also discussed by [9]. The band positions are weakly dependent on the iron content of the corundum; the position of the lowest energy band, for example, ranges from 1.06 μm at 0.8 wt. % [9] to 1.03 μm at 13.2 wt. %. The Mossbauer spectra of the samples are all asymmetric doublets ($IS=0.30$ mm/s; $QS=0.54$ mm/s), in agreement with previous studies which show that effects of paramagnetic relaxation are important in corundum containing ferric iron [10].

The position and general shape of the spectral features for ferric iron in the precipitate annealed at 500°C with 13.5 wt. % Fe_2O_3 are essentially the same as those observed in the martian data. This correspondence includes not only the shallow band minimum near 0.85 μm and the relative reflectivity maximum near 0.76 μm but also the position of and the structure within the absorption edge. Both have changes in slope near 0.52 and 0.65 μm . If our identification of the ferric phase in our samples as embryonic hematite is correct, then such phases are also likely present on Mars.

Refs. [1] Singer et al., *JGR* 84, 8415, 1979; [2] Sherman et al., *JGR* 87, 10169, 1982; [3] Singer, *JGR* 87, 10159, 1982; [4] Morris et al., *JGR* 90, 3126, 1985; [5] Johnson and Norrish, *Aust J Soil Res* 19, 231, 1981; [6] Morris and Lauer, *JGR* 86, 10893, 1981; [7] Constabaris et al., *App Phys Lett* 7, 59, 1965; [8] Levin et al., *Phase Diag Ceram*, Am Ceram Soc, 1964; [9] Lehmann and Harder, *Am Mineral* 55, 98, 1970; [10] Wickman, *Mossbauer Eff Meth* v 2, 39, Plenum Press, 1966.

