

PREPARATION AND CHARACTERIZATION OF A NANOPHASE HEMATITE POWDER;

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INTRODUCTION. In recent papers [1,2], we have characterized the diffuse reflectivity, Mossbauer spectra, and magnetic properties of nanophase-hematite (np-Hm) dispersed at different number densities throughout spectrally white and iron-free matrix materials. Np-Hm particles are hematite particles whose diameters are ~10 nm or less. Np-Hm was studied in a dispersed form (as opposed to a pure powder) because that is the mode of occurrence in natural environments and because reflectivity spectra are also dependent on the nature of the matrix in which the np-Hm is dispersed. We were able to show that np-Hm plus some bulk-Hm can satisfy the spectral constraints of Martian bright region spectra and concluded that hematite is present in Martian surface materials.

Although pure powders of np-Hm are not likely present in natural environments, it is necessary to prepare and characterize such powders for two reasons. First, it is possible that the support materials (silica gel and activated alumina) are not entirely inert during sample preparation and that certain properties of the composite material are dominated by an interaction zone. Second, the composition and other physicochemical properties intrinsic to np-Hm are difficult to determine in the presence of the matrix material. In this abstract, we report the preparation and characterization of a np-Hm powder.

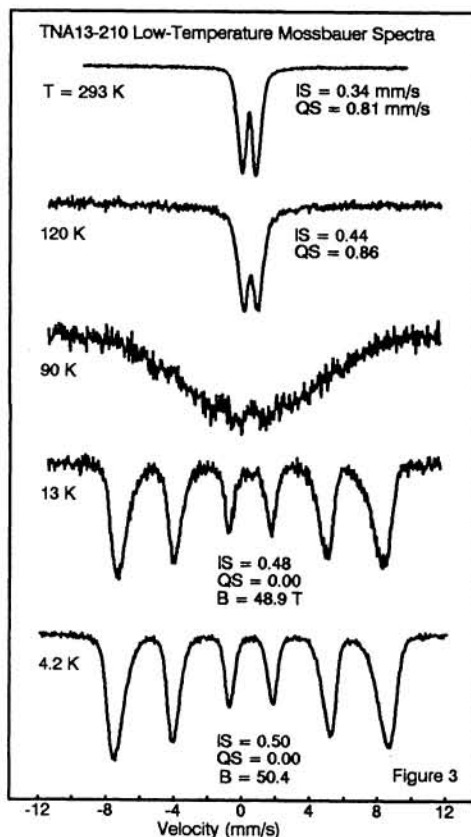
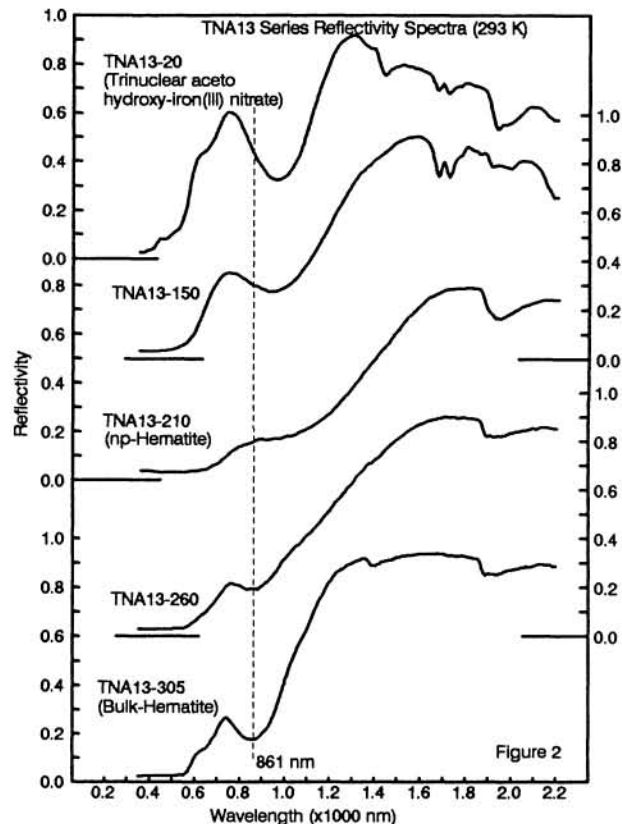
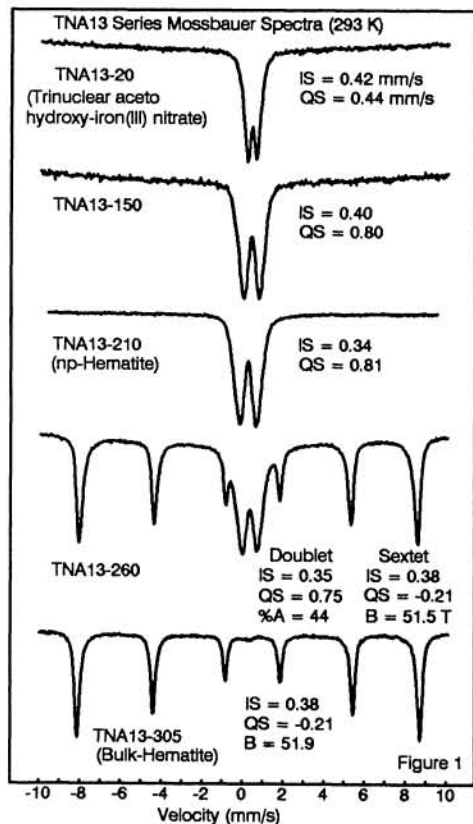
METHODS. Np-Hm was prepared by the slow thermal decomposition (in air) of trinuclear acetato hydroxy-iron(III) nitrate ($\text{Fe}_3(\text{OCOCH}_3)_7\text{OHNO}_3 \cdot 2\text{H}_2\text{O}$). The nitrate was prepared following the procedure described by [3]. The thermal decomposition was done in ~50°C steps (lasting 20-40 hr each) with cooling to ambient between steps to remove some sample for reflectivity and Mossbauer measurements.

RESULTS AND DISCUSSION. Figures 1 and 2 show Mossbauer and reflectivity spectra for the thermal decomposition of $\text{Fe}_3(\text{OCOCH}_3)_7\text{OHNO}_3 \cdot 2\text{H}_2\text{O}$ sample TNA13-20. Numbers following the hyphen are the maximum temperature (in °C) seen by each sample. The Mossbauer and reflectivity spectra of TNA13-210 are equivalent to those obtained previously for supported np-Hm [1,2]. By ~300°C, the np-Hm has converted to bulk hematite (TNA13-305). Both the Mossbauer and reflectivity spectra of the nitrate (TNA13-20), which contains trimers of ferric atoms [e.g., 4], are distinct from those for np-Hm. Thus the sequence shown by Figures 1 and 2 is (1) decomposition of the nitrate with its Fe(III) trimers to particles of np-Hm at ~210°C, and (2) growth of the np-Hm particles to bulk-Hm particles by ~300°C. The transition temperature to bulk-Hm is seemingly in conflict with [1,2] in which np-Hm particles were formed within a matrix material and were stable to growth to bulk-Hm at 550°C. Presumably, the difference can be attributed to the physical isolation of individual np-Hm particles by the matrix, resulting in stability at higher temperatures.

Low-temperature Mossbauer spectra for np-Hm (TNA13-210) are shown in Figure 3. Partial magnetic ordering is apparent at 90K; complete magnetic ordering is present by 13K. The quadrupole splitting (QS) of magnetically ordered np-Hm is zero. This implies the angle between the magnetic field and electric field gradient is a distribution with zero average, which could result from the poor crystallinity of np-Hm [e.g., 5]. XRD patterns for TNA13-210 show only two very broad lines similar in position and shape to those for 2-XRD-line (2L) ferrihydrite ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$) [e.g., 6], and the Mossbauer spectra of np-Hm and 2L-ferrihydrite are qualitatively similar. However, at 4.2K the 50.4 T value of B for np-Hm is larger than the 46.5 T value reported for 2L-ferrihydrite [5].

Np-Hm (TNA13-210) equilibrated with air contains ~7 wt. % H_2O . Approximately half of this water is physically adsorbed because it can be removed at room temperature by passing He gas over the sample. The remaining ~3.5 wt. % is more strongly held, but may still be physically bound. Alternatively, it may be essential in stabilizing the particles. For comparison, ferrihydrite and goethite contain ~17 and ~10 wt. % H_2O , respectively.

Because it does not have defined ferric crystal-field transitions, the reflectivity spectrum of np-Hm is unlike those for powders of crystalline (bulk) ferric oxides and also ferrihydrite [e.g., 7,8]. Its spectrum can be viewed, however, as an extrapolation of that for bulk-Hm; extreme broadening of the hematite ~860 and 620 nm bands would give the step-shaped featured observed for the np-Hm spectrum.



The saturation magnetization (J_s) of TNA13-210 (determined by $1/H$ extrapolation) at 293 K is $\sim 3 \text{ Am}^2/\text{kg}$, which is significantly higher than the 0.0 and $0.2 \text{ Am}^2/\text{kg}$ values for TNA13-20 and TNA-305 (bulk-Hm), respectively. Anomalously high values of J_s for np-Hm have been attributed to lattice defects which increase in importance as particle diameter decreases. The defects cause a net imbalance in the two antiferromagnetic lattices, which gives rise to the net magnetization [e.g., 9].

In summary, the particles we call np-Hm are appropriately named because their properties are most closely an extrapolation of the properties of bulk-Hm to nanometer-sized dimensions. The Mossbauer data show that np-Hm is large enough to be regarded as particles as opposed to atomic clusters of ferric atoms. Because np-Hm plus some bulk-Hm can satisfy Martian spectral constraints [1,2], hematite is likely present on the surface of Mars.

REFERENCES: [1] Morris *et al.*, *JGR* 94, 2760, 1989; [2] Morris *et al.*, *JGR* 95, 5101, 1990; [3] Yamanaka *et al.*, *Mat. Res. Bull.* 19, 161, 1984; [4] Martin-Luengo *et al.*, *Clay Min.* 24, 495, 1989; [5] Murad, *Iron in Soils and Clay Minerals*, D. Reidel, 309, 1988; [6] Eggleton and Fitzpatrick, *Clay & Clay Min.* 36, 111, 1988; [7] Morris *et al.*, *JGR* 90, 3126, 1985; [8] Morris and Schulze, *4th Int. Conf. Mars* (abs), 1989; [9] Rancourt *et al.*, *JMMM* 305, 1985.