

MOSSBAUER STUDY OF ULTRAMICROCRYSTALLINE HEMATITE. D.G. Agresti¹, J.A. Newcomb¹, and R.V. Morris². ¹Univ. of Alabama at Birmingham, Birmingham, AL 35294; ²NASA Johnson Space Center, Houston, TX 77058.

INTRODUCTION. As part of an ongoing attempt to simulate bright-region martian reflectance spectra by production of analog materials, we have investigated by Mossbauer spectroscopy a suite of samples that contain hematite formed on a silica gel support material (6nm pore diameter) [See companion paper, Ref. 1]. These studies are complementary to x-ray diffraction and optical reflectance measurements [1] and help characterize these samples according to particle size distribution, crystallinity, and mineralogical phase.

EXPERIMENTAL PROCEDURES. Mossbauer spectra were obtained over a temperature range from 22 to 300K. The spectra generally consist of an asymmetrically broadened magnetic-hyperfine sextet and a quadrupole doublet (Fig. 1), the relative area of which gradually increases with temperature in a manner characteristic of the superparamagnetic nature [2] of these samples. Each spectrum was least-squares fit with a doublet and up to 9 magnetic sites in order to determine isomer shift (IS), quadrupole splitting (QS), magnetic hyperfine field (H_{eff}) distribution, and relative area of the superparamagnetic doublet (%SP). The variation of %SP with temperature (Fig. 2) is correlated with the size distribution of the ultramicrocrystalline hematite particles [2].

RESULTS AND DISCUSSION. To illustrate the technique and analysis, Mossbauer spectra of 3 samples of Ref. 1 are discussed here: Sample A, 12.8 wt% Fe_2O_3 ; Sample B, 23.7%; and Sample D, 5.76%. Fig. 1 shows a set of spectra obtained for Sample D, with analysis for %SP and particle-size distribution (number per unit volume = derivative of %SP curve [2]) shown in Fig. 2a. Note that the distribution has a peak at ~7 nm, with a broad tail including particle diameters up to ~20 nm. Representative spectra for Sample A are shown in Fig. 3. The doublet at room temperature implies a relatively narrow distribution (mean particle size ~9 nm), in contrast to that of Sample D. Fig. 2b is a %SP plot for Sample B, with a very broad distribution predominantly >20 nm. Fig. 4 includes typical distributions of H_{eff} , obtained for Sample B at 3 temperatures. Note the sharp cutoff at the maximum field (H_{max}), whose values are within 2% of bulk hematite values (~515 kOe at room temperature), and the narrower distributions at lower temperatures where surface effects are reduced. Finally, the values obtained for IS and QS for the samples studied are: sextet, where present, IS = 0.38, QS = -0.22; doublet, IS = 0.34, |QS| = 0.5-0.8, all mm/s, at room temperature.

The Mossbauer results support the conclusion that the samples of Ref. 1 are composed of discrete, nm-size, crystalline (ultramicrocrystalline) particles of hematite. Measured values for IS, QS, and H_{max} are all in close agreement with those of bulk hematite, while QS and H_{max} are not consistent with corresponding values for either maghemite or goethite. The field distribution suggests that H_{max} is associated with the particle cores, which have a similar structure to bulk hematite, while the tail at lower fields results from a reduced exchange coupling at the surface. For all samples studied, a negative value for $\text{QS}_{\text{sextet}}$ was maintained down to 22K, where our bulk value is +0.36 mm/s. This complete suppression of the Morin transition shows the sensitivity of $\text{QS}_{\text{sextet}}$ to small particle size [3], even for Sample B. The broad size distributions for Samples B and D apparently result from sample preparation. Sample A was dried at room temperature (25 °C), while Samples B and D were dried relatively rapidly at ~60 °C.

Mossbauer Study of Ultra... Hematite
 Agresti, D.G., et al.

REFERENCES. [1] R.V. Morris et al., this volume; [2] W. Kundig et al., Phys. Rev. **142**, 327, 1966; [3] See e.g., Greenwood & Gibb, Mossbauer Spectroscopy, Chapman & Hall, 1971.

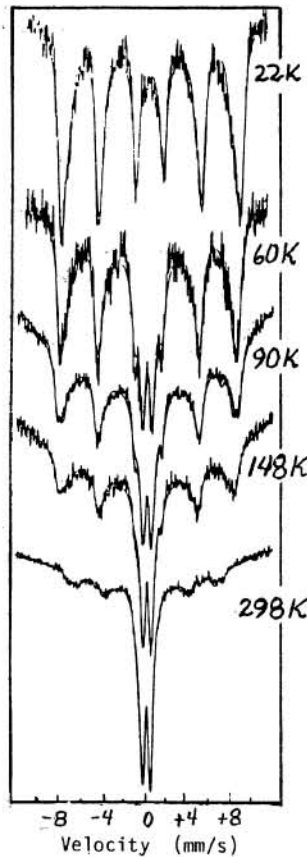


Fig. 1. Mossbauer spectra of Sample D.

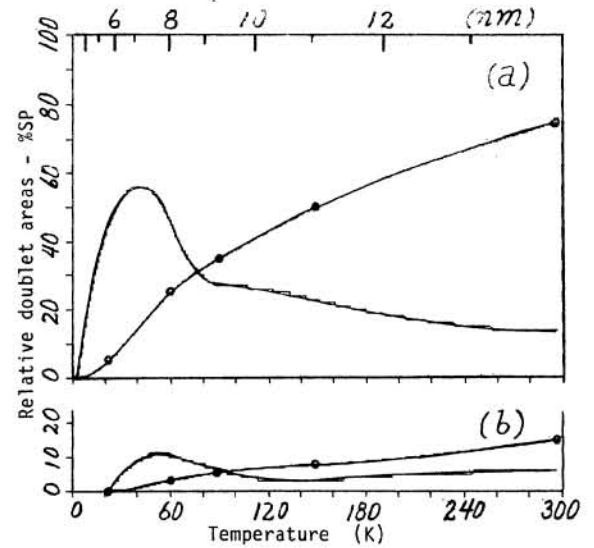


Fig. 2. Relative doublet areas (circles) in spectra of (a) Sample D and (b) Sample B, with cubic-spline fit, and derivative of this curve. The upper scale, diameter of equal-volume spheres, is calibrated from Ref. 2.

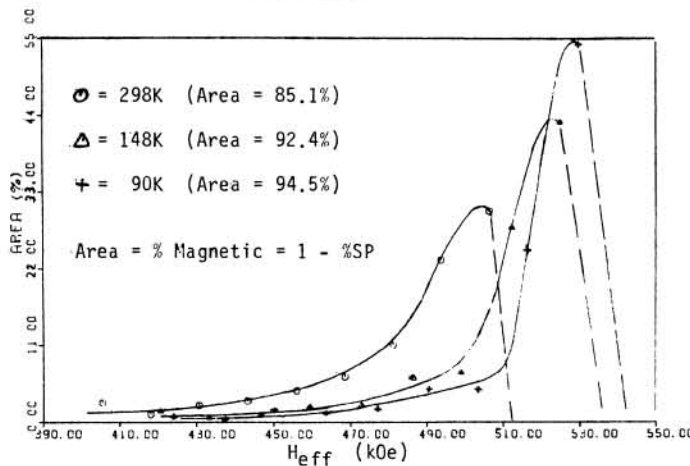


Fig. 4. Distribution of H_{eff} for 9 magnetic sites in 3 spectra of Sample B. The curves are hand-drawn through the data.

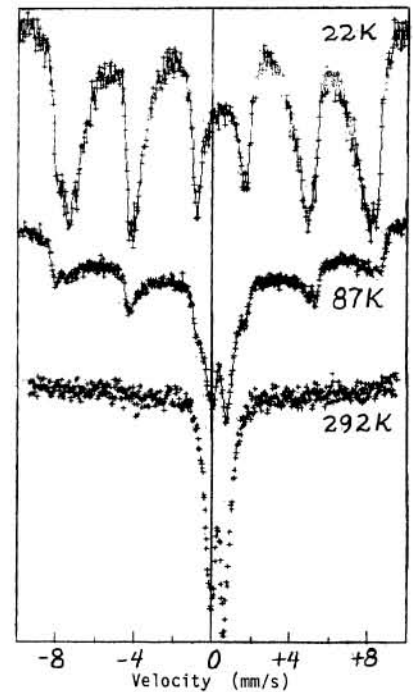


Fig. 3. Mossbauer spectra of Sample A. (For the 87K spectrum, %SP = 54)