Mossbauer Study of Ultramicrocrystalline Hematite. D.G. Agresti, J.A. Newcomb, and R.V. Morris. 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 asymmetrical 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 ($H_{ff}$) 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% $\text{Fe}_2\text{O}_3$; 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 $H_{ff}$, 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 = 0.5-0.8, 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 $QS_{sextet}$ 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 $QS_{sextet}$ 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.
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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. 3. Mossbauer spectra of Sample A. The curves are hand-drawn through the data.

Fig. 4. Distribution of $H_{\text{eff}}$ for 9 magnetic sites in 3 spectra of Sample B. The area = % Magnetic = 1 - %SP.