ULTRAMICROCRYSTALLINE HEMATITE: PROPERTIES AND OCCURRENCE ON THE MARTIAN SURFACE. Richard V. Morris¹, H. V. Lauer², Jr., A. V. Murali³, D. G. Agresti⁴, and J. A. Newcomb⁴. ¹NASA Johnson Space Center, Houston, TX 77058; ²Lockheed, Houston, TX 77058; ³Lunar and Planetary Institute, Houston, TX 77058; ⁴Univ. of Alabama at Birmingham, Birmingham, AL 35294.

INTRODUCTION. Spectral features generally attributed to ferric iron in the martian bright regions spectra are a weak absorption edge extending from -0.4 to 0.75 μm, a relative reflectivity maximum at 0.75 μm, and a shallow band minimum near 0.87 μm [e.g., 1]. Certain poorly crystalline materials containing ferric iron formed in the terrestrial weathering environment have similar spectral characteristics, suggesting that the dominant ferric-containing phases on Mars are also poorly crystalline [e.g., 2, 3]. The implication is that specific mineralogical assignments are not possible. The 0.87 μm band minimum and the 0.75 μm reflectivity maximum are consistent with spectra for crystalline hematite powders having mean particle diameters greater than ~140 nm, but the position of the absorption edge is not [4]. In this abstract we discuss the spectral properties of supported (silica gel) hematite particles having diameters below ~20-100 nm (ultramicrocrystalline hematite) and show that they are consistent with the martian spectral data. In a companion abstract [5], we discuss detailed Mossbauer studies of the same samples.

EXPERIMENTAL PROCEDURES. The ultramicrocrystalline hematite particles were formed on silica gel (chromatographic grade with 6 nm diameter holes) support material by impregnating the gel with ferric nitrate solution. The samples were dried at 25-60°C and calcined at 550°C for approximately 60 hr. The impregnation-calcination cycle was repeated to produce samples with high iron concentrations. In addition to optical spectroscopy, the samples were analyzed by XRD and Mossbauer spectroscopy for particle size and phase information and by instrumental neutron activation analysis for iron content.

RESULTS AND DISCUSSION. The spectra for 9 samples having Fe₂O₃ contents between 0.01 (unimpregnated gel) and 12.8 wt. % are shown in Figure 1. There was sufficient iron in the samples having greater than 0.32 wt. % Fe₂O₃ to obtain room-temperature Mossbauer spectra, and they are all doublets (Is=0.32 mm/s; QS=0.5-0.8 mm/s). The low-temperature spectra [5] show that the doublets are due to superparamagnetic and crystalline hematite particles having mean particle diameters less than ~20 nm. XRD data, obtained for all but the most iron-rich sample, show no diffraction lines. Because of the Mossbauer data, this implies that the particles have dimensions too small to coherently scatter x-rays rather than having a non-crystalline structure. Two trends with increasing iron content are apparent in Figure 1. The absorption edge shifts toward the visible, and the absorption strength at the position of the hematite band minimum near 0.85 μm increases. Note that a resolved minimum is not present, and that this, together with evidence for superparamagnetism [5], is indicative of the presence of ultramicrocrystalline hematite particles. The features near 1.22 and 1.37 μm are OH combination and overtones that are inherent to the silica gel.

The spectra in Figure 2 show that the position of the absorption edge does not necessarily correlate with Fe₂O₃ content. Based on the temperature dependence of their Mossbauer spectra [5], the mean particle diameter of Sample A (12.8 wt. % Fe₂O₃) is ~9 nm, and that for Sample B (23.7 wt. % Fe₂O₃) is at least 20 nm. The presence of a well-defined band minimum for Sample B is consistent with the larger mean particle diameter for Sample B because it implies the presence of a significant fraction of particles that are too large.
to be characterized as ultramicrocrystalline. Sample A thus has a higher number density of hematite particles but significantly lower Fe$_2$O$_3$ content relative to Sample B. As shown in Figure 2, the position of the absorption edge for Sample A is located further into the visible than that for Sample B. This is opposite to the trend in Figure 1 and shows that both the total Fe$_2$O$_3$ content and the mean size of the hematite particles can influence the position of the absorption edge. It is likely that the regular variation in the spectral properties with iron content in Figure 1 is due to a regular increase in the number density of ultramicrocrystalline hematite, which also correlates with iron content.

The position of the absorption edge for the sample with 0.46 wt. % Fe$_2$O$_3$ (Figure 1) closely matches that observed for the martian case, but a shallow band minimum near 0.85 um is not present in the former. The spectrum of Sample C (Figure 2), which is a mixture of the 0.46 % sample with 10 wt. % Sample B, shows that a wide size distribution including ultramicrocrystalline hematite particles preserves the position of the absorption edge of the ultramicrocrystalline hematite particles and produces a shallow band minimum characteristic of the larger hematite particles. It can be concluded, therefore, that the spectral data for Mars are consistent with the presence of hematite as a distinct phase.