SPECTRAL BEHAVIOR OF HEMATITE AT VISIBLE/NEAR INFRARED AND MIDINFRARED WAVELENGTHS.

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Introduction: The oxide mineral hematite (α-Fe_2O_3) is present on Mars as evidenced by spectroscopy using visible/near infrared (VNIR) [1-4] and midinfrared (MIR) wavelengths [5]. The physical nature of this surficial hematite varies from fine-grained, crystalline red hematite (red-Hm) in certain martian bright regions [e.g., 2], to coarser-grained, crystalline gray hematite (gray-Hm) in the Sinus Meridiani equatorial site discovered in the Mars Global Surveyor Thermal Emission Spectrometer (MGS-TES) data [5]. The VNIR spectra require that the red hematite is present in amounts subordinate to a second ferric pigment, which accounts for the general shape and position of the martian ferric absorption edge. By analogy with palagonitic tephra [6] and synthetic samples [1,7], the pigment is a nanophase ferric oxide, possibly nanophase hematite (np-Hm).

The purpose of this abstract is to document the physicospectral properties of hematite in the VNIR (0.35 to 2.2 µm) and MIR (5 to 25 µm) with respect to the terms "nanophase" and "crystalline", "red" and "gray", and "fine-grained" and "coarse-grained". We will show that different "types" of hematite (np-, red-, and gray-Hm) have different spectral responses in the VNIR and MIR regions and that these differences are important for inferring the types of hematite and their relative proportions from remotely sensed spectra of Mars. Because hematite is an alteration product that forms through many different geologic processes, determination of the type of hematite provides important clues about the style and diversity of martian weathering processes.

Nanophase versus Crystalline: As shown by X-ray diffraction and Mössbauer spectroscopy, np-Hm is X-ray amorphous (two broad XRD lines centered near 0.25 and 0.15 nm) and superparamagnetic (Mössbauer doublet at 293 K), and crystalline hematite coherently scatters X-rays (powder pattern with sharp peaks) and has a thermally stable magnetic moment (Mössbauer sextet at 293 K) [1,8,9,10]. Nanophase behavior occurs at diameters <10 nm. VNIR and MIR spectroscopy are also sensitive to hematite crystallinity and particle diameter (Figure 1 and [1,10,11,12,]). The absence (for np-Hm; TNA30-215) and presence (for crystalline-Hm; HMS3) of a well-defined minimum near 860 nm in VNIR spectra results from broad and narrow distributions, respectively, in crystal-field environments [1,10]. Presumably, the absence (np-Hm) and presence (crystalline-Hm) of discrete vibrational bands in the 700 to 400 cm^{-1} region of MIR spectra results from broad and narrow distributions, respectively, in the shape of FeO_6 octahedra. In both cases, the broad distributions in local Fe environments within np-Hm particles results from their high surface-to-volume ratios and attendant inability to establish long-range crystal order [1].

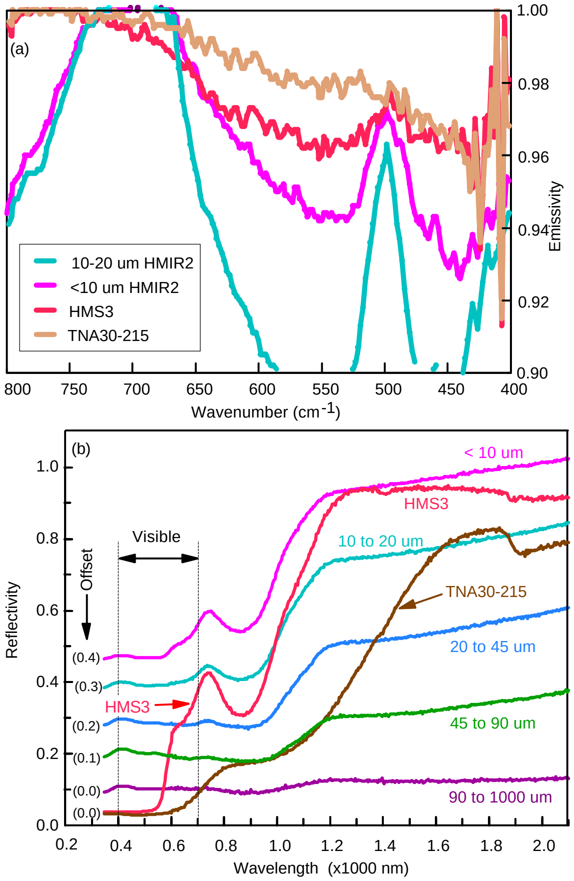

Figure 1: (a) MIR emissivity and (b) VNIR reflectivity spectra of crystalline hematites HMS3 (red, 0.14 µm particle diameter [13]) and HMIR2 size fractions and np-Hm TNA30-215 (<10 nm particle diameter [1]). Sharp features near 400 cm^{-1} in (a) result from water vapor.

Red versus Gray: As shown in Figure 1b, crystalline, fine-grained HMS3 is visibly red because its absorption edge (0.52 to 0.70 µm) is deep and sharp and occurs in the red portion of the visible spectrum. Np-Hm TNA30-215 is very dark purple (nearly black) because the onset of the ferric edge occurs at longer wavelengths (~0.62 µm). In contrast, all size separates of crystalline (by XRD) hematite HMIR2 (Ironton, MN), which we obtained by crushing and wet-sieving a gray-colored hand specimen, are gray except for the <10 µm fraction. As shown in Figure 1b, gray implies a relatively flat reflectivity spectrum over visible wavelengths. The <10-µm fraction is purple, consistent with a shallow absorption edge beginning near 0.52 µm. Because red (shorthand for orange-red-purple) hematite paint pigments have mean particle diameters of 5 µm [e.g., 13,14], the particle diameter at which the red to gray change occurs is ~5-10 µm. Because large (>10 µm) hematite particles can be polycrystalline assemblages of red <5 µm hematite grains, large hematite particles are not necessarily gray. Although np-Hm is nearly black in the visible as a pure powder, it imparts a yellow to brown color when dispersed at moderate concentrations in spectrally white matrix material [1]. In our usage, red-Hm and gray-Hm are always crystalline.

Fine versus Coarse: Operationally, it is convenient to use the diameter of the red to gray boundary (5-10 µm) for the dividing line for fine and coarse hematite. By this convention, fine-grained hematite (either np-Hm or red-Hm) always imparts color (i.e., a ferric absorption edge) and gray-Hm does not. Martian bright regions like Olympus-Amazonis can be described as containing fine-grained hematite because their reflectivity spectra can be reproduced using laboratory mixtures of nanophase ferric oxide (either synthetic np-Hm or palagonitic tephra) and <5 wt% red-Hm HMS3 [1,2,4]. Gray hematite could be present, but this interpretation is equivocal with VNIR data [1].

Figure 2 shows that the fine-grained (np-Hm and red-Hm) and coarse-grained (gray-Hm) hematite powders have weak and strong fundamental vibrational bands, respectively, between 700 and 400 cm^{-1}. Also, the hematite fundamental vibrations decrease in strength with decreasing particle diameter. Comparison of Figures 1 and 2 shows that fine-grained hematites (np-Hm and red-Hm) are more easily detected in VNIR data and that coarse-grained hematites (gray-Hm) are more easily detected in MIR data. Although the spectra are not shown, powders of coarse-grained, composite particles of red-Hm are readily detected in both VNIR and MIR data because they are both "red" in the VNIR and have deep fundamental bands in the MIR.

Hematite in Sinus Meridiani, Mars: An area in Sinus Meridiani (near 0° N, 5° W) stands out as possibly unique. After atmospheric correction and spectral removal of a basalt component [5,15], the residual spectrum clearly shows the hematite fundamental bands between approximately 530 and 200 cm^{-1} and a high, relatively flat emissivity spectrum between approximately 830 and 1300 cm^{-1} [5]. Surface regions where VNIR data indicate the presence of red-Hm and possibly np-Hm (e.g., Olympus-Amazonis [e.g., 2]) apparently do not have such pronounced fundamental hematite absorption bands in the MIR [5]. This observation, coupled with the apparently weak VNIR signature of red hematite in the Sinus Meridiani region [16], suggests that the hematite in Sinus Meridiani is gray-Hm (i.e., >5-10 µm particles), as discussed in [5]. The gray-Hm can occur as discrete particles or as grains in larger composite particles.

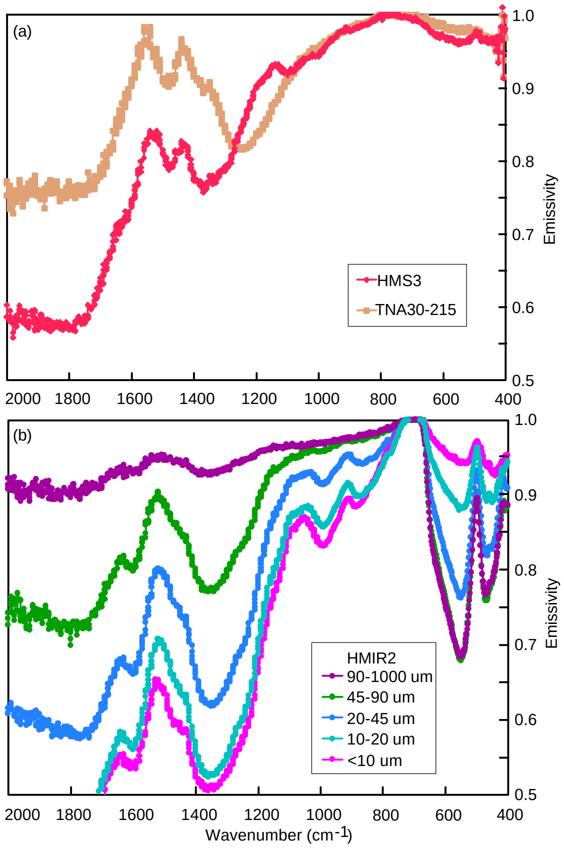

Figure 2: MIR emissivity spectra of (a) HMS3 (red-Hm) and TNA30-215 (np-Hm) and (b) particle size fractions of hematite HMIR2.

References: [1] Morris et al., *JGR*, *94*, 2760, 1989; [2] Morris et al., *JGR*, *102*, 9125, 1997; [3] Bell et al., *JGR*, *95*, 14447, 1990; [4] Morris and Golden, *Icarus*, *134*, 1, 1998; [5] Christensen et al., *JGR*, submitted, 1999; [6] Morris et al., *GCA*, *57*, 4597, 1993; [7] Morris and Lauer, *JGR*, *95*, 5101, 1990; [8] Kundig et al., *Phys. Rev.*, *142*, 327, 1966; [9] Dormann, *Rev. Phys. App.*, *16*, 275, 1985; [10] Morris et al., *LPSXXII*, 927, 1991; [11] Bell et al., *JGR*, *100*, 5297, 1995; [12] Lane et al., *LPSXXX*, #1469, 1999; [13] Morris et al., *JGR*, *90*, 3126, 1985; [14] Hancock, K. R., Mineral Pigments, in *Industrial Minerals and Rocks*, 335, 1975; [15] Smith et al., *JGR*, submitted, 1999; [16] Bell et al., *LPSXXX*, #1751, 1999.