AGGREGATES OF THE SMALLEST NANOPARTICLES MAKE THE BEST "COARSE" GRAY HEMATITE ANALOG. A.S. Elwood Madden[1], V.E. Hamilton[2], M.E. Elwood Madden[1], and A.L. Swindle[3] [1]School of Geology and Geophysics, University of Oklahoma, 100 E. Boyd, Norman, OK 73019, amadden@ou.edu, [2]Southwest Research Institute, Boulder, CO 80302, [3]Department of Geology, Wichita State University, Wichita KS 67260.

Introduction: Links between mineral properties (e.g., mineralogy, chemistry, texture) and spectral characteristics can be used to interpret the geologic history and present activity of water on Mars. Thermal infrared (TIR) spectra of concentrated hematite deposits in Meridiani Planum lack a 390 cm^{-1} emissivity minimum [1], initially interpreted to represent massive, platy/oriented, crystalline (gray) hematite [2] or aggregates of nanoparticulate hematite with platy morphology [3] but later shown to be hematite spherules [4, 5]. In this investigation, we explored the roles of particle size, crystallinity, and aggregation state in generating TIR spectra similar to coarse crystalline hematite on Mars. We synthesized aqueous hematite nanoparticle suspensions with a range of sizes and generated aggregate grains through freezing with subsequent cryodessication. Aggregates were further charactersized by XRD, TEM, and Raman to test hypotheses regarding which sample characteristics were most important for controlling spectral characteristics.

Hematite synthesis and aggregation: We synthesized five distinct batches of nanoparticulate hematite with different size ranges and morphologies (Table 1). We confirmed the phase identification with powder X-ray diffraction (XRD) and size/morphology with transmission electron microscopy (TEM).

ID	description
Hem I	7-10 nm platelets
Hem II	~30 nm rounded platelets
Hem III	200-400 nm platelets with some rhombs
Hem IV	~1 µm pseudocubic
Hem V	Mixture of ~10 nm platelets and ~30 nm sintered aggregates of the 10 nm platelets

Table 1. Synthetic hematite samples used in this study and sizes of primary particle size in solution, before aggregation.

Aggregate visual characteristics: Freezing solutions of aqueous nanoparticles led to formation of grains that are aggregates of primary particles (Fig. 1) [6]. Hem I and V aggregates are smooth, dense, dark purple to gray curved grains at the micron scale (Fig. 1). On the other hand, Hem II and IV grains appear visibly rough at the micron scale, relevant for vibrational spectroscopy. The appearance of Hem III is intermediate between the Hem I/V and Hem II/IV endmembers. Thus, the smallest particles produced the most dense, dark, and smooth aggregates.

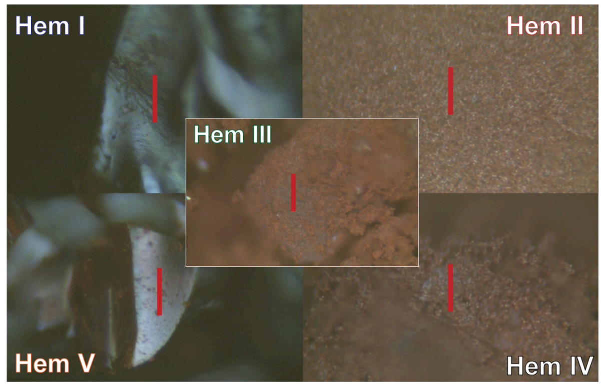

Figure 1. Optical photos of grain areas (150 µm x 95 µm) analyzed by Raman; vertical lines indicate footprint of laser spot on sample surface.

Thermal infrared spectroscopy: Out of the five samples confirmed to be hematite by powder XRD, each exhibited features at the three frequencies expected for hematite, but with wide variation in the strength and character of the emission bands (Fig. 2). Aggregates composed of the smallest fundamental particle sizes (Hem I/ 10 nm and Hem V/ 10-30 nm) were most similar to that observed for Martian hematite. Spectra of Hem III (200 nm) were also similar to Martian hematite, although two of the bands (near 460 cm^{-1} and 420 cm^{-1}) were weaker than expected (Fig. 2). On the other hand, spectra for Hem II (30 nm) and Hem IV were far weaker than expected; the largest fundamental particle size sample (Hem IV) gave to the weakest recorded TIR hematite signal. Hem II, III, and IV all show a double band in the 550-630 cm^{-1} range, rather than the expected single band. Finally, it is important to note that none of the samples show a clear emissivity minimum at 390 cm^{-1}, except perhaps a weak feature in Hem III (200 nm) (Fig. 2).

Raman spectroscopy: All samples exhibited Raman spectra expected for hematite, but with clear variations; 1.) red-shifting and broadening, as would be expected for smaller particle sizes [7], and 2.) increase in the 293 cm^{-1} peak area indicating the presence of minor FeOOH. Similarities between spectra match results from TIR; Hem I and V are most similar to each other (and to a RRUFF database coarse hematite [8]).

Hem III Raman spectra have similar peak positions to Hem I and Hem V but sharper peaks and greater 293 peak areas. Hem II and Hem IV Raman spectra are similar; both are considerably red-shifted and broadened.

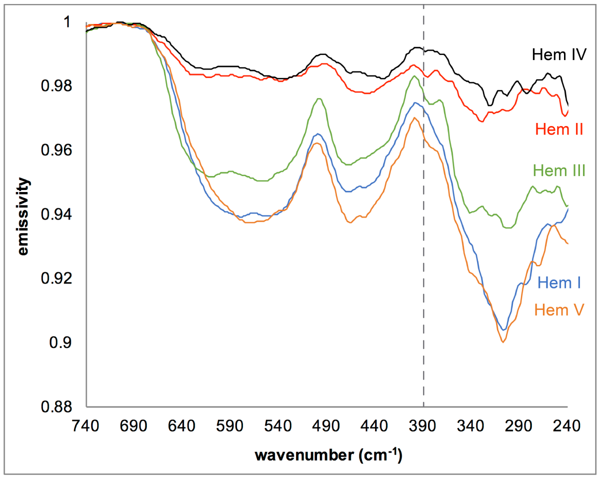

Figure 2. Metal-oxygen region TIR spectra.

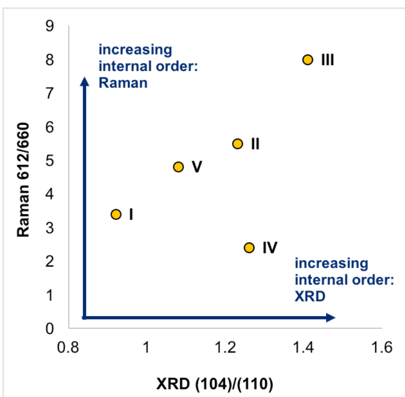

Figure 3. Measures of internal disorder as determined by XRD (x-axis) and Raman (y-axis).

Particle characteristics important for various spectroscopic methods: Comparison of Raman and XRD analyses of hematite nanoparticle aggregates demonstrates that the primary particle size and internal particle disorder provide first-order controls on spectra. Hematites (I and V) are disordered likely due to primary/ individual particle size effects [e.g., 7], with increasing order through the larger Hem II and Hem III samples. The anomalously low internal order of Hem IV (the largest primary/ individual particle size) determined by Raman (Fig. 3) is supported by previous work using the same synthesis method; during growth hematite subunits aggregate in a regular fashion to provide the uniform size and morphology, but that seems to preserve a poorly crystalline network between the individual sub-crystallites [9]. Thus, Hem IV (1000 nm primary particle diameter) appears similar to Hem II (40 nm primary particle diameter) in spectra.

Future work: We observed stronger TIR spectral features for those aggregates that have a dark smooth surface at the micron scale, which were composed of the smallest fundamental particle sizes in our case. We continue to explore relationships between primary particle size, aggregate grain size distribution and roughness, packing/space-filling of fine-grained particles [10], and crystallinity in controlling hematite spectral characteristics.

Relevance to hematite on Mars: All aggregates produced TIR spectra similar to coarse hematite; however, grains composed of primary particles with diameters <30 nm produced dark gray coarse aggregates with TIR spectra most similar to those of the Mars spherules. In agreement with [3], internal radial crystallographic orientation of nanocrystalline aggregates [11] is not required to produce coarse-analog TIR spectra. The 390 cm^{-1} minimum will likely be absent from any nanocrystalline hematite if it is somewhat poorly crystalline or of fine enough fundamental particle size (<30 nm). Our Hem III was the most crystalline according to XRD and Raman and produced the most prominent (albeit minor) feature at 390 cm^{-1}; this feature was weaker in Hem V, weakest in Hem I, and absent in TES spectra of Martian hematite spherules. All of these results agree with previous suggestions that hematite spherules formed at temperatures <300° C [12]. Finally, our results will aid interpreting future Raman spectra of hematite materials collected on Mars, such as those in the planned ExoMars mission [13].

References: [1] Christensen, P. R. et al. (2000) *J. Geophys. Res.-Planets,* 105(E4). [2] Lane M.D. et al. (2002) *J. Geophys. Res.*, 107(E12), 5126, [3] Glotch T. D. et al. (2006) *Icarus,* 181(2), 408-418. [4] Squyres S. W. et al. (2004) *Science,* 306, 1698-1703. [5] Christensen P. R. et al. (2004) *Science*, 306, 1733-1739. [6] Sexton, M.R. et al. (2016) *Icarus*, in press. [7] Chernyshova I. V. et al. (2007) *Phys. Chem. Chem. Phys.*, 9, 1736-1750. [8] Lafuente B. et al. (2015) http://rruff.info. [9] Sugimoto, T., et al. (1998) *J. Coll. Int. Sci.*, 134, 265-279. [10] Kirkland L. E. et al. (2004) *Geophys. Res. Lett.*, 31(5), L05704. [11] Golden, D. C. et al., (2008) *Am. Mineral.*, 93(8-9), 1201-1214. [12] Glotch, T. D. et al. (2004) *J. Geophys. Res.*, 109, E07003. [13] Lopez-Reyes, G. et al. (2013) *Eur. J. Mineral.*, 25(5), 721-733.

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