SPECTRAL CHARACTERISTICS OF NANOPHASE IRON OXIDES AND HYDROXIDES. E. C. Sklute, M. D. Dyar, S. Kashyap, J. F. Holden, and S. Jaret. Mount Holyoke College, Dept. of Astronomy, South Hadley, MA, 01075, esklute@mtholyoke.edu; Univ. of Massachusetts, Amherst, Dept. of Microbiology, Amherst, MA 01003; Stony Brook University, Dept. of Geosciences, 255 ESS Bldg., Stony Brook, NY, 11794-2100.

Introduction: Iron oxides and oxyhydroxides in the nanoscale size range (1-100 nm in at least one direction) are involved in, and often the driving force for, many of Earth’s surface processes [1-3]. Nanophase iron oxides and hydroxides (iron NPOs) are also believed to be ubiquitous on Mars as part of the global dust [4-6], and have been found in many achondrites [7], suggesting that they are present on the planets from which those meteorites originated. Given their known prevalence and importance, it is reasonable to assume that iron NPOs may be common phases on many rocky solar system bodies and could affect surface processes on those bodies.

Accurate identification of type, size, crystallinity, and variation of iron oxides on planetary surfaces has significant implications for the conditions and processes occurring on those planets, but in the nanophase size regime, mineral identification is challenging. The most reliable identifications for iron NPOs come from the few studies where multiple analytical techniques are used in tandem. However, there is a significant deficiency in spectral libraries of well-characterized samples in this size fraction. Here we report the visible near infrared (VNIR), mid-infrared (MIR) attenuated total reflectance (ATR), Raman, and Mössbauer spectral characteristics of a set of synthetic iron NPOs to begin to fill that deficiency.

Methods: Ten iron NPOs: ferrihydrite (Fh), akaganéite (Ak1023), goethite (Goet0115 and Goet0123), lepidocrocite (Lep0304 and Lep1006), hematite (Hem0220 and Hem1009), maghemite (magh0618), and magnetite (Mag0414) were synthesized following the methods of [8-10]. All samples were freeze-dried directly prior to analysis and confirmed to be pure phases at the resolution of XRD. Mössbauer spectra were collected at Mount Holyoke College on a Web Research Co. (now See Co.) W100 spectrometer using a ~80 mCi $^{57}$Co source in Rh with a Janis closed cycle He cryostat. Spectra were collected at 295K, 220K, 150K, 80K, and 7K and calibrated to $\alpha$-Fe foil. Mössbauer data were fit using Mexfield, a program provided by E. DeGrave at the University of Ghent, Belgium. Raman spectra were collected at Stony Brook University (SBU) on a Thermo Fisher Nicolet 6700 FTIR, 256 scans per spectrum. VNIR spectra were collected at SBU on an ASD FieldSpec3 Max with $\iota=30$, $\epsilon=0$.

Results: Mössbauer spectra of the nanophase iron oxides and hydroxides are shown in Fig. 1 (295K) and Fig. 2 (7K). They indicate that there is a minor contaminant in Hem0220 and that Mag0414 is likely a cation-deficient magnetite rather than an end member magnetite. Superparamagnetic character caused by...
small grain size can be seen in Magh0618, Hem1009, and Goet0123 at 295K.

MIR ATR data for iron NPOs display absorptions due to the asymmetric H-O-H and O-H stretching (~3400 cm⁻¹), H-O-H bending (~1630 cm⁻¹), O-H bending (~1170-750 cm⁻¹), and Fe-O vibrations (~ 650 cm⁻¹) [11]. Fig. 3 shows spectra for iron NPOs below 1900 cm⁻¹, where they are most distinguishable. All samples show a limited number of broadened absorption features characteristic of fine grained samples [12].

Raman data for iron NPOs show scattering due to the interaction of IR light with Fe-O vibrations, where the vibration causes a polarization change to the electron density [13]. The Raman data (Fig. 4) show a reduced number of broadened features (w.r.t. literature), characteristic of finer grained and/or poorly crystalline.

VNIR spectra of iron NPOs show Fe³⁺ spin forbidden crystal field transitions (0.35-0.90 μm), absorptions due to overtones and combinations of OH and H₂O stretching, bending, and rotation modes (~1.4 μm, 1.7-1.8 μm, ~1.9 μm, 2.0-2.5 μm). The shape and location of these features can be used to help differentiate iron NPOs (Fig. 5). Spectra for iron NPOs show greater reflectivity than those for their larger grained counterparts and adsorbed water on the greatly increased number of surface sites leads to an increase in intensity and smearing out of hydration features.

Conclusions: Iron NPOs have been synthesized and analyzed by multiple forms of spectroscopy. Although Hem0220 shows an impurity and Mag0414 is nonstoichiometric, results for all other samples indicate that the samples are pure at the resolution of the respective techniques. MIR ATR and Raman features for these nanophase materials are reduced in number and broadened compared to literature reports for coarser samples, while VNIR spectra broader hydration features but increased reflectivity.