EFFECTS OF SURROUNDING MEDIUM (FLUID VS. AIR) ON SPECTRAL PROPERTIES OF NANOPHASE IRON (OXYHYDR)OXIDES. Elizabeth C. Sklute[1], Srishti Kashyap[2], Peng Wang[3], Thomas T. Tague Jr.[3], M. Darby Dyar[1] and James F. Holden[2], [1]Dept. of Astronomy, Mount Holyoke College, 50 College St., South Hadley, MA. 01075, USA, ecsklute@mtholyoke.edu. [2]Dept. of Microbiology, University of Massachusetts, 639 Pleasant St. Amherst, MA. 01003, USA. [3]Bruker Optics Inc., 19 Fortune Dr. Billerica, MA. 01821, USA.

Introduction: Nanophase iron (oxyhydr)oxides (FeNPOs) are prevelant and important phases on Earth, Mars, and potentially many other rocky solar system-bodies [1]. On Earth, these phases fuel microbial metabolisms across many environments and substantially impact fluid chemistry, soil evolution, and nutrient and contaminant cycling [2]. Their size often causes them to be structurally, and thus spectroscopically, distinct from their bulk counterparts and even other FeNPOs of different sizes and shapes. These morphological differences relate to environmental differences at formation and can affect subsequent reactivity. Understanding spectroscopic variability of FeNPOs is critical to evaluating their role in planetary surface processes.

Unlike the case for bulk samples, spectra of nanophase materials are substantially impacted by surface structure. Interactions between the surrounding medium and the particle surface *both at the time of synthesis and at the time of analysis* may therefore create significant changes to particulates' spectra. Understanding of these differences across biologically relevant media is needed to identify definitive spectroscopic biosignatures. Yet, to date, very little work has been done to investigate phenomena that cause spectra of the same particles to be different when wet vs. dry. We report here spectra of seven synthetic FeNPOs dried and analyzed under various levels of hydration to address this issue and set a baseline for experiments utilizing saline solutions, as commonly used in microbial culturing.

Methods: Detailed synthesis procedures for the seven FeNPOs: ferrihydrite (Fh), akaganéite (Akag102315), lepidocrocite (Lep030415), hematite (Hem100915), goethite (Goet012315), maghemite (Magh061815), and magnetite (Mag060516), are given in [1]. Because Hem100915 could not be sufficiently concentrated for Raman fluid analysis, Hem022015 is presented and compared to Hem100915. Hem022015 was synthesized using method #5 as given in [2]. FeNPOs were stored in Milli-Q water (18.2 MΩ•cm) at 4° C until preparation.

Raman analysis was performed at Bruker Optics Inc. on a Bruker Senterra Raman microscope using a 20× objective (connected to a single elbow for fluid samples) and a 532 nm excitation laser powered to either 0.2 or 2 mW, depending on the sensitivity of the sample towards heat transformation. Raman samples were analyzed either as freshly filtered powders or in fluid through the wall of the glass vial. For fluid samples, the vial and water contributions were subtracted from the overall spectrum.

Fourier transform infrared (FTIR) attenuated total reflectance (ATR) data were acquired at Bruker Optics Inc. on a Bruker Vertex 70 FTIR using a diamond ATR accessory, ultra-wide range beam splitter, and DTGS detector. Samples were prepared as (1) freeze-dried powders (or anoxically dried in the case of Mag060516) (2) freshly filtered and highly hydrated gels, (3) freshly filtered air-dried powders, and (4) fluid drops concentrated through the *in situ* drying process on the ATR stage. Goet012315 was also dispersed in isopropanol (IPA) and analyzed as it dried.

Results: *Raman.* **Figure 1** shows Raman spectra of FeNPOs analyzed both in water and as solids in air. Small differences between fluid and dry sample peak positions are seen for several of the oxides. For Lep030415 and Mag060516, the main peak in the liquid sample is shifted to higher energy, while for Goet011515, Goet012315, and Akag102315, the main peak is shifted lower.

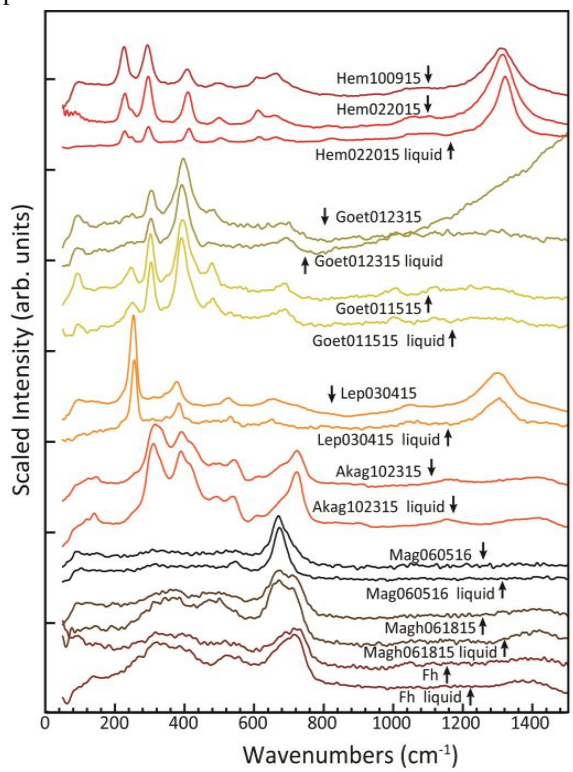

Figure 1. Raman data for FeNPOs analyzed as fluids and dry powders. Only slight shifts in Raman features result from differences in medium and should not hamper identification.

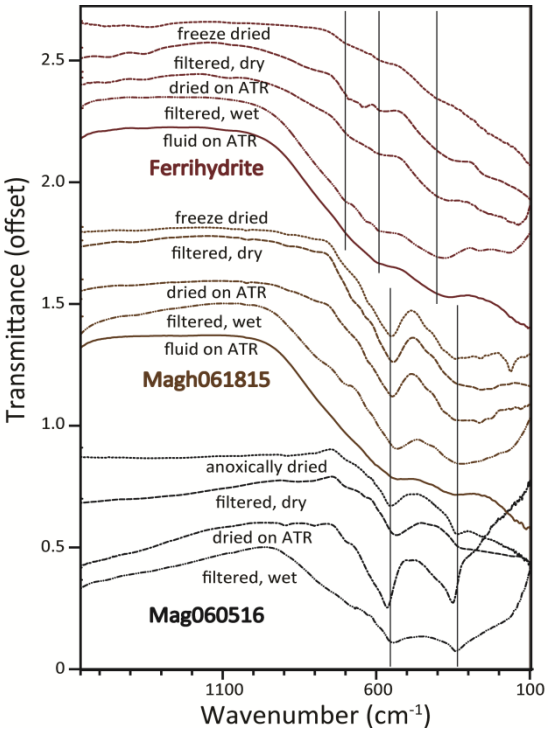

Figure 2. FTIR ATR data for Fh, Magh061815, and Mag060516 from various preparations and in different hydration states. Vertical lines denote absorptions of freeze-dried Fh (top three) and Mag060516 (bottom two).

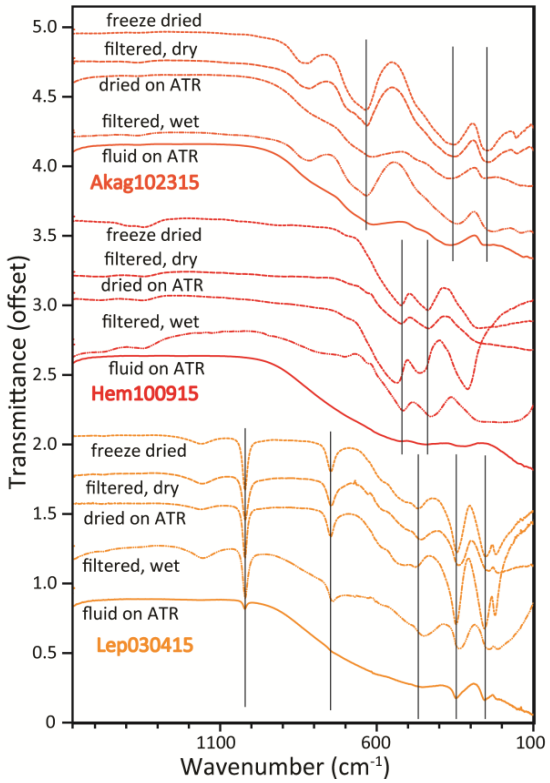

Figure 3. FTIR ATR data for Akag102315, Hem100915, and Lep030415 from various preparations and in different hydration states. Lines denote absorptions of freeze-dried samples.

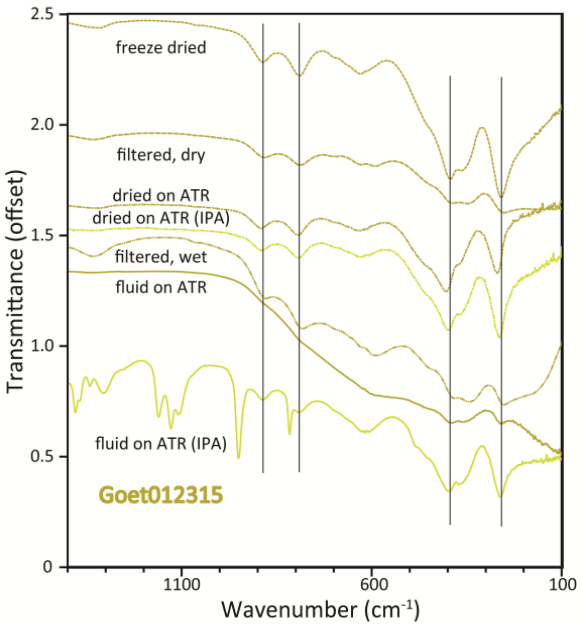

Figure 4. FTIR ATR data for Goet012315 from various preparations, in different hydration states, and in different solvents. Lines denote absortpions of freeze-dried samples. IPA is isoporpopanol.

FTIR. Mid- and far-infrared spectra forFeNPOs (**Figure 1-3**) show that the position of major overlap depends on preparation method. This is particularly important for nanophase magnetite and maghemite spectra, which only differ slightly in absorption position. A significant shift with preparation method is also found in nanophase goethite spectra. The positions of the two main hydroxyl absorptions at ~883 and 788 cm^{-1} shift with degree of hydration and method of drying. This is important because these absorption positions are often correlated to Al substitution [3], but can shift by up to 10 cm^{-1} based on hydration state.

Implications: Spectral variations among FeNPO samples prepared and analyzed under different conditions are small but significant. These shifts can confuse interpretations of cation substitution [e.g., 3] or biosignature presence/absence when they are based on the position(s) of any spectral feature(s). The most significant differences are seen for samples dried on the ATR crystal, for reasons we do not yet understand, but which probably relate (in part) to kintetics and orientation. This work is particularly important to biological investigations in which microbial oxidation or reduction are inferred using air- or freeze-dried samples.

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References: [1] Sklute E. C. et al. (2017) *Phys. Chem. Mineral.* doi:10.1007/s00269-017-0897-y [2] Schwertmann U. and Cornell R. M. (2000) *Wiley, New York*. [3] Schulz D. G. and Schwertmann U. (1987) *Clay Mineral.*, 22, 83-92.