

## D<sub>2</sub>O SUBSTITUTION EXPERIMENT ON HYDRATED IRON AND MAGNESIUM SULFATES & ITS APPLICATION FOR SPECTRAL INTERPRETATION OF MARTIAN SULFATES.

John J. Freeman<sup>1</sup>, Michael Jin<sup>1,2</sup>, Alian Wang<sup>1</sup>, <sup>1</sup>Department of Earth & Planetary Sciences and the McDonnell Center for the Space Sciences, Washington University, St. Louis, MO, 63130, <sup>2</sup>John Burroughs School, Ladue, MO, 63124, (JohnJFreeman@wustl.edu)

**Sulfates were found on Mars** by both surface explorations and orbital remote sensing, but discrepancies exist in the results of these two groups of observations. Mars Exploration Rovers have found Fe-, Ca-, and Mg-sulfates on Mars in the vicinities of their landing sites. Jarosite,  $[\text{KFe}^{3+}_3(\text{SO}_4)_2(\text{OH})_6]$ , has been definitively identified by Mössbauer spectroscopy, and this mineral accounts for  $\sim 10$  wt.% the material in Meridiani outcrop [1]. From the salty soils excavated by the wheels of Spirit rover at Gusev, a tentative mineral identification, also based on Mössbauer spectroscopy, was made for ferric sulfate; although no further specific mineralogy can be extracted at the moment [2]. In MER investigations, compositional correlations seen in APXS data [3, 4] and mineral modeling based on APXS and MB data, have been used to imply the existence Mg-sulfates and Ca-sulfates in Gusev salty soils, the Meridiani outcrop, and in a few Gusev outcrops [3, 4, 5, 6, 7].

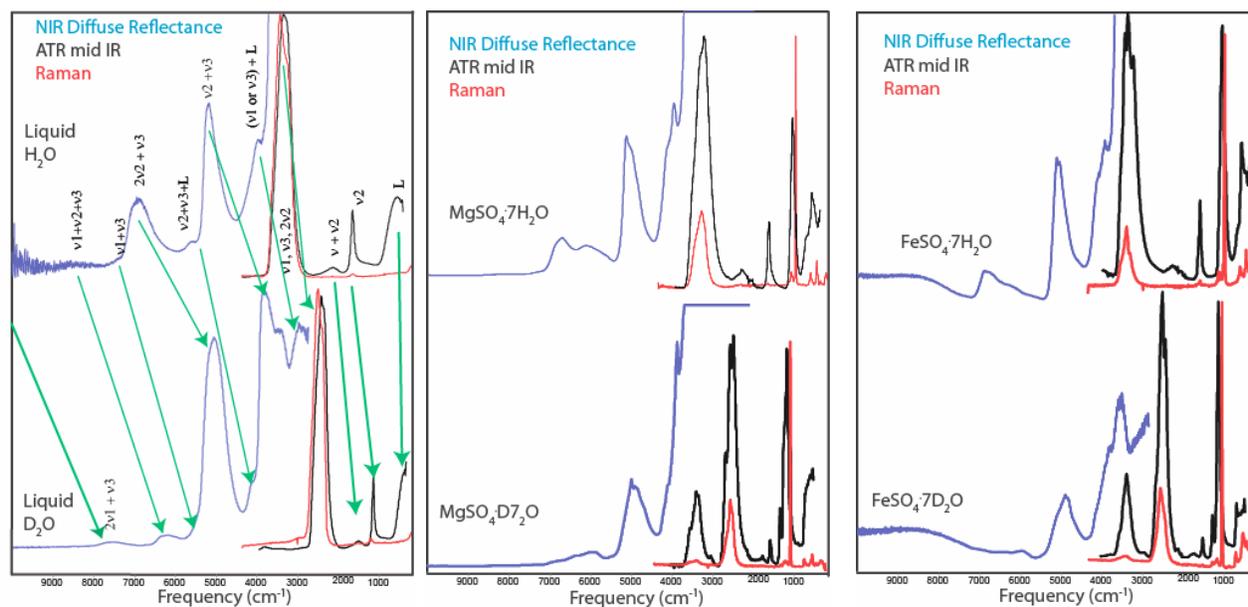
On the other hand, orbital remote sensing based on NIR reflectance spectra by OMEGA on Mars Express and by CRISM on MRO clearly shows the evidence for Mg- and Ca-sulfates but not Fe-sulfates [8, 9]. The general non-detection of iron sulfates on Mars by orbital remote sensing is one of the biggest mysteries in martian sulfate investigation: Iron sulfates of any kind were not seen at Meridiani Opportunity landing site and traversing area [10], where the Meridiani outcrops extend several hundreds km wide and several hundreds meter in depth. We believe the

solution to this mystery may be found in the details of NIR (1 to 5  $\mu\text{m}$ ) spectra of the sulfates -- especially when they are mixed with each other or mixed with basaltic components.

The purpose of the D<sub>2</sub>O substitution experiments described here is to build a reliable set of peak assignments for hydrated metal sulfates in the 1 to 5  $\mu\text{m}$  spectral region as observed by both OMEGA and CRISM -- a spectral region dominated by the OH stretching vibration of the water molecule plus numerous overtone and combinational modes attributed to fundamental modes of both the water molecule and the sulfate ion. These peak assignments help the interpretation of the NIR spectra obtained in OMEGA and CRISM experiments. .

D for H substitution is a traditional technique for determining which bands in the vibrational spectrum of a material are associated with motions involving the H atom. In our case, we substitute D<sub>2</sub>O for H<sub>2</sub>O to identify fundamental, combinational and overtone vibrations associated with the waters of crystallization in the sulfate minerals. . The approach we used here is to build first a basic set of peak assignments of the fundamental vibrational modes seen in Raman and mid-IR spectra of liquid H<sub>2</sub>O and D<sub>2</sub>O and substituted hydrates of the Mg- and Fe-sulfates; and then to use these assignments to understand the overtone and combinational modes observed in the in NIR spectral range of the minerals.

**Spectral features of H<sub>2</sub>O/D<sub>2</sub>O:** Figure 1 shows a



set of Raman, mid-IR, and diffuse reflectance NIR spectra of liquid D<sub>2</sub>O compared to the spectra of liquid H<sub>2</sub>O. Diffuse reflectance spectra of the liquids were obtained with a Nexus 670 FTIR spectrometer fitted with a diffuse reflectance attachment. Samples were in the form a layer of NIR-transparent, powdered CaF<sub>2</sub> moistened with a few drops of the liquid. The ATR spectra were recorded using a diamond anvil ATR attachment. Raman spectra were acquired with a HoloLab5000-532 system. In Figure 1, the % diffuse reflectance data have been converted to Kubela-Munk units, ATR mid-IR spectra are shown in ATR corrected absorbance units, and Raman spectra are shown in relative intensity units.

**D<sub>2</sub>O substitution in Mg-sulfates:** MgSO<sub>4</sub>·7D<sub>2</sub>O was prepared by dissolving MgSO<sub>4</sub>·H<sub>2</sub>O into liquid D<sub>2</sub>O at nearly 100°C and then cooling the solution to room temperature to precipitate crystals. This process was repeated 3 - 4 more times using new liquid D<sub>2</sub>O each time. This procedure converted the majority of structural water into the deuterated form. Dehydration of MgSO<sub>4</sub>·7D<sub>2</sub>O using deuterated, aqueous-salt solutions as relative-humidity buffers is also under way to produce the deuterated hydrates of starkeyite and kieserite. Figure 2 shows a set of Raman, mid-IR, and NIR diffuse reflectance spectra of epsomite and that of its deuterated analog. The mid-IR absorbance spectrum of the deuterated material shows that over 80% of structural waters had been substituted by D<sub>2</sub>O.

**D<sub>2</sub>O substitution in Fe<sup>2+</sup>-sulfates:** FeSO<sub>4</sub>·7D<sub>2</sub>O was prepared in the same way as for MgSO<sub>4</sub>·D<sub>2</sub>O. It was noted that despite our precautions to exclude oxygen from the experiments, some small amount of the ferric ion were produced in the solution. The very high solubility of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in water relative to FeSO<sub>4</sub>, however, insured that only the hydrated ferrous species crystallized on cooling the aqueous solution. Dehydration of the FeSO<sub>4</sub>·7D<sub>2</sub>O over deuterated, aqueous-salt solutions as relative-humidity buffers was used to make deuterated analogs of rozenite and szomolnokite. Figure 3 shows a set of Raman, mid-IR, and NIR spectra of deuterated melanterite, in comparison with those of melanterite.

**Spectral peak assignments for fundamental vibration of H<sub>2</sub>O and D<sub>2</sub>O:** A systematic peak position shift upon deuteration can be seen in every fundamental vibrational mode of the water molecule: ν<sub>1</sub>, Raman active OH stretching; ν<sub>2</sub>, H<sub>2</sub>O bending; ν<sub>3</sub>, IR active OH stretching, and L, low energy lattice modes. These assignments derived from the basic literature [11, 12] are shown in Figure 1. Also shown in Figure 1 are the assignments for the water combi-

nation and overtone bands in the NIR based upon the assignments for gaseous H<sub>2</sub>O [12]. By analogy and with literature assignments, these same bands are assigned in the spectrum of liquid D<sub>2</sub>O. Green arrows in the Figure 1 clearly show the isotopic shift of a band arising from the H-D substitution.

**Spectral peak assignments for overtone and combinational modes:** We are currently in the process of sorting out the detailed NIR vibrational band assignments for the epsomite and melanterite, and their deuterated analogs, and also comparing our data with that of Chio et al. [13] on the hydrates and deuterates of FeSO<sub>4</sub>. The fundamental modes of the (SO<sub>4</sub>)<sup>2-</sup> in the Raman and mid-IR region are easily recognized as those modes were less affected by the D-H substitution. The majority of the vibrational bands in NIR region >3000 cm<sup>-1</sup>, by analogy with the pure water spectrum, are derived from overtones and combination modes of structural waters. While the combination band, ν<sub>1</sub>+ν<sub>3</sub> of the sulfate ion is readily seen in 3000 to 2000 cm<sup>-1</sup> NIR diffuse reflectance spectrum (not shown, [14]). The vibrational modes above 3000 cm<sup>-1</sup>, appear to be dominated almost completely by the overtone and combination bands of structural waters. The crystallographic environment of a structural water in the salt lattice can be detected in the details of the NIR diffuse reflectance overtones and combination bands of the water molecules. We are currently studying these spectra in more careful details to determine if any of the bands in the NIR diffuse reflectance spectra can be assigned unambiguously to combination modes arising from a mix of the fundamental modes of the water of crystallization and the modes of (SO<sub>4</sub>)<sup>2-</sup> tetrahedron.

**Acknowledgement:** This work was supported by Missouri Space Grant Consortium Summer High School Internship Program for MJ, and by a NASA Mars Fundamental Research grant NNX07AQ34G.

**References:** [1] Klingelhöffer et al. (2004), *Science*, V306, 1740-1746. [2] Morris et al. (2007) *7<sup>th</sup> International Conference on Mars*, abs #3393. [3]. Wang et al. (2006), *JGR*, V111, E02S17. [4] Wang et al. (2006), *JGR*, V111, E02S16. [5] Clark et al. (2005), *EPSL*, 73-94. [6] Ming et al. (2006), *JGR*, V111, E02S12. [7] Yen et al. (2007), *JGR*, submitted. [9] Bibring et al. (2005), *Science*, V307, 1576-1580. [9] Murchie et al., (2007), *7<sup>th</sup> International Conference on Mars*, abs#3238. [10] Wiseman et al. (2007), *7<sup>th</sup> International Conference on Mars*, abs#3111. [11] Nakamoto (1978), *The Infrared and Raman Spectra of Inorganic Coordination Compounds*, 3rd. Ed, John Wiley & Sons, NY. [12] Hertzberg (1945), *Infrared and Raman Spectra*, Van Nostrand Reinhold Co., Inc., NY, Chio et al. (2007), *J. Raman Sped.*, V38, 98-99. [14] Wang et al. (2004), *Lunar and Planetary Science XXXV*, 1510.