

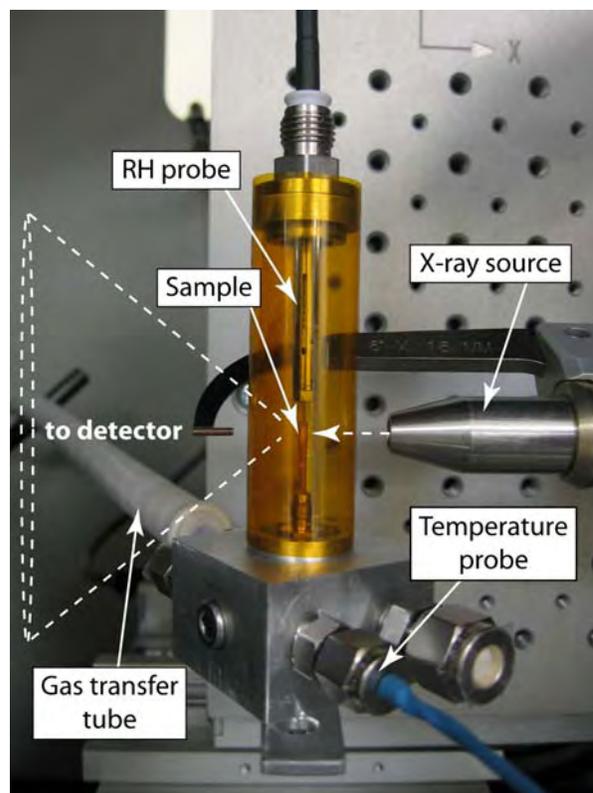
**RELATIVE HUMIDITY-INDUCED PHASE TRANSITIONS OF FE-SULFATE MINERALS: *IN-SITU* X-RAY DIFFRACTION STUDIES.** W. Xu<sup>1</sup>, N. J. Tosca<sup>1</sup>, S.M. McLennan<sup>1</sup> and J. B. Parise<sup>1,2</sup>, <sup>1</sup>Department of Geosciences, <sup>2</sup>Department of Chemistry, SUNY Stony Brook, Stony Brook, NY 11794-2100 USA. ([Wenqian.Xu@sunysb.edu](mailto:Wenqian.Xu@sunysb.edu))

**Introduction:** At least two distinct Fe-sulfate minerals have been positively identified on the martian surface by the MER rovers – jarosite at Meridiani Planum and an unknown ferric sulfate(s) at Gusev Crater [1,2]. Work aimed toward understanding surface processes on Mars suggests that Fe-bearing sulfate minerals are an important component of the chemical sediments that preserve evidence of liquid water on an ancient Mars [3]. Fe-bearing sulfates are capable of yielding uniquely detailed information on the environmental conditions of the past and even present martian surface because their stability is governed by important variables such as pH, redox conditions and relative humidity (RH). In addition, many forms of ferrous and ferric Fe-bearing sulfates are extensively hydrated, which may in part account for the budget of liquid water measured at the near surface by the neutron spectrometer aboard Mars Odyssey.

Fe-sulfate minerals display a complex series of paragenetic reactions observed in the field and laboratory. It is reported that most phase transitions among the Fe-sulfates are induced by subtle shifts in climatic variables such as relative humidity (RH). Interestingly, in terrestrial acid mine drainage environments, the RH-induced phase transitions occur on short time scales under the daily RH fluctuations typical of Earth surface environments. On Mars, present data show that daily local RH can vary from <10% to >90%, allowing a complex series of phase transitions to occur at the martian surface [4]. In addition, mineralogical identification of Fe-sulfates by orbital instruments such as OMEGA and CHRISM will require phase equilibrium data to provide a crucial link in interpreting dehydration/rehydration changes from the mineral phase identified to the phase initially precipitated from liquid water.

There has been previous work concerning RH impacts on sulfate hydration/dehydration processes [4, 5, 6, 7, 8], including some *in-situ* diffractometry investigations under dynamic RH control [4, 7, 8]. However, phase equilibria among many Fe-sulfates have not yet been delineated. Even for the melanterite ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ )-rozenite ( $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ ) system, published data on the phase transition boundary were not in good agreement [9].

Accordingly, the goal of this work is to acquire high-quality time-resolved X-ray scattering data *in-situ* as a function of relative humidity and temperature for a



**Figure 1: Diffraction experiment setup.**

variety of Fe-sulfate minerals of interest. We describe a new experimental method for the acquisition of such data over a wide range of relative humidity and temperature. The method is being adapted for use with a synchrotron X-ray source at the NSLS at Brookhaven National Laboratory. Acquiring *in-situ* diffraction data for Fe-sulfate materials will be of paramount importance in understanding the range of environmental stability for Fe-sulfates on Mars. Such data will also be in high demand for the upcoming Mars Science Laboratory (MSL) mission, which will have combined X-ray diffraction and X-ray fluorescence capabilities.

**Methods:** The *in-situ* X-ray diffraction experiment is carried out on a Bruker AXS diffractometer with a Siemens HI-STAR area detector. Humidity is controlled by a V-Gen II RH Generator, which passes water-saturated air through a condenser to the experiment cell. The desired RH is achieved by adjusting the condenser temperature. Humid air passes through a

heat-sealed transfer tube through a manifold and into a polyimide capillary sealed in a Kapton FN film chamber. The Kapton film exhibits excellent X-ray transparency and is heat sealable. Sample powders, with glass wool substrate, are loaded in the bisected end of the capillary so that the sample retains contact with air and does not block gas flow. The RH probe is placed just above the sample to measure both the temperature and RH. To identify temperature gradients, another probe is mounted in the manifold to measure gas temperature before entering the capillary. The experiment temperature can be increased by wrapping the sample cell with a tape heater (not shown in Fig. 1).

To test the experimental design and data acquisition process, the melanterite ( $\text{Fe}^{2+}\text{SO}_4\cdot 7\text{H}_2\text{O}$ ) - rozenite ( $\text{Fe}^{2+}\text{SO}_4\cdot 4\text{H}_2\text{O}$ ) system was investigated first. Data were collected at ambient temperature and pure rozenite was used as the starting sample. A program built with the RH generator carried out the automated process of increasing RH over the experiments. The initial and final RH were 55% and 85% respectively, with a 2% step size and 50min dwell at each step. RH and T probe measurements were collected every minute. Over the experiment, diffraction frames were collected continuously with a 5min exposure time for each frame, recording 10 frames for each RH step. Cobalt radiation was used as the X-ray source in these experiments. The gas flow rate used was 150 cc/minute.

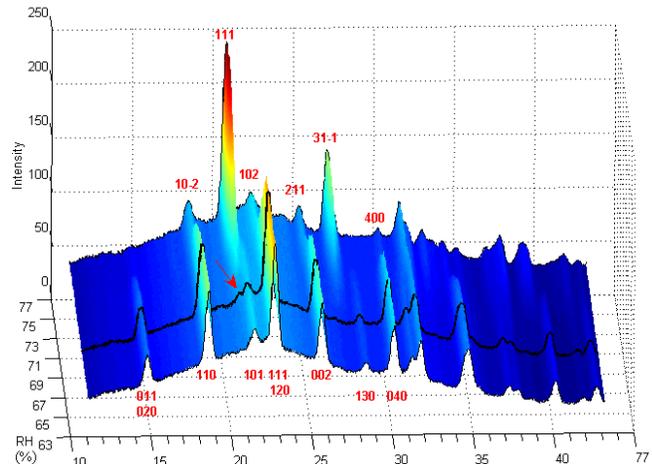
**Results:** Figure 2 depicts diffraction data for the melanterite-rozenite experiment from 63% to 77% relative humidity. The indexed diffraction peaks for

Temperature and RH probe measurements indicated that the actual temperature in the sample cell was  $27.8 \pm 0.3^\circ\text{C}$  during the experiment, but no temperature gradient was detected. There were small RH fluctuations at each step, which were within 0.5%.

The data from the experiment described above at  $27.8^\circ\text{C}$  show that the phase transition between melanterite and rozenite occurred at 67% RH, which is in excellent agreement with Hemingway et al (2002) [9] (~67%) and in fairly good agreement with results reported by Malinin et al. (1979) [5] and Chou et al.(2002) [6] (~64%). Intermediate phases such as ferroxahydrate ( $\text{FeSO}_4\cdot 6\text{H}_2\text{O}$ ) did not appear in this hydration process. Siderotil ( $\text{FeSO}_4\cdot 5\text{H}_2\text{O}$ ) was not observed in this study, as some Cu substitution is required to stabilize the structure [10].

The results discussed above show that relative humidity-induced phase transitions can be recorded *in-situ* as a function of temperature and relative humidity. The flexibility of the experimental design allows the stability of Fe-bearing sulfate minerals to be investi-

gated as a result of changing environmental variables. The data produced from the experiments described here will provide an important link between the remote detection of Fe-sulfate minerals at the martian surface and understanding the environmental conditions re-



**Figure 2:** In-situ diffraction data capturing the rozenite-melanterite phase transition. The x-, y- and z-axes correspond to  $2\theta$ , intensity and RH, respectively. Some peak indexes for melanterite are listed in red at the top of the figure and peak indexes for rozenite are listed at the bottom. The diffraction pattern shown in black was collected ~20 minutes after the RH stabilized at 67%. The red arrow indicates the first appearance of the melanterite (111) reflection in this scan.

sponsible for their formation and stability.

Ongoing work is investigating copiapite ( $\text{Fe}^{2+}\text{Fe}^{3+}_4(\text{SO}_4)_6(\text{OH})_2\cdot 20\text{H}_2\text{O}$ ) and related Fe-sulfates for which few phase equilibrium data have been reported in the literature. A companion laboratory synthesis program is providing necessary mono-mineralic samples with which to investigate. Ultimately, well-characterized samples for which reversible relative-humidity and temperature data are collected will help build a comprehensive understanding of the Fe-sulfate system and its behavior at the martian surface.

**References:** [1] Squyres, S. et al. (2004) *Science*, 306, 1709. [2] Morris, R.V. et al. (2006) *JGR*, 111, E02S13. [3] Burns, R.G. & Fisher, D.S. (1990) *JGR*, 95, 14415. [4] Vaniman et al. (2004) *Nature*, 431, 663. [5] Malinin et al. (1979) *Russ. J. Phys Chem*, 53, 1332-1333. [6] Chou et al. (2002) *Am. Mineral.* 87, 108-114. [7] Peterson & Grant (2005) *Can. Mineral.* 43, 1171-1181. [8] Linnow et al. (2006) *Anal. Chem.* 78, 4683-4689. [9] Hemingway et al. (2002) *U.S. Geol. Surv. Open File Rep.* 02-161. [10] Jambor et al. (1963) *Can. Mineral.* 7, 751-763.