

RELATIVE HUMIDITY-INDUCED PRODUCTION OF FERRICOPIAPITE AND RHOMBOCLASE FROM FERRIC SULFATE ANHYDRATE: X-RAY DIFFRACTION STUDIES UNDER CONTROLLED CONDITIONS. W. Xu¹, N. J. Tosca², S.M. McLennan¹ and J. B. Parise^{1,3}, ¹Department of Geosciences, SUNY Stony Brook, Stony Brook, NY 11794-2100. ²Dept. of Organismic & Evolutionary Biology, Harvard University, Cambridge, MA 02138. ³Department of Chemistry, SUNY Stony Brook, Stony Brook, NY 11794-2100. (Wenqian.Xu@sunysb.edu)

Introduction: Ferric sulfate minerals have been positively identified on the Martian surface, including jarosite [1, 2], and the unknown ferric sulfate phase found in Gusev Crater, which is likely to be a combination of copiapite, fibroferite and rhomboclase [3]. The Fe-bearing “Fe3D3” phase on Meridiani Planum might also contain a ferric sulfate hydrate phase, and shwertmannite has been suggested as a candidate mineral [4]. One interesting property of iron sulfate minerals is that they display complex phase transitions among different hydration states with respect to changes in environmental conditions such as temperature (T) and relative humidity (RH). Because some of these transformations are hysteretic or irreversible and also because Fe-sulfate stability is controlled by acidity and redox conditions, these phases may impose important constraints on the evolution of surface conditions on Mars. This on-going study is aimed at understanding the phase relationships among iron sulfates and the stability of each phase as function of temperature and relative humidity. Here, we report the transition from anhydrous ferric sulfate to mixture of ferricopiapite and rhomboclase under elevated air humidity at room temperature, which has not been reported in previous studies.

Methods: Phase transitions are characterized in this study by X-ray diffraction, using a specially made sample chamber to control both T and RH. The experiment setup on a Bruker AXS diffractometer was previously introduced [5]. Fig. 1 shows a similar system using a scintag PAD-X diffractometer in this study. The chamber wall is made from heat-resistant lucite, with X-ray-transparent windows made of kapton film. A hygrometer can be placed 1cm above the sample plate through the opening on the front panel to monitor RH and T. Two additional openings on the panel allow mounting additional RH and T probes, and can also be used as gas inlet and outlet ports connected to a V-Gen II RH Generator (InstruQuest®) for dynamic RH control. Static RH control, as shown in figure 1, is achieved by humidity-buffer method, placing a container of saturated salt solution inside the chamber. Heat tape is wrapped around the sample to produce an even thermal field and adjust sample temperature up to 90°C.

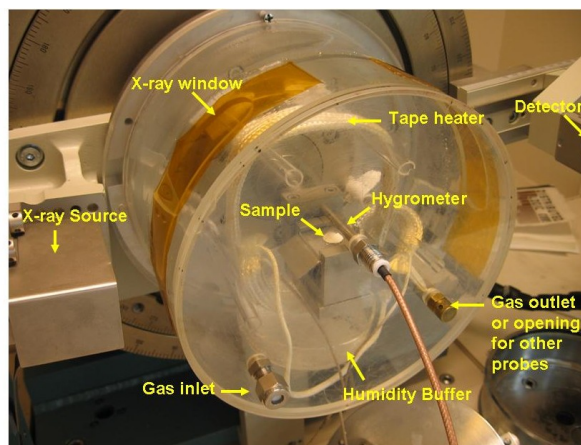


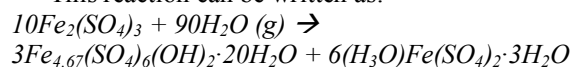
Fig. 1 Set-up on Scintag Diffractometer using static RH control mode

Powder samples are stored in covered humidity buffer containers to allow equilibration with a given relative humidity value. After equilibration with the conditions in the buffer container, the sample is quickly transferred into the X-ray chamber, in which the RH and T are pre-adjusted to match the humidity buffer. This procedure minimizes unwanted changes due to varying RH or T during the short transporting period. To ensure that the equilibrium state is achieved, the sample is preserved at the same conditions for another 48 hours and X-ray data are collected again. Phases are stabilized if this pattern is exactly the same as the one collected before. The main advantage to this setup is that it allows the collection of high quality diffraction data (which generally requires a few hours) under non-fluctuating RH and T.

Our initial study focuses on the Fe(III) -SO₄ - H₂O three component system, which includes ferricopiapite (Fe³⁺_{0.67}Fe³⁺₄(SO₄)₆(OH)₂·20H₂O), rhomboclase ((H₃O⁺)Fe³⁺(SO₄)₂·3H₂O), kornelinite (Fe³⁺₂(SO₄)₃·H₂O_{7.25}), coquimbite (Fe³⁺₂(SO₄)₃·H₂O₉), etc. As the most basic form in this system, anhydrous ferric sulfate provides a simple and logical starting material. The initial sample was pure ferric sulfate anhydrate from Alfa-Aesar (Puratronic®, 99.998%, metals basis). Starting from dry conditions, the humidity-buffer method was used to control and modulate RH, and the entire experiment process was conducted at room temperature (23-25°C).

Results: Fig. 2 shows three of the diffraction patterns recording this hydration process from very low RH to 45%. A portion of the starting sample changed to ferricopiapite and rhomboclase under RH as low as ~33%. At 45% RH, all ferric sulfate anhydrate transformed. Fig. 3 compares our data with theoretical calculated XRD profiles from existing crystal structure models of ferricopiapite [6] and rhomboclase [7], which confirmed the presence of these two phases. Although the subsequent dehydration experiment showed no sign of a reverse in this transition, it is not yet known if it may be kinetically hindered.

This reaction can be written as:



Considering the fact that the products have hydroxyl groups and protons in their structures, this reaction exhibits the strong hydrolysis effect of Fe(III). More specifically, the hydrolysis makes the iron sulfate system more complicated to study, and may also be the reason for the observed hysteresis.

Implications for the martian surface: Our results show that anhydrous sulfate Fe-sulfate phases are strongly hygroscopic and result in complex phase transitions. In addition, the amount of acidity produced by the Fe³⁺ hydrolysis reactions is significant; initially pure water vapor absorbed by anhydrous Fe-sulfate in the above reaction reached a pH low enough to allow ferricopiapite and rhomboclase precipitation, which is approximately pH 0 or less. This process may have been important in locally generating acidity at the martian surface.

As our work continues, we expect to delineate the boundaries of more phase transitions, eventually exploiting the unique sensitivity of Fe-sulfate minerals to a variety of environmental factors.

References:

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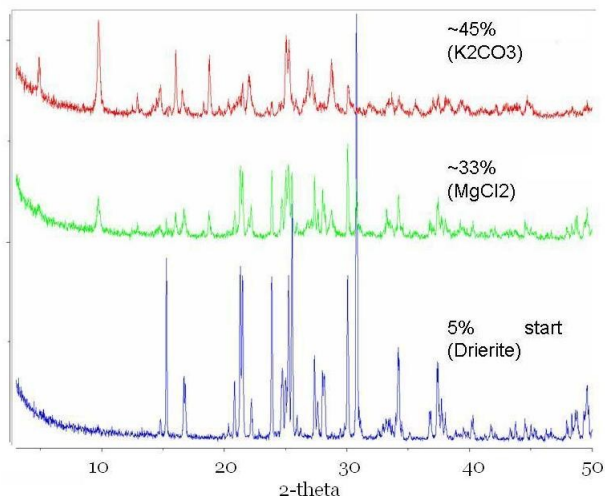


Fig. 2 Diffraction data showing the phase transition as RH was increased. Each profile is noted with the RH in percentage and the humidity buffers used (in parenthesis). Starting sample is $\text{Fe}_2(\text{SO}_4)_3$ in monoclinic system.

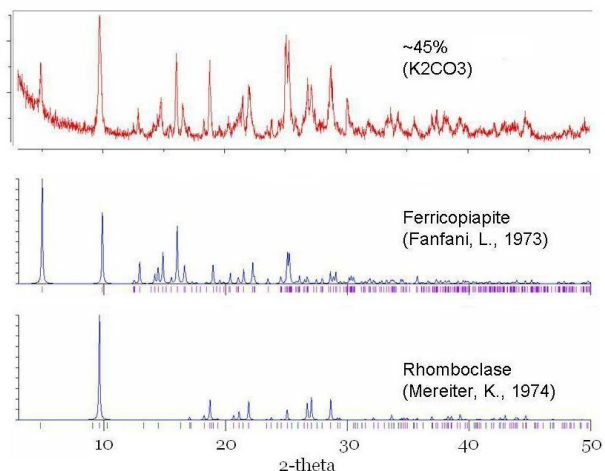


Fig. 3 comparing the experiment data (at the top) with XRD signatures calculated from reported structure models, showing the resultant sample is a mixture of ferricopiapite and rhomboclase.