

THE EFFECT OF TEMPERATURE AND WATER ON FERRIC-SULFATES. S. J. Chipera¹, D. T. Vani-man¹, and D. L. Bish², ¹Group EES-6, MS D469, Los Alamos National Laboratory, Los Alamos, NM 87545 (chipera@lanl.gov), ²Department of Geological Sciences, Indiana University, 1001 E 10th St., Bloomington, IN 47405.

Introduction: We have previously examined stability relationships for Mg-sulfates with application to Mars [1,2,3]. We have begun applying many of the same techniques to ferric-sulfates that are believed to occur on the martian surface as a result of oxidizing-acid conditions [4]. Jarosite has been shown to exist on the surface of Mars [5], and it is likely that other ferric-sulfates exist as well. Like their Mg-cousins, the Fe³⁺-sulfates have complex thermal and hydration/dehydration behaviors. Many of the Fe³⁺-sulfates are readily soluble, some are quite hygroscopic, and although there are numerous crystalline phases, an X-ray amorphous phase is quite prevalent. Of particular interest, when Fe³⁺-sulfates are dissolved in water and then dried, a very viscous “substance” is formed which could be quite problematic for rover and instruments if encountered on the surface of Mars. This material is similar to that previously documented for a variety of ferric-sulfates [4].

Methods: For these preliminary studies, chemical reagents of known composition were used, several phases were synthesized from the reagents, and several natural samples were obtained including fibroferrite from a mine waste dump at Leadville, Colorado, USA (Table 1). The crystalline forms of the ferric sulfates were determined by X-ray diffraction (XRD) analyses using a Siemens D500 diffractometer fitted with a Kevex PSi solid state detector, Cu radiation, and a controlled humidity cell [6].

The Fe³⁺-sulfate-5-hydrate chemical reagent (CAS 142906-29-4) in the form of a fine yellow powder (Figure 1) was confirmed to contain five waters of hydration from heating experiments. When analyzed by XRD, this material produced what we refer to as the “two-hump amorphous” phase (Figure 2). Although similar to ferrihydrite, the peaks do not have the same spacings. A second Fe³⁺-sulfate-reagent advertised as a monohydrate was also purchased (CAS # 10028-22-5) and is composed of small 1-4 mm spheres that are extremely difficult to grind. When analyzed by XRD, this material was found to consist of a mixture of kornelite, rhomboclase, romerite, and ferricopiapite.

Saturated salt solutions were used to control relative humidity at various temperatures. For example, by placing Fe³⁺-sulfate-5-hydrate chemical reagent at 75°C over a saturated SrCl₂ solution to control humid-

ity at ~43%RH, pure kornelite was produced (Figures 1 and 2). Interestingly, the sample has the appearance of first deliquescing to a liquid before crystallizing as kornelite (Figure 1).

Table 1: Minerals and formulas for the phases used or obtained in this preliminary study.

Mineral	Chemical Formula
Fibroferrite	Fe ³ (SO ₄)(OH) • 5H ₂ O
Romerite	Fe ² Fe ³ ₂ (SO ₄) ₄ • 14H ₂ O
Ferricopiapite	Fe ³ _{2/3} Fe ³ ₄ (SO ₄) ₆ (OH) ₂ • 20H ₂ O
Coquimbite	Fe ³ ₂ (SO ₄) ₃ • 9H ₂ O
Kornelite	Fe ³ ₂ (SO ₄) ₃ • 7H ₂ O
Rhomboclase	(H ₅ O ₂)Fe ³ (SO ₄) ₂ • 2H ₂ O
Mikasaite	Fe ³ ₂ (SO ₄) ₃
Amorphous	Fe ³ ₂ (SO ₄) ₃ • 5H ₂ O



Figure 1: Fe³⁺-sulfate-5-hydrate reagent powder on the right. Placing it at 75°C and 43%RH for 14 days produced the kornelite shown on the left.

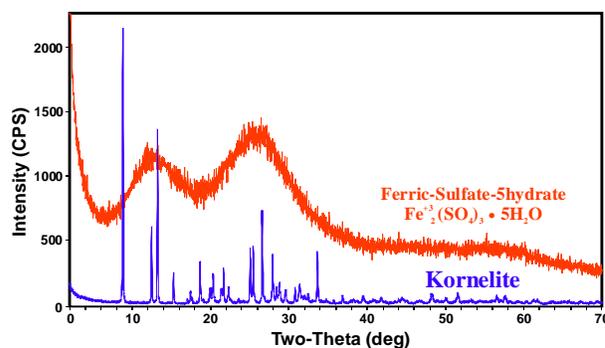


Figure 2: XRD patterns showing the “two-hump” amorphous phase (Figure 1, right side) and the kornelite (Figure 1, left side) samples.

Results: The Fe^{+3} -sulfates are extremely soluble. We were able to dissolve 88 grams of Fe^{+3} -sulfate-5-hydrate into 20ml of deionized water, only stopping at this point as the solution turned quite viscous. Solutions tend to be deep red in color (Figure 3). Placing Fe^{+3} -sulfate solution into a -50°C freezer produced an unexpected result. Rather than freezing solid, the material remained a viscous substance that was quite pliable (Figure 4). Placing this sample into a laboratory freeze-drier at 0.1 torr for 5 days produced a dark-red transparent “glob” that turned into a very viscous liquid when touched. Drying Fe^{+3} -sulfate solutions at 3°C , ambient room temperature, and at 50°C also produced a dark-red transparent “sticky” solid which, when analyzed by XRD, produced the two-hump amorphous phase along with variable amounts of ferricopiapite and rhomboclase. The evaporation pathway from a liquid can be described as 1) transforming to a syrup then a viscous “goo”; 2) development of a hard shell over the goo which slows the drying of the interior; 3) transformation to a dark-red-sticky solid; 4) and in certain conditions, crystallization to a final solid.



Figure 3: Fe^{+3} -sulfate liquid -- in this sample, 5 g of ferric-sulfate was dissolved in 20 ml DI water.

Drying at 75 and 95°C produced samples that were dominated by rhomboclase and other minor as yet undetermined phases. Heating Fe^{+3} -sulfates to 200°C produced the anhydrous mineral, mikasaite.

The Fe^{+3} -sulfate reagents were analyzed at various humidities at the ambient temperature inside the diffractometer ($\sim 28^\circ\text{C}$). The monohydrate was analyzed at 0, 20, 40, 60, and 80%RH and started out as kornelite, rhomboclase, and romerite. At 20%RH, ferricopiapite began to form. In the 80%RH runs, the sample deliquesced, with ferricopiapite the only solid phase in the liquid.

The Fe^{+3} -sulfate-5-hydrate reagent was analyzed at 40, 45, 50, 55, 60, 65, 70, and 75%RH. It began as the two-hump amorphous phase, with minor ferricopiapite forming during the initial runs. At 55%RH, the amorphous material reacted to form significant ferricopiapite along with minor rhomboclase, and kornelite.

At 65%RH, the sample deliquesced, leaving ferricopiapite and rhomboclase with a liquid.

Pure kornelite was analyzed at 60, 65, 70, 75, 80, and 85%RH. At 75%RH, XRD peak intensities began to decrease and at 80%RH the sample deliquesced. These data help to confirm the observation and hypothesis that Fe^{+3} -sulfate-5-hydrate first deliquesces into a liquid before forming the kornelite, as shown in Figure 1.



Figure 4: Fe^{+3} -sulfate solution at -50°C for 12 days.

Relevance to Mars: Of particular interest in a martian environment, when Fe^{+3} -sulfates are either dissolved in water or deliquesce and are then dried, they form a very viscous “goo” which does not freeze, even at -50°C . If such material is encountered on the surface of Mars, it could present problems to a rover and its instruments. Such materials could also be at least partially responsible for the common occurrence of duricrusts on the martian surface [4]. Preliminary results suggest that given sufficient time, Fe^{+3} -sulfates should “dry” to a crystalline or amorphous solid. However, care should be used to ensure that Fe^{+3} -sulfates do not come in contact with liquid water or deliquesce at elevated relative humidities.

References: [1] Vaniman, D.T. et al. (2004) *Nature* 431, 663-665. [2] Chipera, S.J., et al. (2005) Lunar and Planetary Science Conference, XXXVI, #1497. [3] Chipera, S.J. and Vaniman, D.T, (2007) *Geochimica et Cosmochimica Acta*. [4] Hasenmueller, E.A. and Bish, D.L. (2005) Lunar and Planetary Science Conference, XXXVI, #1164. [5] Klingelhöfer G. et al. (2004) *Science*, 306, 1740-1745. [6] Chipera, S.J. et al. (1997) *Advances in X-Ray Analysis*, 39, 719-721.

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