THE HYDRATION AND DEHYDRATION OF HYDROUS FERRIC IRON SULFATES. E. A. Hasenmueller and D. L. Bish, Dept. of Geological Sciences, Indiana Univ., 1001 E. 10th St., Bloomington, IN 47405-1405, USA

Introduction: Data collected by Viking, Pathfinder, and the Mars Exploration Rovers and by orbiters (e.g., Odyssey) provide multiple lines of evidence for the historical and present-day existence of water on Mars. For example, Mars Odyssey detected up to ~10 wt% equivalent H_2O in equatorial regions of Mars where water ice is not stable [1]. It has been theorized that sulfate minerals, including hydrated ferric sulfates, may be part of the inventory of hydrous phases that account for water on the martian surface [2, 3, 4]. Several Fe-bearing minerals, such as jarosite and goethite, as well as Mg and Ca sulfates have already been identified in the martian regolith [5, 6, 7].

Knowledge of the martian regolith mineralogy is essential to understanding Mars' hydrogeologic history, and hydrous minerals may serve as useful records of past aqueous alteration events. Indeed, important inferences about past conditions have been made from the presence of jarosite and goethite [5, 6], and it has been determined that jarosite is thermodynamically stable under assumed martian surface conditions [8]. Laboratory data measured under simulated martian surface conditions are crucial to provide constraints on hydrous mineral stability [9], and guided by current martian soil chemistry data we selected hydrated ferric sulfates for study (in lieu of *ferrous* sulfate minerals).

Methods: Samples were chosen based on their H_2O contents, the presence of independent H_2O molecules that might evolve in a step-wise manner, and availability. Jarosite does not contain H_2O but is OH-bearing and was studied because it has been identified on Mars [5]. Jarosite, ($KFe_3(SO_4)_2(OH)_6$), from Bisbee, AZ; kornelite ($Fe_2(SO_4)_3 \cdot 7H_2O$), from Napa Co., CA; botryogen, ($MgFe(SO_4)_2(OH) \cdot 7H_2O$), from Coso Hot Springs, CA; and coquimbite, ($Fe_2(SO_4)_3 \cdot 9H_2O$), from Alcaparrosa, Chile, were analyzed. Samples were ground dry and were mounted on an Anton-Paar TTK 450 heating stage on a Bruker D8 diffractometer with a VANTEC-1 position-sensitive detector (Cu radiation). Data collection ranges were tailored to each mineral to encompass the strongest peaks and collection times were typically 1-2 hrs. The heating stage was programmed to range from 25°C to 300°C in 50°C increments (25°, 50°, 100°, …) and humidities ranged from room humidity (25-48%RH) to ~0% (roughing-pump vacuum). Initial diffraction experiments evaluated sample purity, and reconnaissance heating measurements were made to determine the gross thermal behavior. Based on initial heating measurements, subsequent heating experiments were conducted on a much finer temperature scale and for longer times.

Results: *Jarosite.* Diffraction data for jarosite changed little from 25° to 300°C, with only minor peak shifts occurring as a function of temperature. Exposure of the sample to vacuum (~20 mtorr) had no effect on the diffraction pattern. These results are consistent with the absence of H_2O molecules in the structure.

Coquimbite. Initial heating experiments from 25°-300°C revealed gradual decomposition beginning at 50°C, evidenced by continuous decrease in peak intensities; no peak shifts or new phases were observed. This reaction was not reversible, which was surprising given the presence of independent H_2O molecules in coquimbite (Fig. 1). The structure of coquimbite was destroyed between 200° and 250°C (Fig. 2), leaving an amorphous material that recrystallized to kornelite and copiapite ($Fe^{+2}Fe^{+3}_4(SO_4)_6(OH)_2 \cdot 20H_2O$) after reexposure to room temperature and humidity. Finer-scale heating at 30°, 40°, and 45°C showed a gradual decrease in peak intensities even at 30°C. Thus, coquimbite is unstable at temperatures as low as 30°C and may be unstable at 25°C in a vacuum; further experiments will evaluate the lower-temperature stability limits.
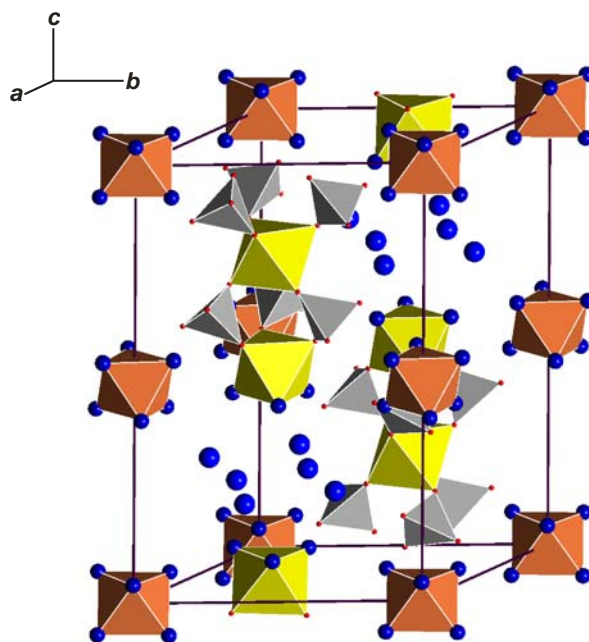

Figure 1. Crystal structure of coquimbite. H_2O molecules are represented by blue spheres, Fe octahedra are yellow, Al octahedra are orange, and SO_4 tetrahedra are grey. Note the independent H_2O molecules not closely coordinated to tetrahedra or octahedra.
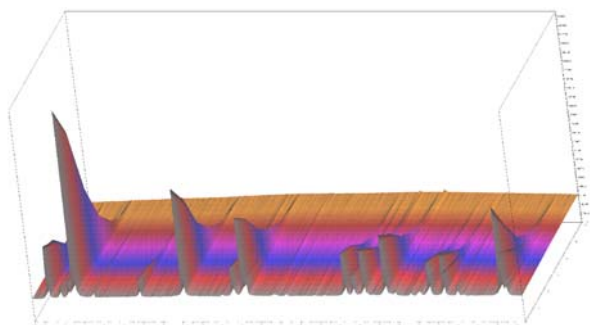
Figure 2. Diffraction data for coquimbite. The *x*-axis is 2θ angle, the *y*-axis shows a colored band for each diffraction pattern at 50ºC increments ranging from 25º-300ºC, and the *z*-axis is intensity.

Botryogen. The botryogen structure consists of linked Fe octahedra and sulfate tetrahedra, with H_2O molecules primarily occupying some octahedral apices. However, one H_2O molecule is independent of the octahedra and tetrahedra, with long bonds to the tetrahedral and octahedral apices. The botryogen diffraction pattern showed progressive intensity decrease between 25º and 50ºC, with a major decrease between 50º and 75ºC, rapidly degrading above 100ºC. This reaction was not reversible, and after heating, the powder sample solidified into a hard ceramic-like crust.

Kornelite. The kornelite structure, like that of botryogen, consists of linked Fe octahedra and sulfate tetrahedra, also with H_2O molecules primarily occupying some octahedral apices. However, two crystallographically distinct H_2O molecules are independent of the octahedra and tetrahedra, with long bonds to the tetrahedral and octahedral apices. Like coquimbite, the kornelite diffraction pattern progressively decreased in intensity with temperature, but anhydrous Fe-sulfate appeared between 50º and 75ºC, which was subsequently destroyed between 200º and 250ºC (Figure 3). These temperature-induced reactions were irreversible.
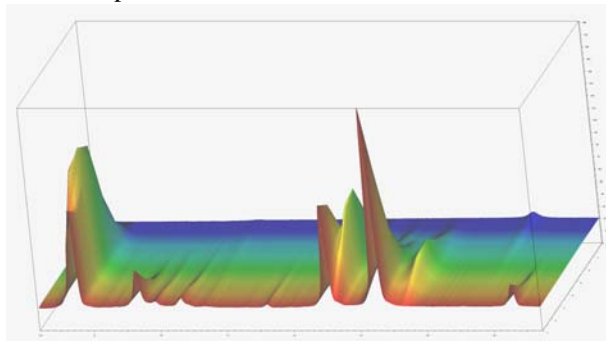

Figure 3. Diffraction data for kornelite. The *x*-axis is 2θ angle, the *y*-axis shows a colored band for each diffraction pattern at 25º, 50º, 75º, 100º, 150º, 200º, 250º, and 300ºC, and the *z*-axis is intensity.

Conclusions: All of the hydrous ferric sulfates studied here were stable at room temperature under vacuum (with the possible exception of coquimbite), suggesting that they are probably stable under present-day martian surface conditions and are possible combined reservoirs of Fe, S, and H_2O. However, unlike zeolites and smectites which reversibly dehydrate and hydrate, none of the hydrated ferric sulfates evaluated in these experiments reversibly dehydrated. Although the coquimbite, botryogen, and kornelite structures all contain independent H_2O molecules, they did not undergo reversible dehydration reactions similar to the epsomite-to-hexahydrite reaction for the Mg sulfates. Diffraction peak intensities for all three hydrates gradually decreased at temperatures just above room temperature, unaccompanied by significant shifts in peak positions (with the exception of jarosite). Apparently, unlike zeolites and smectites but like the lower hydrates of Mg sulfate (e.g., hexahydrite), the independent H_2O molecules in these minerals are integral parts of their structures. Consequently, loss of any H_2O molecules gives rise to structural breakdown.

All three hydrated iron sulfates either became gelatinous or hardened into a ceramic-like crust after dehydration. If similar hydrated Fe-sulfates occur on the martian surface, such reactions, perhaps due to long-term dehydration, might contribute to the cementation of the regolith observed in places (i.e., duricrusts). This effect is so pronounced in the three hydrous sulfates studied here that it is likely that only small amounts of these materials in the regolith could lead to significant cementation. It is noteworthy that only small temperature excursions were required to destroy the structure of these three minerals, creating amorphous phases that could prove difficult to identify unambiguously using spectral or diffraction data.

References: [1] Feldman W. C. et al. (2003) *JGR*, 109, E09006, 13 pp. [2] Cloutis E. A. et al. (2001) *LPS XXXII*, 1375. [3] Vaniman D. T. et al. (2004) *Nature*, 431, 663-665. [4] Zolotov M. Y. et al. (2004) *LPS XXXV*, 1465. [5] Klingelhöfer G. et al. (2004) *Science*, 306, 1740-1745. [6] NASA Press Release, December 13, 2004. [7] Christensen P. R. et al. (2004) *Science*, 306, 1733-1739. [8] Forray F. L. et al. (2004) *2nd Conf. on Early Mars*, 8009. [9] Bish D. L. et al. (2003) *Icarus*, 164, 96-103.