THE HYDRATION AND DEHYDRATION OF HYDROUS MIXED-CATION SULFATES. D. L. Bish and M. K. Scanlan, Dept. of Geological Sciences, Indiana Univ., 1001 E. 10th St., Bloomington, IN 47405-1405, USA

Introduction: Viking, Pathfinder, and the Mars Exploration Rovers and martian orbiters (e.g., Odyssey) all support the historical and present-day existence of water on Mars. Mars Odyssey detected up to ~10 wt% equivalent H_2O in equatorial regions of Mars where water ice is not stable [1], and a variety of hydrated sulfate and chloride minerals have been suggested as possibly contributing to the Mars surface water reservoir [2, 3, 4]. Several studies have suggested the presence of open-system evaporite deposits on Mars, all of which assumed the existence of mixed-cation sulfate and perhaps chlorides. King et al. [5] proposed a model for primordial oceans and lakes on Mars that were enriched in Mg, sulfate, and chloride. They predicted a concentration sequence involving a variety of salts, including many different mixed-salt hydrates. Several Mg and Ca sulfates have been identified in the martian regolith [6, 7, 8] and previous work [3, 9] demonstrated that sulfate minerals can contain considerable H_2O under martian surface conditions. Some evaporite minerals, including blödite, have also been suggested to form by atmospheric deposition [10].

Knowledge of martian regolith mineralogy is essential to understanding Mars' hydrogeologic history, and hydrous minerals can serve as valuable records of past aqueous alteration events. Indeed, important inferences about past conditions can be made from the presence of specific minerals [5]. Laboratory data measured under simulated martian surface conditions are crucial to provide constraints on hydrous mineral stability [11]; guided by current martian soil chemistry data and the simulations of [5], we selected several hydrated mixed-cation sulfates and sulfate-chlorides for study.

Methods: Blödite from Torrance Cty, New Mexico (NM); kainite from Hessen, Hannover, and Thuringia, Germany, and Carlsbad, NM; and polyhalite from Stassfurt and Thuringia, Germany, and Eddy County, NM, were selected for study. None of these contained *independent* H_2O molecules and were not expected to dehydrate reversibly. They were chosen to determine whether the H_2O molecules in their structures can survive low-pressure, slightly elevated-temperature conditions.

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). X-ray diffraction (XRD) data collection ranges were tailored to each mineral to encompass the strongest peaks, and collection times were reduced to ≤30 min to allow rapid, repetitive measurement. Some measurements were tailored to detect very short-term changes (1-2 min) using the detector in fixed mode (no detector movement). Measurement temperatures ranged from 22°C to 420°C in fixed increments (typically 50º, but at times as small as 10ºC) and humidities ranged from room humidity (25-48%RH) to ~0% (roughing-pump vacuum). Initial XRD experiments evaluated sample purity, and reconnaissance heating measurements were made to determine the gross thermal behavior. Based on initial measurements, subsequent XRD experiments were conducted on a much finer temperature scale and for longer times. Thermal behavior was also evaluated using a TA Instruments simultaneous thermogravimetric analyzer (TGA)-differential scanning calorimeter (DSC) up to ~900C, using heating rates of 10ºC/min.

Results: *Blödite, $(Na_2Mg(SO_4)_2 \cdot 4H_2O)$.* The blödite specimen contained minor gypsum and trace glauberite ($Na_2Ca(SO_4)_2$) impurities (for all samples, the presence of impurities did not affect the XRD results but contributed to the overall TGA behavior). Blödite's XRD pattern changed little upon evacuation at 23ºC and the specimen was stable to ~100ºC, when intensities began to decrease and the unit cell began to contract. After repeated measurements at 100ºC, a step to 110ºC caused a transformation to a new, unidentified phase. This new phase broke down at 160ºC, with a phase resembling anhydrous blödite remaining up to 300ºC. This anhydrous phase did not rehydrate under room conditions on a scale of several days. Given the pressure differences (XRD data collected in vacuum), these results are broadly consistent with TGA data, showing two major discrete weight losses beginning at ~130º and ~165ºC and peaking at ~140ºC (4.86%, ~one H_2O molecule) and ~170ºC (7.0%), with two more gradual large weight losses peaking at ~260ºC (4.83% and 3.48%). The observed total weight loss (20.17%) compares well with the calculated value, 21.54%. However, the variety of weight-loss events is inconsistent with the presence of only two crystallographically distinct H_2O molecules in the structure and must result from major structural reorganization accompanying partial to complete dehydration.

The blödite structure can be envisioned as independent Mg octahedral-sulfate tetrahedral pairs that are corner shared, with individual pairs linked via Na atoms. H_2O molecules form two Mg octahedra apices. The lack of reversible dehydration is consistent with the absence of independent H_2O molecules that might evolve without affecting the structure.

Kainite, ($MgSO_4 \cdot KCl \cdot 2.75H_2O$). Specimens from Hannover and NM contained minor halite and sylvite impurities and were used for further studies. XRD data measured every 10ºC to 200ºC (Figure 1) showed that kainite was stable to ~60ºC *in vacuo* (red, figure), whereupon it transformed to an unknown crystalline phase (yellow to green), which subsequently began to break down at ~130ºC. This phase was destroyed by 170ºC (green to blue) and did not change with further heating. Measurements in *air* showed that the first structural transition began >80ºC, was complete by 140ºC, and the new phase decreased in intensity through 190ºC and became amorphous at 200ºC. Amorphous dehydrated kainite slowly (days) rehydrated at 22ºC in air to hexahydrite ($MgSO_4 \cdot 6H_2O$), and minor kainite appeared after ~one week. TGA data revealed a minor weight loss at ~96ºC (1.6%) and two major weight losses, beginning at ~125º (3.3%) and 175ºC (9.2%) and peaking at ~135ºC and ~205ºC. Differences between XRD and TGA transition temperatures (70ºC *in vacuo*; 100ºC in air; 125º in the TGA) are likely due to pressure and heating-rate differences.

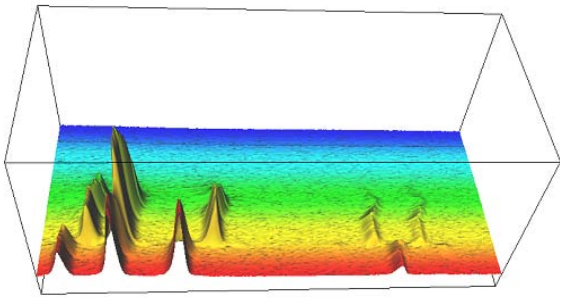

Figure 1. XRD data for Hessen kainite (vacuum); *x* axis is 2θ, *y* axis is intensity, and *z* axis (different colors) represents 23 to 200ºC and back to 23ºC.

The kainite structure consists of layers of SO_4 tetrahedra, corner sharing with some Mg octahedra. Kainite contains seven independent H_2O molecules, and the simplicity of the dehydration behavior shows that multiple H_2O molecules evolve almost simultaneously upon dehydration-induced structural breakdown. The Mg1, Mg2, and Mg4 octahedra all have two H_2O molecules completing their coordination polyhedra, and the Mg3 octahedron includes four equatorial H_2O molecules [12]. Kainite was not expected to exhibit reversible dehydration and hydration as it lacks independent H_2O molecules that could be lost without disrupting the structure. The Mg2-H_2O1 bond distance is considerably longer than the other Mg-H_2O distances, suggesting that H_2O1 may be the first to evolve. In addition, this H_2O molecule is not bonded to any other cation or molecular group. Loss of this H_2O would result in a 1.84% weight loss in a pure specimen, comparing well with the observed loss of 1.83% at 135ºC.

Polyhalite, ($K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$). XRD data measured every 50ºC up to 250ºC and every 10ºC to 430ºC (in vacuum) revealed gradual thermal expansion and peak broadening to 350ºC and then a gradual intensity decrease and contraction to 430ºC. The XRD pattern returned almost to its original state on returning to 23ºC. The lack of obvious structural change on heating to 430ºC is remarkable. The polyhalite structure consists of units of an Mg octahedron sharing two apices with two sulfate tetrahedra. These triplet units are linked through K and Ca cations. Polyhalite contains one independent H_2O molecule (the number in the formula is an artifact of the particular formula unit chosen), at two apices of each Mg octahedron. Thus, like blödite and kainite, polyhalite is not expected to dehydrate reversibly. TGA data show one weight loss of 5.6% beginning at ~285ºC, in agreement with [13]. This weight loss agrees well with the calculated weight loss for pure polyhalite of 5.98%, given the admixture with minor anhydrite, thenardite, and a trace of gypsum. TGA data collection for polyhalite was hampered by the fact that the samples melted and appeared to have frothed out of the sample pans at ~420ºC; subsequent measurements were terminated at 420ºC.

Conclusions: These hydrous mixed-cation sulfate-chlorides contain H_2O molecules that are integral to their structures, and they do not reversibly dehydrate. They were all stable at 22ºC *in vacuo*, strongly suggesting that they would be stable under present-day martian surface conditions. Temperatures of first dehydration in air range from 60ºC for kainite, to 130ºC for blödite, and ~285ºC for polyhalite. All of these minerals have been shown to form in evaporitic conditions and, once formed, should retain their structural H_2O easily on the martian surface. Compared with the ferric iron sulfates investigated by [9], where only small temperature excursions were required to destroy their structures, these mixed-cation sulfate/chlorides are considerably more stable and are reasonable combined reservoirs of S, Cl, and H_2O on Mars.

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