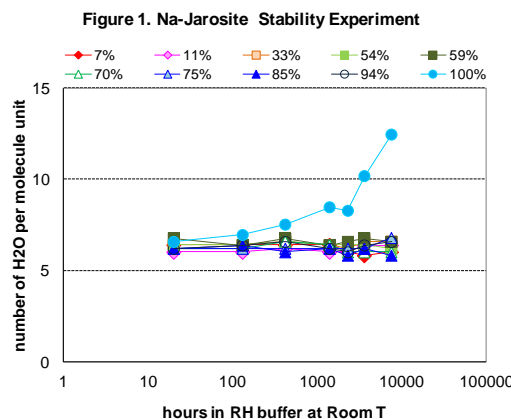


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Previous laboratory investigation of the fundamental properties of ferric sulfates: A few early studies [6,7] investigated the solubility relationships of minerals in the $\text{Fe}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$ system, but only in 200-50 °C temperature range. Xu et al. [8] studied the rehydration of two anhydrous ferric sulfates at 21 °C; Wang et al [9] studies the stability fields and phase transition pathways of five hydrous ferric sulfates at 50 °C, 21 °C, and 5 °C. Kong et al. [10] defined the first phase boundary below 50 °C between two normal ferric sulfates. The ferric sulfates studied in above recent works [8-10] belong to *normal* $[\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}]$, *acidic* $[\text{FeH}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}]$, and *slightly basic* $\text{Fe}_{4.67}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}]$ types.

In these experiments, the humidity buffer technology was used to “drive” the processes towards dehydration or rehydration; the gravimetric measurements at regular time interval were conducted to monitoring the change of $\text{H}_2\text{O}/\text{OH}$ content in each sample; the laser Raman spectroscopic measurements were made on the

Result #1, Stable K-, Na, H3O-jarosites: Figure 1 shows the data from ten experiments on Na-jarosite within ten different RH buffers at 21 ± 1 °C. Similar plots are obtained from the experiments on Na-jarosite at 50 °C, 5 °C, and -10 °C, as well as from the similar two sets of exper-



iments started from K- and H_3O -jarosites. Combining these data with those from the dehydration experiment of Na-jarosite at 95 °C reported last year [12], it is very clear that jarosite structure maintained an extremely high stability in solid-gas interactions at wide T-RH range, especially when compared with the results from the similar experiments on five other ferric sulfates [9]. These experimental results are consistent with the finding of jarosite at the surface in widespread region on Mars (e.g., Maridiani Planum).

The reason for the continuous mass increase of Na-jarosite sample at 100% RH and 21 ± 1 °C as shown in Fig. 1 could only be resulted from the transfer of H_2O from the vapor phase of RH buffer. At early stages, H_2O molecules may be adsorbed as a water film at the surface of jarosite grains, a similar phenomenon observed in the experiments started with other ferric sulfates [9]. The difference in jarosites experiments was that the total deliquescence did not occurred. Instead, a mixture of solid-liquid was formed with total mass increases continuously (Fig. 1). According to the K-jarosite dissolution study of Madden et al. [13], we believe that jarosite dissolution occurred after the formation of water film at grain surface. During the dissolution, the consumption of OH^- by forming ferrihydrite, or maghemite, or hematite would lower the pH of the liquid surrounding jarosite grains, from neutral to acidic. Subsequently in this acidic solution, the dissolution rate of jarosite would increase [13] and lower the pH of solution even further. The low vapor pressure of this aqueous solution would facilitate a continuous transfer of H_2O from the vapor phase (buffered by pure water at 100%RH) to the sample, as indicated by the continuous mass increase of the sample (Fig. 1).

We noticed that the development of this process would change with experimental temperature, while the temperature dependences of the same process for three jarosites are different. For K-jarosite, the process moves faster when T increases, the similar process moves slower for Na-jarosite when T increases, and there is no obvious temperature dependence for H_3O -jarosite.

Result #2, Low-T behaviors of ferric sulfates: 36 Experiments at -10 °C and six RH levels provided additional information on the stability fields of six ferric

Figure 2. Phase boundaries of other types of ferric sulfates

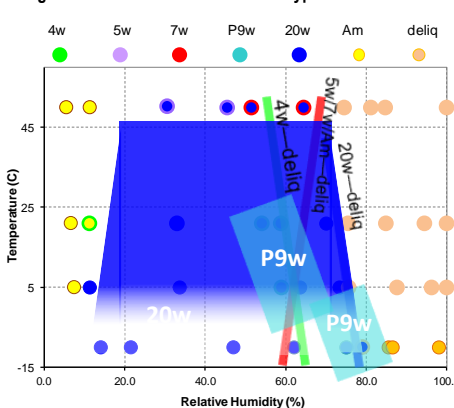
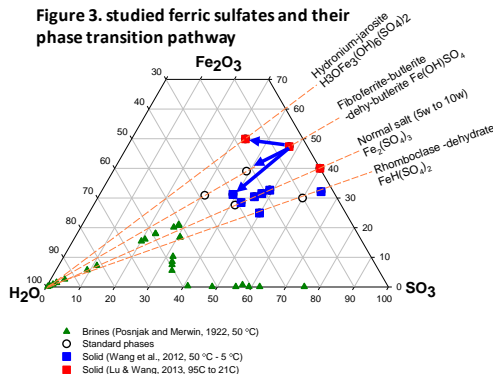


Figure 3. studied ferric sulfates and their phase transition pathway



sulfates whose properties in 50 - 5 °C range were reported previously [9]. The results in Figure 2 firstly confirmed a trend found in hydrous Mg-sulfates to be also true for hydrous ferric sulfates, i.e., the sulfates with high hydration degrees have a large stability field at low temperature. In addition, three deliquescence boundaries found in 50 - 5 °C were also extend to -10 °C.

Result #3, Phase transition of FeOHSO_4 :

The purpose of experimental set (3) was to rehydrate FeOHSO_4 to make fibroferite $[\text{FeOHSO}_4 \cdot 5\text{H}_2\text{O}]$ and butlerite $[\text{FeOHSO}_4 \cdot 2\text{H}_2\text{O}]$. Attempts of synthesizing these two phases by other team were failed in the past [14]. In our experiments, relatively high RHs (>50%)

and high Ts (95 °C, 50 °C, 21 °C) were used to drive the rehydration and also to rise the reaction rate. We found that H_3O -jarosite is the end-product of FeOHSO_4 rehydration at 95 °C and ~100%RH (P_{earth} , >42 days); while parabutlerite $[\text{FeOHSO}_4 \cdot 2\text{H}_2\text{O}]$, ferricopiapite, and H_3O -jarosite appeared at 50 °C and 21 °C with RH > 65%, P_{earth} , and >334 days duration.

These experiments demonstrated again the extreme high stability of OH-bearing ferric sulfates in solid-gas interactions even under high RH levels. Figure 3 shows the phase transition pathways among these OH-bearing phases. Combining with the report of last year [12], these experiments shed light into the genetic connections among three most important hydrous ferric sulfates found on Mars, jarosite, ferricopiapite, and ferric hydroxysulfate, with the environmental conditions.

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