STABILITY AND PHASE TRANSITION PATHWAYS OF OH-BEARING FERRIC SULFATES UNDER THE CONDITIONS RELEVANT TO DIURNAL, SEASONAL, AND OBLIQUITY CYCLES ON MARS.

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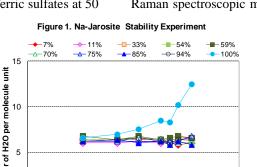
Different forms of ferric sulfates at surface & subsurface on Mars: Among the Fe-sulfates identified on Mars, those being found at the surface are OH-bearing, e.g., jarosite H₃O)Fe₃(SO₄)₂(OH)₆] in Meridiani outcrop [1] and ferric hydroxysulfate [FeOHSO₄] in exposed stratigraphic layers at Aram Crater [2]. In contrast, ferric sulfates of other forms were suggested existing in excavated subsurface regolith (Gusev crater), e.g., ferricopiapite $[Fe_{4.67}(SO_4)_6(OH)_2 \ 20H_2O],$ paraconquimbite and coquimbite [Fe₂(SO₄)₃ 9H₂O], and rhomboclase fibroferrite [FeOHSO₄ 5H₂O], $[FeH(SO_4)_2 \ 4H_2O] \ [3, \ 4].$ Furthermore, the dehydration of highly hydrated phase (ferricopiapite) was suggested by long-duration repeating observations of the Spirit rover [5].

These mission observations emphasized the importance of understanding the fundamental properties of ferric sulfates, especially their preservations and phase transitions under the conditions relevant to Mars' surface and subsurface environments. To build these understanding through laboratory experiments will link the mission observations to the interaction processes between Mars atmosphere and surface materials, and would further shed light into the current water budget of Mars.

Previous laboratory investigation of the fundamental properties of ferric sulfates: A few early studies [6,7] investigated the solubility relationships of minerals in the Fe₂O₃-SO₃-H₂O 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 [Fe₂(SO₄)₃ xH₂O], acidic [FeH(SO₄)₂ 4H2O], and slightly basic Fe_{4.67}(SO₄)₆(OH)₂ 20H₂O] types.

New experimental study of OH-bearing ferric sulfates: Since 2011, we started a new set of experiments on two major



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types of OH-bearing ferric sulfates: jarosite group and butlerite-fibroferrite group. We have successfully synthesized three jarosites KFe₃(SO₄)₂(OH)₆, NaFe₃(SO₄)₂(OH)₆, and H₃OFe₃(SO₄)₂(OH)₆, and a ferric hydroxysulfate FeOHSO₄[11].

Using these newly synthesized basic ferric sulfates, we started three sets of experiments in 2012, which were designed to simulate the post-depositional salts-atmosphere interaction processes on Mars, i.e., the deposited ferric sulfates experienced only the changes in atmospheric conditions (temperature T and relative humidity RH), as those would happened during the diurnal, seasonal, obliquity cycles on Mars. The solid-liquid interactions, that would bring-in additional ions, were not simulated by our experiments.

The three sets of new experiments are: (1) 90 experiments on the stability field and phase transition pathways of K-, Na, H₃O-jarosites, at three temperatures (50 $^{\circ}$ C, 21 $^{\circ}$ C, 5 $^{\circ}$ C) and ten relative humidity levels (from 5% to 100%); (2) 54 experiments on the stability field and phase transition pathways of K-, Na-, & H₃O-jarosites, ferricopiapite, paracoquimbite, kornelite [Fe₂(SO₄)₃ 7H₂O], crystalline and amorphous pentahydrated ferric sulfates [Fe₂(SO₄)₃ 5H₂O], and rhomboclase at -10 $^{\circ}$ C and six RH levels (from 11 % to 98%); (3) 12 experiments on the rehydration of FeOHSO₄ at three Ts (95 $^{\circ}$ C, 50 $^{\circ}$ C, 21 $^{\circ}$ C) and four RH levels from 50% to 100%.

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 H₂O/OH content in each sample; the laser Raman spectroscopic measurements were made on the

intermediate and final reaction products for phase identifications. We report here the preliminary results.

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-

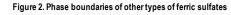
iments started from K- and H₃O-jarosites. Combining these data with those from the dehydration experiment of Na-jarosite at 95 °C reported last year [12], it is very clear that jarosite structure maintained an extremely high stability in solid-gas interactions at wide T-RH range, especially when compared 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).

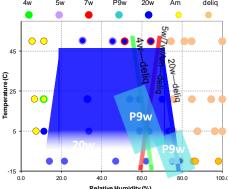
The reason for the continuous mass increase of Na-jarosite sample at 100% RH and 21 ± 1 °C as shown in Fig. 1 could only be resulted from the transfer of H₂O from the vapor phase of RH buffer. At early stages, H₂O molecules may be adsorbed as a water film at the surface of jarosite grains, a similar phenomenon observed in the experiments started with other ferric sulfates [9]. The differ-

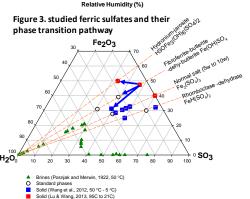
ence in jarosites experiments was that the total deliquescence did not occurred. Instead, a mixture of solid-liquid was formed with total mass increases continuously (Fig. 1). According to the K-jarosite dissolution study of Madden et al. [13], we believe that jarosite dissolution occurred after the 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 H₂O 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 H₃O-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







sulfates whose properties in 50-5 $^{\circ}$ 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 $^{\circ}$ C were also extend to -10 $^{\circ}$ C.

Result #3, Phase transition of FeOHSO₄: The purpose of experimental set rehydrate (3) was to FeOHSO₄ to make fibroferrite [FeOHSO₄ 5H₂O] and butlerite [FeOHSO₄ 2H₂O]. 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 FeOHSO₄ rehydration at 95 °C and ~ 100%RH (P_{earth} , >42 days); while parabutlerite [FeOHSO₄.2H₂O], 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 shad 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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References: [1] Klingelhofer et al., *Science*, 2004; [2] Lichtenberg et al., *JGR*, 2010; [3] Johnson et al., *GRL*, 2007; [4] Wang et al., *JGR*, 2008; [5] Wang & Ling, JGR, 2011; [6] Posnjak & Merwin, *J. Am. Chem.1922*; [7] Merwin & Posnjak, *Am. Mineral.*, 1937; [8] Xu et al., *Am. Mineral.*, 2009; [9] Wang et al.; *Icarus*, 2012; [10] Kong et al., *Chem. Geol.*, 2011; [11] Lu & Wang, *LPSC*, 2012; [12] Liu & Wang, *LPSC*, 2012; [13] Madden et al., *GCA*, 2012; [14] Lombardo, 2010, MS thesis at Queen's University.