

## PHASE BOUNDARIES AMONG THREE HYDROUS $\text{Fe}^{3+}$ SULFATES

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**Introduction:** Sulfates are important secondary minerals produced from the evaporation of fluids involved in the aqueous alteration of Mars' primary lithology[1]. Knowledge on the fundamental properties of sulfates, such as phase boundary, stability field, phase transition pathways and rates, can greatly enhance our understanding of mission observations, as well as Mars hydrologic evolution[2-5]. The experimental studies addressing the above properties of sulfates (Ca, Mg, and Fe, Al) have started since the discovery of sulfates on Mars[6,7], and have been continued for many years. However, the fundamental properties of  $\text{Fe}^{3+}$  sulfates have not been fully revealed, especially the phase boundaries, because of their complicate nature, either in neutral, or acidic, or basic form, observed on Earth and on Mars[8].

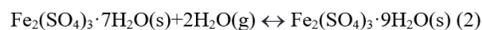
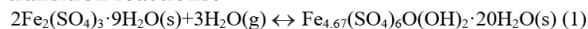
The purpose of this study is to determine the phase relationships between the  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  (**9W**) and  $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$  (**7W**), and that between the **9W** and  $\text{Fe}_{4.67}(\text{SO}_4)_6\text{O}(\text{OH})_2 \cdot 20\text{H}_2\text{O}$  (**20W**) in Mars relevant temperature range, and at the same time, to monitor the potential occurrences of other ferric (neutral, basic, and acidic) sulfates. This study will help the understanding of occurrence of the ferric sulfates and their phase transitions on Mars.

**Experimental methods and processes:** *The starting samples of 7W, 9W and 20W:* were synthesized using the techniques described in literatures[2,4].

The phase identification and the homogeneity of three synthesized samples were determined by Laser Raman spectroscopy. For each sample, Raman data of more than 100 points were collected from a flattened powder sample that is placed on a glass slide.

*Structural or adsorbed water:* we will use gravimetric method plus Raman spectroscopy to monitor the development of phase transition. We notice that two processes can cause the gravimetric change of a salt:

(1) hydration and dehydration, i.e., the loss or gain of structural water; (2) adsorption and desorption, i.e., the loss or gain of adsorbed water. In following phase transition reactions:



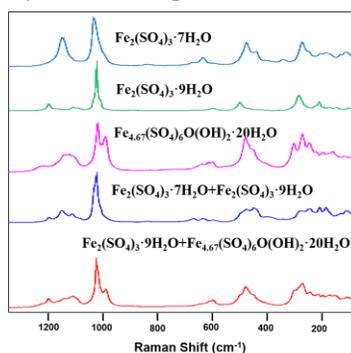
the adding or losing one structural  $\text{H}_2\text{O}$  would cause only 3.2 wt.% mass variations in a **9W** molecule, 1.5 wt.% in **20W**, and 3.7 wt.% in **7W**. Therefore, the mass change caused by the phase changes among different ferric sulfates is difficult to be distinguished from that caused by the changes of adsorbed water at different relative humidity (RH) levels. Thus, we used

a procedure similar to [2,3] as the first step. We would add the adsorbed water under similar T - RH conditions into the starting phases (i.e., *The water adsorption experiment*), which will help to remove the uncertainty in the follow up *phase boundary experiments*.

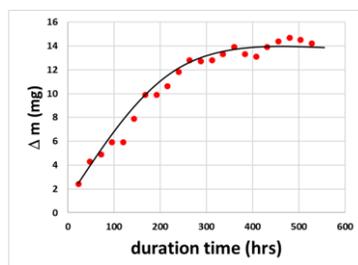
*In the water adsorption experiments,* the amount of added adsorbed water to three starting samples was determined by gravimetric measurements at temperature ranges in 0 - 30°C for **9W** and **7W** and -10 - 30°C for **9W** and **20W** (the T values were close to the values of estimated phase boundary based on [2,3]) in  $\text{H}_2\text{O}$ -NaBr and  $\text{H}_2\text{O}$ - $\text{Mg}(\text{NO}_3)_2$  RH buffers, respectively. After these samples reaching the saturation of adsorbed water (**Fig. 2.**) at relevant conditions but not changing its identification (determined by Raman checking in sealed reaction vials), will the *phase boundary experiments* start.

*The phase boundary experiments:*

After reaching the saturation of adsorbed water, two samples (either **7W** and **9W** or **9W** and **20W**) were mixed with equal portions (1:1), and a total mass of 200-400 mg was used as the starting material. The selection of total mass was decided based on the equation (1) and (2), in order for the mass change (caused by adding or losing one structure  $\text{H}_2\text{O}$  molecule in three different hydrous ferric sulfates) to be larger than the uncertainty in our gravimetric measurement.



**Figure 1.** Raman spectra of the synthetic starting phases of **7W**, **9W**, and **20W** and typical mixing spectra of experimental products.



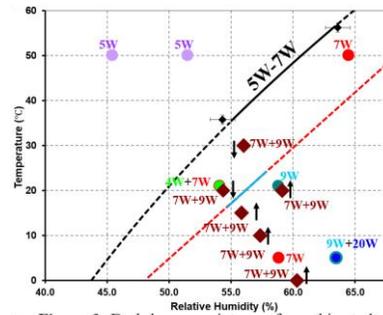
**Figure 2.** Result of water adsorption experiment: the mass increase of **9W** powder reaching a plateau in NaBr RH% buffer at 10°C.

The starting mixture was put into a reaction vial, with carefully measured total mass (precision to  $\pm 0.1$  mg), including the cap of reaction vial. The reaction vial (without cap) was put into a RH buffer bottle filled with a saturated binary salt-water solution, with extra salt grains exposed above the liquid level to avoid RH gradient in the system. On the basis of previous stability field study on ferric sulfates [2], oversaturated aqueous solutions of NaBr and  $\text{Mg}(\text{NO}_3)_2$  were selected for controlling the RH%. The temperature (T) of reactions was controlled by a water bath with precisely controlled temperature (Neslab RTE-110 by Thermo Fisher). The T value was determined by a Pt wire with precision of  $\pm 0.1^\circ\text{C}$ . The experiments were ran at the T range in  $-10$  -  $30^\circ\text{C}$  for **9W** and **20W** mixture and in  $0$  -  $30^\circ\text{C}$  for **7W** and **9W** mixture.

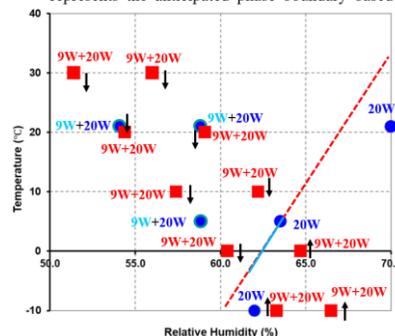
A large increment of temperature ( $\Delta T$ ) was used in the largest initial T range. Based on the gravimetric data (either losing or gaining mass), we would gradually reduce the scale of T range and the T step ( $\Delta T$ ), until the equilibrium of two phase being reached, i.e., no loss or gain of mass will be observed at a T ( $= T_{\text{eq}}$ ). For example, assuming  $T_{\text{eq}}$  is around  $0.5^\circ\text{C}$ , we will use  $\Delta T = 5^\circ\text{C}$  in the  $0 - 10^\circ\text{C}$ ,  $\Delta T = 1^\circ\text{C}$  in the  $0 - 5^\circ\text{C}$ ,  $\Delta T = 0.2^\circ\text{C}$  in the  $0 - 2^\circ\text{C}$ , and  $\Delta T = 0.1^\circ\text{C}$  in the  $0 - 1^\circ\text{C}$ .

At each T step, the time duration of every experiment is 48 - 240 hours. By the end of a  $\Delta T$  step, the reaction vial was taken out from the RH buffer bottle, immediately capped with its own cap. The mass of whole vial was measured and compared with its initial mass. In these experiments, the phase boundary point will be finally determined (a  $T_{\text{eq}}$  at fixed RH%) by almost unchanged samples mass, less or equal to  $\pm 0.1$  mg. At each  $\Delta T$  step, the multiple Raman measurements ( $> 50$ ) were made, in order to check if new phase (other than **7W**, **9W**, **20W**) appeared.

**Preliminary Results after 7 months experiments:** For the phase boundary between **7W** and **9W**, current results suggest that two equilibrium points on the **7W** - **9W** phase boundary might locate between  $20$  -  $30^\circ\text{C}$  and along the RH% curve of NaBr buffer, and around  $18^\circ\text{C}$  and along the RH% curve of  $\text{Mg}(\text{NO}_3)_2$  buffer (**Fig. 3**). During this set of experiments, only the Raman spectra of **7W**, **9W** were found in the start-



**Figure 3.** Dark brown points are from this study on phase boundary of **7W-9W**. A light blue line represents the anticipated phase boundary based



**Figure 4.** Red points are from this study on phase boundary of **9W-20W**. The light blue line represents the anticipated phase boundary based on current results. The relevant data points from a stability field study [2] are shown.

ing materials (after the water adsorption experiment), and in the starting mixture. However, the spectrum of rhomboclase  $\text{FeH}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  (**4W**) was appeared when checking the reaction product at  $30^\circ\text{C}$  in NaBr buffer (RH% = 56.03%). I.e., an acidic ferric sulfate occurred through dehydration of **7W** and **9W**. We used two methods to avoid this happening. Firstly, we run the experiment in NaBr buffer at  $25^\circ\text{C}$ , instead of  $30^\circ\text{C}$ . Secondly, we run the similar experiment in  $\text{CoCl}_2$  buffer (RH% = 64.92%) at  $25^\circ\text{C}$ . Until the writing of this abstract, the second experiment has been running more than 300 hours and no rhomboclase appeared.

During the phase boundary experiment between **9W** and **20W**, only Raman spectra of **9W**, **20W** were encountered in the starting materials (after water adsorption experiment), in the starting mixture, and in reaction products (**Fig. 1**). According to the observed mass changes, we antic-

ipate the two  $T_{\text{eq}}$  points on the **9W** - **20W** phase boundary to be located in  $0 - 10^\circ\text{C}$  and along the RH% curve of NaBr buffer, and in  $-10 - 0^\circ\text{C}$  and along the RH% curve of  $\text{Mg}(\text{NO}_3)_2$  buffer (**Fig. 4**).

**Conclusions and Future Work:** We are in the process to define two pairs of ferric sulfates phase boundaries in Mars relevant temperature range. Within next few months, their precise locations in T-RH space will be identified. Based on them, the thermodynamic parameters of these two pairs ferric sulfates will be calculated.

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