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PHASE BOUNDARIES AMONG THREE HYDROUS Fe^{3+} SULFATES

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Introduction

- 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 [1-5];
- Knowledge of fundamental properties of Fe^{3+} sulfates have not been fully revealed, especially the phase boundaries, because of their complicate nature, e.g., either in neutral, or acidic, or basic form, observed on Earth and on Mars[6].

Goal of this study

- To determine two phase boundaries among three ferric sulfates: 7W, 9W, and 20W, as following in Mars relevant temperature (T) range;

$$2Fe_2(SO_4)_3\cdot 9H_2O(s)+3H_2O(g) \leftrightarrow Fe_{4.67}(SO_4)_6O(OH)_2\cdot 20H_2O(s) \quad (1)$$

$$Fe_2(SO_4)_3\cdot 7H_2O(s)+2H_2O(g) \leftrightarrow Fe_2(SO_4)_3\cdot 9H_2O(s) \quad (2)$$

- To monitor the potential occurrences of other ferric (neutral, basic, and acidic) sulfates, using Raman spectroscopy.

a. H_2O pre-absorption of starting samples

- To let the starting phase absorbing enough H_2O at pre-determined Relative Humidity (RH%) and T to reduce the error in mass measurement [1] ;

b. To define two points on a phase boundary in RH-T space

- To select over-saturated H_2O-NaBr and H_2O-$Mg(NO_3)_2$ as Relative Humidity (RH_a & RH_b) buffers based on [1];
- To use a water-bath to precisely control the temperature (T) of a mixture of ferric sulfates, with precision of ± 0.1°C;
- To use gravimetric measurements (± 0.1 mg) of that mixture to select the changing direction of T, until the mass change Δm = 0, i.e., to define a pair of RH_a & T_a (same for RH_b & T_b).

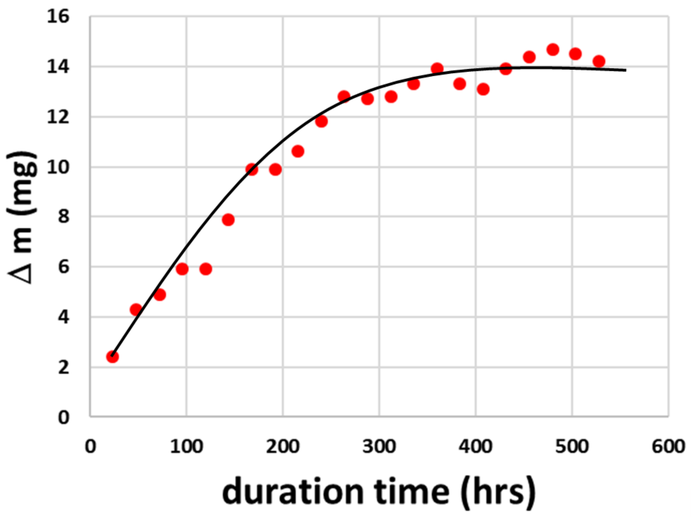

Figure 1. Result of *water adsorption experiment*: the mass increase of 9W powder reaching a plateau in NaBr RH% buffer at 10°C after 300 hrs.

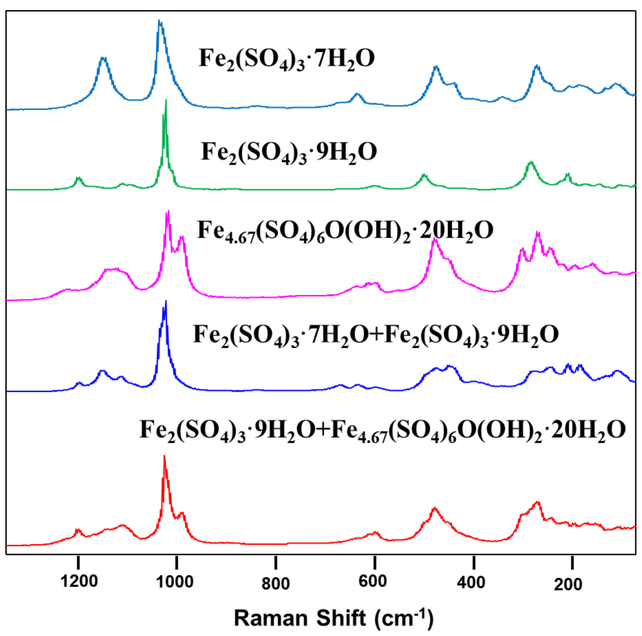

Figure 2. Raman spectra of the synthetic starting phases of 7W, 9W, and 20W and typical mixing spectra of experimental products [1,3].

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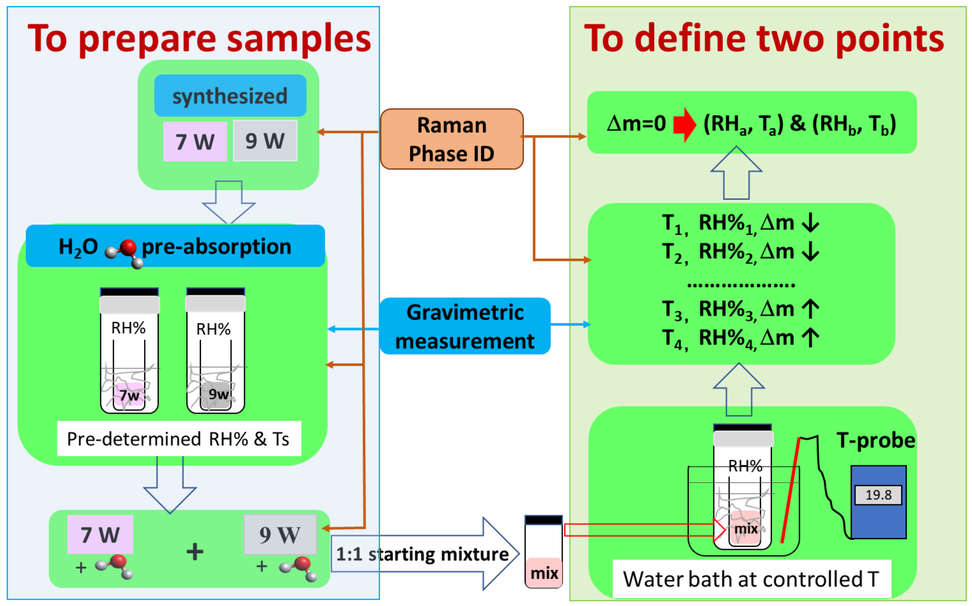

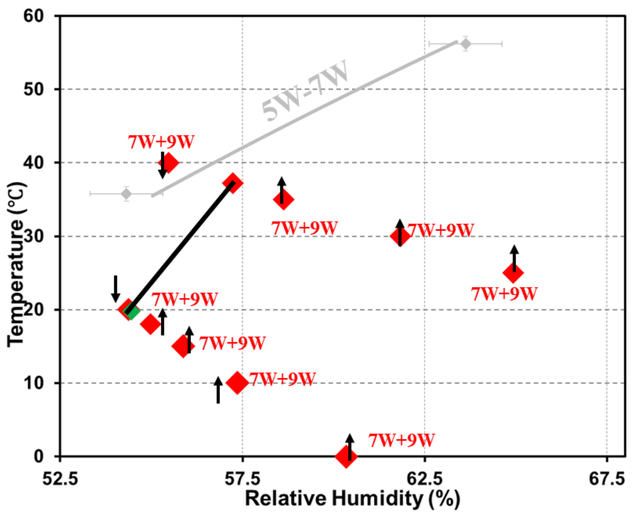

Figure 3. Red diamonds are data of this study searching for the final location (**a black line)** of the phase boundary between **7W** & **9W.** A gray line is the phase boundary between 5W & 7W determined by [2]. In the figure: **5W** = $Fe_2(SO_4)_3\cdot 5H_2O$), ↑ = mass increase, ↓ = mass decrease.

Phase boundary between 7W & 9W

- The two points found on the phase boundary between 7W and 9W were **at T=19.8°C and RH% = 54.45%,** and near 37.2°C and 57.23 RH%, (Fig. 3);
- Only the Raman spectra of 7W, 9W were found in the starting mixture and in reaction products (Fig. 2);
- A caveat: rhomboclase $FeH(SO_4)_2\cdot 4H_2O$ **(4W)** appeared in the reaction product at 30°C in NaBr buffer (RH% = 56.03%). Thus, the $CoCl_2$ buffer (RH% = 64.92% at 30°C) was used to finish the study.

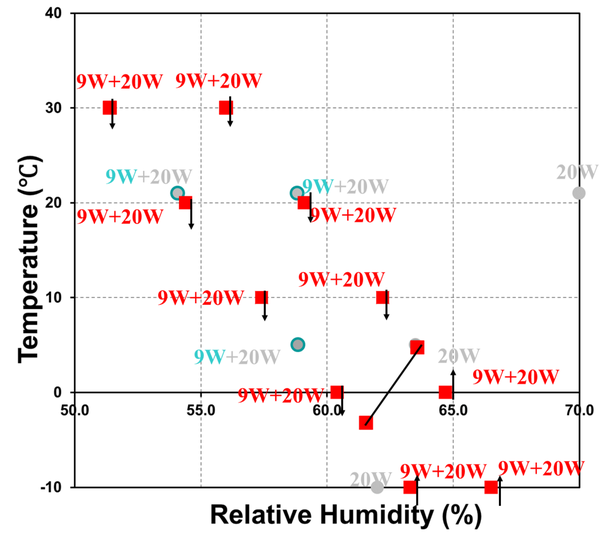

Figure 4. Red squares are data of this study searching for the final location (**a black line**) of the phase boundary between **9W & 20W**. In the figure: the relevant data gray colored data points are from a stability field study [1]; ↑ = mass increase, ↓ = mass decrease.

Phase boundary between 9W & 20W

- The two points found on the phase boundary between 9W and 20 W were near 4.7°C and 63.6 RH%, and near -3.2°C and 61.54 RH% (Fig. 4);
- Only Raman spectra of **9W, 20W** were encountered in the starting mixture and in reaction products (Fig. 2).

Conclusions and Future Work

We are in the process to define the final positions of two phase boundaries among three ferric sulfates in Mars relevant temperature range. Based on them, the thermodynamic parameters of these two pairs of ferric sulfates will be calculated.

References: [1] Wang, A. et al. (2012) Icarus 218, 622-643. [2] Kong, W. G. et al. (2011) CG, 284, 333-338. [3] Ling, Z. C. et al. (2010) Icarus 209, 422-433. [4] Wang, A. et al. (2016) JGR, 121,678-694. [5] Chou, I.M. et al. (2007) JGR, 112, E11004. [6] Druschel, G. K. et al. (2004) GT, 5, 13.