$(H_3O)Fe(SO_4)_2$, A NEW PHASE FORMED BY DEHYDRATING RHOMBOCLASE.

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Introduction: Several ferric sulfate minerals have been discovered or positived confirmed on the Martian surface, including jarosite, rhomboclase, ferricopiapite, fibroferrite and schwertmannite *(1-6)*. These minerals contain structural water or hydroxyls, and may account for the water measured in the equatorial regions by the neutron spectrometer aboard Mars Odyssey. Iron sulfates are sensitive to changes in environmental variables such as temperature (T) and relative humidity (RH), which make them potentially important tracers of paleo-environmental conditions on Mars. Characterizing the reaction pathways among iron sulfates allows a better understanding of the Martian climate and hydrogeologic history. In this abstract, we present a preliminary study on the dehydration behavior of rhomboclase and its dehydrated phase.

Methods: Rhomboclase ($(H_3O)Fe(SO_4)_2{\cdot}3H_2O$) was synthesized according to literature (*7*): mixing 2 g of anhydrous ferric sulfate, 2.5 g of water and 2.5 g of sulfuric acid (95.9% H_2SO_4 by mass). The solution was dried at ambient condition (20°C, 10-30% RH). rhomboclase formed as white product after 3 days.

The dehydration of rhomboclase was chracterized by *in situ* using the temperature-resolved XRD method without humidity control. Data were collected at X7B beamline at the National Synchrotron Light Source. Rhomboclase powders were loaded in a polyimide capillary with a 0.5mm inner diameter, and the x-ray beam matched to the same size using variable slits. An air-blower type heater was used to control the temperature with the thermocouple placed in contact with the outside of the capillary. The heater was programmed to range from 30°C to 180°C at a rate of 1°C/min. XRD data were collected by MAR345 area detector continuously with 120 seconds exposure time, plus 45 seconds readout time before the start of the next exposure. The wavelength used was 0.3184Å.

The effect of RH on the stability of rhomboclase was also investigated using the Rigaku DSC-XRD diffractometer with RH control device. Two heating runs up to 90°C were carried out under 4% and 40% RH, respectively.

Results: Temperature-resolved XRD data revealed a two-step decomposition of rhomboclase at 73°C and 128°C (Fig. 1). The intermediate phase formed starting from 73°C could not be identified from the JCPDS database, but was solved by powder method. The difference in crystal structure between rhomboclase and the dehydrated phase was shown in Fig. 2. Rhomboclase crystallizes in a layered structure with nominally four interlayer water molecules (including a hydronium). The dehydrated phase loses three interlayer water molecules, with the distance between layers shrinking from 9.14 Å of rhomboclase to 7.83Å. The intralyer structures are also different. In the dehydrated phase, Fe-O6 octahedra are fully connected to 6 S-O4 tetrahedra by corner-sharing mode, compared to sharing only 4 corners with S-O4 in rhombolcase, although the Fe/S ratio remains the same. This dehydration step is reversible.

Heating the dehydrated phase up to 128°C led to a sharp transition to form monoclinic $Fe_2(SO_4)_3$, which involved a loss of the last structural water and a desulfation process.

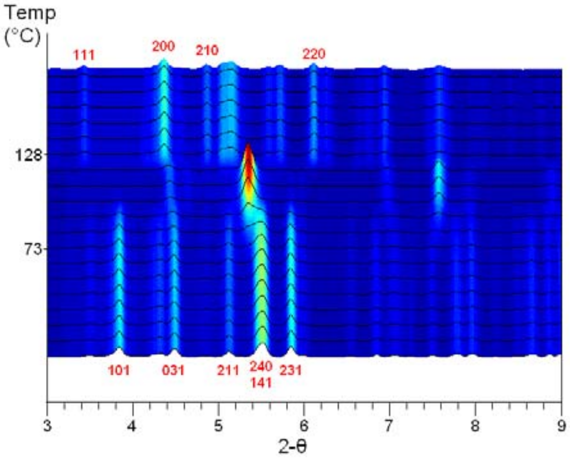

Figure 1. Temperature-resolved XRD data showing the thermal dehydration process of rhomboclase. An intermediate dehydrated phase appeared at 73°C before its decomposition to monoclinic $Fe_2(SO_4)_3$ at 128°C. Some peak indexes for rhomboclase are listed at the bottom and those for monoclinic $Fe_2(SO_4)_3$ are listed at the top.

The RH effect. Results from the Rigaku DSC-XRD showed the same transition to the dehydrated form occurred at 80°C with the RH controled at 4%. At RH 40%, no dehydration was detected up to 90°C. A positive slope is expected for the phase boundary line in the RH-T diagram (Fig.3), which is reasonable as higher RH favors the hydrated form.

Rhomboclase was also preserved in extremely dry condition (RH<1%) at room temperature to study its stability. The dehydrated phase formed after 3 days. This result is important as it implies high temperature is not necessary for the dehydration to occur as long as the RH is low enough. Futher experiments will investigate whether this dehydrated phase could be present under vaccum and under simulated martian environments.

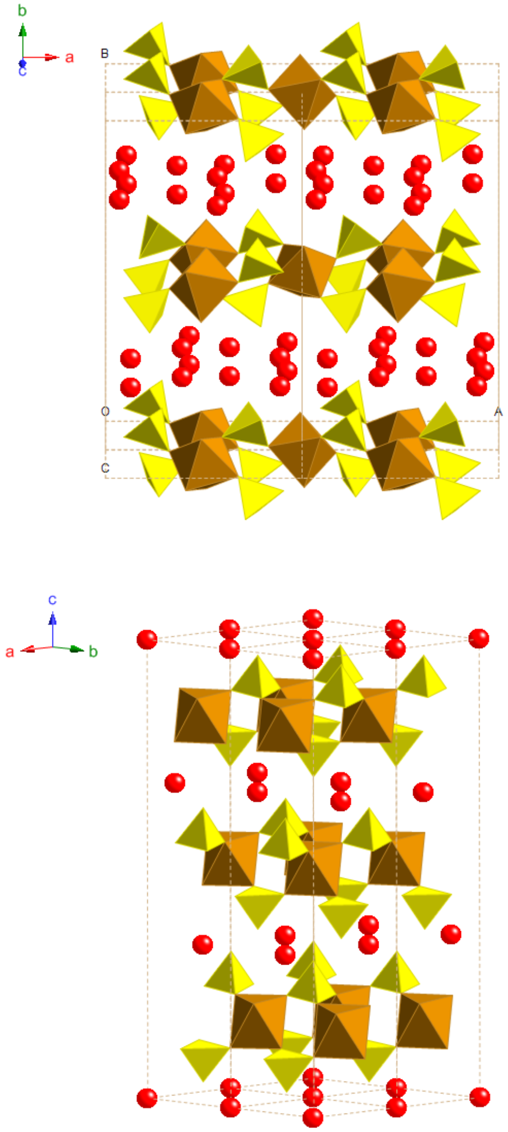

Figure 2. Crystal structure of rhomboclase (at the top) and $(H_3O)Fe(SO_4)_2$. Water and hydronium oxygen are represented by red spheres. FeO_6 octahedra are brown and SO_4 tetrahedra are yellow.

Conclusions: The stability of rhomboclase with respect to T and RH has been examined by *in situ* XRD method. Rhomboclase transforms to $(H_3O)Fe(SO_4)_2$ either by heating to 70~80°C or by dehydration under <1% RH conditions at room termperature. The structure of the dehydrated phase has been solved and the possibility of its existence on Mars is being studied.

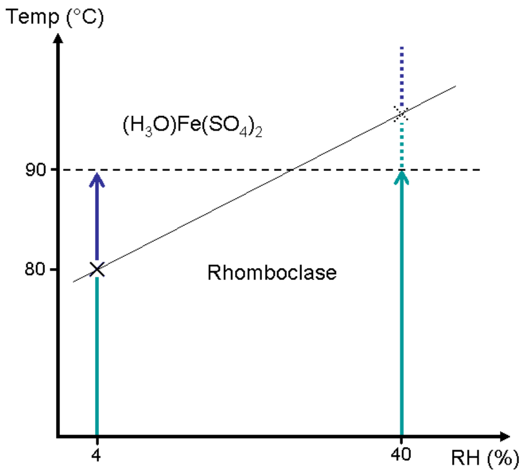

Figure 3. An suspected phase diagram between rhomoboclase and $(H_3O)Fe(SO_4)_2$ based on the RH-controlled XRD data.

References:

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