A Comparison of Dehydration Processes of Al-, Fe^{2+}-, & Mg-Sulfates under Mars Relevant Conditions

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Abstract #1797

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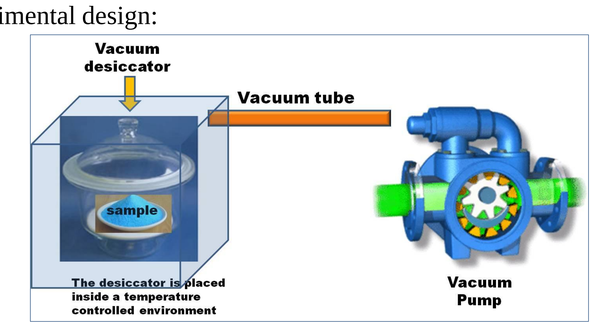
Introduction

- Hydrous sulfates (Ca-, Mg-, Fe-sulfates and recently Al-sulfates) , as markers of aqueous processes on Mars, have been observed on a variety of locations on Mars;
- This set of six experiments studies the dehydration processes and dehydration rates of a Al-sulfate (Alunogen, $Al_2(SO_4)_3$•$17H_2O$) and a Fe^{2+}-sulfate (Melanterite, $FeSO_4$•$7H_2O$);
- The dehydration rate of hydrous sulfates is a function of environment pressure (P), temperature (T), and partial water pressure (P_{H2O}). Our experiments were conducted at Mars relevant P, P_{H2O}, and at three Ts;
- We compared our results with those from the previous experiments on a Mg-sulfate (epsomite, $MgSO_4$•$7H_2O$);
- Our goal is to understand the potential hydration degrees of these sulfates within Mars subsurface and the current water budget of Mars.

Samples & Experiments

Samples are prepared to make sure:
1. Within the same grain size range;
2. At the highest hydration degrees (RH buffer tech.)
3. With confirmed ID and homogeneity (laser Raman 100-point check).

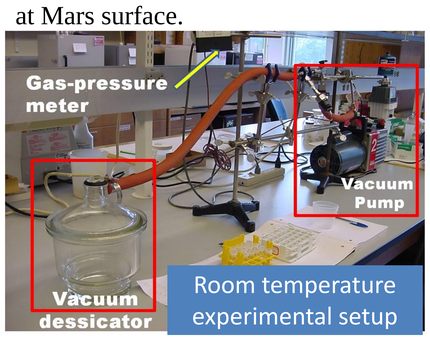
Experimental design:



The P and P_{H2O} in our experiments are relevant to general Mars P and P_{H2O}.

In Lab		On Mars	
the atmospheric pressure in dessicator: 0.16 to 0.26 mbar	<	Mars atmospheric pressure: 7 mbar
PH2O: 0.14 – 0.25 Pa	>	PH2O: 0.04 – 0.15 Pa

Two sets of experiments (for alunogen and melanterite) are conducted at 3 temperatures: 25°C, 0°C, and -12°C， which are within the T range at Mars surface.

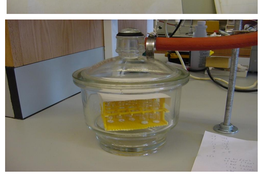


Room temperature experimental setup

0°C experimental setup (immersed in H_2O liquid + ice bath)

Experiments at -12°C were made by placing the vacuum desiccators in a freezer (at -12°C ± 1°C).

- For each of six experiments, 15 sample bottles were used: (60±5 mg per bottle for alunogen, 120±5 mg per bottle for melanterite):
- at each of 9-16 steps during the dehydration, all 10 sample bottles were taken out for mass measurements, from which we obtained the standard deviation of gravimetric measurements;



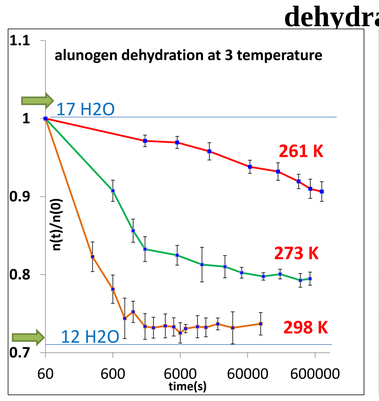
- at five steps during the dehydration, one of the remaining 5 sample bottles was taken out for laser Raman measurements, from which we determined the crystal structural changes.

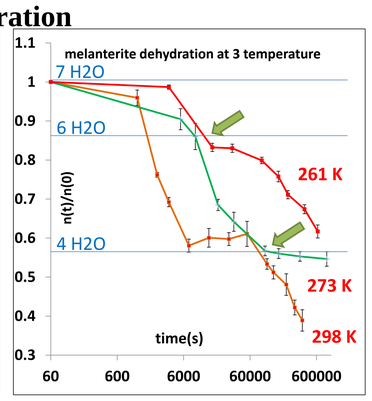
Experiment Results

Alunogen	Duration(Hours)	Dehydration
25°C	26	17 H2O to 12.53 H2O
0°C	141	17 H2O to 13.51 H2O
-12°C	210	17 H2O to 15.41 H2O
Melanterite	**Duration(Hours)**	**Dehydration**
25°C	102	7 H2O to 2.72 H2O
0°C	238	7 H2O to 3.82 H2O
-12°C	174	7 H2O to 4.32 H2O

Among the 6 dehydration experiments , alunogen dehydrated from 17 H_2O to 12.53 H_2O at 21° C. Melanterite dehydrated from 7 H_2O to 2.72 H_2O at 21° C.

Mass reductions of alunogen and melantorite during the dehydration

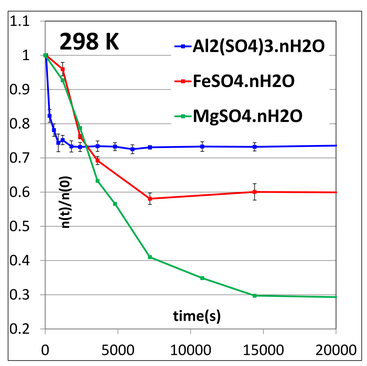


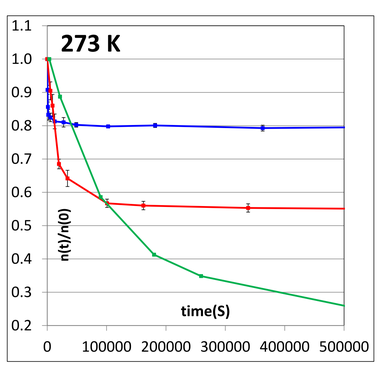


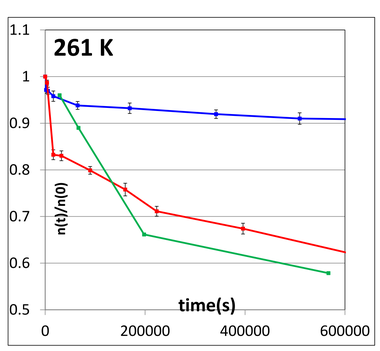
n(t) = the number of structural H_2O per molecule at a time (t)
n(0) = the number of structural H_2O per molecule at a time (0)
Time (s) = time duration of experiment (second)

Alunogen dehydrates fast until reaching 12w, then almost stable at our exp. conditions;
Melanterite dehydration appears as 3 stages: from 7w to 6w, to 4 w, and then further.

Comparison -- three dehydration paths





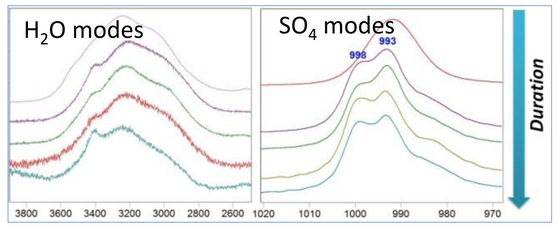


Under very similar P, T, P_{H2O} conditions:

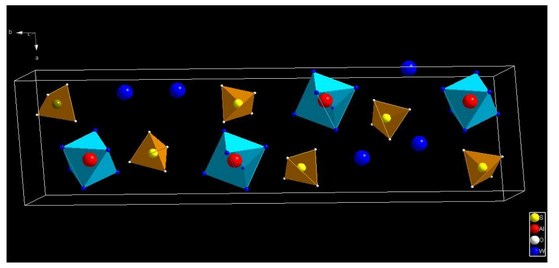
- All three dehydrations are strongly T dependent;
- With very different dehydration pathways:
  - Alunogen – fast at beginning, then stable at ~ 12w;
  - Melanterite – experience three stages;
  - Epsomite – a smooth continuous dehydration (amorphozation, Wang et al., 2006, 2009).

structural changes during the dehydration

A. alunogen → meta-alunogen

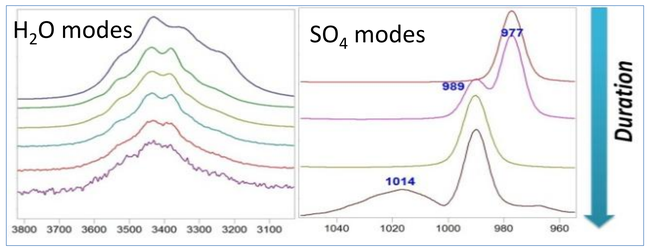


Change of Raman spectra of $Al_2(SO_4)_3$.nH_2O (n = 17 to 12.5) during dehydration at 298 K. XRD analysis confirms the structural change from alunogen [$Al_2(SO_4)_3$ ·$17H_2O$] to meta-alunogen $Al_2(SO_4)_3$ ·$12H_2O$].

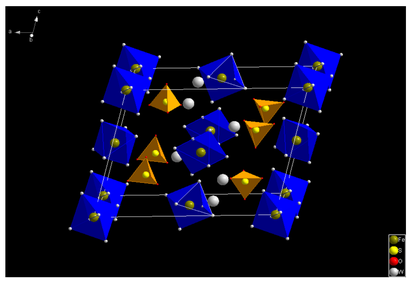


Crystal structure study of alunogen reveals that among the total structural 17 H_2O per molecule, 5 H_2O that are hydrogen bonded. Their weak bonding strength makes them easy to loss, while other 12 H_2O are coordinated with Al, thus more structurally stable.

B. Melanterite → rozenite → mixture of rozenite & amorphous Fe^{2+}- sulfates



Change of Raman spectra of FeSO4.nH2O (n = 7, 4, 1) during dehydration at 298 K (Choi et al., 2006).



Crystal structure study of melanterite reveals that among the total 7 structural H_2O, only one is hydrogen bonded, which will be removed first during the dehydration. Then, structural change happens from ferrohexahydrite [$FeSO_4$ $6H_2O$, C2/c] to rozenite [$FeSO_4$ $4H_2O$, P21/c]. The appearance of broad Raman peak at 1014 cm^{-1} suggests the formation of amorphous Fe^{2+}-sulfates with hydration degree between 1-4.

Conclusion

A comparison of the dehydration processes of alunogen, melanterite, and epsomite reveals:

- **The dehydration rates of all three processes are strong temperature dependent. At low T, all three dehydrations invariably go very slow;**
- **Under the similar P, T, P_{H2O} conditions, the pathways of dehydration of three hydrous sulfates are very different: alunogen lost only the hydrogen bonded H_2O; melanterite went through three steps in which crystalline structures were maintained during almost entire duration; epsomite lost first hydrogen bonded H_2O and then become amorphous during almost entire duration. The differences in the bonding strength are the causes for their different dehydration pathways.**
- **Under the similar P, T, P_{H2O} conditions, the dehydration of epsomite goes faster than that of melanterite, the dehydration of melanterite goes faster than that of alunogen.**

Acknowledgement

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References

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