

PATHWAYS AND RATES OF Mg-SULFATE DEHYDRATION AND REHYDRATION ON MARS.

Alian Wang, John J. Freeman, Dept Earth and Planetary Sciences and McDonnell Center for Space Sciences, Washington University, St. Louis, MO, 63130 USA (alianw@levee.wustl.edu)

We report a new understanding developed on the basis of experimental study [1,2,3] of the hydrous Mg-sulfates, using humidity buffer technology and non-invasive Raman spectroscopy.

Stability field and phase transition pathways:

Information came from direct Raman phase identifications and gravimetric measurements (Fig. 1):

At $T < 50^\circ\text{C}$, hexahydrate ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, 6w), epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 7w), and meridianiite ($\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$, 11w) precipitate from Mg-S-solution. Kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$, 1w) only precipitates from high temperature (T) aqueous solution (95°C in our experiments).

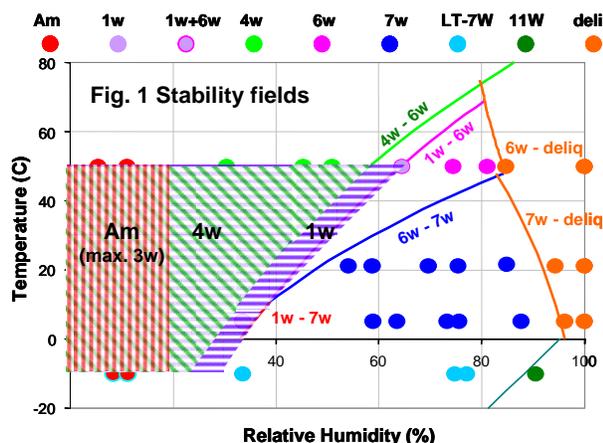
At $T < 50^\circ\text{C}$, starkeyite ($\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$, 4w) (not kieserite) is the dehydration end product from 11w, 7w, 6w. Amorphous Mg-sulfates (Am) form by fast dehydration of 11w, 7w, 6w (not from 4w or 1w), and it can hold a maximum 3 water per SO_4 .

At $T < 50^\circ\text{C}$, kieserite is only formed through two pathways from the dehydration of 6w, 7w, 11w; (1) if these salts were originally mixed with Ca- and Fe-sulfates, Fe-hydroxide and Fe-oxide; or (2) the salts were first converted to amorphous phases.

We found that $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ has two polymorphs, LH-1w and MH-1w (kieserite). The LH-1w forms from the dehydration of 6w, 7w, 11w by above two pathways. The MH-1w precipitates from high T aqueous solution, and can also be formed from the conversion of LH-1w at mid-range relative humidity (RH).

We found that $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ has two polymorphs, 7w (epsomite) and LT-7w. LT-7w is stable at $T \leq -10^\circ\text{C}$. Fig. 1 shows the phase boundary between 11w and LT-7w. The extent of the stability fields of LT-7w and 11w below -10°C has not been undetermined yet.

Above 0°C , the rehydration pathways of LH-1w, 4w, Am are different. Amorphous phase rehydrates to 4w first, then to 6w/7w, while LH-1w rehydrates to 6w without go through 4w. 4w rehydrates to 6w/7w.



In the $-10^\circ\text{C} \leq T \leq 50^\circ\text{C}$ range, the stability fields of LH-1w, MH-1w, 4w, and Am are partially overlap in low-mid RH range (Fig. 1).

Rate of dehydration and rehydration: Rate information was extracted from Raman ID of intermediate reaction products measured at regular time interval during the dehydration/rehydration experiments. Most experiments (except vacuum desiccation for amorphization [4]) were conducted under terrestrial $P_{\text{H}_2\text{O}}$ (with selected RHs) which would increase the general rate of reaction. Therefore, only the ratio of rates at different temperatures is meaningful for their applications to Mars. Sources of errors affecting the rate estimations are (1) the limited number of experiment temperatures (three) used for rate extraction and (2) the limited number of intermediate stages when Raman ID was made on the reaction products. For these reasons, we use only the order of magnitude of rate ratios in the discussions to judge whether a process has the potential to happen on Mars.

The rate of amorphization is strongly controlled by temperature [4]. The amorphization process matches a first-order reaction whose rate can be estimated by $k(T) = \ln 2 / t_{1/2}(T)$. The rate k at 21°C is ~ 120 times the k at -8°C in our experiments. When extrapolating into 210-240 K range (4 to 8 o'clock at Spirit site [5,6,7] while RH drops from 10% to $\sim 0\%$), the rate of amorphization would be 10^{-4} to 10^{-7} of that at 21°C .

The dehydration and rehydration processes of most Mg-sulfates match roughly the first-order forward reaction within the errors stated above.

The rate of 7w dehydration at 21°C is ~ 50 times the rate at 5°C , in our experiments for total conversion to 4w at 11% RH (Earth $P_{\text{H}_2\text{O}}$). Extrapolating to 240K would decrease the rate of dehydration ~ 5000 times. In 240K - 290K daytime ground temperature at Spirit site [5,6,7], this dehydration can proceed steadily.

Using the same method (experimental data plus extrapolation), we found that the rehydration rates of 1w, 4w, and Am would be very low in temperature range 180K-210K (0 to 4 o'clock at Spirit site [5,6,7] while RH increases from 10% to 100%). For example (Fig. 2), the rehydration rate of Am (to 4w, 6w, 7w) at 180 K for 100% RH and for 35% RH would be 5×10^{-4} and 10^{-6} times of that at 21°C . At Earth $P_{\text{H}_2\text{O}}$, that means >5 years at 100%RH and > 83000 years at 35%RH, and hundreds times more at Mars $P_{\text{H}_2\text{O}}$.

Application to Mg-sulfates on Mars: Based on the information of pathways and reaction rates from ours and other experiments [8], we developed the following hypotheses (Fig. 3).

Precipitation – 7w would be the major Mg-sulfate phase precipitated from Mg-S aqueous solutions on Mars, because the surface temperature in Mars’ general area was never above 50°C, even in its warm and wet past. During a localized hydrothermal event, MH-1w (kieserite) would precipitate from aqueous solution. For low temperature Mg-S aqueous solutions ($2^{\circ}\text{C} \leq T \leq -3^{\circ}\text{C}$), the freezing point suppression by saturated MgSO_4 is only $\sim 3^{\circ}\text{C}$, 11w would precipitate.

Dehydration – With Mars getting colder and drier, 7w and 11w (if they do not coexist with water ice) would start to dehydrate. The kinetic barrier at $<50^{\circ}\text{C}$ would prevent the direct dehydration of 7w/11w to 1w. The dehydration would stop at starkeyite (4w).

At the locations where the chemistry of original brine allowed the co-precipitation of Ca-sulfates, Fe-sulfates, and Fe-hydroxides, or the processes built up the mixture of Mg-sulfates with other minerals (including Fe-oxides), the coexisting species would function as a catalyst in the dehydration of 7w/11w, overcoming the kinetic barrier to reach LH-1w as the final dehydration product. Rapid dehydration of 7w/11w during the early stage (when temperature on Mars was not very low) would form amorphous Mg-sulfates. However, the gradual decreasing of $P_{\text{H}_2\text{O}}$ in Mars atmosphere can cause the continuation of Am dehydration, thus to form LH-1w.

In mid-low obliquity period like current Mars, the MH-1w (precipitated from hydrothermal aqueous solution), LH-1w and 4w (formed from the dehydration of 7w/11w) would be stable/metastable over most of Mars. The 11w could occur and be stable near the Polar Regions where it might co-exist with water ice.

Rehydration -- In high obliquity period on Mars, water ice would form at low altitude regions. The coexisting water ice (100%RH) will stimulate the rehydration of 1w and 4w. Because the low obliquity period can last for millions of years, the rehydration can progress steadily even at extremely low rates to form 7w (LT-7w). The 7w would gradually convert to 11w.

During the diurnal cycle – During a diurnal cycle on Mars, the high RH(s) that can induce the rehydration of 1w, 4w, Am would last only a few hours in the early morning on Mars (i.e. 1-2 hrs at 100% RH and <4 hrs at $>10\%$ RH derived from T measurements at MER sites [5, 6, 7]). In addition, this period would be immediately followed by a >20 hrs dehydration period at RH of $\sim 0\%$. Therefore we believe that it is almost impossible for these rehydrations to occur and to proceed during a diurnal cycle on Mars.

Similarly, the probability of forming amorphous Mg-sulfates during a diurnal cycle is also extremely low, because of the very low rate of amorphization (from the 6w/7w phases) at this low temperature (210K-240K while RH drops from 10% to $\sim 0\%$). Note

the critical condition to form amorphous Mg-sulfates is to rapidly extract H_2O from 7w/6w causing structural collapse. This condition can not be satisfied if the reaction rate is too low. In addition, because of the low rate of 1w and 4w rehydration at low T, not much 7w can be formed during diurnal cycles, while Am can only be formed from 11w, 7w, or 6w, but not from 4w or 1w.

Conclusion: Our hypothesis developed based on a set of experiments referred to in this abstract indicates that 1w, 4w, and 11w should be the current stable/metastable Mg-sulfates on Mars.

Acknowledgement: This study was funded by a Mars Fundamental Research project (NNX07AQ34G).

References: [1] Wang et al (2006), *GCA*, 70, 6118-6135. [2] Wang et al. (2008), *JGR*, 114, JE003266. [3] Freeman et al (2009), *this volume*. [4] Wang et al (2007), *38th LPSC*, #1196. [5] Smith et al (2004), *Science*, 306, 1750-1752. [6] Spanovich et al (2006), *Icarus*, 180, 314-320. [7] Smith et al (2006), *JGR*, 111, E12S13. [8] Chipera et al. (2007), *GCA*, 71, 241-250.

Figure 2. Rehydration of Am to 4w or 6w or 7w

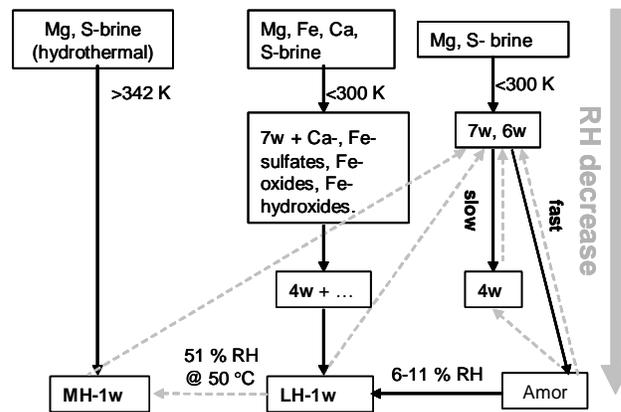
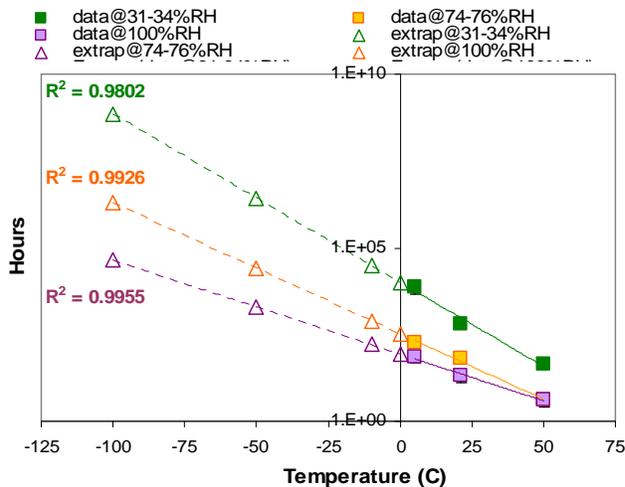


Figure 3. Pathways of forming martian Mg-sulfates