

**SUBSURFACE HYDROUS SALTS AND OBLIQUITY CYCLE ON MARS.** Alian Wang, Dept. of Earth & Planetary Sciences, McDonnell Center for the Space Sciences, Washington University in St. Louis ([alianw@levee.wustl.edu](mailto:alianw@levee.wustl.edu))

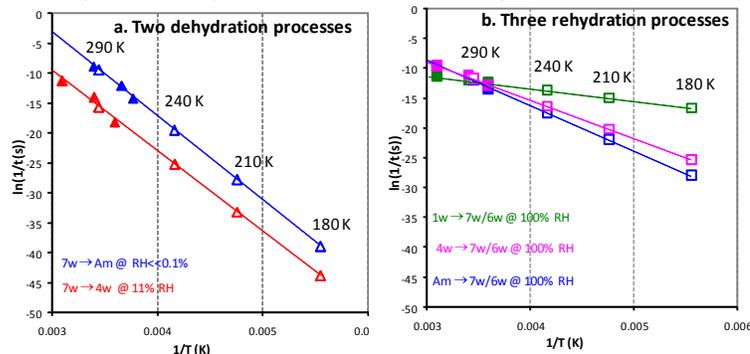
**Introduction:** We report a study that uses the reaction rates [1] derived from experimental data on the dehydration-rehydration processes of Mg-sulfates at low P, T conditions relevant to Mars, correlates with Mars obliquity cycles [2], and evaluates the preservation potential of highly hydrated sulfates in the subsurface of equatorial regions on Mars. These potentials are supported by mission observations and analog study in a hyperarid region on Earth (Tiber Plateau).

**T-RH conditions in salt-rich subsurface:** Subsurface hydrous sulfates were found at Gusev and Meridiani Planum by two MER Rovers [3,4]. A thermal model of the temperature profile for a two-layer regolith [5] suggests that a layer of ice-rich regolith of *high thermal inertia*, when covered by a layer of dry soil, would have low environmental  $T_{ave}$  and small  $\Delta T$ . For example, with a surface temperature swing from 150K to 240K,  $T_{ave}$  of ice-rich regolith at 0.5 meter depth can be in the range of 175 K to 185 K. Because hydrous sulfates (for which dehydration/rehydration follows *first order kinetics* [6]) have *even higher thermal stability* than H<sub>2</sub>O ice (for which sublimation/deposition follows *zero order kinetics*), this model can be extrapolated to salt-rich subsurface regolith. Under a known atmospheric  $P_{H_2O}$ , lower  $T_{ave}$  and smaller  $\Delta T$  would translate directly to a higher RH (relative humidity) and smaller  $\Delta RH$ .

**Stability field of hydrous sulfates at low T:** We conducted two sets of laboratory experiments [1, 7-11] to study the stability fields of hydrous Mg- and Fe<sup>3+</sup>-sulfates. They demonstrate (1) a tendency of enlarged stability field of highly hydrated sulfates towards low RH range at low T [1, 7, 8]; (2) hydrous Fe<sup>3+</sup>-sulfates have greater thermal stability than hydrous Mg-sulfates [9, 10, 11]; (3) Fe<sup>3+</sup>-sulfates, especially ferricopiapite, have the capability to adsorb large amount of H<sub>2</sub>O on grain surfaces, with a maximum of ~12.5 H<sub>2</sub>O/ ferricopiapite molecule at 5 °C [11]; (4) at low T, highly hydrated sulfates can maintain a high RH level in an enclosure, e.g., 96-97% RH by epsomite and 75-79% RH by ferricopiapite at -10 °C.

**$T_{env}$  effects on dehydration/rehydration rates:** The reaction rates (as functions of T) of five dehydration/rehydration processes for Mg-sulfates were derived from experimental data under 1 atm pressure and 50 °C, 21 °C, and 5 °C [1]. For Mars application, the  $\ln(1/t)$  vs.  $T$  correlations were extrapolated to a  $T_{env}$

Figure 1. T effect on the reaction rates of Mg-sulfates (solid symbol = exp. Data, unfilled symbols = extrapolations to Mars relevant T range).



range relevant to Mars surface and subsurface (Fig. 1). From the regression lines in Figure 1, the activation energy  $E_a$  and pre-exponential factor ( $A$ ) in the Arrhenius equation can be calculated for each of five dehydration/ rehydration processes. We found that *the dehydration rates have much strong T-dependences than the rehydration rates* (Fig. 1). This difference means that at low T, dehydration would slow down greatly, but rehydration (e.g., LH-1w  $\rightarrow$  7w) would maintain a moderate rate.

**$P_{env}$  effects on dehydration rates:** During the dehydration of a hydrous sulfate, environmental pressure ( $P_{env}$ ) affects the collision rate of released H<sub>2</sub>O with surrounding gas molecules. A high collision rate induced by high  $P_{env}$  would increase the probability of recondensing H<sub>2</sub>O into sulfate once they hit the grain surface. Thus the derived  $E_a$  of dehydration would be affected by  $P_{env}$  in an experiment.

For example, an ultra-high vacuum chamber ( $10^{-9}$  torr,  $1.33 \times 10^{-7}$  Pa) was used for epsomite dehydration by McCord et al. [6], from which an  $E_a$  of  $0.9 \pm 0.10$  eV and a  $\nu$  of  $3.2 \times 10^{14}$  s<sup>-1</sup> were obtained. Following *first order kinetics* to estimate the number density of H<sub>2</sub>O in epsomite,  $n(t) = n(0)e^{-\alpha t}$ , where  $\alpha = \nu e^{-E_a/kT}$ ,  $\nu$  is the *effective attempt frequency* that has typically the order of vibrational frequency of crystal lattice (s<sup>-1</sup>),  $k$  is Boltzmann's constant (eV/K). The half-life ( $t_{1/2}$ ) of dehydration is thus equal to  $0.693/\alpha$ . The calculated  $t_{1/2}$  at 294K is 57 seconds for epsomite dehydration under McCord's experimental condition.

In contrast, using the  $E_a$  value of 1.15 eV derived from our experiments ( $P=1$  atm,  $RH=11\%$  [1]), and a  $\nu$  of  $1.01 \times 10^{14}$  s<sup>-1</sup> determined from the frequency of the stretching-vibration mode of structural H<sub>2</sub>O in epsomite, the calculated  $t_{1/2}$  at 294K is 97.2 hr. The obvious difference in  $t_{1/2}$ (s) shows the effect of  $P_{env}$ . In order to derive a proper  $E_a$  for Mars relevant  $P_{env}$ , we con-

ducted a set of epsomite dehydrations under  $P < 1$  mbar and  $0.05 \text{ Pa} < P_{\text{H}_2\text{O}} < 0.34 \text{ Pa}$ , approaching the average atmospheric conditions in equatorial regions on Mars ( $P \sim 7$  mbar,  $P_{\text{H}_2\text{O}} \sim 0.04 - 0.15 \text{ Pa}$ , [12]). The measured  $t_{0.57}$  at 294K is 80 minutes. These experiments were conducted in three subsets: at 21 °C, 0 °C, and -8 °C. The data set at 21 °C was used to refine  $a$  *Ea* value of 1.049 eV. The data sets at 0 °C and -8 °C were used to validate this *Ea* value. Using the new P-corrected *Ea* and  $v$ , we can make rough estimations on the  $t_{1/2}$  (order of magnitude) of epsomite dehydration for the  $T$ (s) relevant to Mars salt-rich subsurface (predicted by [5]), e.g.,  $t_{1/2}$  at 190K, 185K, and 180K are about 1.4Myr, 8.0Myr, and 50Myr.

The  $t_{1/2}$  of rehydration at low  $T$  would be much shorter than those of dehydration, because the rehydration rates have very weak  $T$ -dependences (Fig. 1). For example, the dehydration rate at 180K is  $\sim 10^{-13}$  of that at 294K, while the LH-1w  $\rightarrow$  7w rehydration rate at 180K is only  $\sim 10^{-2}$  of that at 294K (Table 4 in [1]).

**Correlating  $t_{1/2}$  with obliquity cycle on Mars:** Mars is a dynamic system. Its obliquity changes quasi-periodically. Laskar et al [1] provided a precise solution for the evolution of Mars obliquity values over 10 to 20 Myr. They showed that Mars obliquity cycled between 35° to 15° in the period of now to 5 Myr ago, between 45° to 25° in the period of 5–21 Myr ago.

Ice sublimation and deposition at various regions on Mars are controlled by the obliquity cycles. Quantitative climate models predict that when obliquity exceeds 30°, water ice is stable in the near surface down to lower mid-altitude [13]. When obliquity exceeds 45°, the water ice persists at equator [14].

The rehydration/dehydration of hydrous sulfates at the equatorial regions on Mars would follow the same cycle, with lower rates (*first order kinetics*) than water ice deposition/sublimation. The slow dehydration of epsomite at low  $T$  (180-190K) implies that when the period of low obliquity is comparable with the  $t_{1/2}$ , considerable amounts highly hydrated Mg-sulfates would be kept in subsurface before the start of next high obliquity period. Conversely, during a high obliquity period, the less  $T$ -dependent moderate rehydration rate would induce full rehydrations of Mg-sulfates.

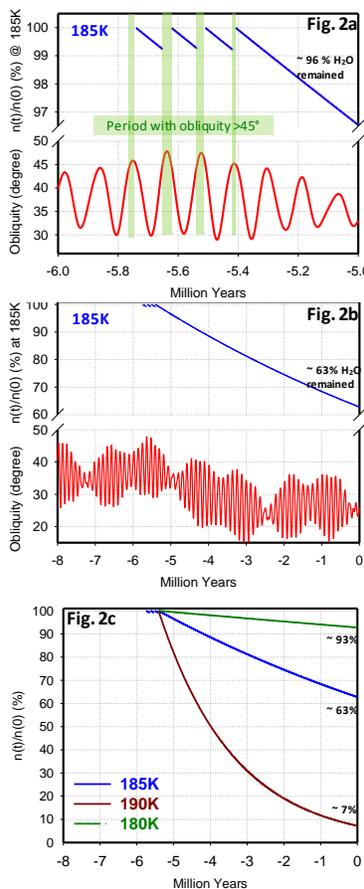


Figure 2 shows a schematic relationship between the cycles of obliquity (red line) and the dehydration/rehydration (other colors) of subsurface Mg-sulfates *in equatorial regions on Mars*. As indicated by climate model [14], water ice would persist at equator during the periods with obliquity  $>45^\circ$  (colored in green) between 5 and 6 Myr ago. The Mg-sulfates co-existing with the ice would reach full rehydration (to epsomite 7w or meridianiite 11w) with a moderate rehydration rate [1]. When obliquity is  $<45^\circ$ , the subsurface Mg-sulfates (7w or 11w) in equatorial region would dehydrate (blue line) at a very low dehydration rate. With a  $T_{\text{env}} \sim 185\text{K}$ ,  $\sim 96\%$  structural  $\text{H}_2\text{O}$  would remain at 5 Myr (Fig.2a). Between 5 Mys ago and the present, the obliquity was never beyond  $45^\circ$ , thus the equatorial subsurface Mg-sulfates would continue their dehydrations (Fig. 2b). Depending on the actual  $T_{\text{env}}$  (a function of altitude, buryal depth, and the amount of buried salts and ice), the remaining (until today) structural water in subsurface Mg-sulfates ( $T_{\text{env}}=180\text{-}190\text{K}$ ) would vary from 93-7% (Fig. 2c).

**Conclusion:** The potential preservation of highly hydrated sulfates in the subsurface of equatorial regions on Mars does exist. This potential is supported by the mission observations [9, 15] and by a terrestrial analog study [16].

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**References:** [1] Wang et al., (2011a), *JGR*, doi:10.1029/2011JE003818. [2] Laskar et al. (2004) *Icarus*, doi:10.1016/j.icarus.2004.04.005. [3] Haskin et al., (2005) *Nature*, v436, p66. [4] Klingelhofer et al. (2005), *Science*, v306, p1740. [5] Mellon et al. (2004), *Icarus*, v169, p324. [6] McCord et al (2001) *JGR*, V106, p3311. [7] Wang et al., (2006) *GCA*, v70, p6118. [8] Wang et al. (2009) *JGR*, doi:10.1029/2008JE003266. [9] Ling & Wang (2010) *Icarus*, doi:10.1016/j.icarus.2010.05.009. [10] Wang & Ling (2011b) *JGR*, doi:10.1029/2010JE003665. [11] Wang et al., (2012), submitted to *Icarus*. [12] Smith (2002) *JGR*, doi:10.1029/2001JE001522. [13] Mellon and Jakosky (1995) *JGR*, V100, p11781. [14] Richardson and Wilson, (2002) *JGR*, V107, doi:10.1029/2001JE001536. [15] Maurice et al (2011) *JGR*, doi:10.1029/2011JE003810. [16] Wang & Zheng (2009) *40<sup>th</sup> LPSC*, abs#1858.