

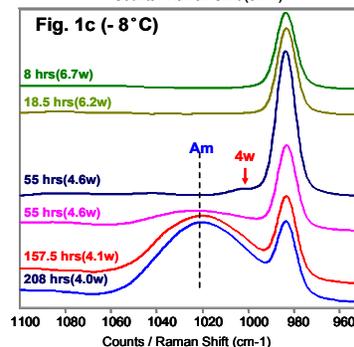
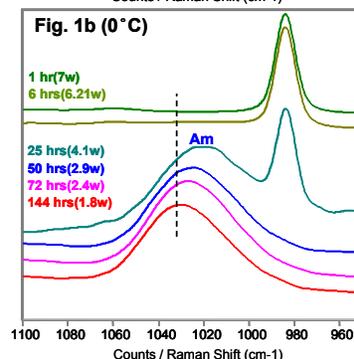
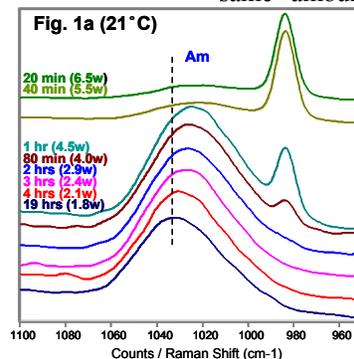
FORMATION RATE OF AMORPHOUS MAGNESIUM SULFATES AT LOW TEMPERATURES APPROACHING THE CURRENT SURFACE CONDITIONS ON MARS. Alian Wang, John J. Freeman, Bradley L. Jolliff, Department of Earth & Planetary Sciences and the McDonnell Center for the Space Sciences, Washington University, St. Louis, MO, 63130 (alianw@levee.wustl.edu)

Amorphous Mg-sulfates: The existence of hydrous Mg-sulfates in martian surface materials has been implied by all landed missions on Mars to date [1-7], and has been identified by orbital remote sensing (OMEGA and CRISM) [8-10]. Well-controlled laboratory experiments on hydrous sulfates [11-19] provide the fundamental underpinning to link the surface and orbital observations, as well as to address possible reasons for observational discrepancies (e.g., water contents). Among various Mg-sulfates, the existence of amorphous Mg-sulfate on Mars has been postulated since it can be readily formed in the laboratory from rapid dehydration of epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) or hexahydrate ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$) [13,15,18], and it has been demonstrated to be stable under very dry conditions (5-10% RH) [19]. Thus, amorphous Mg-sulfate has been proposed to be one of the major forms of Mg-sulfate existing over broad regions of Mars' surface [13,17]. We have previously reported on the formation of amorphous Mg-sulfate within 2 hrs at room temperature ($21 \pm 1^\circ\text{C}$) by fast, vacuum dehydration of epsomite. We also showed that the hydration state of amorphous Mg-sulfate (i.e., number of water molecules per formula unit of MgSO_4 , WMPFU) can be determined by the position of the ν_1 Raman peak near 1030 cm^{-1} (despite its non-crystalline nature) [15,18]. We report here new results on the formation rates of amorphous Mg-sulfate at low temperatures.

Low T experiments at current surface water-vapor pressure: Epsomite used in our experiments as a starting-phase was prepared at 21°C over a saturated aqueous NaCl solution ($\sim 75\%$ RH), and was verified by multiple Raman measurements. The fast dehydration of epsomite was done by placing a number of open sample vials containing pre-weighed amounts of epsomite into a vacuum desiccator. The temperature of the desiccator was maintained at either $0^\circ\text{C} \pm 0.5^\circ\text{C}$ using a water-ice bath, or $-8^\circ\text{C} \pm 3^\circ$ using a saturated aqueous KCl solution bath cooled by a water-ice bath

and dry ice. The maximum vacuum attained in the desiccator was measured as 60 millitorr. With a 22–36% RH range in our laboratory, the approximate water vapor pressures inside the desiccator during the period of our experiments were estimated to be within the range of annual water vapor pressures at equatorial regions on Mars, e.g., 0.04–0.15 Pa at the Opportunity site [20]. Sample vials were removed from the vacuum desiccator at scheduled times, sealed immediately, weighed, and analyzed *in situ* using the laser Raman spectrometer.

Time for total amorphization at low T: A key result of these experiments is that at low temperatures approaching the current Mars surface temperature range, the time required for total amorphization of the same amount of epsomite increases tremendously.



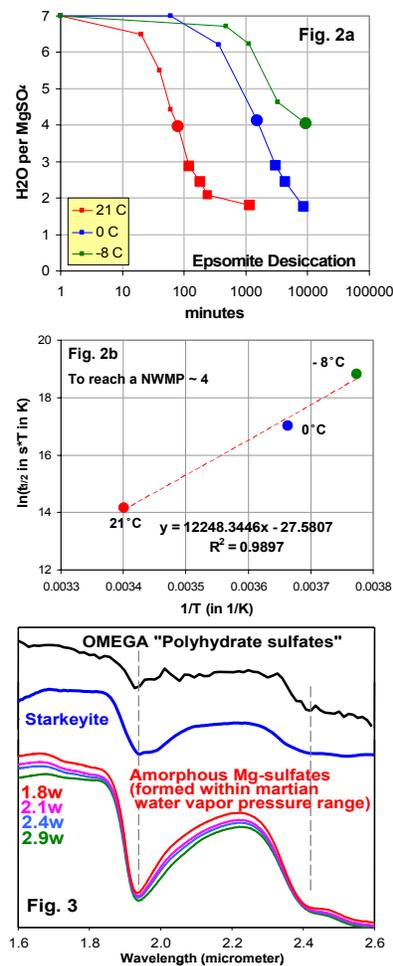
Raman spectra in Fig. 1a show that at 21°C , a $\sim 50\text{ mg}$ epsomite sample totally converts into amorphous Mg-sulfate in 2 hrs (light blue spectrum). The same amount of epsomite takes 50 hrs (Fig. 1b, light blue spectrum) for total amorphization at 0°C . At -8°C , total amorphization was not reached after 208 hrs (Fig. 1c, light blue spectrum).

Maximum water content of amorphous Mg-sulfates: Our experiments indicate an upper limit for the WMPFU that an amorphous structure can hold. At both 21°C and 0°C , total amorphization (light blue spectra in Fig. 1 and large square symbols in Fig. 2a) occurred only after a WMPFU value ~ 3 was attained. These observations are in agreement with experimental results at 50°C during the process of *re-hydration* of amorphous Mg-sulfate in eight different relative humidity buffers, where the *in situ* Raman and weight-gain measurements indicated the persistence of amorphous structure until a WMPFU value ~ 3.1 . Thereafter, crystalline starkeyite and epsomite began to appear from amorphous Mg-sulfate with a WMPFU value > 3.3 .

Formation rate of amorphous Mg-sulfate at low T: Figure 2a shows the

results of weight-loss measurements on three sets of vacuum dehydration experiments. Although the absolute rate of amorphization would relate to specific experimental setting, the relative rates appear to be inversely correlated with the experimental temperature. Since epsomite can readily lose one water molecule to become hexahydrate (even by slight grinding), the conversion of hexahydrate (WMPFU=6) to amorphous Mg-sulfate (with a WMPFU \sim 2 in our experiments) would be the rate limiting step during the amorphization process. We can use the time needed to reach a WMPFU value \sim 4 as the approximate half life ($t_{1/2}$) of the process, which is represented by the three large circular symbols in Fig. 2a. A combination of the first-order rate equation with the Arrhenius equation shows that the temperature dependence of $t_{1/2}$ can be expressed by $\ln[t_{1/2} * T] = [G^*/R][1/T] - \ln[0.693k_B/h]$, where R , k_B and h are the universal gas, Boltzmann's, and Planck's constants, respectively, and G^* is the activation free energy for the process. By putting our experimental data into a $\ln[t_{1/2} * T]$ vs. $(1/T)$ plot (Fig. 2b), it appears that a linear regression line can fit the experimental data with a $R \approx 0.995$ ($R = 0.988$ is significant at the 90% level for three points). This fit suggests that the amorphization process matches a first-order forward reaction whose rate can be estimated by $k(T) = \ln 2 / t_{1/2}(T)$, thus the reaction rate k at 21 °C is 18.6 times $k(0^\circ\text{C})$, and 118 times $k(-8^\circ\text{C})$, and the activation free energy can be estimated using the slope of regression line in Fig. 2b.

Extrapolating the regression line in Fig. 2b to lower and higher temperatures suggests that >50 days at -20°C and >3530 days at -40°C would be needed to reach a WMPFU \approx 4, but only 2 minutes at 50°C . The observed surface temperature ranges at Meridiani are 280–210 K in the aphelion season and 290–215 K in the perihelion season [21]. During a daily diurnal cycle, the most rapid RH decrease (from 100% to 10%) that would cause amorphization occurs from dawn to early morning when the temperature range is centered around 235 K (-40°C) or 253 K (-20°C) for the two seasons. In an environment similar to our experimental setting, the amorphization half life would be on the



order of *two months to ten years* in these temperature ranges.

Formation of starkeyite at low T: During the -8°C experiments, a weak Raman peak at 1000 cm^{-1} belonging to the ν_1 mode of starkeyite ($\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$) was observed (dark blue spectrum in Fig. 1c) without evidence of amorphous Mg-sulfate, in the intermediate dehydration products taken out of vacuum at 18.5 hrs and 55 hrs. After a few days of storage at 21°C , the Raman peak of amorphous Mg-sulfate, not starkeyite, was observed from the same samples. The appearance of starkeyite in low-T vacuum dehydration experiments is not unexpected because we find starkeyite to be the *common* end product of *slow* dehydration from epsomite at 5°C , 21°C , and 50°C [22]. When the rate of dehydration drops further at $T \ll -8^\circ\text{C}$, it could be starkeyite, not amorphous Mg-sulfate, that is the end product of near vacuum dehydration of epsomite.

NIR reflectance spectra of amorphous Mg-sulfates: We acquired the NIR diffuse reflectance spectra of amorphous Mg-sulfates with varying amounts of MWPFU (Fig. 3). The de-

gree of hydration of amorphous Mg-sulfate does not affect the general shape or the position of $1.9\text{ }\mu\text{m}$ spectral band, but does affect the band width. Figure 3 also compares spectra of amorphous Mg-sulfates with the spectrum of starkeyite and the typical OMEGA spectrum assigned to “polyhydrated sulfates”. The similarity in spectral patterns suggests that both starkeyite and amorphous Mg-sulfate are good candidates for the “polyhydrated sulfate” assigned by OMEGA team.

Acknowledgement: We thank Prof. R. Arvidson for providing the OMEGA spectrum. This work is supported by NASA funding NAG5-12114, NAG5-12684, and for the MER Athena Science team.

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