

CONVERSION OF CRYSTALLINE $\text{MgSO}_4\cdot\text{XH}_2\text{O}$ TO THE HYDRATED AMORPHOUS PHASE – A RAMAN, NIR, AND XRD STUDY. Alian Wang, John F. Freeman, Bradley L. Jolliff, and Raymond E. Arvidson, Department of Earth & Planetary Sciences and McDonnell Center for Space Sciences, Washington University, St. Louis, MO 63130 (alianw@levee.wustl.edu)

Introduction: Recent orbital and landed missions, OMEGA on Mar Express and two Mars Exploration rovers [1-5] have found Mg-sulfates on Mars. In order to further advance our knowledge on the hydrologic history of Mars and to evaluate its potential for hosting life, *in situ* identification of hydration states of magnesium sulfates, as well as the Ca-, Fe-, hydrated sulfates, will be crucial for future landing missions.

Because of the large daily temperature variation at the surface of Mars [$>100\text{K}$] and the full-scale swing in relative humidity (RH) of $\sim 0\%$ to $\sim 100\%$ occurring during these temperature excursions, it is anticipated that the hydration state and degree of crystallinity of Mg-sulfates may change during the Martian diurnal cycle [2]. During the rapid dehydration processes, a magnesium sulfate with high degree of hydration such as hexahydrite and epsomite may transform into less hydrated, amorphous phases. Because the re-hydration of these amorphous phases may be extremely sluggish at the cold night temperatures of Mars when the RH is higher, it has been suggested that non-crystalline magnesium sulfates holding more water than kieserite would be the most commonly seen sulfate phase on the surface of Mars [6].

In addition to the Raman study of eight hydrated crystalline magnesium sulfates that we report elsewhere [7], we report here our use of Raman, XRD, and reflectance NIR spectroscopy to study the conversion of crystalline, hydrated magnesium sulfates into an amorphous, hydrated phase. We also compare the NIR spectra of this amorphous, hydrated phase with NIR spectra obtained by the OMEGA instrument on Mars Express – data that were obtained from the dark etched terrain at Meridiani Planum where the Opportunity rover landed.

Experiments and results: Amorphous, hydrated magnesium sulfate was prepared from finely powdered, crystalline epsomite and hexahydrite. The samples were placed in a vacuum desiccator and evacuated to ~ 650 millitorr at $21^\circ\text{C} \pm 1^\circ\text{C}$ for 14 days. The weight-loss measurements showed that 5

moles of water were lost per mol epsomite and 4 moles of water were lost per mole of hexahydrite. The XRD powder pattern of crystalline epsomite shown in Fig 1a is converted to the amorphous phase (Fig. 1b) where all crystalline diffraction lines associated with the orthorhombic structure of epsomite have disappeared. The powder diffraction now shows only a broad featureless hump at a 2θ angle centered at $\sim 29^\circ$. Although this dehydration product has a featureless XRD pattern, the Raman spectrum of this material (Fig. 1c) contains a prominent, broad water band centered at 3460 cm^{-1} and a shoulder at $\sim 3290\text{ cm}^{-1}$. Furthermore the $\text{SO}_4\text{ v}_1$ fundamental band lies at $\sim 1030\text{ cm}^{-1}$ (Fig. 2a), having a much broader peak width than any crystalline hydrated or anhydrous Mg-sulfate (Fig. 2a) [7].

Unlike XRD, the translational symmetry in the structure is not a necessary condition to produce Raman and infrared spectral peaks. Gases, liquids, and glasses all have characteristic vibrational spectra. Nevertheless, disordered solids such as glasses, polymers, and disordered crystalline lattices, arising during rapid changes in chemical composition or shocks due to sudden changes in pressure and/or temperature, will have broadened peak width. The crystalline and amorphous forms of a chemically identical species can generally be distinguished. A disordering of the lattice of epsomite or hexahydrite due to rapid vacuum dehydration would be reflected in a broadening of the Raman bands of the product such as was observed in this study. The broadened Raman bands in the XRD-amorphous, hydrated magnesium sulfate that we have produced are thus indicative of a highly disordered, non-crystalline hydrated magnesium sulfate.

The presence of a water band in the Raman spectrum of this amorphous phase (Fig. 1c) plus the position of its fundamental $\text{SO}_4\text{ v}_1$ band at $\sim 1030\text{ cm}^{-1}$ (Fig. 2b) -- lying between the 1047 cm^{-1} band crystalline kieserite ($\text{MgSO}_4\cdot\text{H}_2\text{O}$) and the 1000 cm^{-1} band of crystalline starkeyite ($\text{MgSO}_4\cdot 4\text{H}_2\text{O}$) -- supports the weight-loss evidence which shows only two moles of water in this amorphous magnesium sulfate phase.

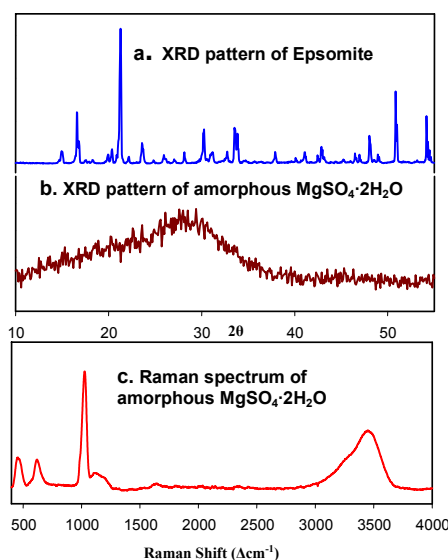


Figure 1. Characterization of amorphous $\text{MgSO}_4\cdot 2\text{H}_2\text{O}$

The loss in crystallinity of epsomite under evacuation at RT happens very quickly (Fig. 2b) – starting within the first 30 minutes and an up shift of the $\text{SO}_4 \nu_1$ was observed during the progress of dehydration.

We also observed the similar conversion of hexahydrate, at RT and vacuum dehydration, resulting in a similar less hydrated amorphous phase. When kieserite and starkeyite were put under the same rapid dehydration conditions, however, no weight loss was observed nor did any changes occur in the Raman spectra of the crystalline phases.

In the crystal structures of kieserite and starkeyite, the water molecules are more tightly coordinated with Mg cations whose octahedral coordination spheres are closely links with SO_4 groups, which make them very stable towards vacuum dehydration at RT. The crystal structures of hexahydrate and epsomite salts are, however, more loosely packed, evidenced by the larger volume per formula and ~ 79 to 88 % less dense than starkeyite. The water molecules in epsomite and hexahydrate are associated with the magnesium coordination sphere and only linked to the sulfate tetrahedra by hydrogen bonding. Additionally in epsomite, the 7th water molecule is not linked to any of the polyhedra. The rapid loss of water molecules from these two higher hydrates would thus cause the collapsing of the crystal framework resulting in the observed amorphous phases.

Implications for Martian Magnesium Hydrates: In a separate study of phase transformations among the hydrated Mg sulfates [7], we found no evidence of any rehydration of the kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) at 30%

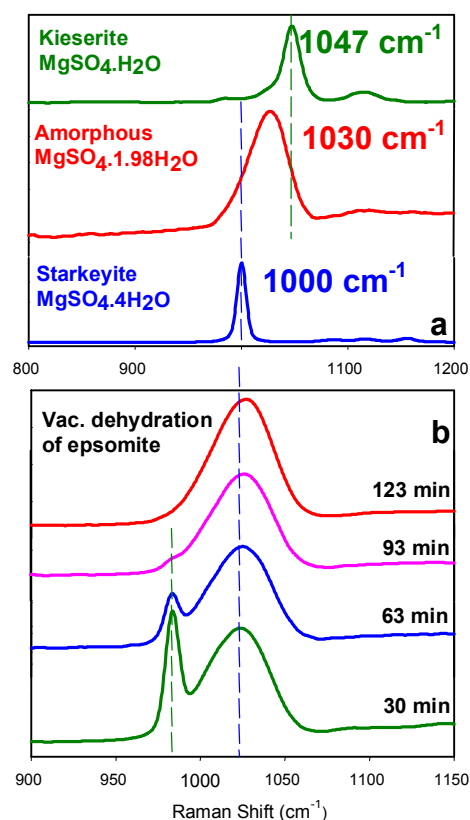


Figure 2. The Raman ν_1 band of amorphous and crystalline $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$

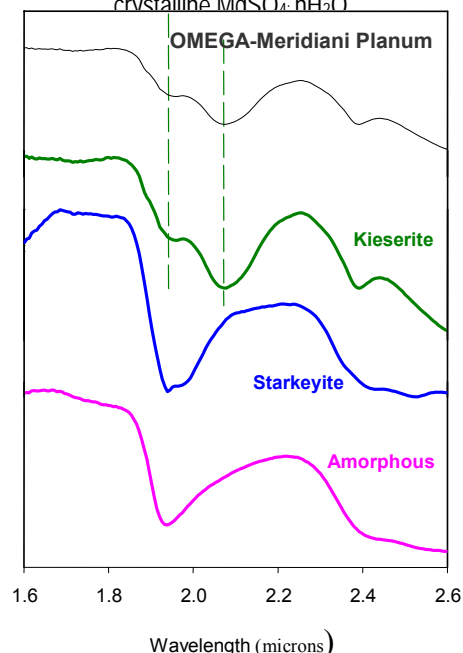


Figure 3. Comparison of OMEGA and laboratory NIR spectra

RH and 50°C within the first 24 hours. We found no evidence of re-crystallization of amorphous Mg-sulfates at ~ 30% RH and RT within a few days. It would thus appear unlikely that rehydration and re-crystallization of the amorphous Mg-sulfates would progress to a detectable level during a 2-3 hours period of high RH at extremely cold temperatures (<200K) in the martian night [8]. The %RH drops very quickly as the warming of the martian day starts. Based on our experiments, starkeyite and kieserite (if they existed) would survive the 10-12 hours extra dry condition of the martian daytime, while epsomite and hexahydrate would quickly convert to hydrous amorphous Mg-sulfates.

Figure 3 presents the NIR diffuse reflectance spectrum of amorphous $\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$ compared with the NIR spectra of kieserite, starkeyite, and an OMEGA spectrum from the dark etched terrain at Meridiani Planum where the Opportunity rover landed. The OMEGA spectrum shows a better match with kieserite than with the amorphous Mg-sulfate dihydrate produced in this study.

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References: [1] Bibring et al. (2005), *Science*, p1576. [2] Arvidson et al. (2005), *Science*, p1591. [3] Gendrin et al. (2005) *Science*, p 1587. [4] Gellert et al. (2004), *Science*, p829. [5] Rieder et al. (2004), *Science*, p1746. [6] Vaniman et al. (2004), *Nature*, p663. [7] Wang et al., *this issue* [8] Smith et al. (2004), *Science*, p1750.