STUDY OF TWO STRUCTURAL POLYMORPHS OF MgSO4·H2O BY RAMAN, IR, XRD, AND HUMIDITY BUFFER EXPERIMENTS – IMPLICATION FOR MARTIAN KIESERITE. Alian Wang, John J. Freeman, Raymond Arvidson, Department of Earth & Planetary Sciences and the McDonnell Center for the Space Sciences, Washington University, St. Louis, MO, 63130 (alianw@levee.wustl.edu)

Mystery of martian kieserite: Kieserite ($MgSO_4 \cdot H_2O$) was identified on Mars based on NIR reflectance spectra obtained by OMEGA instrument on the Mars Express and CRISM instrument on the MRO [1, 2, 3]. Nevertheless, the pathway of forming kieserite on Mars is quite perplexing. Laboratory experiments [4, 5, 6, 7] have demonstrated that if epsomite ($MgSO_4 \cdot 7H_2O$) or hexahydrite ($MgSO_4 \cdot 6H_2O$) precipitated from SO_4-rich aqueous solutions were the origin of martian kieserite, then under current (& past) Mars surface temperatures, martian kieserite _was not formed by direct dehydration_ of these two phases. Our experiments show that at $T \leq 50°C$ [4,5], the dehydration products of epsomite or hexahydrite is starkeyite ($MgSO_4 \cdot 4H_2O$), which is stable within -10°C to 50°C range and 5% -51% RH (RH range varies with T). In addition, amorphous Mg-sulfates (holding up to 3 structural waters) can be formed by fast dehydrations of epsomite or hexahydrite [8].

Pathways for forming kieserite at T≤ 50°C: Our experiments [5] indicated that kieserite can be formed from epsomite or hexahydrite through two pathways: (1) through an intermediate stage -- amorphous Mg-sulfates; (2) by dehydrating a mixture of epsomite with anhydrite ($CaSO_4$). Furthermore, on-going experiments in our laboratory suggest that when epsomite was mixed with ferrous and ferric sulfates ($FeSO_4 \cdot 7H_2O$, $Fe_2(SO_4)_3 \cdot 7H_2O$, and $Fe_2(SO_4)_3 \cdot 5H_2O$), kieserite can also be produced by low T dehydration of epsomite.

It appears that the anhydrous calcium- and hydrous iron-sulfates provided a mini-scale local environment surrounding epsomite grains. This local environment has overridden the effect of large scale environmental conditions (provided by humidity buffers in laboratory experiments, or by atmospheric and surface conditions .on Mars), and has facilitated the dehydration process at low T (e.g. dehydration of starkeyite) that is otherwise barred by the activation energy.

Structural polymorphs of MgSO4·H2O seen by Raman, XRD and IR: The mystery of martian kieserite is further complicated by two structural polymorphs of $MgSO_4 \cdot H_2O$ (as LH-monohydrate and HH-monohydrate in figures, named after their formation pathways, where LH stands for Low Humidity and HH stands for High Humidity), which have distinct XRD, Raman, and IR spectra,; and have different formation pathways and stability fields. These two polymorphs are the

topic of this study. Both polymorphs were produced from the same pure reagent monohydrate magnesium sulfate. A set of baking experiments (and possible TGA) is going-on, to obtain the exact $H_2O/MgSO_4$ ratios.
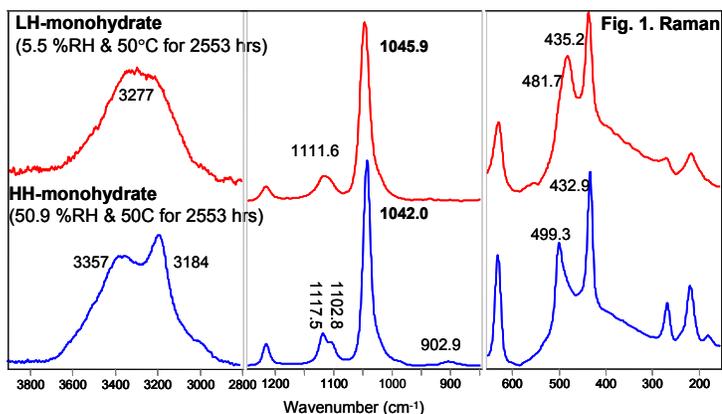
Figure 1 shows the Raman spectra of two polymorphs. The major spectral differences are (1) the positions of strongest Raman peak, ν_1 of SO_4 tetrahedron (symmetric stretching vibration), at 1046 or 1042 cm^{-1}; (2) the peak shapes of structural water in 3400-3000 cm^{-1} spectral region (singlet or doublet); (3) the positions of other peaks with mid to low intensities.
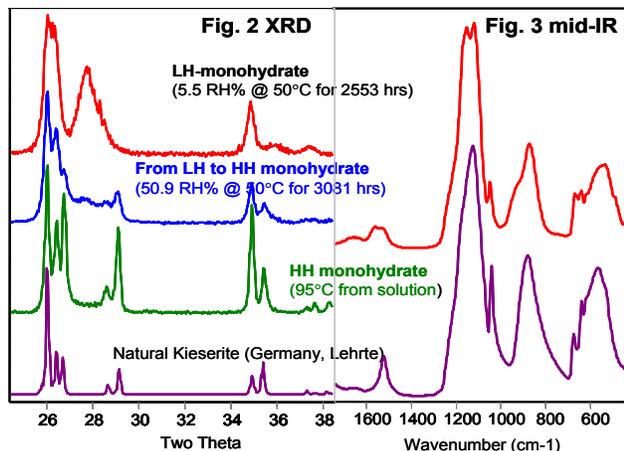
Figure 2 shows the XRD patterns of two polymorphs. They are also compared with a natural kieserite from Lehrte, Germany [9], whose XRD pattern is a perfect match to the standard kieserite in XRD database and also to the calculated XRD pattern based on structural refinement [10]. The XRD pattern of HH-monohydrate basically matches with terrestrial natural kieserite. In addition, the XRD pattern of LH-monohydrate does not match with the standard $MgSO_4 \cdot 1.25H_2O$.

Figure 3 shows the mid-IR spectra (ATR) of two polymorphs. The differences in spectral patterns and peak positions are obvious, especially the strongest ν_3 peak of SO_4 tetrahedron (asymmetric stretching vibration). The weaker but sharp ν_1 peak positions are consistent with Raman observations.

Formation pathways and stability fields of two polymorphs: Chipera et al (2007, [7]) have noticed that a reagent monohydrate Mg-sulfate has a different XRD pattern from the standard kieserite in XRD PDF database. In their humidity buffer experiments (using XRD for phase identification), this monohydrate partially converted to standard kieserite at mid RH levels (37 -53 %, vary with T), and was totally converted at higher RH levels (43 – 74%, vary with T).

In our humidity buffer experiments (using Raman

Fig. 1. Raman

LH-monohydrate (5.5 %RH & 50°C for 2553 hrs)

HH-monohydrate (50.9 %RH & 50C for 2553 hrs)

3277

3357 3184

1111.6

1045.9

1102.8
1117.5

1042.0

902.9

435.2

481.7

432.9

499.3

Wavenumber (cm^{-1})

Fig. 2 XRD   **Fig. 3 mid-IR**

LH-monohydrate
(5.5 RH% @ 50°C for 2553 hrs)

From LH to HH monohydrate
(50.9 RH% @ 50°C for 3081 hrs)

HH monohydrate
(95°C from solution)

Natural Kieserite (Germany, Lehrte)

Two Theta   Wavenumber (cm-1)

spectra for phase identification), we found that (1) LH-monohydrate partially converted to HH-monohydrate in 30-45 %RH at 21°C and 50°C, and almost totally converted at 50.9 %RH and 50°C; (2) from a saturated solution of Mg-sulfates at 95°C, the precipitated crystals have a structure of HH-monohydrate (Fig.2); (3) from the dehydration of epsomite when it was originally mixed with anhydrite or Fe-sulfates, or when it was first converted to amorphous Mg-sulfates then dehydrated further, the final dehydration product is always LH-monohydrate.

These observations mean: (1) HH-monohydrate (i.e. natural-kieserite-like phase) only forms at mid to high relative humidity: either directly crystallized from aqueous solution at high temperature (hydrothermal process); or slowly converted from LH-monohydrate at mid-high relative humidities. Some terrestrial natural kieserite may have formed in this way, and the conversion can benefit from a higher temperature. The HH-monohydrate was never observed as the final dehydration product of Mg-sulfates of higher hydration degrees (epsomite, hexahydrite, or starkeyite) [4, 5, 7]. (2) On the other hand, LH-monohydrate is observed as the end phase of dehydration process of Mg-sulfates with higher degrees of hydration, i.e. epsomite, hexahydrite, and amorphous Mg-sulfate, and especially at relatively lower temperatures (T ≤50°C). both polymorphs are stable at low relative humidity [5, 7].

Implication to Martian kieserite: based on the formation pathways and the stability fields of two polymorphs revealed by our experiments, we hypothesize that the structure of martian kieserite would be that of LH-monohydrate if they were originated from low humidity dehydration of epsomite, hexahydrite, and meridianite ($MgSO_4 \cdot 11H_2O$) that were originally precipitated from SO_4-rich aqueous solutions.

In some special locations, where martian kieserite was formed directly from a hydrothermal process with local temperatures > 69°C, it would have the structure of HH-monohydrate (i.e. terrestrial natural-kieserite-like phase).

To verify this hypothesis, we compare (Fig. 4) an OMEGA "kieserite" NIR spectrum with the diffuse reflectance NIR spectra of LH- and HH-monohydrates synthesized in our laboratory. The HH-monohydrate has slightly red shifted 1.9 and 2.4 µm bands compared with LH-monohydrate, and a flattened top of its 2.1 µm band that may relate to the double shape of water band in fundamental vibration region (Fig. 1a, Raman spectra). The central positions of 2.1 µm bands of two polymorphs are almost the same.

The OMEGA "kieserite" spectrum shows a better match at 1.9 and 2.4 µm bands with the spectrum of LH-monohydrate, suggesting it to be the dehydration product of $MgSO_4 \cdot xH_2O$ that was precipitated from aqueous solution. However, the 2.1 µm band of this particular OMEGA spectrum appears flat on top, which could be real or false, considering that the effect of spectral calibration and correction on the detail band positions and band shapes of OMEGA and CRISM spectra should be thoroughly investigated. Figure 4 also includes a diffuse reflectance NIR spectrum of $FeSO_4 \cdot H_2O$. It does not match this particular OMEGA "kieserite" spectrum.

Conclusion: The formation pathways and stability fields of two structural polymorphs of $MgSO_4 \cdot H_2O$ and their spectral features provide the important clues to gain understanding on the origin of martian kieserite. Further detailed study of the spectra from OMEGA and CRISM, with full knowledge on the effect of spectral calibrations and corrections, are needed, in order to apply our experimental results to mission data interpretation.

References : [1]. Arvidson et al. (2005) *Science 307,* 1591-1593. [2] Gendrin et al. (2005), *Science 307,* 1587-1591. [3] Murchie et al. (2007), *7th International Conference on Mars,* abs #3238. [4] Wang *et al.* (2006), *Geochem. Cosmochem. Acta* (2006). [5] Wang et al. (2007), *38th LPSC,* abs #1298. [6] Vaniman et al. (2006), *Am. Minerals.* V91, 1628-1642. [7] Chipera et al. (2007), *Geochem. Cosmochem. Acta,* 241-250. [8] Wang et al., *38th LPSC,* abs #1195. [9] Papike et al. (2008), *this volume.* [10] Hawthorne, et al. (1987), *Neues Jahnbuch for Mineralogie, Monatshefte,* **157,** 121-132.

Fig. 4. NIR

LH-monohydrate

OMEGA_Kieserite

HH-monohydrate

$FeSO_4.H_2O$

Wavelength (µm)