Mystery of martian kieserite: Kieserite (MgSO₄·H₂O) 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 (MgSO₄·7H₂O) or hexahydrite (MgSO₄·6H₂O) precipitated from SO₄-rich aqueous solutions were the origin of martian kieserite, then under current (and past) Mars surface temperatures, martian kieserite was not formed by direct dehydration of these two phases. Our experiments show that at T ≤ 50°C [4,5], the dehydration products of epsomite or hexahydrite are starkeyite (MgSO₄·4H₂O), 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 (CaSO₄). Furthermore, on-going experiments in our laboratory suggest that when epsomite was mixed with ferrous and ferric sulfates (FeSO₄·7H₂O, Fe₂(SO₄)₃·7H₂O, and Fe₂(SO₄)₃·5H₂O), 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 MgSO₄·H₂O (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 H₂O/MgSO₄ ratios.

Figure 1 shows the Raman spectra of two polymorphs. The major spectral differences are (1) the positions of strongest Raman peak, ν₁ of SO₄ 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 MgSO₄·1.25H₂O.

Figure 3 shows the mid-IR spectra (ATR) of two polymorphs. The differences in spectral patterns and peak positions are obvious, especially the strongest ν₃ peak of SO₄ tetrahedron (asymmetric stretching vibration). The weaker but sharp ν₁ 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

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>LH-monohydrate</th>
<th>HH-monohydrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>3277</td>
<td>3357</td>
<td>1111.0</td>
</tr>
<tr>
<td>1045.9</td>
<td>1042.8</td>
<td>432.9</td>
</tr>
<tr>
<td>435.2</td>
<td>496.3</td>
<td>481.7</td>
</tr>
<tr>
<td>902.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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precipitated from SO$_4$-rich aqueous solutions. (MgSO$_4$·11H$_2$O) that were originally pre-
somite, hexahydrite, and meridianite from low humidity dehydration of ep-
LH-monohydrate if they were originated 
ture of martian kieserite would be that of  
experiments, we hypothesize that the struc-
t fields of two polymorphs revealed by our  
morphs are stable at low relative humidity  
relatively lower temperatures (T $\leq$ 50°C). The  
end phase of dehydration process of Mg-sulfates  
was first converted to amorphous Mg-sulfates then  
finally mixed with anhydrite or Fe-sulfates, or when it  
from the dehydration of epsomite when it was origi-
tals have a structure of HH-monohydrate (Fig.2); (3)  
be 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 natu-
r al 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 de-
hydration product of Mg-sulfates of higher hydration 
degrees (epsmite, 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, hexa-
hydrite, and amorphous Mg-sulfate, and especially at  
relatively lower temperatures (T $\leq$50°C). both poly-
morphs 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  
epsmite, hexahydrite, and meridianite (MgSO$_4$·11H$_2$O) 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 lo-
cal 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 $\mu$m bands com-
pared with LH-monohydrate, and a flattened top of its  
2.1 $\mu$m 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 $\mu$m bands  
of two polymorphs are almost the same.  
The OMEGA “kieserite” spectrum shows a better  
match at 1.9 and 2.4 $\mu$m bands with the spectrum of  
LH-monohydrate, suggesting it to be the dehydration  
product of MgSO$_4$·xH$_2$O that was precipitated from  
aqueous solution. However, the 2.1 $\mu$m 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$_4$·H$_2$O. It does not match this particular OMEGA  
“kieserite” spectrum.

**Conclusion:** The formation pathways and stability  
fields of two structural polymorphs of MgSO$_4$·H$_2$O and their spectral features  
provide the important clues to gain understanding on the origin of martian kieser-

e. 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 interpre-

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