

ORIGIN OF MARTIAN KIESERIT. K. Connor and Alian Wang, Dept of Earth and Planetary Sciences and McDonnell Center for the Space Sciences, Washington University in St. Louis, St. Louis, MO, 63130, USA (alianw@levee.wustl.edu).

Kieserite on Mars: Kieserite is one of the two (another is polyhydrated sulfate) most commonly seen and widely spread hydrous sulfates observed at the surface of Mars, identified by orbital remote sensing, using vis-NIR spectroscopic technique (OMEGA and CRISM instruments on ESA's Mars Express and NASA's MRO missions). Due to its distinct reflectance double band in 1.95 & 2.07 μm , kieserite was definitively identified, especially on its hydration degree, as monohydrate $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ [1]. However, there are two very different schools of thoughts on the origin of these martian kieserite, especially when interpreting the *interbedded layers of kieserite and polyhydrated sulfate*, observed at several locations on Mars [2, 3].

a. Kieserite from dehydration: laboratory experimental investigation on the thermodynamic properties of hydrous Mg-sulfates have the following findings:

- 1) Kieserite can *only* directly precipitate at $T \geq 69^\circ\text{C}$ from $\text{Mg-SO}_4\text{-H}_2\text{O}$ solution [4, 5];
- 2) Kieserite *cannot* be formed from direct dehydration of pure Mg-sulfates, epsomite and hexahydrite, at $T \leq 50^\circ\text{C}$ [6, 7, 8]
- 3) However, kieserite *can* be formed by dehydrations at $T \leq 50^\circ\text{C}$ through two pathways: (a) from epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) mixed with hydrous Ca-, Fe-sulfates, and Fe-oxides and Fe-hydroxides, (b) from amorphous Mg-sulfates, e.g., $\text{MgSO}_4 \cdot 2\text{-}3\text{H}_2\text{O}$ [8];

The current understanding of Mars' historical surface temperature is generally $< 50^\circ\text{C}$ except within very localized hydrothermal zones. Therefore above experimental findings suggest that the most observed martian kieserite should be the dehydration products from epsomite (or hexahydrite depending on the T of precipitation) which was precipitated *together* with (Ca, Fe)-sulfates and Fe-oxides/hydroxides.

b. Kieserite directly precipitated from brines at $T < 50^\circ\text{C}$: Another school of thought [9] based on geochemical modeling suggests when Mg-sulfates precipitate from a brine with high ionic strength, other salts, especially chlorides and chloride-sulfate (kainite $\text{KClMgSO}_4 \cdot 3\text{H}_2\text{O}$, carnallite $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$, bischofite $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) would also precipitate. *The low H_2O activity* environment provided by those salts would facilitate the precipitation of kieserite, at temperature below 69°C . This concept of low-T kieserite precipitation has been used to interpret the observed *interbedded kieserite-polyhydrated sulfates* on Mars [3].

Experimental evaluation: we conducted two sets of precipitation experiments at temperature $T=21^\circ\text{C}$ and 5°C to evaluate the second model-derived concept.

Brine samples: We made five mixtures of epsomite $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and bischofite $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, with molar ratios of 1:9, 3:7, 5:5, 7:3, and 9:1. These mixtures are dissolved in small amounts of Millipore H_2O to build brines in Mg- SO_4 -Cl- H_2O system, with extremely high ionic strength. Thus they are very good simulations for over-saturated brines right before the happening of salt precipitation on Mars.

Evaporation and precipitation: Two open Petri Dishes were used for each brine, containing small quantities of brines that barely cover the bottom. One set of five brines was maintained at the counter-top of a laboratory ($21 \pm 1^\circ\text{C}$, variable RH). Another set was maintained in a refrigerator ($5 \pm 1^\circ\text{C}$, variable RH). In addition, we placed the two Petri Dishes that contain the brine of bischofite:epsomite=9:1 (Cl: SO_3 =18:1), the highest Cl-concentration, into an abnormally low RH environment in a sealed desiccator buffered by saturated LiCl- H_2O solution (RH=11.3% at 21°C and at 5°C) (Fig.1). These experiments lasted for nearly three months.



Figure 1. Experiment – a brine started from a 1:9 mixture of epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) was maintained at 21°C and 11%RH.

In situ Measurements:

Continuous Laser Raman Spectroscopic (LRS) measurements were made directly on the precipitated crystalline materials from the second day after the experiments started, until the full solidifications of all brine samples were reached. Figure 2 shows the standard LRS spectra of bischofite and Mg-sulfates with hydration degree from zero to 11 H_2O per MgSO_4 molecule. These Mg-sulfates and bischofite all have finger-print LRS spectra, which facilitate the definitive identification of them (chemistry & hydration degrees) in mixtures.

The LRS measurement was made by directly targeting a focused 532 nm laser beam (~ 9 mW) onto a salt grain. Each spectrum was recorded in 10 second. Previous experimental study [6] have demonstrated that no change in the hydration degree of Mg-sulfates would happen in such short measurement time. For the early products of evaporations, 10 spots per sample were checked by LRS each time. For final products,

automatic and manual LRS scan via 100 spots per sample were made.

No kieserite observed in low-T precipitations: Table 1 shows the hydration degrees of final Mg-sulfates from all ten samples.

Our experiments simulate the precipitation of Mg-sulfates from oversaturated Mg-SO₄-Cl-H₂O brine at Mars relevant low temperatures (21°C and 5°C). The extremely low water activities in these experiments were controlled by (a) a salt-brine system with saturated Mg-SO₄-Cl-H₂O solution and co-precipitated bischofite MgCl₂·6H₂O salt, as suggested by geochemical modeling [9]; (b) an atmospheric environment buffered by LiCl-H₂O saturated solution (11% RH at 21°C, xx% RH at 5°C, [10]). *Yet, kieserite was not observed in any of these experiments.*

Furthermore, we have observed in all these experiments, bischofite precipitated in much late stage (solubility of MgSO₄ at 25°C is 36 g/100gH₂O, MgCl₂ is 56 g/100gH₂O, [11]). It means during Mg-sulfates precipitation, the local RH was controlled by MgCl₂-H₂O saturated solution, which has been experimentally determined to be 33% RH at 21°C and 33.6%RH at 5°C [10].

Origin of martian kieserite: *we have not found experimental evidence for the direct precipitation of kieserite at T<50°C from the brines with very high Cl-concentration as geochemical model suggested.* Although we cannot exclude kieserite formation from brines with even higher Cl-concentration (e.g., Cl:SO₃ ~ 100:1, 1000:1, 10000:1), giving the huge amount of kieserite found at Mars surface by orbital remote sensing and the almost constant Cl:SO₃ ratio (~1:10) found in Mars' rocks and soils by landed missions, it seems that direct precipitation at low-T is highly unlikely to be the origin of martian kieserite. Our previous and current experimental investigations support the low-T dehydration of epsomite or hexahydrite (and of starkeyite when co-existing with Ca, Fe-sulfates) to be

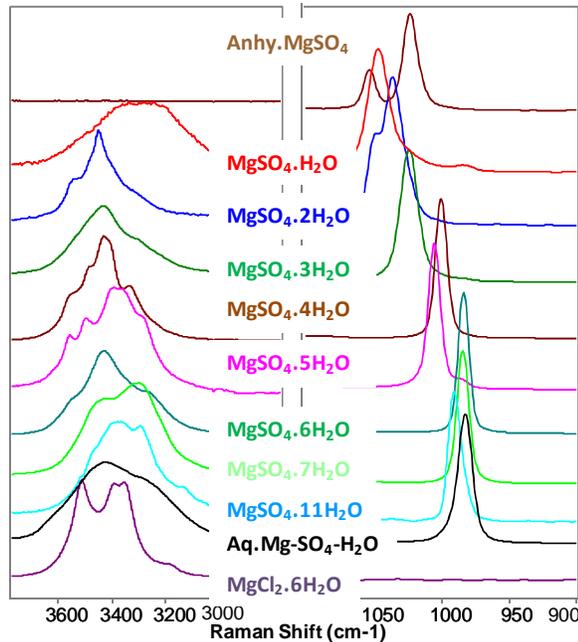


Figure 2. Standard LRS spectra of bischofite and Mg-sulfates with hydration degree from zero to 11 H₂O per MgSO₄ molecule. Phase ID in this study is definitive.

the origin of martian kieserite.

We believe the formation of *interbedded layers of kieserite and polyhydrated sulfate should be induced by the episodic changes of brine chemistry*, which would generate two types of precipitates: (1) almost pure epsomite (or hexahydrite depending on T), and (2) epsomite mixed with other sulfates and chlorides. When dehydration started in later time at T < 50°C, the one from almost pure epsomite would stop after forming starkeyite MgSO₄·4H₂O [6,

7], that would be seen by orbital remote sensing as *polyhydrated sulfates*; while the dehydration of epsomite mixtures (with other sulfates and chloride) proceeded further to generate *kieserite*, as identified by orbital remote sensing.

Giving the difference in dehydration rates of starkeyite and rozenite FeSO₄·4H₂O, experimentally determined by another set of experiments [12], we anticipate the *polyhydrated sulfates to be mainly starkeyite*.

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Table 1. LRS identified hydration degree of Mg-sulfates in precipitations from brines of epsomite-bischofite-H₂O

T	21°C					5°C				
	RH	<50%				RH	<50%			
Epsom: Bisch	1:9	3:7	5:5	7:3	9:1	1:9	3:7	5:5	7:3	9:1
hydration degree	5w, 6w _{base}	5w, 6w	5w	4w, 6w	4w, 5w, 6w	5w, 6w	6w, 5w	6w	7w	7w