

**NATURE, FORMATION, AND CLIMATIC MEANING OF INTERBEDDED SULFATE STRATIGRAPHY ON MARS.** 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).

**Interbedded sulfate stratigraphy** was observed at many locations on Mars [1, 2, Fig. 1]. The two types of hydrous sulfates occurred in these layers are: *kieserite* (*K-layer*)  $MgSO_4 \cdot H_2O$  that was identified based on its distinct double band at 1.95 & 2.07  $\mu m$  in reflectance Near-IR spectra [3]; and *polyhydrated sulfates* (*P-layer*) whose nature remained largely unknown [4].

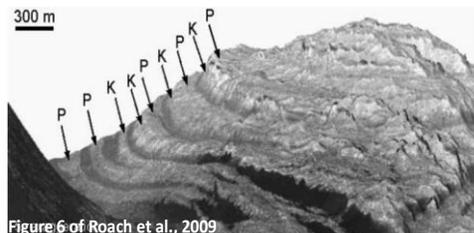


Figure 1. interbedded sulfates stratigraphy on Mars

We report a new understanding on the natures of two hydrous sulfates observed in interbedded stratigraphy and their formation processes, based on the thermodynamic and kinetic properties of hydrous sulfates revealed by laboratory experiments through NASA Mars Fundamental Research Program (MFRP) [5-8], and a terrestrial field observation of hydrous salts [9, 10]. Laser Raman spectroscopy (LRS) was the major analytic tool to determine the molecular forms and the hydration degrees in these investigations.

**Nature of observed polyhydrated sulfates:** Direct spectra comparison would exclude hydrous  $Fe^{3+}$ , Ca-, Al-sulfates from the candidates to contribute the spectral features of *polyhydrated sulfates*. Furthermore, highly hydrated Mg- and  $Fe^{2+}$ -sulfates, e.g.,  $MgSO_4 \cdot xH_2O$  ( $x=11, 7, 6$ ) and  $FeSO_4 \cdot xH_2O$  ( $x=7, 6$ ) are excluded because: (1) OMEGA or CRISM instruments sense the species in top layer ( $\sim mm$  thick) of Martian materials which is in equilibrium for long period with the current Mars atmosphere (extremely low  $P_{H_2O}$ ); (2) stability fields of highly hydrated Mg/Fe-sulfates [5-7] suggest they would immediately dehydrate (in hours or days) in current Mars atmosphere. Remain candidates for *polyhydrated sulfates*, starkeyite  $MgSO_4 \cdot 4H_2O$  and rozenite  $FeSO_4 \cdot 4H_2O$ , are intermediate dehydration products from highly hydrated sulfates. However, *how can they retain mid-level hydration degree on hyper-arid Mars? What is the climatic significance?*

In an early set of experiments on Mg-sulfates ( $T=50\text{ }^\circ\text{C}, 21\text{ }^\circ\text{C}, 5\text{ }^\circ\text{C}, -10\text{ }^\circ\text{C}$ , relative humidity  $RH=6-100\%$ ) [5-7], we have demonstrated that the dehydration of a pure  $MgSO_4 \cdot xH_2O$  ( $x=11, 7, 6$ , meridianite, epsomite, hexahydrate) at temperature  $\leq 50\text{ }^\circ\text{C}$  would

“stop” at the stage of starkeyite  $MgSO_4 \cdot 4H_2O$ , no further dehydration to kieserite ( $MgSO_4 \cdot H_2O$ ) would progress. We recently, finished a new set of similar experiments on  $Fe^{2+}$ -sulfates ( $T=50\text{ }^\circ\text{C}, 21\text{ }^\circ\text{C}, 5\text{ }^\circ\text{C}, RH=6-100\%$ ), it revealed that, opposite to Mg-sulfates, the dehydration of  $FeSO_4 \cdot 7H_2O$  at  $T \leq 50\text{ }^\circ\text{C}$  did not stop at rozenite  $FeSO_4 \cdot 4H_2O$  stage, further dehydration towards szomolnokite  $FeSO_4 \cdot H_2O$  was accomplished [11].

We found that a sub-structural unit in starkeyite, a four-member ring made of two  $SO_4$  tetrahedra and two  $MgO_2(H_2O)_4$  octahedra by sharing corner oxygen, would help maintaining the structural meta-stability against dehydration at low  $T$ , because additional activation energy would be needed to break-off the ring in order to form kieserite  $MgSO_4 \cdot H_2O$  [5, 6]. We also found that the stability of these intermediate dehydration phases is heavily influenced by the size of octahedra, i.e., the electrostatic force employed by metal cation in a smaller  $M(H_2O)_6$  ( $M=Mg, Fe, Al$ ) octahedron would hold its coordinating  $H_2O$  tighter, thus more resistant to dehydration [10]. Although similar four-member-rings exist in the structure of rozenite, it has a slightly longer S-O bond length (average 1.489  $\text{\AA}$ ) and larger  $FeO_2(H_2O)_4$  (average Fe-O/ $H_2O$  length 2.120  $\text{\AA}$ ) than in starkeyite (1.472  $\text{\AA}$  and 2.074  $\text{\AA}$ ) which explain the observed less stable rozenite.

Based on these new comparison on dehydration pathways of Mg-sulfates and  $Fe^{2+}$ -sulfates, we now conclude that *Starkeyite*  $MgSO_4 \cdot 4H_2O$  is the most possible candidate for *polyhydrated sulfates*.

**Origin of observed Martian kieserite:** at  $T \geq 69\text{ }^\circ\text{C}$ , kieserite would precipitate directly from  $MgSO_4$ -rich brine [12], which can happen during hydrothermal events on Mars but cannot explain the large quantity of kieserite on Mars with such wide spreading. A pathway to form the majority of observed kieserite at relatively low temperature (a general understanding was  $T_{\text{surface}} < 50\text{ }^\circ\text{C}$  in Mars history) needs to be found. There have been two schools of thoughts: #1, kieserite is the dehydration product from  $MgSO_4 \cdot xH_2O$  ( $x=11-2$ ) through specific pathways (experiments, 5-8] at  $T < 69\text{ }^\circ\text{C}$ ; #2, kieserite can precipitate directly from Cl-enriched Mg-SO<sub>4</sub>-brine at  $T < 69\text{ }^\circ\text{C}$  (modeling, 13, 14).

To evaluate the model-driven concept #2, we conducted a set of evaporation-precipitation experiments of Cl-enriched brines. Brine samples of Mg-SO<sub>4</sub>-Cl system, with molar ratios of  $SO_4:Cl_2$  of 9:1, 7:3, 5:5, 3:7, and 1:9 (note almost constant  $SO_3:Cl$  ratio of 10:1

was found in Mars' surface materials by many landed missions), were put into open Petri Dishes and maintained at  $T = 21 \pm 1^\circ\text{C}$  and  $T = 5 \pm 1^\circ\text{C}$  for evaporation. The RH levels for most samples were maintained at 33% ( $\text{MgCl}_2\text{-H}_2\text{O}$  buffer), but were 11% ( $\text{LiCl-H}_2\text{O}$ ) and 6% ( $\text{LiBr-H}_2\text{O}$ ) for the brine sample with the highest Cl-content ( $\text{SO}_4:\text{Cl}_2 = 1:9$ ). During the whole evaporation processes of ten brine samples, continuous LRS measurements were made directly on the precipitated crystalline materials from Day-2 until the full solidifications of all brine samples were reached, and then continuous LRS monitoring on dry crystals until Day-124 of experiments.

The LRS spectra taken until the full solidification of brine samples indicate, in addition to  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , only  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  were precipitated directly from all brine samples. I.e., no directly precipitated kieserite was observed from these Cl-enriched Mg- $\text{SO}_4$  brines. The LRS spectra taken until Day-124 indicate the appearance of  $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$  (without  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ), apparently generated by dehydration of epsomite & hexahydrate, based on previous study [5-7]. Furthermore, no kieserite was observed from the precipitates of a natural brine of K-Na-Ca-Mg- $\text{SO}_4$ -Cl system.

These experiments support that the dehydration from  $\text{MgSO}_4 \cdot x\text{H}_2\text{O}$  ( $x=11, 7, 6$ ) is the origin for the majority of martian kieserite. The model-driven concept #2 maybe based on thermodynamics, but is not supported by kinetics. Furthermore, this conclusion was validated by the observed hydration degrees of Mg-sulfates from DLT saline playa in a hyper-arid region on Earth (Qaidam basin, Tibet) [9,10].

**Meta-stability of the four-member-ring units in starkeyite** is the key thermodynamic and kinetic property responsible for the formation of interbedded sulfate stratigraphy. Firstly, this meta-stability in a relatively low temperature range ( $T_{\text{surface}} < 50^\circ\text{C}$  over Mars history) is the reason for "polyhydrated" sulfates to retain their mid-level hydration degree in hyper-arid environment (Mars surface) for extremely long period (billions years). Secondly, we found that in specific chemical environments that do exist on Mars, this meta-stability can be broken by catalysis effect thus further dehydration towards kieserite have been accomplished. Our experiments [7, 10] demonstrated when  $\text{MgSO}_4 \cdot x\text{H}_2\text{O}$  ( $x=11, 7, 6$ ) precipitated together with other sulfates (Ca- and  $\text{Fe}^{2+}$ -sulfates) and chlorides (NaCl, KCl) from a chemical complex brine, the co-existences of these sulfates (and  $\text{Fe}^{3+}$ -sulfates,  $\text{Fe}_2\text{O}_3$ , and  $\text{FeOOH}$  as possible alteration products from  $\text{Fe}^{2+}$ -sulfates) and chlorides have functioned as catalysis that helped the breaking of meta-stability of starkeyite  $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$  and facilitated the formation of kieserite

at  $T \leq 50^\circ\text{C}$ . Knowing chemical complex K-Na-Mg-Fe-Ca- $\text{SO}_4$ -Cl brines can be generated from chemical weathering of various basaltic rocks on Mars, the probability of forming kieserite through this pathway on hyper-arid Mars at low T would be quite high.

**Formation of interbedded sulfates stratigraphy on Mars:** We believe that the interbedded Kieserite-Starkeyite (K-S) layers are formed from episodic brines with differences in chemistry at  $T < 50^\circ\text{C}$ . Shown in Figure 2, the dehydration of Mg-sulfates precipitated from a complex Mg-Ca-Fe- $\text{SO}_4$ -Cl brine would develop to the stage of kieserite thus to form K-layer (red arrows in Fig. 2); the dehydration of Mg-sulfates precipitated from a relatively pure Mg- $\text{SO}_4$  brine would stop at the stage of starkeyite thus to form S-layer (blue arrows in Fig. 2). Depending on the actual sequences and their locations on Mars, a K- and S-layer pair can be the result of *two different brines came at different episodes*; it can also be the result of *two dehydration processes of Mg-sulfates precipitated from single Mg-Ca-Fe- $\text{SO}_4$ -Cl brine*. In later case, since  $\text{CaSO}_4$  and  $\text{FeSO}_4$  have lower solubility (0.205 and 29.5 g/100g $\text{H}_2\text{O}$  at  $25^\circ\text{C}$ ) than  $\text{MgSO}_4$  (35.7 g/100g $\text{H}_2\text{O}$ ), the early precipitated sulfates would deplete the Ca, Fe cation from the brine and leave it as relatively pure in Mg- $\text{SO}_4$ . Therefore, the early precipitated Mg-sulfates co-existing with other catalysis species would dehydrate to kieserite and form K-layer; the later precipitated Mg-sulfates from later stage brine would dehydrate to starkeyite and form S-layer.

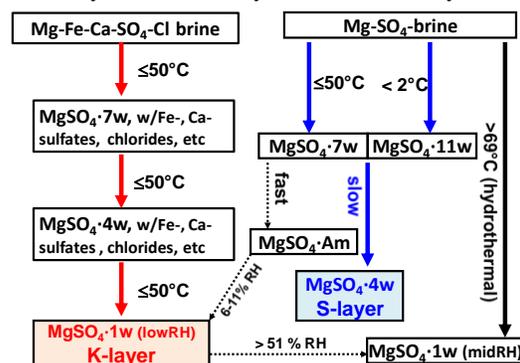


Figure 2. Pathways of Mg-sulfates dehydration under different environmental and chemical conditions relevant to Mars.

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