

**STABILITY OF MAGNESIUM SULFATE MINERALS IN MARTIAN ENVIRONMENTS.** G.M. Marion<sup>1</sup> and J.S. Kargel<sup>2</sup>, <sup>1</sup>Desert Research Institute, 2215 Raggio Parkway, Reno, NV 89512, giles.marion@dri.edu, <sup>2</sup>U.S. Geological Survey, 2255 N. Gemini Dr., Flagstaff, AZ 86001, jkargel@usgs.gov.

**Introduction:** *Viking Lander*, *Pathfinder*, and *Mars Exploration Rover* missions to Mars have found abundant sulfur in surface soils and rocks, and the best indications are that magnesium sulfates are among the key hosts [1-6]. At Meridiani Planum, MgSO<sub>4</sub> salts constitute 15 to 40 wt.% of sedimentary rocks [3-5,7]. Additional S is hosted by gypsum and jarosite. Reflectance and thermal emission spectroscopy is consistent with the presence of kieserite (MgSO<sub>4</sub>•H<sub>2</sub>O) and epsomite (MgSO<sub>4</sub>•7H<sub>2</sub>O) [3]. Theoretically, the dodecahydrate (MgSO<sub>4</sub>•12H<sub>2</sub>O) should also have precipitated [8].

We first examine theoretically which MgSO<sub>4</sub> minerals should have precipitated on Mars, and then how dehydration might have altered these minerals.

**Methods and Materials:** FREZCHEM is an equilibrium chemical thermodynamic model parameterized for concentrated electrolyte solutions using the Pitzer equations [9] for temperatures from <-70 to 25°C, pressures from 1 to 1000 bars, and the system Na-K-Mg-Ca-Fe-H-Cl-SO<sub>4</sub>-NO<sub>3</sub>-OH-HCO<sub>3</sub>-CO<sub>3</sub>-CO<sub>2</sub>-CH<sub>4</sub>-H<sub>2</sub>O [8,10-15]. The model includes 58 solid phases including ice, 11 chloride minerals, 14 sulfate minerals, 15 carbonate minerals, five solid-phase acids, three nitrate minerals, six acid-salts, one iron oxide, and two gas hydrates.

FREZCHEM was used to establish equilibria with respect to composition and temperature among magnesium sulfate minerals [MgSO<sub>4</sub>•H<sub>2</sub>O (kieserite), MgSO<sub>4</sub>•6H<sub>2</sub>O (hexahydrate), MgSO<sub>4</sub>•7H<sub>2</sub>O (epsomite), and MgSO<sub>4</sub>•12H<sub>2</sub>O]. To determine the equilibrium partial pressure of water, P<sub>(g),H<sub>2</sub>O</sub>, for a reaction such as MgSO<sub>4</sub>•12H<sub>2</sub>O(cr) ⇌ MgSO<sub>4</sub>•7H<sub>2</sub>O(cr) + 5H<sub>2</sub>O(l), (1) we used the following equation:

$$P_{(g),H_2O} = \frac{1}{K_{H,H_2O}} \left[ \frac{K_{MgSO_4 \cdot 12H_2O}}{K_{MgSO_4 \cdot 7H_2O}} \right]^{0.2} \quad (2)$$

where K<sub>H,H<sub>2</sub>O</sub> is the Henry's law constant controlling water equilibrium between atmospheric and aqueous phases, and K<sub>MgSO<sub>4</sub>•12H<sub>2</sub>O</sub> and K<sub>MgSO<sub>4</sub>•7H<sub>2</sub>O</sub> are the solubility products for the specified solid phases. All three constants, and others needed for other equilibria, are quantified as functions of temperature in FREZCHEM.

**Results:** We first examine the stability of magnesium sulfate minerals in pure binary and ternary solutions; then we examine the stability of these hydrates exposed to a cold, dry Martian atmosphere. Figure 1 shows the stability of ice, epsomite, and MgSO<sub>4</sub>•12H<sub>2</sub>O between 25°C and the eutectic at

-3.6°C for a pure MgSO<sub>4</sub>-H<sub>2</sub>O system. In this system, the lower hydrates, hexahydrate and kieserite, only form at higher temperatures (48°C and 69°C, respectively).

The presence of other constituents in ternary (or higher) systems can lower the temperatures at which lower hydrates are stable. For example, hexahydrate is stable at 25°C in a MgSO<sub>4</sub>-MgCl<sub>2</sub>-H<sub>2</sub>O system at 3.8 m MgCl<sub>2</sub> [12]. This requires high chloride concentrations that may occur in Martian environments that have previously undergone extensive sulfate precipitation and chloride concentration due to extreme freezing or desiccating conditions [3-5].

Based on the Rover mission to Meridiani Planum, it is likely that the sedimentary rocks at this site formed from acidic brines [3-5, 16-17]. Figure 2 illustrates the stability of magnesium sulfate minerals in a liquid briny MgSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O system. At high H<sub>2</sub>SO<sub>4</sub> concentrations (> 4 m), both kieserite and hexahydrate are stable, but only over the narrow temperature range from 18 to 25°C. It is still the case that epsomite and MgSO<sub>4</sub>•12H<sub>2</sub>O are thermodynamically the most stable minerals over the greatest temperature range (Fig. 2) and particularly at the cold temperatures most relevant to the Martian surface. Epsomite is dominant at high temperatures and high acidities; MgSO<sub>4</sub>•12H<sub>2</sub>O is dominant at low temperatures and low acidities. Note that ice is never stable in the presence of epsomite in this acidic system (Fig. 2), which is also the case in the pure MgSO<sub>4</sub>-H<sub>2</sub>O system (Fig. 1).

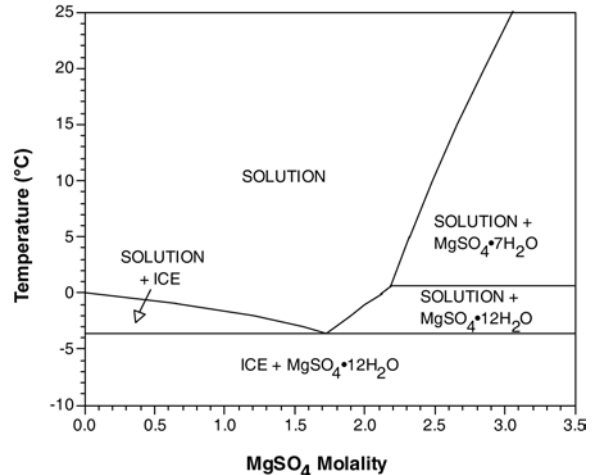
Using Eqn. 2 (or appropriate analogues), we calculated stability lines for ice, MgSO<sub>4</sub>•12H<sub>2</sub>O-MgSO<sub>4</sub>•7H<sub>2</sub>O, and MgSO<sub>4</sub>•7H<sub>2</sub>O-MgSO<sub>4</sub>•H<sub>2</sub>O at temperatures from 0 to -50°C (Fig. 3). This temperature range covers the majority of the summertime diurnal range at low latitudes on Mars, and the colder end of this range is approximately the annual mean temperature at the warmest areas on the planet, such as parts of Meridiani Planum. An average Martian atmospheric P<sub>(g),H<sub>2</sub>O</sub> line is included in Fig. 3 for reference. In the current cold, dry atmosphere of Mars, ice, MgSO<sub>4</sub>•12H<sub>2</sub>O, and epsomite are unstable at the warmer areas on the Martian surface, but kieserite is instead stable. Dehydration of higher hydrates probably accounts for the apparent presence of lower hydrates of magnesium sulfate hydrates in reflection/thermal emission spectroscopy [3] and the microporous structure and polygonal cracks of the laminated

sedimentary rocks imaged by *Opportunity* [16]. Note, however, that if ice is present for whatever reason (e.g., at depth in soil, protected by a duricrust, or at high latitudes), then both epsomite and  $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$  are thermodynamically stable. Zolotov and Shock [18] also concluded that the higher hydrates of  $\text{MgSO}_4$  are stable in the presence of ice for the much colder surface of Europa (-133 to  $-193^\circ\text{C}$ ).

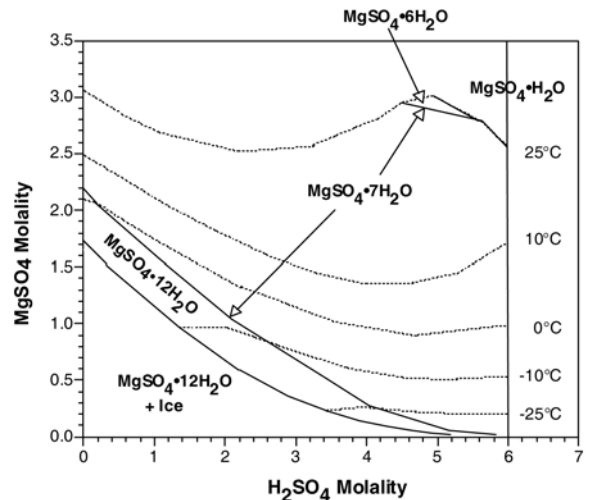
The presence of hydrated sulfates could account for  $\text{H}_2\text{O}$  buried at shallow levels on Mars [19]. The unusual softness of the sedimentary rocks at the Meridiani Planum [3-5] also can be explained by a high abundance of notably soft hydrated sulfate minerals. If epsomite (molar volume =  $146.71 \text{ cm}^3/\text{mol}$ , [15]) is dehydrated to kieserite (molar volume =  $56.60 \text{ cm}^3/\text{mol}$ ), then there would be a 61.4% loss of volume. If epsomite initially constitutes 25% of the rock mass [3-5,7], then there would be a rock volume loss of 15.4%, which could contribute to rock softness and development of tensile stresses that may drive polygon formation.

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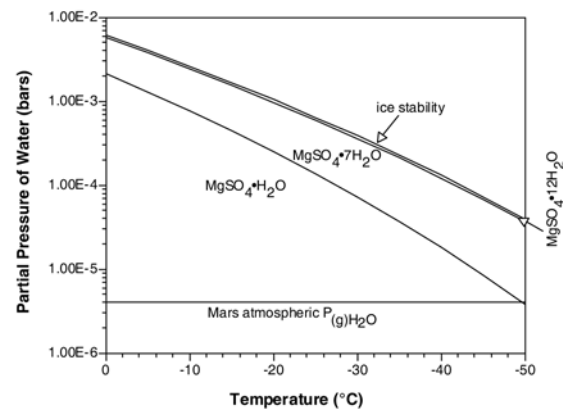
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**Figure 1.** Stability diagram for a pure  $\text{MgSO}_4\text{-H}_2\text{O}$  system over the temperature range from  $25^\circ\text{C}$  to the eutectic at  $-3.6^\circ\text{C}$ .



**Figure 2.** The stability of  $\text{MgSO}_4$  minerals in  $\text{MgSO}_4\text{-H}_2\text{SO}_4$  systems between  $-25$  and  $25^\circ\text{C}$ . Solid lines are equilibrium lines; dashed lines are temperature lines.



**Figure 3.** The stability of ice and  $\text{MgSO}_4$  hydrates in a Martian environment.