



Modeling calcium sulfate chemistries with applications to Mars



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ABSTRACT

On Mars, evidence indicates widespread calcium sulfate minerals. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) seems to be the dominant calcium sulfate mineral in the north polar region of Mars. On the other hand, anhydrite (CaSO_4) and bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) appear to be more common in large sedimentary deposits in the lower latitudes. The tropics are generally warmer and drier, and at least locally show evidence of acidic environments in the past. FREZCHEM is a thermodynamic modeling tool used for assessment of equilibrium involving high salinity solutions and salts, designed especially for low temperatures below 298 K (with one version adapted for temperatures up to 373 K), and we have used it to investigate many Earth, Mars, and other planetary science problems. Gypsum and anhydrite were included in earlier versions of FREZCHEM and our model Mars applications, but bassanite (the CaSO_4 hemihydrate) has not previously been included. The objectives of this work are to (1) add bassanite to the FREZCHEM model, (2) examine the environments in which thermodynamic equilibrium precipitation of calcium sulfate minerals would be favored on Mars, and (3) use FREZCHEM to model situations where metastable equilibrium might be favored and promote the formation or persistence of one of these phases over the others in violation of an idealized equilibrium state.

We added a bassanite equation based on high temperatures (343–373 K). A Mars simulation was based on a previously published Na–Ca–Mg–Cl– SO_4 system over the temperature range of 273 to 373 K. With declining temperatures, the first solid phase under equilibrium precipitation is anhydrite at 373 K, then gypsum forms at 319 K (46 °C), and epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) at 277 K. This sequence could reflect, for example, the precipitation sequence in a saturated solution that is slowly cooled in a deep, warm aquifer.

Because FREZCHEM is based on thermodynamic equilibrium, a crude approach to problems involving metastable equilibria is available by removing phases that may have kinetically inhibited formation. Removing anhydrite allows bassanite to precipitate at 373 K, followed by gypsum at 351 K (78 °C), and epsomite at 277 K. Removing anhydrite and gypsum allows bassanite to form from 373 to 273 K. But bassanite formation from warm to cold temperatures does not seem appropriate for Mars and Earth.

An explanation for spatial patterns of gypsum, anhydrite, and bassanite on Mars and Earth could be past environmental differences. Anhydrite and bassanite are favored near Mars' equator with higher temperatures, along with drier, more saline, and more acidic environments. Gypsum would be favored at the lower temperatures in the Mars polar region with wetter, lower salinity, and less acidic environments. On Earth, Ca-sulfate would likely over time largely finish re-precipitating as the more insoluble gypsum. But Mars was not in long-term moderate climates compared to Earth that strongly influenced the dominance of gypsum on Earth. So while temperature and water/acid environments for CaSO_4 minerals on Mars may have been a major factor for these precipitations, the short-term moderate climates on Mars may also have influenced the prevalence of higher soluble CaSO_4 species in the lower Mars latitudes.

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1. Introduction

On Mars, there is abundant evidence for the presence of calcium sulfate minerals in sediments and soil (e.g., Clark et al., 2005; Langevin et al., 2005; McLennan et al., 2005; Catling et al., 2006; Vaniman and Chipera, 2006; Chou and Seal, 2007; Fishbaugh et al., 2007; Plaut et al., 2007; Combe et al., 2008; Harrison et al., 2008; Kereszturi et al., 2008; Kuzmin et al., 2008; Szyrkiewicz et al., 2008, 2010, 2013; Vaniman et al., 2008; Horgan et al., 2009; Massé et al., 2010, 2012; Wray et al., 2010; Wilson and Bish, 2011; Sefton-Nash et al., 2012; Sqyres et al., 2012; Van Driessche et al., 2012; Weitz et al., 2013, 2015). Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) seems to be the dominant calcium sulfate mineral in the north polar region of Mars (Langevin et al., 2005; Fishbaugh et al., 2007). Preliminary reports of sedimentary gypsum in equatorial layered deposits were refuted by subsequent analyses (Bishop et al., 2009; Wray et al., 2010). But more recent papers again suggest that gypsum is present in equatorial layered deposits (Sefton-Nash et al., 2012; Sqyres et al., 2012; Weitz et al., 2013, 2015). On the other hand, anhydrite (CaSO_4) and bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) are more common in the lower latitudes (Harrison et al., 2008; Wray et al., 2010; Van Driessche et al., 2012), which are warmer and drier, and show evidence of acidic environments in the past (McLennan et al., 2005; Ming et al., 2006). Anhydrite, bassanite and gypsum are also inferred to be present in calcium sulfate veins at the Curiosity Rover site (Nachon et al., 2014; Vaniman et al., 2014; Rapin et al., 2015). Sulfate is also present within drill tailings, not always obviously associated with discrete veins (Vaniman et al., 2014). The light toned veins in Gale have been identified as pure sulfate by ChemCam, Laser Induced Breakdown Spectroscopy (LIBS), and APXS analyses (McLennan et al., 2013; Nachon et al., 2014). ChemCam detected hydrated sulfates, e.g., at target named ‘Reddik Bight’ and ‘Denault’ in sols 316 and 317 (Anderson et al., 2015). Hydrated sulfates are found in light toned fracture fills, but anhydrite has been found locally (Nachon et al., 2014; Schröder et al., 2015). Recent work by Rapin et al. (2015) used H analyses by LIBS/ChemCam to show that the veins were predominantly bassanite, formed by dehydration of gypsum after the veins’ formation.

Some Martian meteorites contain anhydrite, bassanite, and/or gypsum. In some cases analysis has suggested that the hydrated calcium sulfate phases are secondary minerals formed on Mars (Ling and Wang, 2014), whereas in other cases analysis has shown that a likely explanation is secondary weathering on Earth (Greenwood et al., 2009). The common coexistence of two or three calcium sulfate phases along with other evaporitic minerals (such as halite) in the same parts of the same meteorites indicates that there was a dynamic environment (either changing conditions or gradual alteration sequences with sluggish kinetics) during secondary alteration (Bridges and Grady, 2000).

Calcium sulfate minerals are also of interest regarding Mars and extreme Earth analog environments for their ability to trap and preserve organic compounds (Aubrey et al., 2006). These phases can even host endolithic microbiological communities (Parnell et al., 2004).

The FREZCHEM (FC) model has included gypsum and anhydrite from an early version (FC-3, Marion and Farren, 1999) to the present (FC-17, Marion et al., 2015). However, none of these versions include bassanite. Almost all FREZCHEM models deal with low temperatures (173–298 K). The only exception is FC-14 (Marion et al., 2011) that deals with higher temperatures (273–373 K). Bassanite should tend to form at higher temperatures, as we will illustrate in Section 3. The objectives of this work are to (1) add bassanite to the FREZCHEM model (FC-14, 273–373 K), (2) examine the environments in which thermodynamic equilibrium precipitation of calcium sulfate minerals would be favored on Mars, and (3) use FREZCHEM to model situations where metastable equilibrium

might be favored and promote the formation or persistence of one of these phases over the others in violation of an idealized equilibrium state.

2. Methods and materials

2.1. FREZCHEM model

FREZCHEM is an equilibrium chemical thermodynamic model parameterized for concentrated electrolyte solutions (to ionic strengths = 20 molal) using the Pitzer approach (Pitzer, 1991, 1995) for the temperature range from 173 to 298 K (except version FC-14 or ‘CHEMCHAU’, which has temperature range from 273 to 373 K) and the pressure range from 1 to 1000 bar (Marion and Kargel, 2008; Marion et al., 2009a, 2009b, 2010a, 2010b, 2011, 2012, 2013, 2014, 2015). Earlier papers are summarized in Marion and Kargel, 2008; papers cited above beyond 2008 have progressive additions and applications of new chemistries. All FREZCHEM models are structured to deal with acidity, neutrality, and alkalinity, which are important for calcium sulfate minerals on Earth and Mars. The last published version of the model, which includes ethane and propane gas hydrates (Marion et al., 2015), is parameterized for the Na–K–NH₄–Mg–Ca–Fe(II)–Fe(III)–Al–H–Cl–ClO₄–Br–SO₄–SO₃–S₂–NO₃–OH–HCO₃–CO₃–CO₂–O₂–CH₄–NH₃–N₂–C₂H₆–C₃H₈–Si–H₂O system and includes 119 solid phases including ice, 16 chloride minerals, 37 sulfate minerals, 16 carbonate minerals, five solid-phase acids, four nitrate minerals, seven perchlorates, six acid-salts, six sulfites, 1 sulfide, five iron oxide/hydroxides, four aluminum hydroxides, two silica minerals, two ammonia hydrate minerals, five gas hydrates, and two bromide-bearing solid solutions (see above references for these model parameters, especially Marion and Kargel, 2008). In this paper, we re-examine calcium sulfate minerals on Mars, with the aforementioned addition of bassanite.

2.2. Pitzer approach

In the Pitzer approach, the activity coefficients (γ) as a function of temperature at 1.01 bar pressure for cations (M), anions (X), and neutral aqueous species (N), such as CO₂(aq) or CH₄(aq), are given by

$$\begin{aligned} \ln(\gamma_M) = & z_M^2 F + \sum m_a (2B_{Ma} + ZC_{Ma}) \\ & + \sum m_c \left(2\Phi_{Mc} + \sum m_a \Psi_{Mca} \right) \\ & + \sum \sum m_a m_{a'} \Psi_{Ma'a'} + z_M \sum \sum m_c m_c C_{ca} \\ & + 2 \sum m_n \lambda_{nM} + \sum \sum m_n m_a \zeta_{nMa} \end{aligned} \quad (1)$$

$$\begin{aligned} \ln(\gamma_X) = & z_X^2 F + \sum m_c (2B_{cX} + ZC_{cX}) + \sum m_a \left(2\Phi_{Xa} + \sum m_c \Psi_{cXa} \right) \\ & + \sum \sum m_c m_{c'} \Psi_{cc'X} + |z_X| \sum \sum m_c m_c C_{ca} \\ & + 2 \sum m_n \lambda_{nX} + \sum \sum m_n m_c \zeta_{nCX} \end{aligned} \quad (2)$$

$$\ln(\gamma_N) = \sum m_c (2\lambda_{Nc}) + \sum m_a (2\lambda_{Na}) + \sum \sum m_c m_a \zeta_{Nca} \quad (3)$$

where B , C , Φ , Ψ , λ and ζ are Pitzer-equation interaction parameters, m_i is the molal concentration, and F and Z are equation functions. In these equations, the Pitzer interaction parameters and the F function are temperature dependent. The subscripts c , a , and n refer to cations, anions, and neutral species, respectively. The coefficients c' and a' refer to cations and anions, respectively, that differ from c and a . The activity of water (a_w) at 1.01 bar pressure

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