

Modeling salt precipitation from brines on Mars: Evaporation versus freezing origin for soil salts



Jonathan D. Toner^{a,*}, David C. Catling^a, Bonnie Light^b

^a University of Washington, Box 351310, Dept. Earth & Space Sciences, Seattle, WA 98195, USA

^b Polar Science Center, Applied Physics Laboratory, University of Washington, Seattle, WA 98195, USA

ARTICLE INFO

Article history:

Received 10 September 2014

Revised 6 December 2014

Accepted 8 December 2014

Available online 16 December 2014

Keywords:

Mars, surface

Regoliths

Mars

ABSTRACT

Perchlorates, in mixture with sulfates, chlorides, and carbonates, have been found in relatively high concentrations in martian soils. To determine probable soil salt assemblages from aqueous chemical data, equilibrium models have been developed to predict salt precipitation sequences during either freezing or evaporation of brines. However, these models have not been validated for multicomponent systems and some model predictions are clearly in error. In this study, we built a Pitzer model in the Na–K–Ca–Mg–Cl–SO₄–ClO₄–H₂O system at 298.15 K using compilations of solubility data in ternary and quaternary perchlorate systems. The model is a significant improvement over FREZCHEM, particularly for Na–Mg–Cl–ClO₄, Ca–Cl–ClO₄, and Na–SO₄–ClO₄ mixtures. We applied our model to the evaporation of a nominal *Phoenix Lander* Wet Chemistry Laboratory (WCL) solution at 298.15 K and compare our results to FREZCHEM. Both models predict the early precipitation of KClO₄, hydromagnesite (3MgCO₃·Mg(OH)₂·3H₂O), gypsum (CaSO₄·2H₂O), and epsomite (MgSO₄·7H₂O), followed by dehydration of epsomite and gypsum to kieserite (MgSO₄·H₂O) and anhydrite (CaSO₄) respectively. At low residual water contents, our model predicts the precipitation of halite (NaCl), NaClO₄·H₂O, and Mg(ClO₄)₂·6H₂O, whereas halite and NaClO₄·H₂O never precipitate in FREZCHEM. Our model predicts that calcite does not precipitate from evaporating WCL solutions at 298.15 K, which conflicts with other evidence for calcite in *Phoenix* soils. Previous studies that modeled freezing of WCL solutions found that calcite does form. Furthermore, our model predicts that ~0.3 wt.% H₂O is held in hydrated salts after the WCL solution has completely evaporated at 298.15 K, whereas previous studies have found that ~1.3 wt.% H₂O is held in hydrated salts if WCL solutions freeze. Given minimum water contents in Mars soils of 1.5–2 wt.% H₂O measured from orbital spectra and in situ measurements, our modeling results suggest that salts at the *Phoenix* site were not formed during evaporation near 298.15 K, whereas formation during freezing remains possible.

© 2014 Elsevier Inc. All rights reserved.

1. Introduction

Perchlorate salts have been found on Mars by the *Phoenix* Wet Chemistry Laboratory (WCL) experiment (Hecht et al., 2009; Kounaves et al., 2010a; Toner et al., 2014b) and have been inferred at other locations from pyrolysis experiments (Leshin et al., 2013; Ming et al., 2013; Navarro-González et al., 2010), suggesting that perchlorate is globally distributed on Mars. Martian perchlorate is thought to derive from atmospheric processes (Catling et al., 2010), albeit probably involving heterogeneous chemistry (Smith et al., 2014), and is much more abundant (~0.5 wt.%) than trace concentrations found in Earth deserts (Calderón et al., 2014;

Kounaves et al., 2010b). Perchlorates on Mars are of significant interest because they are among the most hygroscopic salts known (Gough et al., 2011), and can depress the freezing point of water down to 198 K (Chevrier et al., 2009; Marion et al., 2010) or even lower due to supercooling (Toner et al., 2014a). This suggests that liquid water could be present on Mars in the form of perchlorate brines, despite the present-day cold and dry conditions. Such brines could support certain extremophile forms of life (Coates and Achenbach, 2004; Davila et al., 2010), facilitate weathering reactions in the martian regolith, influence water and CO₂ cycling between the regolith and atmosphere (Clark, 1978; Niles et al., 2013), and have even been proposed as lubricants for flowing ice masses (Fisher et al. 2010; Lenferink et al., 2013).

Thermodynamic Pitzer models (Pitzer, 1991) have proven successful in predicting water activities, ion activities, and salt precip-

* Corresponding author.

E-mail address: toner2@uw.edu (J.D. Toner).

itation sequences in complex brine mixtures on Earth (e.g. Harvie et al., 1984; Marion, 2001; Spencer et al., 1990). Applied to Mars, water activity predictions are useful for evaluating the potential habitability of brines (Davila et al., 2010). Furthermore, the identity of salt phases on Mars has implications for the past aqueous history (Boynton et al., 2009; Marion et al., 2010; Toner et al., 2014b) and the potential for salts to deliquesce to form brine (Gough et al., 2011, 2014). Marion et al. (2010) presented the first comprehensive Pitzer treatment of perchlorate brines by incorporating perchlorate into the FREZCHEM model (Marion and Kargel, 2008). Because FREZCHEM is already parameterized for many other salt systems (Marion, 2001; Marion and Farren, 1999; Marion and Kargel, 2008), FREZCHEM can theoretically be used to model salt precipitation from multicomponent brines, such as were measured in the Phoenix WCL experiments.

Pitzer models, such as FREZCHEM, predict solution properties by accounting for ionic interactions that occur in binary salt systems (comprised of a single salt in solution with water) and ternary salt systems (two salts in solution with water). FREZCHEM is primarily based on thermodynamic data in binary salt systems, and many of the model parameters governing ternary systems are either assumed to be similar to parameters in ‘analogous salt systems’ or are set to zero. In discussing potential errors in FREZCHEM ternary parameters, Marion et al. (2010) concludes that shortcoming in the ternary parameters should only have a small effect on model predictions. However, Toner et al. (2014b) found that FREZCHEM predicts unusual freezing point depressions, salt precipitation sequences, and ion activities when multicomponent WCL solutions are modeled. Multicomponent mixtures with Ca–Mg–ClO₄ never reach their eutectic in FREZCHEM and ion activity coefficients for Mg²⁺ can be in excess of 10⁵, leading to significant ‘salting out’ effects for salts of Mg²⁺. These effects do not occur when pure, binary solutions are modeled, and so are likely model artifacts caused by inaccurate ternary parameters.

In this study, we develop a Pitzer model for multicomponent perchlorate brines using solubility data at 298.15 K compiled primarily by Chan and Khoo (1988) and Chan et al. (1989, 1995). Although present-day Mars is much colder than 298.15 K (the global average is about 220 K), a model parameterized to 298.15 K can be applied to understanding warmer conditions in the past and provides a rigorous test of the current FREZCHEM parameterization. Furthermore, a robust model at 298.15 K provides a foundation for extrapolating perchlorate models to lower temperatures.

2. Methods

In FREZCHEM, the osmotic coefficient of water (ϕ) and the ion activity coefficients for cations (γ_M) and anions (γ_X) in multicomponent solutions are given by (Marion and Kargel, 2008; Pitzer, 1991) (excluding neutral species for simplicity):

$$\phi = 1 + \frac{2}{\sum m_i} \left\{ \frac{-A_\phi I^{3/2}}{1 + bI^{1/2}} + \sum \sum m_c m_a (\beta_{ca}^\phi + ZC_{ca}) + \sum \sum m_c m'_c \left(\Phi_{cc'}^\phi + \sum m_a \psi_{cc'a} \right) + \sum \sum m_a m_{a'} \left(\Phi_{aa'}^\phi + \sum m_c \psi_{ca'a} \right) \right\} \quad (1)$$

$$\ln \gamma_M = z_M^2 F + \sum m_a (2\beta_{Ma} + ZC_{Ma}) + \sum m_c \left(2\Phi_{Mc} + \sum m_a \psi_{Mca} \right) + \sum \sum m_a m_{a'} \psi_{Maad'} + |z_M| \sum \sum m_c m_a C_{ca} \quad (2)$$

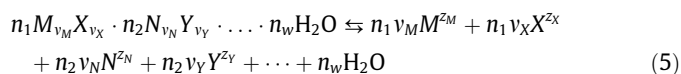
$$\ln \gamma_X = z_X^2 F + \sum m_c (2\beta_{cX} + ZC_{cX}) + \sum m_a \left(2\Phi_{Xa} + \sum m_c \psi_{cXa} \right) + \sum \sum m_c m_{c'} \psi_{cc'X} + |z_X| \sum \sum m_c m_a C_{ca} \quad (3)$$

where m (mol kg⁻¹) is the molality of cations (c) and anions (a), z is the ion charge, I is the ionic strength, A_ϕ is the Debye–Hückel limiting law slope (0.3917 kg^{1/2} mol^{-1/2} at 298.15 K), b is a constant (1.2 kg^{-1/2} mol^{-1/2}), and F and Z are functions. β^ϕ and β are functions of $\beta^{(0)}$, $\beta^{(1)}$, and $\beta^{(2)}$, C is a function of C^ϕ , and Φ^ϕ and Φ are functions of θ . The osmotic coefficient in Eq. (5) is related to the water activity of a solution (a_w) by:

$$a_w = \exp \left(\frac{-\phi \sum m_i}{55.50844} \right) \quad (4)$$

The $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^ϕ Pitzer parameters are derived by fitting the Pitzer equations to experimental data in binary salt systems. In binary systems, the Pitzer model has been shown to reproduce experimental data to within experimental errors for ionic strengths less than six (Pitzer, 1991), although good fits to experimental data can often be obtained for many systems at much higher ionic strengths ($I \approx 20$ mol kg⁻¹) (e.g. Harvie and Weare, 1980; Pabalan and Pitzer, 1987). The binary perchlorate salt systems modeled here have ionic strengths up to 24 mol kg⁻¹, in the case of Ca(ClO₄)₂, and so are near the limits of what can be modeled by the Pitzer equations. In this study, all binary Pitzer parameters ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^ϕ) are assumed to be the same as in FREZCHEM version 13.3. All other references to the FREZCHEM program in this paper refer to this version.

We derive θ and ψ parameters by fitting the Pitzer equations to experimental data in multicomponent salt solutions. In most cases, the only experimental data available for multicomponent systems are solubility data. To fit the Pitzer equations to solubility data, we exploit the relationship between the measured solubility and the Pitzer parameters as follows. The equilibrium solubility of a salt in aqueous solution is described by the mass action equation:



where M and N indicate cations, X and Y indicate anions, n and v indicate stoichiometric numbers of ions, and z indicates ion charge. For the case of a simple hydrated salt, like NaCl·2H₂O, the solubility product (K) corresponding to reaction (5) is given by:

$$K = (a_w)^{n_w} (a_M)^{z_M} (a_X)^{z_X} = (a_w)^{n_w} (m_M \gamma_M)^{z_M} (m_X \gamma_X)^{z_X} \quad (6)$$

where m_M and m_X are experimentally derived solubilities (mol kg⁻¹) of the salt. Given that the solubility product in Eq. (6) is invariant at constant temperature and pressure, Eq. (6) serves as a basis for fitting experimental solubility data (m_M and m_X) to modeled activity coefficients (a_w , γ_M , and γ_X), which are functions of the Pitzer parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, C^ϕ , θ , and ψ .

More specifically, to fit θ and ψ parameters we first calculate solubility products at 298.15 K and 1 atm using Eq. (6) in binary salt systems (Table 1). Solubilities for perchlorate salts are taken from Chan and Khoo (1988) and Chan et al. (1989, 1995), and solubility products are calculated using FREZCHEM. Solubilities and solubility products for non-perchlorate chemistries are taken directly from FREZCHEM. Then, for multicomponent salt systems in equilibrium with a given salt phase, we fit the θ and ψ Pitzer parameters using a sum-least-squares approach, in which we minimize the function:

$$F = \sum_n (\log K_{mod} - \log K_{calc})^2 \quad (7)$$

Download English Version:

<https://daneshyari.com/en/article/8136919>

Download Persian Version:

<https://daneshyari.com/article/8136919>

[Daneshyari.com](https://daneshyari.com)