Modeling aqueous perchlorate chemistries with applications to Mars

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ABSTRACT

NASA's Phoenix lander identified perchlorate and carbonate salts on Mars. Perchlorates are rare on Earth, and carbonates have largely been ignored on Mars following the discovery by NASA's Mars Exploration Rovers of acidic precipitated minerals such as jarosite. In light of the Phoenix results, we updated the aqueous thermodynamic model FREZCHEM to include perchlorate chemistry. FREZCHEM models the $Na–K–Mg–Ca–Fe(II)–Fe(III)–Al–H–Cl–Br–SO_4–NO_3–OH–HCO_3–CO_3–CO_2–O_2–CH_4–Si–H_2O$ system, with 95 solid phases. We added six perchlorate salts: $NaClO_4·H_2O$, $NaClO_4·2H_2O$, $KClO_4$, $Mg(ClO_4)_2·6H_2O$, $Mg(ClO_4)_2·8H_2O$, and $Ca(ClO_4)_2·6H_2O$. Modeled eutectic temperatures for Na, Mg, and Ca perchlorates ranged from 199 K (-74 °C) to 239 K (-34 °C) in agreement with experimental data.

We applied FREZCHEM to the average solution chemistry measured by the Wet Chemistry Laboratory (WCL) experiment at the Phoenix site when soil was added to water. FREZCHEM was used to estimate SO_4^{2-} and alkalinity concentrations that were missing from the WCL data. The amount of SO_4^{2-} is low compared to estimates from elemental abundance made by other studies on Mars. In the charge-balanced solution, the dominant cations were Mg^{2+} and Na^+ and the dominant anions were ClO_4^-, SO_4^{2-}, and alkalinity. The abundance of calcite measured at the Phoenix site has been used to infer that the soil may have been subject to liquid water in the past, albeit not necessarily locally; so we used FREZCHEM to evaporate (at 280.65 K) and freeze (from 280.65 to 213.15 K) the WCL-measured solution to provide insight into salts that may have been in the soil. Salts that precipitated under both evaporation and freezing were calcite, hydromagnesite, gypsum, $KClO_4$, and $Mg(ClO_4)_2·8H_2O$. Epsomite ($MgSO_4·7H_2O$) and $NaClO_4·H_2O$ were favored by evaporation at temperatures >0 °C, while meridianite ($MgSO_4·11H_2O$), $MgCl_2·12H_2O$, and $NaClO_4·2H_2O$ were favored at subzero temperatures. Incongruent melting of such highly hydrated salts could be responsible for vug formation elsewhere on Mars.

All K^+ precipitated as insoluble $KClO_4$ during both evaporation and freezing simulations, accounting for 15.8% of the total perchlorates. During evaporation, 35.8% of perchlorates precipitated with Na^+ and 48.4% with Mg^{2+}. During freezing, 58.4% precipitated with Na^+ and 24.8% with Mg^{2+}. Given its low eutectic temperature, the existence of $Mg(ClO_4)_2$ in either case allows for the possibility of liquid brines on Mars today. FREZCHEM also showed that $Ca(ClO_4)_2$ would likely not have precipitated at the Phoenix landing site due to the strong competing sinks for Ca as calcite and gypsum. Overall, these results help constrain the salt mineralogy of the soil. Differences between evaporites and cryogenites suggest ways to discriminate between evaporation and freezing during salt formation. Future efforts, such as sample return or in situ X-ray diffraction, may make such a determination possible.

1. Introduction

Among the most interesting findings of the Phoenix Mission to Mars was the presence of the perchlorate anion when soil was mixed with water in the North Polar region of Mars (Catling et al., 2009a,b; Fisher et al., 2008, 2009; Hecht et al., 2008, 2009a,b; Kounaves et al., 2009a,b). Naturally occurring perchlorate

salts are so rare on Earth that no perchlorate salt has yet been given an official "mineral" name (Orris et al., 2003), despite its known occurrence as a salt in the Atacama Desert in Chile (Orris et al., 2003; Trumpolt et al., 2005). The high solubility of most perchlorates could lead to very low eutectic temperatures (e.g., -68.6 °C [$Mg(ClO_4)_2·8H_2O$] and -74.6 °C [$Ca(ClO_4)_2·6H_2O$]) (Pestova et al., 2005) that may play an important role in cold aqueous processes on Mars. Another interesting finding at the Phoenix Mission site were alkalinities attributed to $CaCO_3$ equilibrium (Boynton et al., 2009a,b; Kounaves et al., 2009a,b; Smith, 2009a; Smith et al., 2009b). A decade ago, some models of martian

geochemistry emphasized carbonate mineralization as a logical consequence of the CO_2-rich atmosphere in the past presence of water (e.g., Catling, 1999; Morse and Marion, 1999). But this changed when the Opportunity rover found jarosite in Meridiani Planum. Jarosite implies highly acidic soils (Clark et al., 2005; Klingelhöfer et al., 2004; Navrotsky et al., 2005; Tosca et al., 2005). These disparate findings clearly indicate that geochemical processes on Mars are locally or temporally variable, or both.

On Earth in arid environments, perchlorates are often found associated with nitrate salts where these nitrates, such as those in the Atacama, are deposited from atmospheric sources (Catling et al., 2009a,b; Michalski et al., 2004). This analog suggests that perchlorate may be a useful tracer of atmospheric processes. But solution chemistry is necessary to understand any subsequent aqueous or thermodynamic transformation of the perchlorate. Given that perchlorate is a useful metabolite for certain microbes while it also is a contaminant for drinking water (Coates and Achenbach, 2004), modeling its behavior is important for future Mars missions both to look for life and safely explore Mars with humans.

The equilibrium chemical thermodynamic FREZCHEM model (Marion and Kargel, 2008) had been parameterized for the Na–K–Mg–Ca–Fe(II)–Fe(III)–Al–H–Cl–Br–SO$_4$–NO$_3$–OH–HCO$_3$–CO$_3$–CO$_2$–O$_2$–CH$_4$–Si–H$_2$O system. Given the Phoenix result, we added perchlorate chemistries so that we could simulate the behavior of the actual measured solutions. In particular, the relatively high concentration of ~4 wt.% of calcium carbonate measured by Phoenix's Thermal Evolved Gas Analyzer (TEGA) experiment suggests that the soil interacted with liquid water in the past because it is difficult to form this amount of carbonate by purely dry processes on Mars (Boynton et al., 2009a). Consequently, salts may have dissolved and reprecipitated in the martian soil once or many times in the past. FREZCHEM allows us to simulate evaporite salts that form during evaporation or "cryogenite" salts that form during freezing from the actual solution chemistry measured on Mars by Phoenix. In this way, we can gain insight into the salts that likely exist in the soil at the Phoenix site.

The specific objectives of this study were to: (1) add perchlorate chemistries to the FREZCHEM model and (2) identify the salts that are likely present in the Phoenix soils.

2. Methods and materials

2.1. FREZCHEM model

FREZCHEM is an equilibrium chemical thermodynamic model parameterized for concentrated electrolyte solutions (to ionic strengths >20 m) using the Pitzer approach (Pitzer, 1991, 1995) for the temperature range from <−70 to 25 °C and the atmospheric pressure (P_{atm}) range from <1 to 1000 bars (Marion and Farren, 1999; Marion, 2001, 2002; Marion et al., 2003, 2005, 2006, 2008, 2009a,b; Marion and Kargel, 2008). The current version of the model is parameterized for the Na–K–Mg–Ca–Fe(II)–Fe(III)–Al–H–Cl–Br–SO$_4$–NO$_3$–OH–HCO$_3$–CO$_3$–CO$_2$–O$_2$–CH$_4$–Si–H$_2$O system and includes 95 solid phases including ice, 15 chloride minerals, 35 sulfate minerals, 15 carbonate minerals, 5 solid phase acids, 3 nitrate minerals, 6 acid-salts, 5 iron oxide/hydroxides, 4 aluminum hydroxides, 2 silica minerals, 2 gas hydrates, and 2 bromide sinks (see above references for these model parameters). An objective of this work was to develop perchlorate parameterizations based on classical chemical thermodynamic principles that can be incorporated seamlessly into FREZCHEM. This involved the incorporation of six new perchlorate solid phases into FREZCHEM. A FORTRAN code with user instructions of the resulting model (Version 13) is available from the senior author (giles.marion@dri.edu) or from http://frezchem.dri.edu. The Internet-accessible working

model (Version 10) at http://frezchem.dri.edu also includes perchlorate chemistry.

2.2. Pitzer approach

In the Pitzer approach (Pitzer, 1991, 1995), 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 $CO_2(aq)$ or $CH_4(aq)$, are given by

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

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

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

where B, C, Φ, Ψ, γ and ζ are Pitzer-equation interaction parameters, m_i is the molal concentration, z_i is the ionic valence, 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. 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 is given by

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

where ϕ is the osmotic coefficient, which is given by

$$
\begin{aligned}
(\phi - 1) = \frac{2}{\sum m_i}\Bigg\{ &\frac{-A_\phi I^{3/2}}{1 + bI^{1/2}} + \sum\sum m_c m_a\left(B_{ca}^\phi + ZC_{ca}\right) \\
&+ \sum\sum m_c m_{c'}\left(\Phi_{cc'}^\phi + \sum m_a\Psi_{cc'a}\right) \\
&+ \sum\sum m_a m_{a'}\left(\Phi_{aa'}^\phi + \sum m_c\Psi_{caa'}\right) + \sum\sum m_n m_c\lambda_{nc} \\
&+ \sum\sum m_n m_a\lambda_{na} + \sum\sum\sum m_n m_c m_a\zeta_{n,c,a}\Bigg\}
\end{aligned}
\tag{5}
$$

The binary B parameters in Eqs. (1), (2), and (5), are functions of $B_{ca}^{(0)}$, $B_{ca}^{(1)}$, and $B_{ca}^{(2)}$; similarly, the C parameters in these equations are a function of C_{ca}^ϕ. FREZCHEM specifies the pressure dependence of equilibrium constants (K), activity coefficients (γ), and the activity of water (a_w). The corresponding volumetric (pressure) parameters are functions of $B_{ca}^{(0)V}$, $B_{ca}^{(1)V}$, $B_{ca}^{(2)V}$, and C_{ca}^V. See Marion et al. (2005), Marion and Kargel (2008), or Marion et al. (2008) for a complete description of these temperature–pressure equations.

The temperature and pressure dependencies of Pitzer parameters (discussed above) and solubility products (discussed below) are defined by the equation

$$
P = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5/T + a_6\ln(T)
\tag{6}
$$

where P is the Pitzer parameter or $\ln(K_{sp})$ and T is absolute temperature (K).

3. Results

3.1. Pitzer parameterization and solubility products

The Pitzer parameters for the Na–ClO$_4$ interactions at 298.15 K were taken from Pitzer (1991). These parameters were extended to

lower temperatures by fitting to NaClO$_4$–ice data from Linke (1965) (Fig. 1) using the equation:

$$P_T = P_{298.15} + A(298.15 - T) \qquad (7)$$

where P is the Pitzer parameter and A is a derived constant. Knowing the freezing point depression of a solution in equilibrium with pure ice allows one to directly determine the activity of water (a_w) and the solution osmotic coefficient [ϕ, Eq. (4)], which then can serve as the thermodynamic foundation for estimating the value of Pitzer parameters (Eq. (5)). While Eq. (7) was used to estimate the temperature dependence, this equation was converted to our standard format (Eq. (6)) in Table 1. Parameterization of Na–ClO$_4$ interaction parameters to 239 K (Fig. 1) allowed us to estimate the solubility products for NaClO$_4$·H$_2$O and NaClO$_4$·2H$_2$O (Table 2) based on solubility data (Linke, 1965; Chretien and Kohlmuller, 1966). The model calculated eutectic for this system occurred at 238.95 K with NaClO$_4$ = 9.20 m, which is in excellent agreement with the literature values of 238.95 K with NaClO$_4$ = 9.21 m (Fig. 1; Chretien and Kohlmuller, 1966). The model peritectic for NaClO$_4$·H$_2$O–NaClO$_4$·2H$_2$O occurs at 12.47 m with T = 260.15 K, which is in good agreement with the literature values of 12.46 m with T = 259.90 K (Fig. 1; Chretien and Kohlmuller, 1966).

We could have supplemented the a_w data based on ice equilibria (Fig. 1) with a_w data based on vapor pressure measurements for saturated NaClO$_4$·H$_2$O data for the temperature range from 278.15 to 298.15 K (Apelblat and Manzurola, 2007). However, including the latter data led to poor activity coefficient values near the eutectic that failed to precipitate NaClO$_4$·2H$_2$O. The reason for this discrepancy is that the Apelblat and Manzurola (2007) a_w data are inconsistent with the ice a_w data. For example, the Apelblat and Manzurola, 2007 a_w values at 278.15 and 298.15 K are 0.502 and 0.446 for equilibrium with NaClO$_4$·H$_2$O. On the other hand, the comparable a_w values at 278.15 and 298.15 K are 0.564 and 0.440 based on parameterization with ice data (Fig. 1). Since the latter data led to a better model fit (Fig. 1), we will rely on that parameterization.

The Pitzer parameters for K–ClO$_4$ interactions at 298.15 K were taken from Chan and Khoo (1988). These parameters were extended to lower temperatures by assuming that the validity of the "A" parameters from Eq. (7) based on Na–ClO$_4$ would also work for K–ClO$_4$. From Linke (1965) solubility data, we estimated the solubility product for KClO$_4$ (Table 2). This salt is relatively insolu-
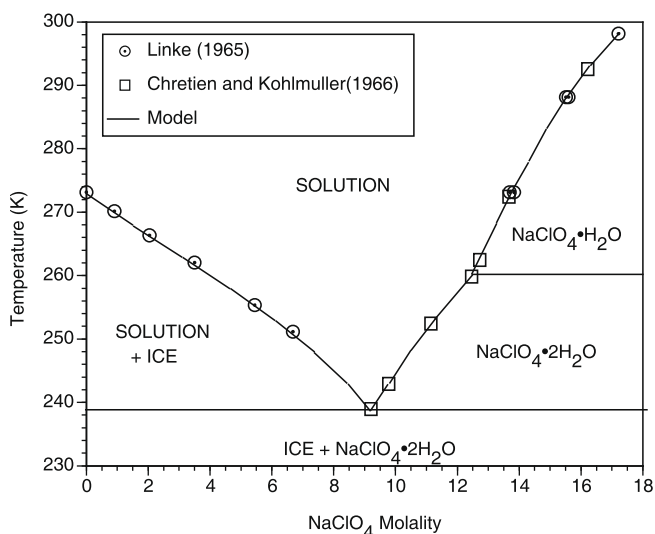
ble. Integrating the Pitzer parameters (Table 1) and the solubility product for KClO$_4$ (Table 2) into the FREZCHEM model allowed us to estimate the temperature and composition of KClO$_4$ at the eutectic point, which was calculated to be 272.974 K (-0.176 °C) at 0.0535 m, not far removed from the experimental value of 0.0545 m at 0 °C (Linke, 1965).

We also had the option with KClO$_4$ to include salt saturation a_w data from Apelblat and Manzurola (2007) as was the case for NaClO$_4$·H$_2$O (see discussion above). However, the only calculated a_w value listed in Apelblat and Manzurola (2007) over the temperature range from 278.15 to 298.15 K for KClO$_4$ was 0.9937, while our model predicts values of 0.9982–0.9952 based on the above parameterizations for KClO$_4$. Our model estimate of a_w for a saturated KClO$_4$ solution (0.15 m) at 298.15 K is 0.9952, which is close to a KClO$_3$ value of 0.9951 at 0.15 m (Robinson and Stokes, 1970). Similarly, NaClO$_3$ and NaClO$_4$ at 0.15 m have near-identical values of 0.9950 (Robinson and Stokes, 1970). Because our KClO$_4$ parameterizations are compatible with the Robinson and Stokes database, we will retain the above described KClO$_4$ parameterization.

The Pitzer parameters for H–ClO$_4$ interactions at 298.15 K were taken from Pitzer (1991). These parameters were extended to lower temperatures by fitting to HClO$_4$ (perchloric acid)–ice data from Linke (1958) using Eq. (7) (Fig. 2). In contrast to how we dealt with NaClO$_4$ (Fig. 1), Mg(ClO$_4$)$_2$ (Fig. 3), and Ca(ClO$_4$)$_2$ (Fig. 5), no attempt was made to include solid phase perchloric acids in our model as we had done in the past for HCl, HNO$_3$, and H$_2$SO$_4$ (Marion, 2002). The degree of hydration of solid phase perchloric acids are highly uncertain (see data in Linke (1958)), so we ignored solid phase perchloric acid chemistries beyond the ice eutectic point (Fig. 2).

The Pitzer parameters for Mg–ClO$_4$ interactions at 298.15 K were taken from Pitzer (1991). These parameters were extended to lower temperatures by fitting Mg(ClO$_4$)$_2$–ice data from Nicholson and Felsing (1950), Dobrynina et al. (1980), and Pestova et al. (2005) (Fig. 3). Parameterization of the ice line to 205 K allowed us to estimate equilibrium constants for Mg(ClO$_4$)$_2$·XH$_2$O. The Linke (1965) and Dobrynina et al. (1980) data listed the hydration as 6H$_2$O, while the data from Pestova et al. (2005) listed the hydration as 8H$_2$O. There are no distinct differences among these three datasets with respect to the solubility of Mg(ClO$_4$)$_2$·XH$_2$O (Fig. 3). In Fig. 4, we lumped all three datasets as either 6H$_2$O or 8H$_2$O. There are no distinct differences within either equation dependent on the experimentally-designated XH$_2$O values. In an earlier paper (Marion et al., 2009b), experimental values for Al$_2$(SO$_4$)$_3$·XH$_2$O (alunogen) varied from X = 16 to 18. In that study, we lumped all data into 17H$_2$O. In this paper, we lumped all the data into 8H$_2$O because there exists independent data that supports the 8H$_2$O hydration (Besley and Bottomley, 1969; Pestova et al., 2005). Also, the 8H$_2$O equation is slightly better fitting than the 6H$_2$O equation (Fig. 4). But either of the equations in Fig. 4 (or Table 2) could be used in the FREZCHEM model (see discussion below). For the above reasons, we use 8H$_2$O as the dominant Mg(ClO$_4$)$_2$ hydrate for cold aqueous processes (Fig. 3). Our model estimate for the eutectic temperature and concentration of Mg(ClO$_4$)$_2$ are 204.95 K and 3.48 m, in good agreement with experimental values of 204.55 K and 3.48 m (Pestova et al., 2005) and 206.15 K and 3.45 m (Dobrynina et al., 1980) (Fig. 3). Had we run the model with the 6H$_2$O equation (Fig. 4), the eutectic occurs at 205.55 K and 3.47 m, which is not significantly different from the 8H$_2$O calculations.

The Pitzer parameters for Ca–ClO$_4$ interactions at 298.15 K were taken from Pitzer (1991). These parameters were extended to lower temperatures with Ca(ClO$_4$)$_2$–ice data from Nicholson and Felsing (1950) and Pestova et al. (2005) (Fig. 5). Parameterization of the ice line to 199 K allowed us to estimate the solubility product for Ca(ClO$_4$)$_2$·6H$_2$O based on data from Linke (1958) (one

Fig. 1. Equilibria for NaClO$_4$ solutions from 25 °C to the eutectic. Symbols are experimental data; lines are model estimations.

Table 1
Binary, ternary, and volumetric Pitzer-equation parameters derived in this work or taken from the literature (numbers are in computer scientific notation where e±xx stands for $10^{\pm xx}$).

Pitzer-equation parameters	a_1	a_2	a_3	Temperature range (K)	Data sources
$B_{Na,ClO4}^{(0)}$	−4.1270e−1	1.57e−3		239–298	Linke (1965), Chretien and Kohlmuller (1966), and Pitzer (1991), this work
$B_{Na,ClO4}^{(1)}$	1.9422e0	−5.59e−3		239–298	Linke (1965), Chretien and Kohlmuller (1966), and Pitzer (1991), this work
$C_{Na,ClO4}^{\phi}$	3.907e−2	−1.35e−4		239–298	Linke (1965), Chretien and Kohlmuller (1966), and Pitzer (1991), this work
$B_{K,ClO4}^{(0)}$	−3.245e−1	5.517e−4		273–298	Linke (1965) and Chan and Khoo (1988), this work
$B_{K,ClO4}^{(1)}$	−3.824e0	1.333e−2		273–298	Linke (1965) and Chan and Khoo (1988), this work
$C_{K,ClO4}^{\phi}$	0.00			273–298	Linke (1965) and Chan and Khoo (1988), this work
$B_{H,ClO4}^{(0)}$	1.747e−1			213–298	Linke (1958) and Pitzer (1991), this work
$B_{H,ClO4}^{(1)}$	−1.8394e−1	1.60e−3		213–298	Linke (1958), and Pitzer (1991), this work
$C_{H,ClO4}^{\phi}$	4.9104e−3	1.10e−5		213–298	Linke (1958), and Pitzer (1991), this work
$B_{Mg,ClO4}^{(0)}$	−9.8977e−2	1.996e−3		205–298	Nicholson and Felsing (1950), Linke (1965), Dobrynina et al. (1980), Pitzer (1991), and Pestova et al. (2005), this work
$B_{Mg,ClO4}^{(1)}$	2.8335e1	−8.830e−2		205–298	Nicholson and Felsing (1950), Linke (1965), Dobrynina et al. (1980), Pitzer (1991), and Pestova et al. (2005), this work
$C_{Mg,ClO4}^{\phi}$	1.6468e−1	−5.202e−4		205–298	Nicholson and Felsing (1950), Linke (1965), Dobrynina et al. (1980), Pitzer (1991), and Pestova et al. (2005), this work
$B_{Ca,ClO4}^{(0)}$	2.4839e−1	6.80e−4		199–298	Nicholson and Felsing (1950), Linke (1958), Pitzer (1991), and Pestova et al. (2005), this work
$B_{Ca,ClO4}^{(1)}$	8.1965e0	−2.16e−2		199–298	Nicholson and Felsing (1950), Linke (1958), Pitzer (1991), and Pestova et al. (2005), this work
$C_{Ca,ClO4}^{\phi}$	4.1510e−2	−1.56e−4		199–298	Nicholson and Felsing (1950), Linke (1958), Pitzer (1991), and Pestova et al. (2005), this work
$\Psi_{Na,K,ClO4}$	1.16e−2			298	Chan and Khoo (1988), this work
$\Psi_{Na,Mg,ClO4}$	−1.07e−2			298	This work[a]
$\Psi_{Na,Ca,ClO4}$	−1.07e−2			298	Chan and Khoo (1988)
$\Psi_{K,Mg,ClO4}$	−1.07e−2			298	This work[a]
$\Psi_{K,Ca,ClO4}$	−1.07e−2			298	This work[a]
$\Psi_{Mg,Ca,ClO4}$	−2.38e−2			298	This work[b]
$\Psi_{Na,H,ClO4}$	−1.60e−2			298	Pitzer, 1991
$\Psi_{K,H,ClO4}$	−1.60e−2			298	This work[a]
$\Psi_{Mg,H,ClO4}$	−7.70e−3			298	This work[b]
$\Psi_{Ca,H,ClO4}$	−1.42e−2			298	This work[b]
$\Theta_{Cl,ClO4}$	3.41e−2			298	Chan and Khoo (1988)
$\Psi_{Cl,ClO4,Na}$	−5.23e−2			298	This work[a]
$\Psi_{Cl,ClO4,K}$	−5.23e−2			298	Chan and Khoo (1988), this work
$\Psi_{Cl,ClO4,Mg}$	4.60e−3			298	This work[c]
$\Psi_{Cl,ClO4,Ca}$	−4.09e−2			298	This work[c]
$\Psi_{Cl,ClO4,H}$	0.00			298	This work[c]
$\Theta_{HCO3,ClO4}$	8.1e−2			298	Königsberger et al. (1992)
$\Psi_{HCO3,ClO4,Na}$	−1.9e−2			298	Königsberger et al. (1992)
$\Psi_{HCO3,ClO4,K}$	−1.9e−2			298	This work[a]
$\Psi_{HCO3,ClO4,Mg}$	−3.6e−1			298	Königsberger et al. (1992)
$\Psi_{HCO3,ClO4,Ca}$	−3.6e−1			298	This work[a]
$\Theta_{CO3,ClO4}$	7.1e−2			298	Königsberger et al. (1992)
$\Psi_{CO3,ClO4,Na}$	−6.0e−3			298	Königsberger et al. (1992)
$\Psi_{CO3,ClO4,K}$	−6.0e−3			298	This work[a]
$\Psi_{CO3,ClO4,Mg}$	0.0			298	Königsberger et al. (1992)
$\Psi_{CO3,ClO4,Ca}$	0.0			298	This work[a]
$\Theta_{HSO4,ClO4}$	8.1e−2			298	This work[d]
$\Psi_{HSO4,ClO4,Na}$	−1.9e−2			298	This work[d]
$\Psi_{HSO4,ClO4,K}$	−1.9e−2			298	This work[d]
$\Psi_{HSO4,ClO4,Mg}$	−3.6e−1			298	This work[d]
$\Psi_{HSO4,ClO4,Ca}$	−3.6e−1			298	This work[d]
$\Theta_{SO4,ClO4}$	7.1e−2			298	This work[e]
$\Psi_{SO4,ClO4,Na}$	−6.0e−3			298	This work[e]
$\Psi_{SO4,ClO4,K}$	−6.0e−3			298	This work[e]
$\Psi_{SO4,ClO4,Mg}$	0.00			298	This work[e]
$\Psi_{SO4,ClO4,Ca}$	0.00			298	This work[e]
Volumetric parameters					
$B_{Na,ClO4}^{v(0)}$	6.475e−6			298	Krumgalz et al. (1996)
$B_{Na,ClO4}^{v(1)}$	2.0790e−5			298	Krumgalz et al. (1996)
$C_{Na,ClO4}^{v}$	−2.230e−7			298	Krumgalz et al. (1996)
$B_{K,ClO4}^{v(0)}$	−7.162e−6			298	Krumgalz et al. (1996)[f]
$B_{K,ClO4}^{v(1)}$	−2.7555e−4			298	Krumgalz et al. (1996)[f]
$C_{K,ClO4}^{v}$	0.00			298	Krumgalz et al. (1996)[f]
$B_{Mg,ClO4}^{v(0)}$	−7.061e−6			298	Krumgalz et al. (1996)
$B_{Mg,ClO4}^{v(1)}$	1.3878e−5			298	Krumgalz et al., 1996
$C_{Mg,ClO4}^{v}$	5.040e−6			298	Krumgalz et al. (1996)

Table 1 (continued)

Pitzer-equation parameters	a_1	a_2	a_3	Temperature range (K)	Data sources
$B_{Ca,ClO4}^{v(0)}$	3.122e−5			298	Krumgalz et al. (1996)
$B_{Ca,ClO4}^{v(1)}$	6.368e−6			298	Krumgalz et al. (1996)
$C_{Ca,ClO4}^{v}$	−1.0443e−6			298	Krumgalz et al. (1996)
$V_{ClO4}^{(0)}$	4.409e1			298	Krumgalz et al. (1996), this work
$K_{ClO4}^{(0)}$	−5.75e−3			298	Millero (2001)[g]

[a] Assumed the same as similar perchlorates.
[b] Assumed the same as Cl salts.
[c] Assumed the same as Cl, NO_3 salts.
[d] Assumed the same as HCO_3, ClO_4 salts.
[e] Assumed the same as CO_3, ClO_4 salts.
[f] Assumed the same as K, ClO_3.
[g] Assumed the same as $B(OH)_4^-$.

Table 2
Equilibrium constants (as ln(K)) derived in this study (numbers are in computer scientific notation where e±xx stands for $10^{\pm xx}$).

Solution–solid phase equilibria	a_1	a_2	a_3	Solid phase molar volumes ($cm^3\,mol^{-1}$)	Temperature range (K)
$NaClO_4 \cdot H_2O \Longleftrightarrow Na^+ + ClO_4^- + H_2O$	−2.575938e1	1.910375e−1	−2.942941e−4	69.53	260–298
$NaClO_4 \cdot 2H_2O \Longleftrightarrow Na^+ + ClO_4^- + 2H_2O$	−9.445939e0	4.950649e−2		85.00	239–260
$KClO_4 \Longleftrightarrow K^+ + ClO_4^-$	−7.125203e0	−6.100201e−2	2.337460e−4	54.98	273–298
$Mg(ClO_4)_2 \cdot 6H_2O \Longleftrightarrow Mg^{2+} + 2ClO_4^- + 6H_2O$	2.133243e1	−2.785519e−2		167.32	205–298
$Mg(ClO_4)_2 \cdot 8H_2O \Longleftrightarrow Mg^{2+} + 2ClO_4^- + 8H_2O$	2.152861e1	−3.469271e−2		189.43	205–298
$Ca(ClO_4)_2 \cdot 6H_2O \Longleftrightarrow Ca^{2+} + 2ClO_4^- + 6H_2O$	−1.786378e1	2.253556e−1	−4.013223e−4	156.47	199–298

Fig. 2. Equilibria for $HClO_4$ solutions from 0 °C to the eutectic. Symbols are experimental data; lines are model estimations.
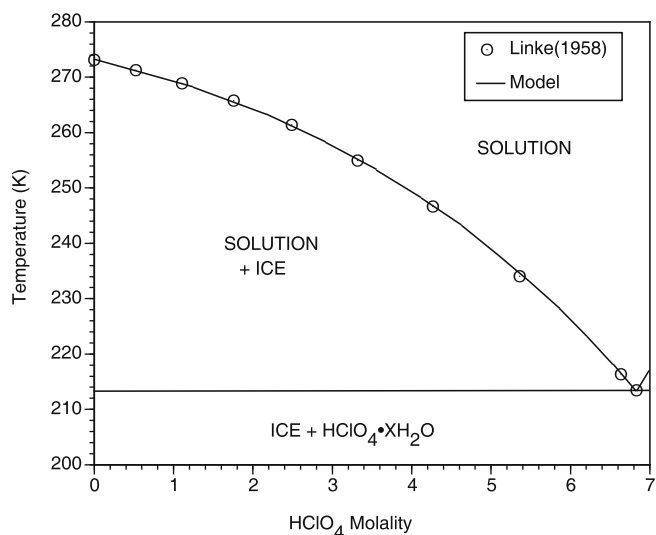

Fig. 3. Equilibria for $Mg(ClO_4)_2$ solutions from 25 °C to the eutectic. Symbols are experimental data; lines are model estimations.

datum) and Pestova et al. (2005) (eight data). Our model estimate of the eutectic for this system is 198.75 K at 4.16 m, which is in good agreement with Pestova et al. (2005) experimental measurements of 198.55 K and 4.20 m (Fig. 5).

There is also plotted in Fig. 5 a dataset from Dobrynina et al. (1984). But this dataset places the eutectic at 212.65 K (4.62 m) for $Ca(ClO_4)_2 \cdot 8H_2O$–ice, which is in contrast to the Linke (1958) and Pestova et al. (2005) datasets that assume the solid phase salt is $Ca(ClO_4)_2 \cdot 6H_2O$ with a lower eutectic (Fig. 5). In the Dobrynina et al. (1984) dataset, a peritectic for $Ca(ClO_4)_2 \cdot 8H_2O$–Ca $(ClO_4)_2 \cdot 4H_2O$ occurs at 258.65 K (6.94 m). Perchlorate concentrations above this point are more soluble than the Linke–Pestova datasets, which suggests that the $6H_2O$ is the more stable state
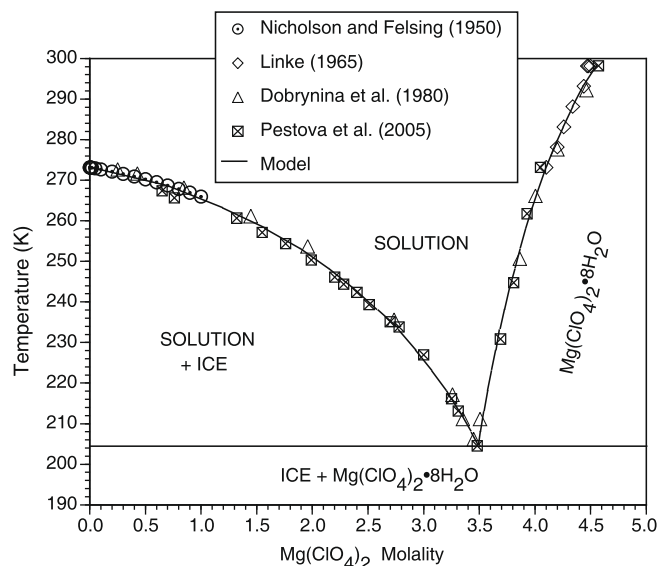
(less soluble). For that reason, we did not include the Dobrynina et al. (1984) data in our parameterization of $Ca(ClO_4)_2$ chemistry.

Also included in Table 1 are ternary Pitzer parameters for 298 K that are used for mixtures. The cited references in Table 1 for these parameters only defined the parameters for 298 K. Also, in many cases, we had to make assumptions for undefined parameters; see the "a–g" footnotes in Table 1. For example, we set $\Psi_{HSO4,ClO4,cation}$ equal to $\Psi_{HCO3,ClO4,cation}$ (footnote d); similarly, we set $\Psi_{SO4,ClO4,cation}$ equal to $\Psi_{CO3,ClO4,cation}$ (footnote e). So how important are these shortcomings in temperature and specific ternary parameters for modeling perchlorate chemistries? Here is a direct quote from Pitzer (1991, p. 113) that states: "It should be
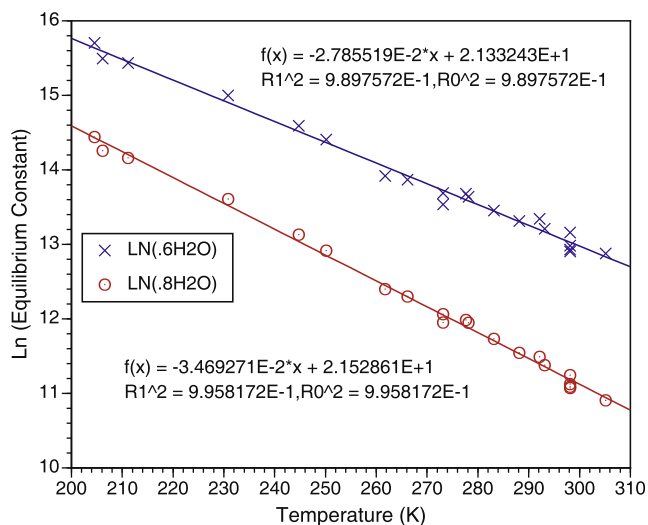
Fig. 4. A comparison of the equilibrium constants for $Mg(ClO_4)_2 \cdot 6H_2O$ and $Mg(ClO_4)_2 \cdot 8H_2O$.

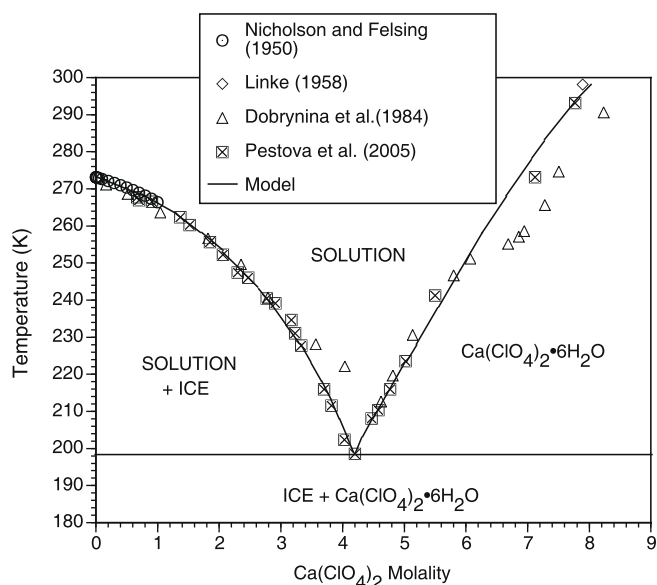**Fig. 5.** Equilibria for $Ca(ClO_4)_2$ solutions from 25 °C to the eutectic. Symbols are experimental data; lines are model estimations.

remembered that the principal effects on mixing electrolytes arise from differences in the pure electrolyte parameters $B^{(0)}$, $B^{(1)}$, and C^ϕ and that the parameters Θ and Ψ have only a small effect, if any". So the shortcomings due to temperature and specific parameterizations of the ternary parameters (Θ and Ψ) are expected to be minor.

3.2. Density and pressure parameterizations

The FREZCHEM model is structured to predict density and the effects of pressure on chemical equilibria (Marion et al., 2005, 2008, 2009b; Marion and Kargel, 2008). Implementation of these equations requires a specification of the partial molar volume $\left(V_i^0\right)$ and compressibility $\left(K_i^0\right)$ of individual species (e.g., ClO_4^-) and binary Pitzer-equation volumetric parameters ($B_{c,a}^v$, Table 1).

All of the volumetric Pitzer parameters at 298 K were taken from Krumgalz et al. (1996) (Table 1). The molar volume for

ClO_4^- ($V_{ClO4}^{(0)}$) was estimated from data in Krumgalz et al. (1996). In that publication, the molar volumes were listed as cation–anion assemblages (e.g., $V_{Na,ClO4}^{(0)}$), but FREZCHEM requires individual ion parameters (e.g., $V_{ClO4}^{(0)}$). We took molar volumes for Na, Mg, and Ca from Millero (2001) at 298 K and subtracted them from molar volumes for $NaClO_4$, $Mg(ClO_4)_2$, and $Ca(ClO_4)_2$ from Krumgalz et al. (1996) to estimate a $V_{ClO4}^{(0)} = 44.09 \pm 0.23$ cm³ mol⁻¹ (Table 1). The compressibility of ClO_4^- (K_{ClO4}^0) (Table 1) was assumed to be the same as $B(OH)_4^-$ due to the similar charge and oxygen contents. The final terms needed for pressure calculations are the molar volumes of the solid phases (Table 2); compressibilities for these phases are minor factors that can safely be ignored (Marion et al., 2005). The molar volumes for $NaClO_4 \cdot H_2O$, $KClO_4$, and $Mg(ClO_4)_2 \cdot 6H_2O$ were derived from atomic weight/density data (Lide, 1994). Similar data for $Mg(ClO_4)_2$ and $Mg(ClO_4)_2 \cdot 6H_2O$ were used to develop a linear equation between molar volume (Y axis) and ·hydrate (X axis). This equation was extrapolated to $8H_2O$ to estimate the molar volume of $Mg(ClO_4)_2 \cdot 8H_2O$, and the slope of this equation was used to estimate the molar volume of $Ca(ClO_4)_2 \cdot 6H_2O$ based on a single $Ca(ClO_4)_2$ datum (Lide, 1994). In Marion et al. (2005), we showed why these molar volume/hydrate data lead to excellent linear fits ($r^2 = 0.9979$–0.9993).

There is a scattering of density data among the Linke (1958, 1965) datasets that were used in model development (Figs. 1–3 and 5, Tables 1 and 2). For example, the experimental data for $NaClO_4$ solution density in equilibrium with $NaClO_4 \cdot H_2O$ at 288 and 298 K (Fig. 1) were 1.663 and 1.683 g cm⁻³, which compares to model calculations of 1.671 and 1.693 g cm⁻³, respectively. Similarly, the experimental density of $Ca(ClO_4)_2$ solution at mineral saturation at 298 K (Fig. 5) was 1.719 g cm⁻³, which compares to the model calculated value of 1.681 g cm⁻³. A possible reason for these discrepancies is that the saturated solutions of these highly soluble salts are higher in concentration than the experimental data used in the Krumgalz et al. (1996) study. For example, the maximum solution concentrations for the $NaClO_4$ and $Ca(ClO_4)_2$ experimental data in the latter study were 11.1 and 2.4 m, respectively, which compares to the saturated solution concentrations for $NaClO_4$ that were 15.6 m (288 K) and 17.2 m (298 K), and for $Ca(ClO_4)_2$ was 7.9 m (298 K). A more dilute example deals with saturated $KClO_4$ solutions where experimental data at 273, 288, 293, and 298 K had densities of 1.005, 1.0076, 1.0085, and 1.0096 g cm⁻³ (Linke, 1965), which are in good agreement with model calculations of 1.0046, 1.0075, 1.0086, and 1.0100 g cm⁻³, respectively. Had we completely ignored the volumetric parameters (Table 1), then the model calculated density for the saturated $NaClO_4$ solution at 298 K would be 3.00 g cm⁻³, an absurd value compared to the experimental value of 1.683 g cm⁻³ and the model value of 1.693 g cm⁻³. This absurd calculation occurred because "unspecified" parameters in the FREZCHEM model are generally assigned values of 0.0, which can lead to highly inaccurate calculations. So using the volumetric parameters of Tables 1 and 2 is a significant improvement over ignoring these parameters totally.

4. Validation and limitations

Figs. 1–3 and 5 indicate the accuracy of model fits to experimental data down to eutectic temperatures. Mean activity coefficients ($\gamma \pm$) at 298.15 K for $NaClO_4$ and $HClO_4$ (Fig. 6) and $Mg(ClO_4)_2$ and $Ca(ClO_4)_2$ (Fig. 7) are compared between Robinson and Stokes (1970) data (hereafter referred to as R&S) and Pitzer (1991) parameterizations based on those datasets (hereafter referred to as Pitzer). The $NaClO_4$–$HClO_4$–$Ca(ClO_4)_2$ datasets cover the concentration range from 0.1 to 6 m, while $Mg(ClO_4)_2$ covers the concentration range from 0.1 to 4.0, due to the lesser solubility of this salt (Fig. 3). The magnitude of activity coefficients is highly
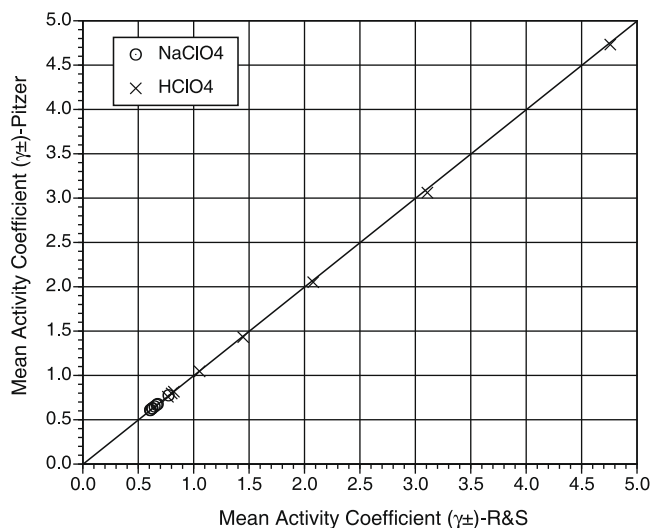
Fig. 6. A comparison of Pitzer model activity coefficients for sodium perchlorate and perchloric acid to experimental data from Robinson and Stokes (1970).
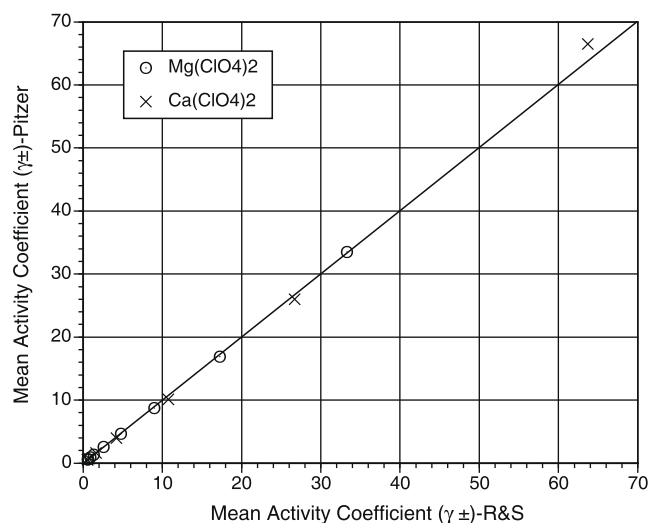

Fig. 7. A comparison of Pitzer model activity coefficients for magnesium perchlorate and calcium perchlorate to experimental data from Robinson and Stokes (1970).

variable among these salts. $NaClO_4$ activity coefficients over these concentrations only vary from 0.609 to 0.775, while $HClO_4$ covers the range from 0.769 to 4.76 (Fig. 6). The $Mg(ClO_4)_2$ and $Ca(ClO_4)_2$ activity coefficients, on the other hand, cover a much broader range of values, up to 63.7 (Fig. 7). In general, the Pitzer parameterizations are in good agreement with the R&S data ($NaClO_4$ $r^2 = 0.99986$; $HClO_4$ $r^2 = 0.99995$; $Mg(ClO_4)_2$ $r^2 = 0.99978$), except for the highest $Ca(ClO_4)_2$ value (Fig. 7) ($Ca(ClO_4)_2$ $r^2 = 0.99912$). This limitation may simply reflect that the Pitzer parameterizations only included $Mg(ClO_4)_2$ and $Ca(ClO_4)_2$ data up to 2 m, while the upper datum in Fig. 7 is at 6.0 m (ionic strength = 18 m). Any activity coefficient in Fig. 7 beyond 2.6 is an extrapolation of the Pitzer parameterization, which is critically important for modeling $Mg(ClO_4)_2$ and $Ca(ClO_4)_2$ solubilities beyond 2.0 m (Figs. 3 and 5).

While model fits to experimental data are encouraging and point out the self-consistency of the model and data inputs (Figs. 1–3 and 5–7), they are not a substitute for validation that requires comparison to independent data for aqueous solutions. The only independent data cited in this paper that were not used in model parameterizations were the density data for $NaClO_4$, $KClO_4$,

and $Ca(ClO_4)_2$. The seven model-calculated densities agreed with the experimental data with a standard error of 0.48% (sign ignored) or 0.16% (sign considered) (see Section 3.2 for details).

Potentially, real limitations of this perchlorate parameterization are the general lack of a temperature dependence and our use of surrogate substitutes for specific ternary parameters (Table 1). Only time and perchlorate importance will result in a more complete set of data for perchlorate chemistries. Fortunately, ternary parameters will likely only have a small effect (see Pitzer comment in Section 3.1).

5. Applications to Mars

Several initial reports documented the aqueous chemistries in the WCL cells at the Phoenix Mission site on Mars (e.g., Boynton et al., 2009a,b; Hecht et al., 2008, 2009a,b; Kounaves et al., 2009a,b). The most recent interpretation suggests that the pH was 7.7 (Boynton et al., 2009a; Hecht et al., 2009b; Kounaves et al., 2009a,b) under the prevailing P_{CO2} conditions of the WCL experiment. In what follows, we will rely on Hecht et al. (2009b) for specifying the chemical compositions of the Phoenix soil solutions. Data were given for three separate solutions formed by mixing soil samples with water that had similar chemical compositions (see Table 1 in Hecht et al. (2009b)). We used their "average" values for the chemistries in our simulations (Table 3). The actual concentrations given in the Hecht et al. (2009b) paper were in molarity (M) units (moles/liter). But the FREZCHEM model requires molality (m) units [moles/kg(H_2O)]. Fortunately, FREZCHEM can calculate a conversion factor (CF) for changing molarity to molality (Marion, 2007). In this particular case, the CF = 1.000252, an insignificant conversion factor given the reported uncertainty of ±20% in monovalent ions and ±50% in divalent ions. For example, a 1.4e−3 M is equal to a 1.4004e−3 m. Sample temperatures were 5–10 °C, so we assigned a value of 7.5 °C (280.65 K) (Table 3) for the starting point in our simulations.

Critical for the ensuing model calculations is the partial pressure of CO_2 (P_{CO2}) which was estimated as 3.0e−3 bars in the WCL cell (Hecht et al., 2009b); we used this P_{CO2} in our model simulations (Table 3). Much less critical is the atmospheric pressure (P_{atm}), which we arbitrarily assigned a value of 1.0 bars (Table 3). The simulations could have been run at lower P_{atm}, but that would only marginally have affected properties such as activity coefficient (γ), density (ρ), and water activity (a_w). For example, a 1.0 m NaCl solution at 25 °C with P_{atm} = 1.0 bars has $\gamma = 0.6590$,

Table 3
Aqueous chemical compositions for the Phoenix Mission soils based on Hecht et al. (2009b), except for the calculated SO_4 and alkalinity that were estimated with the FREZCHEM model.

Ionic species	Experimental values
Na	1.4e−3 m
K	0.38e−3 m
Mg	3.3e−3 m
Ca	0.58e−3 m
Cl	0.54e−3 m
ClO_4	2.4e−3 m
SO_4	1.7e−3 m[a]
Carbonate alkalinity	3.2e−3 (equivalents/kg(H_2O))[a]
pH	7.70
P_{CO2}	3.0e−3 bars[a]
T	7.5 °C
P_{atm}	1.0 bars

[a] SO_4 and alkalinity were estimated by partitioning the excess cation charge [6.6e−3 equilvalents/kg(H_2O)] among SO_4 and alkalinity assuming t = 7.5 °C, P_{CO2} = 3.0e−3 bars, and pH = 7.70. The P_{CO2} value is not the external martian atmosphere but that inferred to have been inside the wet chemistry cells on the Phoenix Lander in equilibrium with the solution measurements.

ρ = 1.0362 g cm^{-3}, and a_w = 0.96679. The same case with P_{atm} = 0.01 bars has γ = 0.6589, ρ = 1.0361 g cm^{-3}, and a_w = 0.96679.

Missing from this dataset were concentrations for SO_4^{2-} and alkalinity. The "average" measured cation charges exceeded the measured anion charges by 6.6e−3 equivalents/kg(H$_2$O). We used the FREZCHEM model to partition this excess charge into SO_4^{2-} and alkalinity concentrations. The FREZCHEM model can calculate the system pH given the ionic concentrations, P_{CO2}, and temperature (Table 3). Our initial estimate of SO_4^{2-} = 8.0e − 4 m with alkalinity = 5.0e−3 equivalents/kg(H$_2$O) led to a model-calculated pH of 7.89. By adjusting SO_4 and alkalinity, we were able to assign SO_4 = 1.7e−3 m and alkalinity = 3.2e−3 equivalents/kg(H$_2$O) that led to a model-calculated pH = 7.70, which Hecht et al. (2009b) estimated for this system. If we assume a soil sample mass of ~1 g was added to the 25 cm^3 WCL leaching solution, this amount of soil sulfate is equivalent to (96 g/mol SO_4^{2-}) × (1.7e−3 mol SO_4^{2-}/(kg(H$_2$O))) × (0.025 kg(H$_2$O)) = 0.4 wt.% sulfate. This is considerably less than the 5–8 wt.% sulfate inferred in soils elsewhere on Mars from elemental abundance (e.g., Yen et al., 2005). Also, a paper currently in submission by Kounaves et al. (soluble sulfate in the martian soil at the Phoenix landing site) has made an estimate of the soluble SO_4 concentration in the WCL cell, which they calcu-

lated as 5.3e−3 m, substantially higher than our estimate of 1.7e−3 m Table 3. Also, in turn, their estimate of the soil sulfate content is ⩾1.4 wt.% compared to our estimate of 0.4 wt.%. But this Kounaves et al. paper leads to similar assemblages of solid phases during the evaporation process as we predicted in our model simulation (Fig. 8), albeit at different relative concentrations. Our simulation of mineral formation during the freezing process (Fig. 9) adds several new potential minerals to the Phoenix site. Overall, the cations of the Phoenix soils were dominated by Mg^{2+} and Na$^+$, and the anions were dominated by ClO_4^-, SO_4^{2-}, and carbonate alkalinity. The compositions given in Table 3 are the basis for our subsequent evaporation and freezing simulations.

We used the data in Table 3 to simulate evaporation of this dilute geochemistry using the fractional crystallization option (once a solid phase precipitates, it is not allowed to dissolve and reprecipitate). Equilibrium crystallization, on the other hand, allows precipitation, dissolution, and reprecipitation. In Figs. 8 (evaporation) and 9 (freezing) examples, the number of independent solid phases were 7 and 8 (includes ice), respectively, which is exactly how many solid phases that would have precipitated had we used the equilibrium option. The fractional crystallization option allowed 8 and 9 solid phases to precipitate, respectively, which
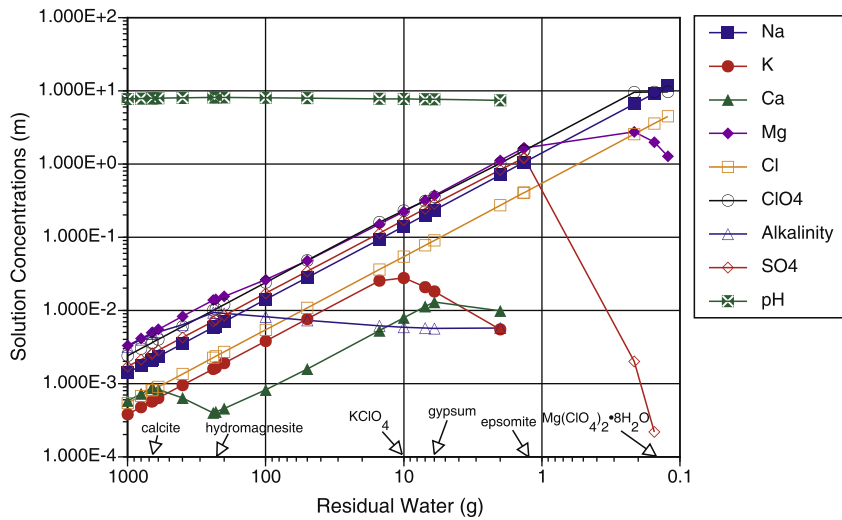

Fig. 8. The model concentrations of a Phoenix martian brine during evaporation at 280.65 K. Arrows indicate where salt phases start to precipitate.
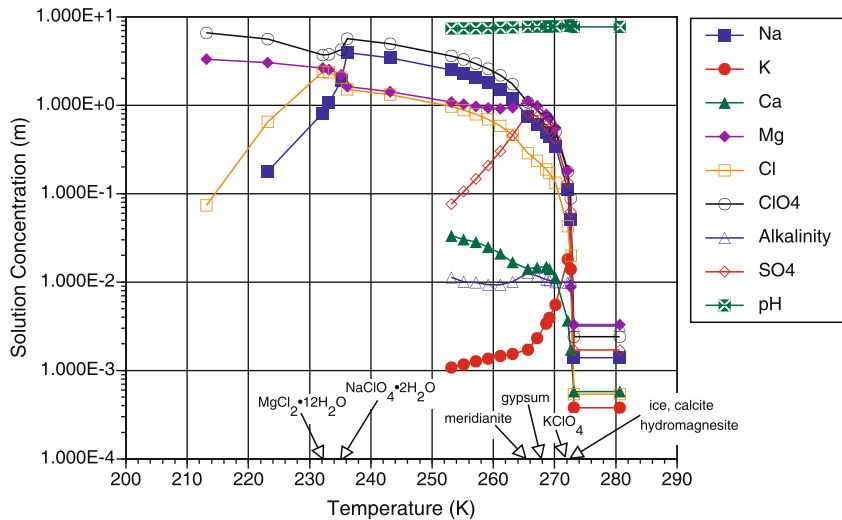

Fig. 9. The model concentrations of a Phoenix martian brine during freezing from 280.65 K to 213.15 K. Arrows indicate where salt phases start to precipitate.

increased the list of potential minerals for Mars. Given the uncertainties in the exact chemical compositions and the processes controlling mineral precipitation on Mars, it is more useful to consider a broader range of solid phases, which is what fractional crystallization provides.

Obviously, this simulation is not driven by the physico-chemical properties of today's Mars, but rather represents hypothetical environments for Mars when temperature and water were more conducive for aqueous processes, which must have happened in the past. On the other hand, there are evaluations of the potential for aqueous phases at the Phoenix site today (e.g., Hanley et al., 2009; Chevrier et al., 2009), but this will not be the focus of our Mars application. Also our simulations do not imply that salts in these Phoenix soils formed in situ. There are abundant aeolian processes on Mars. While carbonates indicate a past interaction with liquid water (Boynton et al., 2009a,b), these interactions could have occurred elsewhere in the distant past, with carbonates and other salts added to the Phoenix sites through aeolian processes. Again, one of our main objectives was to simply identify the salts present in these soils, but not how they may have originated, here or elsewhere.

Because $CaCO_3$ (probably calcite) minerals are likely present in these Phoenix soils (Boynton et al., 2009a,b; Kounaves et al., 2009a,b; Smith, 2009a; Smith et al., 2009b), we removed dolomite and magnesite from the mineral database. Had we retained insoluble dolomite and magnesite, they would likely have precipitated rather than $CaCO_3$, which runs counter to current martian understanding, at least with respect to the Phoenix site. Removal of dolomite and magnesite in simulations is commonly done with Earth seawater (e.g., Marion, 2001; Marion and Kargel, 2008), where $CaCO_3$ is known to be the dominant carbonate that precipitates from seawater. Under these mineral assumptions, the first salts to precipitate were calcite and hydromagnesite (Fig. 8). This initially caused Ca concentrations to decrease, until hydromagnesite became the dominant sink for carbonate minerals. Later, $KClO_4$ and gypsum began precipitating. The pH of this system began at 7.70 (Table 3), rose to 8.11 where hydromagnesite began precipitating, and then slowly dropped to 7.39 by the time the residual water reached 2 g (Fig. 8). Because of the minerals that precipitated, the Ca, K, and alkalinity concentrations dropped to much lower values than Na, Mg, Cl, ClO_4, and SO_4 (Fig. 8). By the time the residual water reached 2 g, 96.6% of Ca, 97.1% of K, and 99.87% of alkalinity contents (moles) had precipitated. Because minor constituents can lead to mathematical convergence problems with major constituents, we removed the minor constituents from model simulations for lower water contents. For example, Ca was set equal to 0.0 m by assuming the residual Ca would have precipitated as gypsum; and equivalent amounts of SO_4 were also removed to balance the Ca removed. Similarly, K was assumed to have precipitated as $KClO_4$, and the residual alkalinity was removed as hydromagnesite.

At residual water values below 2 g, the first salt to precipitate was epsomite ($MgSO_4 \cdot 7H_2O$), which caused a precipitous drop in solution-phase SO_4 concentrations (Fig. 8). At a residual water <0.2 g, the $Mg(ClO_4)_2 \cdot 8H_2O$ salt started to precipitate. Had we carried this simulation to residual water <0.1 g, eventually $NaClO_4 \cdot H_2O$ and NaCl would have precipitated.

We took the data from Table 3 at 280.65 K and decreased the temperature to 213.15 K (−60 °C) in our freezing simulation (Fig. 9). Because this solution was dilute, nothing happened to the constituents between 280.65 and 273.15 K (Fig. 9); but by the time the temperature dropped to 272.65 K (−0.5 °C), 972.85 g of the original 1000 g of water have turned to ice. Note the sharp rise in all salt concentrations when ice formed (Fig. 9). Ice, calcite, and hydromagnesite started precipitating by 272.65 K. Between 272 and 265 K, $KClO_4$, gypsum, and meridianite ($MgSO_4 \cdot 11H_2O$)

began precipitating. The initial pH at 280.65 K was 7.70 (Table 3), which rose to a high value of 8.01 at 272.65 K where the solution started to freeze, then dropped slowly to 7.37 at 253.15 K.

We ran the initial simulation down to 253.15 K. At that point, 99.84% of K had precipitated as $KClO_4$, 96.8% of Ca had precipitated as calcite and gypsum, 99.84% of alkalinity had precipitated as calcite and hydromagnesite, and 97.5% of SO_4 had precipitated as gypsum and meridianite. So we removed these minor constituents at 253.15 K to facilitate simulations at lower temperatures for the major species: Na, Mg, Cl, and ClO_4. Another reason for removing alkalinity is that this chemistry is only valid in FREZCHEM down to ≈251 K (−22 °C) (Marion, 2001).

At lower temperatures, $NaClO_4 \cdot 2H_2O$ and $MgCl_2 \cdot 12H_2O$ began precipitating (Fig. 9). The last salt to precipitate was $Mg(ClO_4)_2 \cdot 8H_2O$. At 213.15 K, Mg (=3.32 m) and ClO_4 (=6.57 m) were the dominant ions remaining in solution. A pure $Mg(ClO_4)_2$ solution has a eutectic of 3.48 m at 204.95 K (Fig. 3). So our simulation is approaching the eutectic for $Mg(ClO_4)_2 \cdot 8H_2O$–ice along the "Ice" line of Fig. 3. For comparative purposes between Figs. 8 and 9, the amount of water that remains in solution at 213.15 and 253.15 K in Fig. 9 were 0.095 g and 0.56 g H_2O. The 0.095 g at 213.15 (Fig. 9) is slightly off the lower limit of Fig. 8 (0.1 g water).

6. Discussion

So what, if anything, do these simulations convey about Mars? One of the obvious outcomes is that several identical minerals formed during evaporation at 280.65 K and freezing between 280.65 and 213.15 K (calcite, hydromagnesite, gypsum, $KClO_4$, and $Mg(ClO_4)_2 \cdot 8H_2O$) (Figs. 8 and 9). On the other hand, there were some differences in mineral formation between evaporation and freezing. During evaporation at 280.65 K, epsomite, $NaClO_4 \cdot H_2O$, and NaCl formed (Fig. 8), while during the freezing process, meridianite, $NaClO_4 \cdot 2H_2O$, and $MgCl_2 \cdot 12H_2O$ formed (Fig. 9). This is because highly hydrated salts such as meridianite ($MgSO_4 \cdot 11H_2O$) and $MgCl_2 \cdot 12H_2O$ tend to be unstable at higher temperatures. While they easily form at subzero temperatures, they can readily decompose at temperatures above freezing. The transition from meridianite to epsomite occurs according to model calculations at 273.76 K (Marion and Farren, 1999), while the transitions among $MgCl_2 \cdot 6H_2O$, $MgCl_2 \cdot 8H_2O$, and $MgCl_2 \cdot 12H_2O$ occur at subzero temperatures (Spencer et al., 1990). Incongruent melting of these highly hydrated salts could cause vug formations in martian rocks, as has been suggested for rover images of sedimentary rocks (Squyres et al., 2004, 2006; Clark et al., 2005; Tosca et al., 2005; Marion et al., 2008).

Because $KClO_4$ is a relatively insoluble perchlorate salt, it readily formed during both evaporation (Fig. 8) and freezing (Fig. 9) processes. In both cases, all of the K likely precipitated as $KClO_4$. This is similar to what models predict for K in the presence of low pH, Fe(III) chemistries that lead to rapid depletion of K due to jarosite [$KFe_3(SO_4)_2(OH)_6$] formation (Marion et al., 2009b). None of the reports on Phoenix Mission perchlorates (Catling et al., 2009a,b; Fisher et al., 2008, 2009; Hecht et al., 2008, 2009a,b; Kounaves et al., 2009a,b) mention the role of $KClO_4$, which seems important based on our model calculations. For example, in both cases (Figs. 8 and 9), it is likely that all K would precipitate as $KClO_4$, which implies 15.8% [(0.38e−3 m/2.40e −3 m) × 100] of perchlorate. During evaporation, 35.8% of perchlorate precipitated with Na, and 48.4% with Mg. During freezing, 58.3% of perchlorate precipitated with Na, and 24.8% with Mg. On the other hand, $Ca(ClO_4)_2 \cdot 6H_2O$ has been mentioned as a potential perchlorate on Mars (Hecht et al., 2009b). But our model calculations indicate that this is highly unlikely for, at least, the Phoenix

site. That is because insoluble calcite and gypsum are much more likely to serve as sinks for Ca than highly soluble Ca(ClO$_4$)$_2$·6H$_2$O. A similar argument was made discrediting highly soluble CaCl$_2$·6H$_2$O formation on Mars (Marion et al., 2009a).

There were nuanced differences among Na–Mg precipitation with Cl–ClO$_4$ ions. Mg(ClO$_4$)$_2$·8H$_2$O precipitated earlier than Na-ClO$_4$·H$_2$O during evaporation at 280.65 K (Fig. 8); and NaClO$_4$·2H$_2$O precipitated earlier than Mg(ClO$_4$)$_2$·8H$_2$O at subzero temperatures (Fig. 9). Also, NaCl is the dominant sink for Cl at higher temperatures (Fig. 8), while MgCl$_2$·12H$_2$O is the dominant Cl sink at subzero temperatures (Fig. 9). Fractional crystallization that does not allow precipitates to dissolve and reprecipitate seems to favor the initial precipitate (less soluble solid phase), which for evaporation led to 48.4% of perchlorates precipitating as Mg(ClO$_4$)$_2$·8H$_2$O, and for freezing led to 58.3% of perchlorates precipitating as Na-ClO$_4$·2H$_2$O (Fig. 9) (see discussion above). Interestingly, despite Mg being the dominant cation, it did not become the dominant perchlorate salt at subzero temperatures. The bottom line is that precipitation of salts is a function of equilibrium constants and their temperature dependence. These results seem largely to depend on the more rapid decrease in the solubility of NaClO$_4$ salts with temperature (Fig. 1) than is the case for Mg(ClO$_4$)$_2$ salts (Fig. 3).

The simulations of martian perchlorate chemistries rest on the assumption that perchlorates interacted with water. On Earth, there is evidence that perchlorates likely formed through atmospheric processes (Catling et al., 2009a,b; Michalski et al., 2004; Trumpolt et al., 2005), which could also be the case for Mars (Catling et al., 2009a,b). But given the prevalence of aqueous salts in these martian soils and the 5 cm depth to ice at the Phoenix WCL sample site (Kounaves et al., 2009a,b), it is highly likely that perchlorates would have interacted with water on Mars at some time in the past.

The results of this modeling effort help constrain speculation about the minerals that likely occur in the Mars Phoenix soils. But the results rest largely on the chemical compositions that were measured and used in our simulations (Table 3). For example, there are large error bars associated with monovalents (±20%) and divalents (±50%) in Table 3. Also, the Kounaves et al., paper (soluble sulfate in the martian soil at the Phoenix landing site) cited earlier that is currently in submission estimated a much higher SO$_4$ concentration (5.3e−3 m) than that used in our study (1.7e−3 m, Table 3). However, this SO$_4$ difference had no effect on the prediction of exactly which solid phases would likely have precipitated during the evaporation process. Whether evaporation or freezing were the dominant processes that led to mineral precipitation is still an open question. But the model results provide a guide to future discrimination between these two possibilities. If salts such as halite and epsomite are found on Mars, this would favor evaporative processes at temperatures >0 °C (Fig. 8). If salts such as NaClO$_4$·2H$_2$O, MgCl$_2$·12H$_2$O, and meridianite are found on Mars, this would favor freezing processes at subzero temperatures (Fig. 9). When soil samples are returned from Mars or mineralogy is defined in situ by X-ray diffraction, we will be able to more tightly constrain the geochemical history of Mars, in part, due to experimental processes, and, in part, due to modeling efforts.

Acknowledgments

References

Apelblat, A., Manzurola, E., 2007. The vapour pressures over saturated aqueous solutions of sodium and potassium acetates, chlorates, and perchlorates. J. Chem. Thermodyn. 39, 1176–1181.

Besley, L.M., Bottomley, G.A., 1969. The water vapour equilibria over magnesium perchlorate hydrates. J. Chem. Thermodyn. 1, 13–19.

Boynton, W.V., and 13 colleagues, 2009a. Evidence for calcium carbonate at the Mars Phoenix landing site. Science 325, 61–64.

Boynton, W.V., Ming, D.W., Sutter, B., Arvidson, R.E., Hoffmann, J., Niles, P.B., Smith, P., Phoenix Science Team, 2009b. Evidence for calcium carbonate at the Phoenix landing site. 40th Lunar Planet. Sci. Conf., Houston, TX. Abstract #2434.

Catling, D.C., 1999. A chemical model for evaporates on early Mars: Possible sedimentary tracers of the early climate and implications for exploration. J. Geophys. Res. 104, 16453–16469.

Catling, D.C., Claire, M.W., Quinn, R.C., Zahnle, K.J., Clark, B.C., Kounaves, S., Hecht, M.H., 2009a. Possible atmospheric origins of perchlorate on Mars. 40th Lunar Planet. Sci. Conf., Houston, TX. Abstract #1567.

Catling, D.C., Claire, M.W., Zahnle, K.J., Quinn, R.C., Clark, B.C., Hecht, M.H., Kounaves, S., 2009b. Atmospheric origins of perchlorate on Mars and in the Atacama. J. Geophys. Res.. doi:10.1029/2009JE003425.

Chan, C.-Y., Khoo, K.H., 1988. Calculation of activities and solubilities of alkali metal perchlorates at high ionic strengths in multicomponent aqueous systems. J. Soln. Chem. 17, 547–567.

Chevrier, V.F., Hanley, J., Altheide, T.S., 2009. Stability of perchlorate hydrates and their liquid solutions at the Phoenix landing site, Mars. Geophys. Res. Lett. 36. L10202. 10.1029/2009GL037497.

Chretien, A., Kohlmuller, R., 1966. Perchlorate de sodium. In: Pascal, P. (Ed.), Nouveau Traite de Chimie Minerale, Sodium and Lithium, vol. 2(#1). Masson & Cie, Paris, pp. 344–354.

Clark, B.C., and 23 colleagues, 2005. Chemistry and mineralogy of outcrops at Meridiani Planum. Earth Planet. Sci. Lett. 240, 73–94.

Coates, J.D., Achenbach, L.A., 2004. Microbial perchlorate reduction: Rocket-fuelled metabolism. Nat. Rev./Microbiol. 2, 569–580.

Dobrynina, T.A., Chernyshova, A.M., Akhapkina, N.A., Rosolovskii, V.Ya., 1980. Fusion diagram of the magnesium perchlorate–water system. Russ. J. Inorg. Chem. 25, 1237–1239.

Dobrynina, T.A., Akhapkina, N.A., Rosolovskii, V.Ya., 1984. The fusion diagram of the calcium perchlorate–water system. Russ. J. Inorg. Chem. 29, 1043–1045.

Fisher, D.A., Hecht, M.H., Kounaves, S., Catling, D., 2008. Effects of deliquescent salts in soils of polar Mars on the flow of the Northern Ice Cap. Eos Trans. AGU (Fall Meet. Suppl.) 89(53). Abstract U11B-0019.

Fisher, D.A., Hecht, M.H., Kounaves, S., Catling, D., 2009. Perchlorate found by Phoenix could provide a mobile brine sludge at the bed of Mars northern ice cap that would allow flow with very low basal temperatures: Possible mechanism for water table re-charge. Lunar Planet. Sci. Conf., Houston, TX. Abstract #2281.

Hanley, J., Chevrier, V.F., Altheide, T.S., 2009. Low temperature aqueous perchlorate solutions on the surface of Mars. 40th Lunar Planet. Sci. Conf., Houston, TX. Abstract #1380.

Hecht, M.H., and 10 colleagues, 2008. Discovery of perchlorate at the Phoenix landing site. Eos Trans. AGU (Fall Meet. Suppl.) 89(53). Abstract U14A-04.

Hecht, M.H., and 10 colleagues, 2009a. Perchlorate in martian soil: Evidence and implications. 40th Lunar Planet. Sci. Conf., Houston, TX. Abstract #2420.

Hecht, M.H., and 13 colleagues, 2009b. Detection of perchlorate and the soluble chemistry of martian soil at the Phoenix lander site. Science 325, 64–67.

Klingelhöfer, G., and 18 colleagues, 2004. Jarosite and hematite at Meridiani Planum from Opportunity's Mössbauer Spectrometer. Science 306, 1740–1745.

Königsberger, E., Schmidt, P., Gamsjäger, H., 1992. Solid–solute phase equilibria in aqueous solution. VI. Solubilities, complex formation, and ion-interaction parameters for the system Na$^+$–Mg^{2+}–ClO$_4^-$–CO$_2$–H$_2$O at 25 °C. J. Soln. Chem. 21, 1195–1216.

Kounaves, S.P., Catling, D., Clark, B.C., DeFlores, L., Gospodinova, K., Hecht, M.H., Kapit, J., Ming, D.W., Quinn, R.C., Phoenix Science Team, 2009a. Aqueous carbonate chemistry of the martian soil at the Phoenix landing site. 40th Lunar Planet. Sci. Conf., Houston, TX. Abstract #2489.

Kounaves, S.P., and 15 colleagues, 2009b. The wet chemistry experiments on the 2007 Phoenix Mars Scout Lander Mission: Data analysis and results. J. Geophys. Res. doi:10.1029/2009JE003424.

Krumgalz, B.S., Pogorelsky, R., Pitzer, K.S., 1996. Volumetric properties of single aqueous electrolytes from zero to saturation concentration at 298.15 K represented by Pitzer's ion-interaction equations. J. Phys. Chem. Ref. Data 25, 663–689.

Lide, D.R., 1994. Handbook of Chemistry and Physics, 75th ed. CRC Press, Boca Raton, FL, 2411 pp.

Linke, W.F., 1958. Solubilities of Inorganic and Metal Organic Compounds, vol. 1, fourth ed.. Am. Chem. Soc., Washington, DC, 1487 pp.

Linke, W.F., 1965. Solubilities of Inorganic and Metal Organic Compounds, vol. II, fourth ed.. Am. Chem. Soc., Washington, DC, 1914 pp.

Marion, G.M., 2001. Carbonate mineral solubility at low temperatures in the Na–K–Mg–Ca–H–Cl–SO$_4$–OH–HCO$_3$–CO$_3$–CO$_2$–H$_2$O system. Geochim. Cosmochim. Acta 65, 1883–1896.

Marion, G.M., 2002. A molal-based model for strong acid chemistry at low temperatures (<200–298 K). Geochim. Cosmochim. Acta 66, 2499–2516.

Marion, G.M., 2007. Adapting molar data (without density) for molal models. Comput. Geosci. 33, 829–834.

Marion, G.M., Farren, R.E., 1999. Mineral solubilities in the Na–K–Mg–Ca–Cl–SO$_4$–H$_2$O system: A re-evaluation of the sulfate chemistry in the Spencer–Møller–Weare model. Geochim. Cosmochim. Acta 63, 1305–1318.

Marion, G.M., Kargel, J.S., 2008. Cold Aqueous Planetary Geochemistry with FREZCHEM: From Modeling to the Search for Life at the Limits. Springer, Berlin, 251 pp.

Marion, G.M., Catling, D.C., Kargel, J.S., 2003. Modeling aqueous ferrous iron chemistry at low temperatures with application to Mars. Geochim. Cosmochim. Acta 67, 4251–4266.

Marion, G.M., Kargel, J.S., Catling, D.C., Jakubowski, S.D., 2005. Effects of pressure on aqueous chemical equilibria at subzero temperatures with applications to Europa. Geochim. Cosmochim. Acta 69, 259–274.

Marion, G.M., Catling, D.C., Kargel, J.S., 2006. Modeling gas hydrate equilibria in electrolyte solutions. CALPHAD 30, 248–259.

Marion, G.M., Kargel, J.S., Catling, D.C., 2008. Modeling ferrous–ferric iron chemistry with application to martian surface geochemistry. Geochim. Cosmochim. Acta 72, 242–266.

Marion, G.M., Catling, D.C., Kargel, J.S., 2009a. Br/Cl portioning in chloride minerals in the Burns formation on Mars. Icarus 200, 436–445.

Marion, G.M., Crowley, J.K., Thomson, B.J., Kargel, J.S., Bridges, N.T., Hook, S.J., Baldridge, A., Brown, A.J., Ribeiro da Luz, B., Souza Filho, C.R., 2009b. Modeling aluminum–silicon chemistries and application to Australian acidic playa lakes as analogues for Mars. Geochim. Cosmochim. Acta 73, 3493–3511.

Michalski, G., Böhlke, J.K., Thiemens, M., 2004. Long-term atmospheric deposition as the source of nitrate and other salts in the Atacama Desert, Chile: New evidence from mass-independent oxygen isotopic compositions. Geochim. Cosmochim. Acta 68, 4023–4038.

Millero, F.J., 2001. Physical Chemistry of Natural Waters. Wiley-Interscience, New York, 654 pp.

Morse, J.W., Marion, G.M., 1999. The role of carbonates in the evolution of early martian oceans. Am. J. Sci. 299, 738–761.

Navrotsky, A., Lázár, F.F., Drouet, C., 2005. Jarosite stability on Mars. Icarus 176, 250–253.

Nicholson, D.E., Felsing, W.A., 1950. The determination of the activity coefficients of the alkaline earth and magnesium perchlorates from freezing point data. J. Am. Chem. Soc. 72, 4469–4471.

Orris, G.J., Harvey, G.J., Tsui, D.T., Eldrige, J.E., 2003. Preliminary analyses for perchlorate in selected natural materials and their derivative products. Open-file Report 03-314, US Geol. Surv.

Pestova, O.N., Myund, L.A., Khripun, M.K., Prigaro, A.V., 2005. Polythermal study of the systems M(ClO$_4$)$_2$–H$_2$O (M^{2+} = Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}). Russ. J. Appl. Chem. 78, 409–413.

Pitzer, K.S., 1991. Ion interaction approach: Theory and data correlation. In: Pitzer, K.S. (Ed.), Activity Coefficients in Electrolyte Solutions, second ed. CRC Press, Boca Raton, pp. 75–153.

Pitzer, K.S., 1995. Thermodynamics, third ed. McGraw-Hill, New York, 626 pp.

Robinson, R.A., Stokes, R.H., 1970. Electrolyte Solutions, second ed. Butterworths, London (revised).

Smith, P.H., 2009a. Water at the Phoenix landing site. 40th Lunar Planet. Sci. Conf., Houston, TX. Abstract #1329.

Smith, P.H., and 35 colleagues, 2009b. H$_2$O at the Phoenix landing site. Science 325, 58–61.

Spencer, R.J., Moller, N., Weare, J.H., 1990. The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na–K–Ca–Mg–Cl–SO$_4$–H$_2$O system at temperatures below 25 °C. Geochim. Cosmochim. Acta 54, 575–590.

Squyres, S.W., and 18 colleagues. 2004. In situ evidence for an ancient aqueous environment at Meridiani Planum, Mars. Science 306, 1709–1714.

Squyres, S.W., and 17 colleagues, 2006. Two years at Meridiani Planum: Results from the Opportunity rover. Science 313, 1403–1407.

Tosca, N.J., McLennan, S.M., Clark, B.C., Grotzinger, J.P., Hurowitz, J.A., Knoll, A.H., Schröder, C., Squyres, S.W., 2005. Geochemical modeling of evaporation processes on Mars: Insight from the sedimentary record at Meridiani Planum. Earth Planet. Sci. Lett. 240, 122–148.

Trumpolt, C.W., Crain, M., Cullison, G.D., Flanagan, S.J.P., Siegel, L., Lathrop, S., 2005. Perchlorate: Sources, uses, and occurrences in the environment. Remediat. J. Environ. Cleanup Costs Technol. Tech. 16, 65–89.

Yen, A.S., and 35 colleagues, 2005. An integrated view of the chemistry and mineralogy of martian soils. Nature 436, 49–54.