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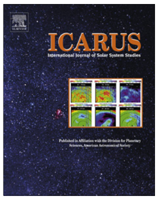

Modeling salt precipitation from brines on Mars: Evaporation versus freezing origin for soil salts

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

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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–SO_4–ClO_4–H_2O 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–ClO_4, Ca–Cl–ClO_4, and Na–SO_4–ClO_4 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 $KClO_4$, hydromagnesite ($3MgCO_3{\cdot}Mg(OH)_2{\cdot}3H_2O$), gypsum ($CaSO_4{\cdot}2H_2O$), and epsomite ($MgSO_4{\cdot}7H_2O$), followed by dehydration of epsomite and gypsum to kieserite ($MgSO_4{\cdot}H_2O$) and anhydrite ($CaSO_4$) respectively. At low residual water contents, our model predicts the precipitation of halite (NaCl), $NaClO_4{\cdot}H_2O$, and $Mg(ClO_4)_2{\cdot}6H_2O$, whereas halite and $NaClO_4{\cdot}H_2O$ 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.% H_2O 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.% H_2O is held in hydrated salts if WCL solutions freeze. Given minimum water contents in Mars soils of 1.5–2 wt.% H_2O 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.

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 CO_2 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-

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

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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–ClO_4 never reach their eutectic in FREZCHEM and ion activity coefficients for Mg^{2+} can be in excess of 10^5, leading to significant ‘salting out’ effects for salts of Mg^{2+}. 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):

$$\begin{aligned}\phi = 1 + \frac{2}{\sum m_i}\Bigg\{&\frac{-A_\phi I^{3/2}}{1+bI^{1/2}} + \sum\sum m_c m_a(\beta^\phi_{ca} + ZC_{ca}) \\ &+ \sum\sum m_c m'_c\left(\Phi^\phi_{cc'} + \sum m_a \psi_{cc'a}\right) \\ &+ \sum\sum m_a m_{a'}\left(\Phi^\phi_{aa'} + \sum m_c \psi_{ca'a}\right)\Bigg\} \end{aligned} \tag{1}$$

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

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

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:

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

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 ($I = {\sim}20$ 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 $Ca(ClO_4)_2$, 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:

$$\begin{aligned}n_1 M_{\nu_M} X_{\nu_X} \cdot n_2 N_{\nu_N} Y_{\nu_Y} \cdot \ldots \cdot n_w H_2O \leftrightarrows n_1\nu_M M^{z_M} + n_1\nu_X X^{z_X} \\ + n_2\nu_N N^{z_N} + n_2\nu_Y Y^{z_Y} + \cdots + n_w H_2O\end{aligned} \tag{5}$$

where M and N indicate cations, X and Y indicate anions, n and ν indicate stoichiometric numbers of ions, and z indicates ion charge. For the case of a simple hydrated salt, like $NaCl{\cdot}2H_2O$, the solubility product (K) corresponding to reaction (5) is given by:

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

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 $\beta^{(0)}, \beta^{(1)}, \beta^{(2)}, C^\phi, \theta$, 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:

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

Table 1
The solubility (mol kg^{-1}) and the log solubility product (log K) for different salt phases used to fit solubility data in this study at 1 atm and 298.15 K. Unless otherwise noted, all solubilities and solubility products are taken from FREZCHEM.

Salt	Solubility (mol kg^{-1})	log K
NaCl (halite)	6.106	1.576
$NaClO_4 \cdot H_2O$	17.165[a]	2.181
Na_2SO_4 (thenardite)	4.423	−0.288
$Na_2SO_4 \cdot 10H_2O$ (mirabilite)	1.960	−1.216
KCl (sylvite)	4.789	0.898
$KClO_4$	0.149[c]	−1.982
$Ca(ClO_4)_2 \cdot 4H_2O$	7.923[b]	7.635
$CaSO_4 \cdot 2H_2O$ (gypsum)	0.015	−4.597
$MgCl_2 \cdot 6H_2O$ (bischofite)	5.810	4.627
$Mg(ClO_4)_2 \cdot 6H_2O$	4.460[b]	5.593
$MgSO_4 \cdot 7H_2O$ (epsomite)	3.054	−1.881

[a] From Chan et al. (1995); $NaClO_4 \cdot H_2O$ ($n = 25$, $\sigma = 0.01$); n is the number of samples and σ is the standard deviation.
[b] From Chan et al. (1989); $Ca(ClO_4)_2 \cdot 4H_2O$ ($n = 11$, $\sigma = 0.01$), $Mg(ClO_4)_2 \cdot 6H_2O$ ($n = 19$, $\sigma = 0.02$).
[c] From Chan and Khoo (1988); $KClO_4$ ($n = 12$, $\sigma = 0.001$).

where K_{calc} is the solubility product in Table 1 for the salt phase, and K_{mod} is the modeled solubility product (i.e. the ion activity product) using the Pitzer equations. For ternary systems that share parameters, most often the $\theta_{\mathrm{Cl}^-,\mathrm{ClO}_4^-}$ parameter, we simultaneously fit all systems having the same parameter. All θ and ψ parameters that do not involve perchlorate are assumed to be the same as in FREZCHEM (with one exception for $\psi_{\mathrm{Na}^+,\mathrm{Mg}^{2+},\mathrm{Cl}^-}$, as described in Section 3.4). The Pitzer parameters we derive and use in our later modeling are given in Tables 2–4.

3. Results

3.1. (Na,Ca,Mg)–Cl–ClO$_4$ systems

The Na–Cl–ClO$_4$ system is determined by the $\psi_{\mathrm{Na}^+,\mathrm{Cl}^-,\mathrm{ClO}_4^-}$ and $\theta_{\mathrm{Cl}^-,\mathrm{ClO}_4^-}$ parameters. Our model predicts experimental solubility data well in this system (Fig. 1A and Table 5), whereas FREZCHEM predicts an extremely large 'salting in' effect (when the ion activity coefficient decreases) for both $NaClO_4 \cdot H_2O$ and NaCl, such that ion concentrations rapidly diverge to unphysical values in Na–Cl–ClO$_4$ mixtures. This is primarily due to the large negative value for the Pitzer interaction parameter $\psi_{\mathrm{Na}^+,\mathrm{Cl}^-,\mathrm{ClO}_4^-}$ in FREZCHEM (−0.0523), which is assumed to be the same as the $\psi_{\mathrm{K}^+,\mathrm{Cl}^-,\mathrm{ClO}_4^-}$ parameter (Marion et al., 2010); in contrast, the value of $\psi_{\mathrm{Na}^+,\mathrm{Cl}^-,\mathrm{ClO}_4^-}$ in our model is ten times smaller (−0.0055). Our model predictions are also consistent with experimental data on mean ion activity coefficients of NaCl in the Na–Cl–ClO$_4$ system (Lanier, 1965) (Fig. 1B), whereas FREZCHEM underestimates ion activity coefficients, leading to the large 'salting in' effect seen in Fig. 1A.

Table 2
$\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^{ϕ} parameters in the Na–K–Ca–Mg–Cl–ClO$_4$–SO$_4$ system from FREZCHEM used to fit solubility data in this study.

Salt	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}
NaCl	7.627E−02	2.804E−01	–	1.271E−03
$NaClO_4$	5.540E−02	2.755E−01	–	−1.180E−03
Na_2SO_4	2.617E−02	1.054E+00	–	2.804E−03
KCl	4.834E−02	2.104E−01	–	−8.392E−04
$KClO_4$	−1.600E−01	1.500E−01	–	–
K_2SO_4	3.795E−03	1.052E+00	–	1.485E−02
$CaCl_2$	3.041E−01	1.708E+00	–	−1.986E−03
$Ca(ClO_4)_2$	4.511E−01	1.757E+00	–	−5.001E−03
$CaSO_4$	1.154E−01	3.560E+00	−6.169E+01	3.975E−02
$MgCl_2$	3.515E−01	1.821E+00	–	6.507E−03
$Mg(ClO_4)_2$	4.961E−01	2.009E+00	–	9.581E−03
$MgSO_4$	1.265E−01	3.492E+00	−6.244E+00	5.291E−02

Table 3
θ parameters in the Na–K–Ca–Mg–Cl–ClO$_4$–SO$_4$ system used in this study.

i–j	$\theta_{i,j}$
Na–K	−9.480E−03[a]
Na–Ca	4.854E−02[a]
Na–Mg	7.000E−02[a]
K–Ca	5.642E−02[a]
K–Mg	1.167E−01[a]
Ca–Mg	1.244E−01[a]
Cl–ClO$_4$	3.099E−02
Cl–SO$_4$	4.597E−02[a]
SO$_4$–ClO$_4$	1.694E−01

[a] From FREZCHEM.

Table 4
ψ parameters in the Na–K–Ca–Mg–Cl–ClO$_4$–SO$_4$ system used in this study.

i–j–k	$\psi_{i,j,k}$
Na–Cl–ClO$_4$	−5.469E−03
K–Cl–ClO$_4$	−5.230E−02[a]
Ca–Cl–ClO$_4$	−3.913E−03
Mg–Cl–ClO$_4$	−7.618E−04
Na–Cl–SO$_4$	−1.451E−03[a]
K–Cl–SO$_4$	−3.829E−03[a]
Ca–Cl–SO$_4$	−5.444E−02[a]
Mg–Cl–SO$_4$	−1.833E−02[a]
Na–SO$_4$–ClO$_4$	−1.411E−02
K–SO$_4$–ClO$_4$	−1.411E−02[b]
Ca–SO$_4$–ClO$_4$	−8.138E−01
Mg–SO$_4$–ClO$_4$	−7.493E−02
Na–K–Cl	−2.539E−03[a]
Na–Ca–Cl	−3.297E−03[a]
Na–Mg–Cl	−2.482E−02
K–Ca–Cl	−2.856E−02[a]
K–Mg–Cl	−4.948E−02[a]
Ca–Mg–Cl	−2.381E−02[a]
Na–K–SO$_4$	3.968E−03[a]
Na–Ca–SO$_4$	−7.342E−02[a]
Na–Mg–SO$_4$	−9.911E−03[a]
K–Ca–SO$_4$	–[a]
K–Mg–SO$_4$	−1.244E−01[a]
Ca–Mg–SO$_4$	2.400E−02[a]
Na–K–ClO$_4$	1.160E−02[a]
Na–Ca–ClO$_4$	−1.178E−02
Na–Mg–ClO$_4$	−2.831E−02
K–Ca–ClO$_4$	−1.070E−02[a]
K–Mg–ClO$_4$	−1.070E−02[a]
Ca–Mg–ClO$_4$	−2.287E−02

[a] From FREZCHEM.
[b] Assumed to be the same as $\psi_{\mathrm{Na}^+,\mathrm{SO}_4^{2-},\mathrm{ClO}_4^-}$.

Solubility data in the Ca–Cl–ClO$_4$ system is restricted to two data points for $CaCl_2 \cdot 4H_2O$–$Ca(ClO_4)_2 \cdot 4H_2O$ and $CaCl_2 \cdot 4H_2O$–$CaCl_2 \cdot 6H_2O$ equilibrium; however, osmotic coefficients have been determined in this system using the isopiestic method (Robinson and Lim, 1971). Our model predictions are in much better agreement with experimental osmotic coefficient data than FREZCHEM (Fig. 1C). Similar to the Na–Cl–ClO$_4$ system, FREZCHEM underestimates measured osmotic coefficients due to a large negative value for the $\psi_{\mathrm{Ca}^{2+},\mathrm{Cl}^-,\mathrm{ClO}_4^-}$ parameter (−0.0409), which is assumed to be the same as the $\psi_{\mathrm{Ca}^{2+},\mathrm{Cl}^-,\mathrm{NO}_3^-}$ parameter in FREZCHEM (Marion et al., 2010). In contrast, our value for $\psi_{\mathrm{Ca}^{2+},\mathrm{Cl}^-,\mathrm{ClO}_4^-}$ is ten times smaller (−0.0039). The solubility data available for the Ca–Cl–ClO$_4$ system indicates that $CaCl_2 \cdot 4H_2O$ precipitates instead of $CaCl_2 \cdot 6H_2O$ at high perchlorate concentrations. FREZCHEM only includes $CaCl_2 \cdot 6H_2O$ as a solid $CaCl_2$ phase, but just above 298.15 K, $CaCl_2 \cdot 6H_2O$ transitions to three different tetrahydrate polymorphs: α, β, and γ-$CaCl_2 \cdot 4H_2O$ (Pátek et al., 2008) (Table 6). If these polymorphs

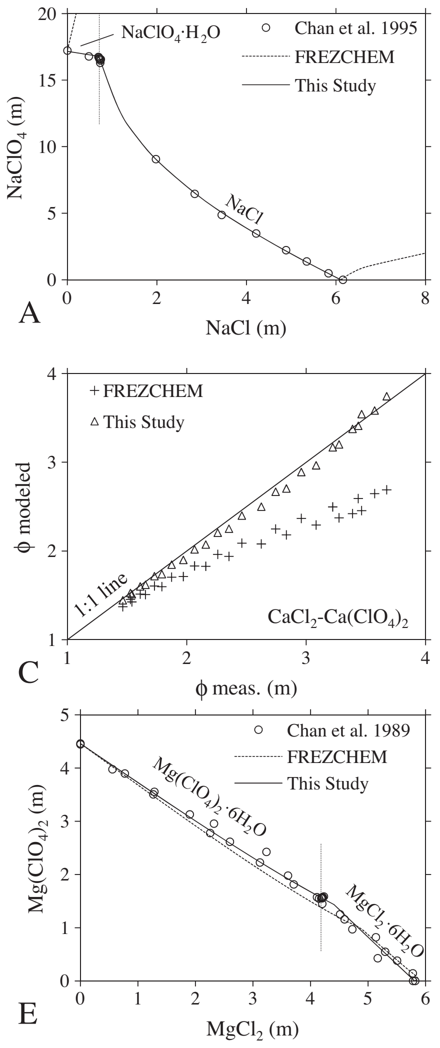

Fig. 1. Measured and modeled values at 298.15 K for (A) solubility in the Na–Cl–ClO_4 system, (B) mean activity coefficients (γ_X) of NaCl in the Na–Cl–ClO_4 system, (C) osmotic coefficients (ϕ) in the Ca–Cl–ClO_4 system, (D) solubility in the Ca–Cl–ClO_4 system, and (E) solubility in the Mg–Cl–ClO_4 system. Model results are shown for FREZCHEM and for this study. Dotted vertical lines indicate experimental points of equilibrium between two salt phases.

Table 5
Comparisons between model predictions and experimental values for selected salt equilibria. Concentrations are given in mol kg^{-1}. Note that this table does not include equilibria involving K^+ or equilibria in quaternary systems.

Salt equilibria	Model prediction		Experimental values	
$NaClO_4 \cdot H_2O \rightleftharpoons NaCl$	16.79 m $NaClO_4$	0.70 m NaCl	16.56 m $NaClO_4$	0.72 m NaCl
$CaCl_2 \cdot 4H_2O \rightleftharpoons Ca(ClO_4)_2 \cdot 4H_2O$	3.83 m $CaCl_2$	5.61 m $Ca(ClO_4)_2$	3.69 m $CaCl_2$	5.72 m $Ca(ClO_4)_2$
$CaCl_2 \cdot 4H_2O \rightleftharpoons CaCl_2 \cdot 6H_2O$	1.78 m $CaCl_2$	6.85 m $Ca(ClO_4)_2$	1.21 m $CaCl_2$	7.26 m $Ca(ClO_4)_2$
$MgCl_2 \cdot 6H_2O \rightleftharpoons Mg(ClO_4)_2 \cdot 6H_2O$	4.42 m $MgCl_2$	1.42 m $Mg(ClO_4)_2$	4.18 m $MgCl_2$	1.57 m $Mg(ClO_4)_2$
$Na_2SO_4 \rightleftharpoons Na_2SO_4 \cdot 10H_2O$	1.08 m Na_2SO_4	4.32 m $NaClO_4$	1.07 m Na_2SO_4	4.27 m $NaClO_4$
$Na_2SO_4 \cdot 10H_2O \rightleftharpoons NaClO_4 \cdot H_2O$	0.06 m Na_2SO_4	17.17 m $NaClO_4$	0.06 m Na_2SO_4	17.23 m $NaClO_4$
$MgSO_4 \cdot 7H_2O \rightleftharpoons Mg(ClO_4)_2 \cdot 6H_2O$	0.09 m $MgSO_4$	4.41 m $Mg(ClO_4)_2$	0.17 m $MgSO_4$	4.36 m $Mg(ClO_4)_2$
$NaClO_4 \cdot H_2O \rightleftharpoons Ca(ClO_4)_2 \cdot 4H_2O$	2.04 m $NaClO_4$	7.83 m $Ca(ClO_4)_2$	–	–
$Mg(ClO_4)_2 \cdot 6H_2O \rightleftharpoons NaClO_4 \cdot H_2O$	3.89 m $Mg(ClO_4)_2$	5.93 m $NaClO_4$	3.11 m $Mg(ClO_4)_2$	7.87 m $NaClO_4$
$Mg(ClO_4)_2 \cdot 6H_2O \rightleftharpoons Ca(ClO_4)_2 \cdot 4H_2O$	0.13 m $Mg(ClO_4)_2$	7.78 m $Ca(ClO_4)_2$	0.17 m $Mg(ClO_4)_2$	7.5 m $Ca(ClO_4)_2$

are included in our model, then our model predicts that α-$CaCl_2 \cdot 4H_2O$ precipitates. Our model prediction for α-$CaCl_2 \cdot 4H_2O$–$Ca(ClO_4)_2 \cdot 4H_2O$ equilibrium is close to the experimental measurement, whereas our model prediction for α-$CaCl_2 \cdot 4H_2O$–$CaCl_2 \cdot 6H_2O$ equilibrium differs somewhat from the experimental value (Table 5 and Fig. 1D). We note that concentrated $CaCl_2$ solutions are difficult to model with the Pitzer equations due to the formation of $CaCl^+$ ion pairs (Phutela and Pitzer, 1983; Rard and Clegg,

Table 6
Solubilities (m) and log solubility products (log K) calculated using FREZCHEM for different $CaCl_2$ salts at 298.15 K, taken from the critical analysis of Pátek et al. (2008).

Salt	Solubility (mol kg^{-1})	log K
$CaCl_2 \cdot 6H_2O$	7.425	3.8026
α-$CaCl_2 \cdot 4H_2O$	8.478	5.3878
β-$CaCl_2 \cdot 4H_2O$	9.415	5.7155
γ-$CaCl_2 \cdot 4H_2O$	9.773	5.8225

1997), so we expect some misfit in our model for the Ca–Cl–ClO_4 system.

For the Mg–Cl–ClO_4 system, both our model predictions and the original FREZCHEM parameterization are in reasonable agreement with average experimental values (Table 5).

3.2. (Na,Ca,Mg)–SO_4–ClO_4 systems

Equilibria in the ternary Na–SO_4–ClO_4 and Mg–SO_4–ClO_4 systems are determined by the $\theta_{SO_4^{2-},ClO_4^-}$, $\psi_{Na^+,SO_4^{2-},ClO_4^-}$, and $\psi_{Mg^{2+},SO_4^{2-},ClO_4^-}$ parameters. We fit the $\theta_{SO_4^{2-},ClO_4^-}$ and $\psi_{Na^+,SO_4^{2-},ClO_4^-}$ parameters using only solubility data from the Na–SO_4–ClO_4 system, excluding data from the Mg–SO_4–ClO_4 system due to the probable formation of $MgSO_4^0$ ion pairs, as discussed below. In the Na–SO_4–ClO_4 system, our model predictions for Na_2SO_4–$Na_2SO_4{\cdot}10H_2O$ and Na_2SO_4–$NaClO_4{\cdot}H_2O$ equilibrium are in excellent agreement with experimental data (Fig. 2A and Table 5).

In the Mg–SO_4–ClO_4 system, our model predictions underestimate salt concentrations and are little better than model predictions in FREZCHEM (Fig. 2B and Table 5). The difficultly with modeling the Mg–SO_4–ClO_4 system is likely due to the formation of $MgSO_4^0$ ion pairs in solution. The formation of $MgSO_4^0$ ion pairs is given by:

$$Mg^{2+} + SO_4^{2-} \leftrightarrows MgSO_4^0 \tag{8}$$

with a solubility product of:

$$K_{MgSO_4^0} = \frac{a_{MgSO_4^0}}{a_{Mg^{2+}}a_{SO_4^{2-}}} = \frac{\gamma_{MgSO_4^0}}{\gamma_{Mg^{2+}}\gamma_{SO_4^{2-}}}\frac{m_{MgSO_4^0}}{m_{Mg^{2+}}m_{SO_4^{2-}}} \tag{9}$$

In pure $MgSO_4$ solutions, the Pitzer equations implicitly account for $MgSO_4^0$ ion pairs in the binary $\beta^{(2)}$ term (Pitzer and Mayorga, 1974). However, in $MgSO_4$–$Mg(ClO_4)_2$ mixtures, the formation of $MgSO_4^0$ ion pairs should be much more extensive than in pure $MgSO_4$ solutions due to higher Mg^{2+} activity coefficients in $Mg(ClO_4)_2$ solutions. For example, the mean ion activity coefficient of saturated $MgSO_4$ (3.05 m) is 0.05, whereas a 3.05 m $Mg(ClO_4)_2$ solution has a mean ion activity coefficient of 9.3. The large increase in Mg^{2+} activity coefficients with increasing perchlorate concentration will drive the reaction in Eq. (8) forward, forming $MgSO_4^0$ ion pairs. Given that the Pitzer model often performs poorly in systems with extensive ion-pairing (Phutela and Pitzer, 1983; Rard and Clegg, 1997), a more accurate representation of $MgSO_4{\cdot}7H_2O$ solubility in $Mg(ClO_4)_2$ solutions may only be possible if $MgSO_4^0$ ion pairs are explicitly accounted for.

Solubilities in the ternary Ca–SO_4–ClO_4 system have not been measured experimentally, but a number of studies have investigated gypsum ($CaSO_4{\cdot}2H_2O$) solubility in quaternary and quinary systems (Elgquist and Wedborg, 1975; Kalyanaraman et al., 1973a,b; Nakayama, 1971; Nilsson et al., 1958). Using the ternary parameters determined above for Na–SO_4–ClO_4, Na–Cl–ClO_4, and Ca–Cl–ClO_4 systems, we simultaneously fit all quaternary and quinary data to our Pitzer model by varying the $\psi_{Ca^{2+},SO_4^{2-},ClO_4^-}$ parameter. The resulting fits (Fig. 2C and D) are close to experimental values, whereas FREZCHEM overestimates gypsum solubility. Our fitted value for the $\psi_{Ca^{2+},SO_4^{2-},ClO_4^-}$ parameter (−0.814) is unusually large for a ternary Pitzer parameter, which are typically between ±0.001 and ±0.1. The large negative value of $\psi_{Ca^{2+},SO_4^{2-},ClO_4^-}$ is likely accounting for increased ion pairing between Ca^{2+} and SO_4^{2-}. As with the Mg–SO_4–ClO_4 system, the formation of $CaSO_4^0$ ion pairs in Ca–SO_4–ClO_4 systems would be favored by high Ca^{2+} activities in concentrated perchlorate solutions.

3.3. Ca–Na–ClO_4, Mg–Na–ClO_4, Ca–Mg–ClO_4, Na–K–ClO_4, and Mg–K–ClO_4 systems

Ternary equilibria in Ca–Na–ClO_4, Mg–Na–ClO_4, and Ca–Mg–ClO_4 systems are determined by the $\theta_{Na^+,Ca^{2+}}$, $\theta_{Na^+,Mg^{2+}}$, $\theta_{Ca^{2+},Mg^{2+}}$, $\psi_{Na^+,Ca^{2+},ClO_4^-}$, $\psi_{Na^+,Mg^{2+},ClO_4^-}$, and $\psi_{Ca^{2+},Mg^{2+},ClO_4^-}$ parameters. Because $\theta_{Na^+,Ca^{2+}}$, $\theta_{Na^+,Mg^{2+}}$, and $\theta_{Ca^{2+},Mg^{2+}}$ parameters are shared with many

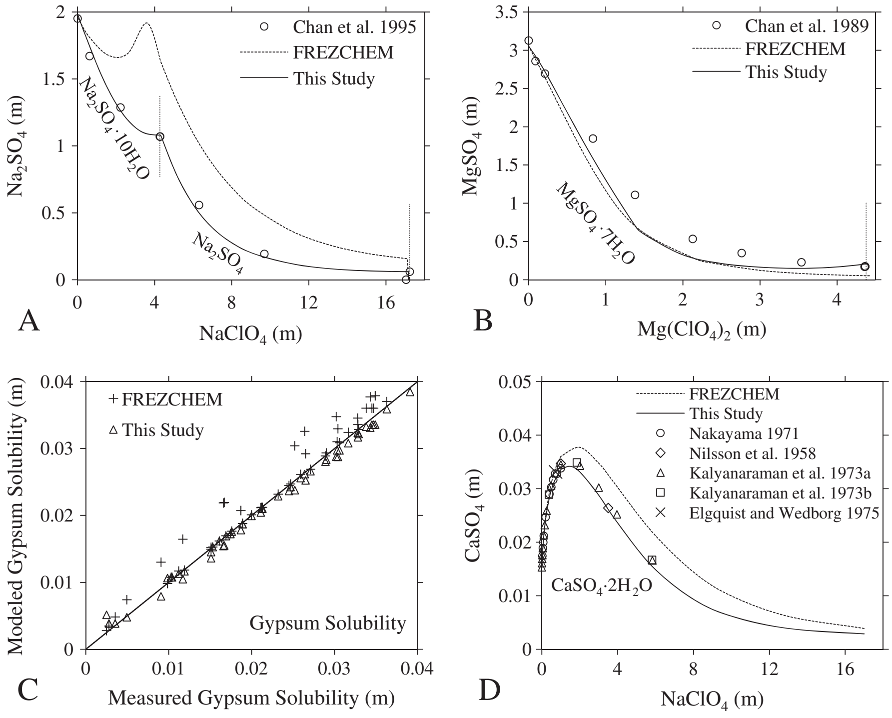

Fig. 2. Measured and modeled solubilities in the (A) ternary Na–SO_4–ClO_4 and (B) ternary Mg–SO_4–ClO_4 systems at 298.15 K. (C) Measured and modeled gypsum solubilities in the quaternary and quinary systems involving Ca–SO_4–ClO_4, and (D) gypsum solubilities in the quaternary Na–Ca–SO_4–ClO_4 system. Model results are shown for FREZCHEM and for this study. Dotted vertical lines indicate experimental points of equilibrium between two salt phases.

other salt systems in FREZCHEM, we retain the values in FREZCHEM. This allows the Pitzer parameters in this study to be integrated with other salt systems in FREZCHEM. Even if these parameters are allowed to vary, there is little improvement to the model fits.

For the Ca–Na–ClO_4 system, our model fit is similar to FREZCHEM, although both models show some misfit for equilibrium with $NaClO_4{\cdot}H_2O$ (Fig. 3A).

In the Mg–Na–ClO_4 system, both our model and FREZCHEM fit the experimental solubility data poorly, although our model is a significant improvement over FREZCHEM (Fig. 3B). If $\theta_{Na^+,Mg^{2+}}$ is also allowed to vary, there is a slight improvement to the model fit; $\theta_{Na^+,Mg^{2+}}$ changes from its FREZCHEM value of 0.07 to −0.015, and $\psi_{Na^+,Mg^{2+},ClO_4^-}$ changes to −0.0205. We recommend these values if only the Mg–Na–ClO_4 system is being modeled; however, for more complex salt mixtures the FREZCHEM $\theta_{Na^+,Mg^{2+}}$ value should be used because this parameter is used in several other ternary systems.

The difficulty with fitting the Mg–Na–ClO_4 system may be due to either high ionic strengths in this system or the formation of ion pairs. For $Mg(ClO_4)_2{\cdot}6H_2O$–$NaClO_4{\cdot}H_2O$ equilibrium, the experimental solubility data indicates that the ionic strength is 17.5 mol kg^{-1}, which is higher than the ionic strength of a saturated $Mg(ClO_4)_2$ solution (13.4 mol kg^{-1}). Because experimental data in the $Mg(ClO_4)_2$ system only extends up to I = 13.3 mol kg^{-1} (Stokes and Levien, 1946), $Mg(ClO_4)_2$ Pitzer parameters must be extrapolated into the supersaturated region in $Mg(ClO_4)_2$–$NaClO_4$ mixtures. However, the Pitzer model typically performs poorly when extrapolated beyond the limits of experimental data (Pitzer, 1991). To determine if our model fit in Fig. 3B could be improved by altering binary $Mg(ClO_4)_2$ parameters in the supersaturated region, we simultaneously fit binary and ternary data in the Na–Mg–ClO_4 system by allowing $\beta^{(0)}_{Mg^{2+},ClO_4^-}$, $\beta^{(1)}_{Mg^{2+},ClO_4^-}$, $C^{\phi}_{Mg^{2+},ClO_4^-}$, $\theta_{Na^+,Mg^{2+}}$, and $\psi_{Na^+,Mg^{2+},ClO_4^-}$ to vary. However, this did not improve our model fit to the experimental data, which indicates that high ionic strengths in the Mg–Na–ClO_4 system are not causing the misfit in our model. As an alternative explanation for the misfit in our model, there is some evidence indicating that $NaClO_4$ solutions are prone to extensive contact ion-pairing above 8 molal, whereas $Mg(ClO_4)_2$ solutions do not form contact ion pairs because the Mg^{2+} ion is strongly hydrated (Zhang and Chan, 2003). In saturated $Mg(ClO_4)_2$–$NaClO_4$ mixtures, Mg^{2+} ions will be preferentially hydrated over Na^+ ions, which would likely lead to even greater ion pairing between Na^+ and ClO_4^- than in pure $NaClO_4$ solutions. This suggests that a more accurate representation of the Na–Mg–ClO_4 system may need to account for ion pairing.

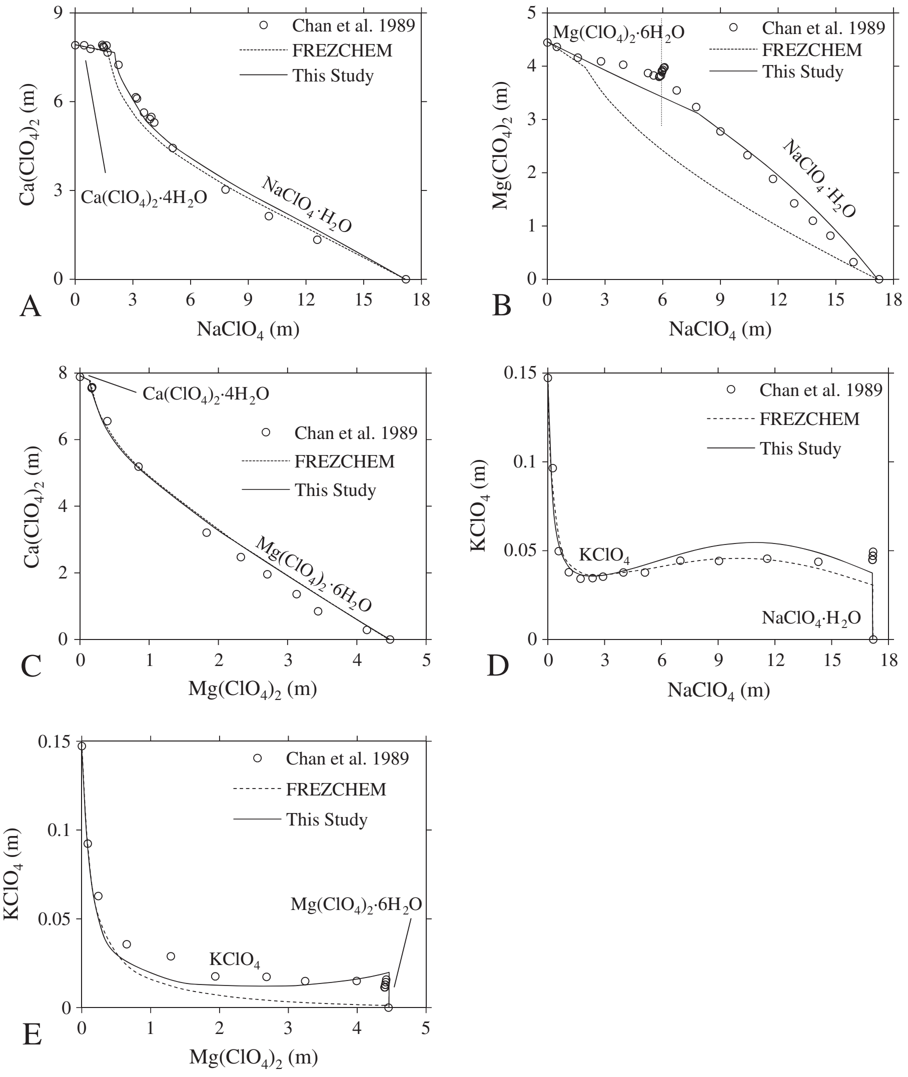

Fig. 3. Measured and modeled solubilities in the (A) Na–Ca–ClO_4, (B) Na–Mg–ClO_4, and (C) Ca–Mg–ClO_4, (D) K–Na–ClO_4, and (E) K–Mg–ClO_4 ternary systems at 298.15 K. Model results are shown for FREZCHEM and for this study. Dotted vertical lines indicate experimental points of equilibrium between two salt phases.

In the Ca–Mg–ClO_4 system, our model is similar to FREZCHEM; both models fits the experimental data well at low $Mg(ClO_4)_2$ concentrations, but the fit becomes poorer as $Mg(ClO_4)_2$ concentrations increase (Fig. 3C and Table 5).

Our model fits in the Na–K–ClO_4 and Mg–K–ClO_4 systems are generally poor, particularly at high perchlorate concentrations (Fig. 3D). Because FREZCHEM better reproduces experimental $KClO_4$ solubilities for $NaClO_4$ concentrations less than 15 m, we retain the FREZCHEM parameterization of this system in our model. In the Mg–K–ClO_4 system, our model is more consistent with experimental $KClO_4$ solubilities at high $Mg(ClO_4)_2$ concentrations; however, we find that our parameterization leads to a large salting in effect for $KClO_4$ when we model Mg–Na–K–ClO_4 mixtures. For example, the solubility of $KClO_4$ in saturated $NaClO_4$–$Mg(ClO_4)_2$ mixtures is on the order of 1 m $KClO_4$ using our parameterization. This is clearly an artifact of the model given the low experimental $KClO_4$ solubilities shown in Fig. 3D and E. Because this salting in effect does not occur in FREZCHEM, we retain the FREZCHEM parameterization for the Mg–K–ClO_4 system. As with other systems where the Pitzer model fits the experimental data poorly, the difficultly with accurately modeling ternary perchlorate systems involving K^+ is likely due to ion pairing between K^+ and ClO_4^- ions. As discussed by Pitzer and Mayorga (1973), the low solubility of $KClO_4$ and the negative value for $\beta^{(0)}_{K^+,ClO_4^-}$ (−0.16) indicates that K^+ and ClO_4^- have a tendency to form ion pairs in solution. Just as we found for the Mg–SO_4–ClO_4 and Ca–SO_4–ClO_4 systems, we expect extensive ion pairing in concentrated $Mg(ClO_4)_2$ or $Ca(ClO_4)_2$ solutions owing to the high ion activity coefficients that occur in these solutions.

3.4. Quaternary Mg–Na–Cl–ClO_4 system

Experimental investigations into quaternary systems involving perchlorate include the Mg–Na–Cl–ClO_4 and K–Mg–Cl–ClO_4 systems. We exclude experimental data from a single study on the K–Mg–Cl–ClO_4 system because the data is inconsistent with other, ternary datasets. For example, four different studies in Chan et al. (1989) agree that equilibrium between $MgCl_2{\cdot}6H_2O$ and $Mg(ClO_4)_2{\cdot}6H_2O$ in the Mg–Cl–ClO_4 system occurs at 4.18 m $MgCl_2$ and 1.57 m $Mg(ClO_4)_2$; however, experimental data in the K–Mg–Cl–ClO_4 system indicates that equilibrium between $KClO_4$, $MgCl_2{\cdot}6H_2O$ and $Mg(ClO_4)_2{\cdot}6H_2O$ occurs at 0.006 m $KClO_4$, 2.59 m $MgCl_2$, and 0.96 m $Mg(ClO_4)_2$. Given that the solubility of $KClO_4$ is low, it should have a negligible effect on the solubility of $MgCl_2{\cdot}6H_2O$ and $Mg(ClO_4)_2{\cdot}6H_2O$. Regardless of the inconsistencies in the quaternary K–Mg–Cl–ClO_4 dataset, the experimental data indicate that carnalite ($KCl{\cdot}MgCl_2{\cdot}6H_2O$) and $KClO_4$–KCl solid solutions precipitate from solution at high K^+ concentrations. Because K^+ concentrations are low at the Phoenix site and K^+ strongly precipitates as $KClO_4$ during freezing or evaporation (Marion et al., 2010), we do not consider systems with high K^+ concentrations here.

The Mg–Na–Cl–ClO_4 system is particularly relevant to the Phoenix WCL chemistry because the residual brine chemistry after evaporation or freezing will likely be dominated by these ions. Our model predictions for this system, using the ternary parameters determined previously, are in reasonable agreement with experimental solubility data; in contrast, FREZCHEM fails to fit the experimental data in Mg–Na–Cl–ClO_4 mixtures (Fig. 4). The misfit in our model is likely due to the poor Pitzer parameterization in the Mg–Na–ClO_4 system, which is causing our model to predict NaCl–$Mg(ClO_4)_2{\cdot}6H_2O$–$NaClO_4{\cdot}H_2O$ equilibrium at higher Na^+ and ClO_4^- concentrations than the experimental point. We find that our model fit to experimental solubility data is greatly improved by varying the ψ_{Na^+,Mg^{2+},Cl^-} parameter from its FREZCHEM value (the solid line in Fig. 4).

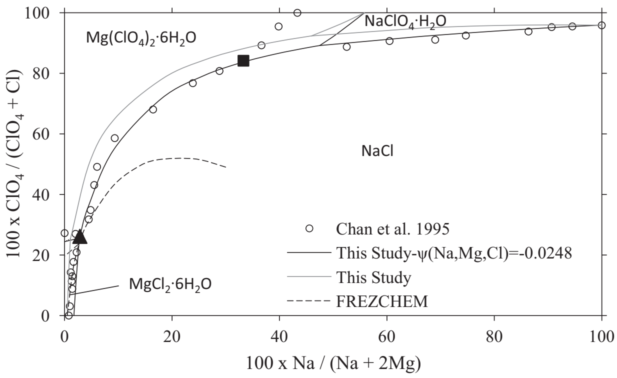

Fig. 4. The phase diagram for the quaternary Na–Mg–Cl–ClO_4 system, showing modeled results from this study (dotted line), modeled results from FREZCHEM (dashed line), and modeled results from this study by varying the ψ_{Na^+,Mg^{2+},Cl^-} parameter (solid line). Experimental points of equilibrium between NaCl–$Mg(ClO_4)_2{\cdot}6H_2O$–$NaClO_4{\cdot}H_2O$, and NaCl–$MgCl_2{\cdot}6H_2O$–$Mg(ClO_4)_2{\cdot}6H_2O$ are indicated by (■) and (▲) respectively.

4. Application to the WCL solution

A major goal for developing equilibrium models for perchlorate-rich salt solutions is the identification of the parent salts at the Phoenix site i.e. the salts originally in the soil that dissolved in the WCL experiments (Chevrier et al., 2009; Hanley et al., 2012; Marion et al., 2010; Toner et al., 2014b). These models assume that soluble salts are at some point completely dissolved in water or in equilibrium with a salt solution, and that salts precipitate from solution during freezing or evaporation. There are several lines of evidence indicating that liquid water is or has been present at the Phoenix site, including: the existence of 3–5 wt.% carbonates in the soil, which are typically formed at this abundance though aqueous processes (Boynton et al., 2009), perchlorate distributions in the soil suggesting salt transport in brines (Cull et al., 2010), the existence of segregated ice in soils (Mellon et al., 2009; Smith et al., 2009), soil dielectric signatures suggesting eutectic melting and/or salt crystallization (Stillman and Grimm, 2011), and tentative observations of liquid brines on the *Phoenix Lander* struts (Rennó et al., 2009). Assuming that liquid water is present at the Phoenix site for at least part of the year, probably as brine, the ∼600 Ma surface age of the soil (Heet et al., 2009) suggests that brines and highly soluble salts will have equilibrated, although sparingly soluble salts like calcite may remain in disequilibrium. In addition, the north polar regions of Mars were likely seasonally warmer in the past during orbital cycles (Laskar et al., 2002; Stoker et al., 2010), which would be more favorable for the formation of liquid water. The 298.15 K model presented in this paper is more relevant for salt assemblages formed during such past, warmer conditions than for present-day conditions.

We add the caveat that Kounaves et al. (2014) advanced the alternative argument that the Phoenix site has been continuously dry since the region was resurfaced by ejecta from the Heimdal Crater ∼600 Ma ago, based on their inference of $Ca(ClO_4)_2$ as the main perchlorate parent salt. The presence of $Ca(ClO_4)_2$ at the Phoenix site is suggested by the absence of a transient spike in Ca^{2+} Ion Selective Electrode (ISE) potentials after sample addition in the WCL experiment. Kounaves et al. (2014) found that measured Ca^{2+} ISE potentials can only be replicated in flight spare WCL units if a mixture of ∼60%/40% $Ca(ClO_4)_2/Mg(ClO_4)_2$ is added. Glavin et al. (2013) have also suggested that $Ca(ClO_4)_2$ may be present at Gale Crater based on O_2 release curves from the Sample Analysis on Mars (SAM) instrument; however, Glavin et al. (2013) notes that all of the perchlorate salts tested fit the SAM data poorly. If $Ca(ClO_4)_2$ is present at the Phoenix site, then the soil must be extremely arid because $Ca(ClO_4)_2$ salts are strongly deliquescent and will readily combine with carbonates and sulfates in aqueous solutions to precipitate insoluble $CaCO_3$ and $CaSO_4$ salts. Hence, the presence of $Ca(ClO_4)_2$ would indicate that the soil is in disequilibrium, and that equilibrium models mean little for the soil mineralogy.

However, we are cautious about interpreting transient signals in the WCL data because there are many aspects of the noisy WCL data that are not well understood, as discussed in Toner et al. (2014b). In particular, we find that the response of the Ca^{2+} ISE after sample addition is unclear (Fig. 5). Three samples were analyzed in the Phoenix WCL experiment: Rosy Red, Sorceress 1, and Sorceress 2. In Rosy Red, the Ca^{2+} ISE potential after sample addition decreases slowly over $\sim$200 s to a constant value, whereas the tests presented in Kounaves et al. (2014) indicate that the Ca^{2+} ISE responds rapidly within several seconds of sample addition. The slow response of the Rosy Red Ca^{2+} ISE would probably have masked the transient signals found by Kounaves et al. (2014). Both Sorceress 1 and 2 show a highly irregular Ca^{2+} ISE response upon sample addition. Note that the Sorceress 1 Ca^{2+} ISE data presented in Kounaves et al. (2014) (their Fig. 1b) shows sample addition occurring about 500 s later than Fig. 5B. We base the exact timing of sample addition on the sharp decrease in the ClO_4^- ISE potential upon sample addition, and this timing agrees well with the sample addition time shown in Kounaves et al. (2010a). The cause of the unusual responses in Ca^{2+} ISE potentials is not known, but the ISE sensors may have been adversely affected by diurnal thermal cycling on Mars because the signal response appears to degrade on later sols. Regardless, given the irregularities shown in Fig. 5, particularly for Sorceress 1 and 2, we conclude that there is no evidence for $Ca(ClO_4)_2$ in Phoenix soils in the WCL data.

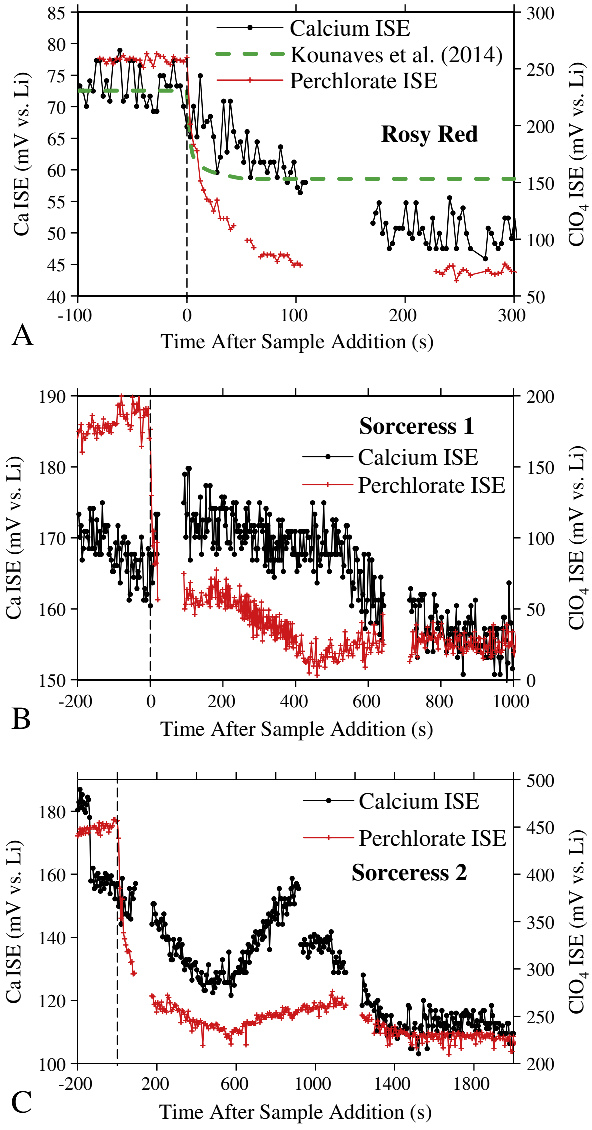

Fig. 5. The Ca^{2+} and ClO_4^- ISE response in the Rosy Red (A), Sorceress 1 (B), and Sorceress 2 (C) WCL experiments. The addition of soil is indicated by the black-dashed vertical lines. The exact timing of soil addition is determined from the rapid decrease in the ClO_4^- ISE potential after sample addition. In Fig. 5A, we also show the Ca^{2+} ISE response measured by Kounaves et al. (2014) for a 60%/40% mixture of $Ca(ClO_4)_2$/$Mg(ClO_4)_2$. Note: concentration is directly proportional to ISE potential for cations, and inversely proportional for anions.

To model the WCL solution, we use ion concentrations for a 'nominal' Rosy Red WCL solution from the revised WCL analysis of Toner et al. (2014b) that includes corrections for ion-pairs and alkalinity; $Ca^{2+} = 0.186$, $Mg^{2+} = 3.459$, $Na^{+} = 1.472$, $K^{+} = 0.329$, $Cl^{-} = 0.407$, $SO_4^{2-} = 1.511$, $ClO_4^{-} = 2.743$ mM, Alk. = 2.919 meq, and pH = 7.67. Toner et al. (2014b) also used this solution composition in their chemical divide modeling. Our new model was run at a temperature of 298.15 K, and the pCO_2 was assumed to be that in the WCL cell, 4 mbar (Kounaves et al., 2010a). In our modeling, we prevent dolomite ($CaMg(CO_3)_2$) and magnesite ($MgCO_3$) phases from precipitating because the formation of these salts is kinetically inhibited at low temperatures (Land, 1998; Langmuir, 1965). We model equilibrium evaporation by sequentially removing water from the solution until all salt phases have precipitated. This is in contrast to the fractional crystallization modeling done by Marion et al. (2010), which assumes that precipitated minerals cannot redissolve into solution. (However, we note that the choice of equilibrium or fractional crystallization makes little difference in the modeling results.) To implement our model we use the geochemical program PHREEQC (Appelo and Postma, 2005), which uses the same Pitzer equations as FREZCHEM. We choose to use PHREEQC because it has fewer convergence issues than FREZCHEM, and it is easier to make changes to Pitzer parameters and solubility products. Toner and Sletten (2013) previously incorporated Pitzer parameters from FREZCHEM into PHREEQC and found excellent agreement between the two models. We have validated our 298.15 K Pitzer model in PHREEQC by comparing our model results to FREZCHEM.

At low concentrations, our model predictions are similar to FREZCHEM, but the two models diverge at very high salt concentrations (compare Fig. 6A, B, and C). In both our model and FREZCHEM, hydromagnesite ($3MgCO_3{\cdot}Mg(OH)_2{\cdot}3H_2O$), gypsum ($CaSO_4{\cdot}2H_2O$), $KClO_4$, and epsomite ($MgSO_4{\cdot}7H_2O$) all precipitate relatively early during evaporation. Subsequently, gypsum and epsomite dehydrate to kieserite ($MgSO_4{\cdot}H_2O$) and anhydrite ($CaSO_4$) respectively. In our model halite (NaCl) then precipitates from solution, followed shortly thereafter by $NaClO_4{\cdot}H_2O$ and $Mg(ClO_4)_2{\cdot}6H_2O$. At this point, the solution composition attains a constant Mg–Na–ClO_4–Cl-rich composition because all phases are precipitating from solution. Note that our model does not accurately predict equilibrium between NaCl–$NaClO_4{\cdot}H_2O$–$Mg(ClO_4)_2{\cdot}6H_2O$, as shown in Fig. 4 and discussed in Section 3.4. Experimental solubility data indicate that equilibrium between these three phases occurs at $Mg^{2+} = Na^{+} = 4.5$ m, $Cl^{-} = 2.13$ m, and $ClO_4^{-} = 11.3$ m; our model predicts a water activity of 0.28 at this point. In FREZCHEM, neither halite nor $NaClO_4{\cdot}H_2O$ precipitate from solution because the FREZCHEM parameterization in the Na–Cl–ClO_4 system causes an extreme 'salting in' effect for these salts. At the lowest residual water content shown in Fig. 6A, the ion activity coefficient for Mg^{2+} increases exponentially to $>10^4$ in FREZCHEM, which causes convergence failures in the model.

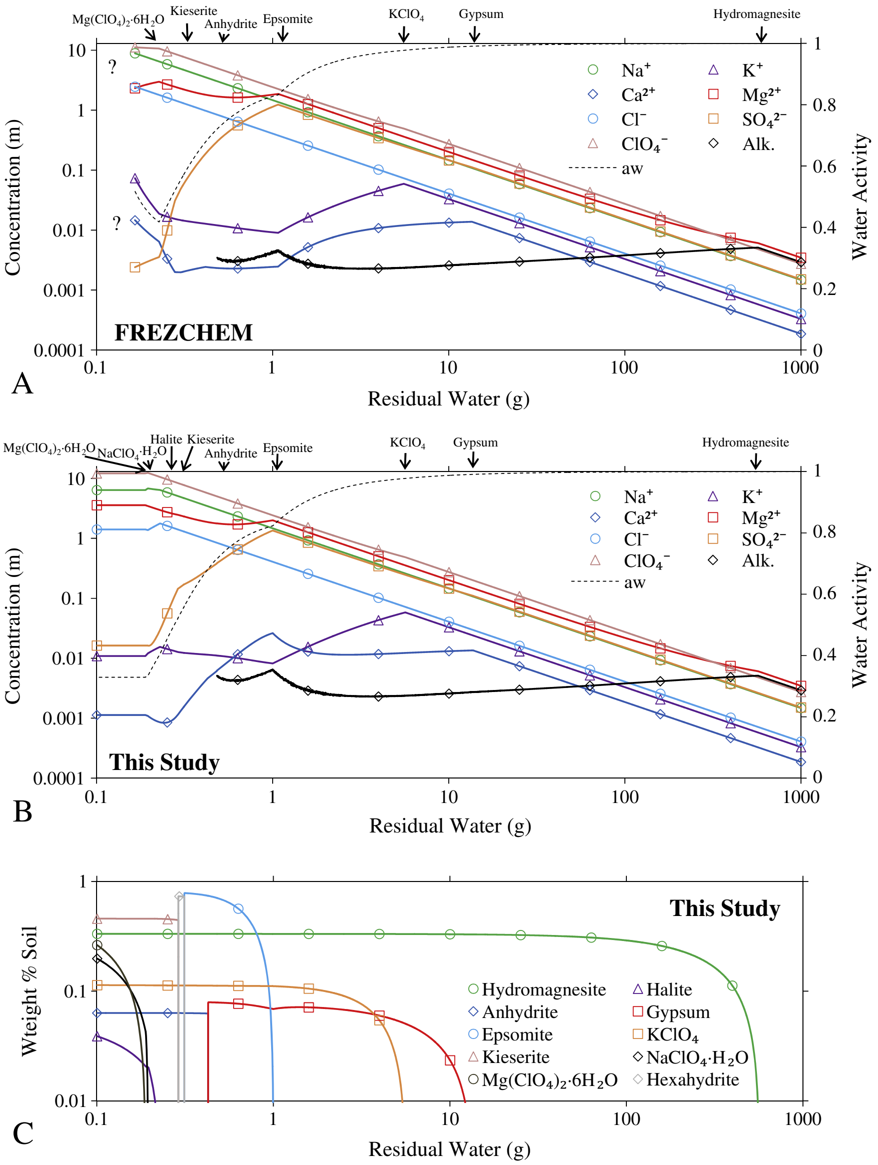

Fig. 6. Modeled ion concentrations (mol kg^{-1}), salt precipitates (wt.%), and water activities predicted in FREZCHEM (A) and this study (B and C), starting from the 'nominal' Rosy Red WCL solution in Toner et al. (2014b). Salt precipitates were converted to wt.% by assuming that 1 g of soil had been added to solution in the WCL experiment. Arrows indicate precipitation events for various salts.

Hence, equilibrium brine chemistries in FREZCHEM could not be evaluated beyond this point.

If all the water is allowed to evaporate in our model, then the total soil water content held in hydrated salt phases is 0.29 wt.% H_2O. This is considerably less than minimum water contents between 1.5 and 2 wt.% measured in Mars' soils from global spectral data (Boynton et al., 2007; Feldman et al., 2004) and from Gale Crater as measured by the Sample Analysis on Mars (SAM) instrument on the Mars Science Laboratory (MSL) (Leshin et al., 2013; Ming et al., 2013). Starting from the same initial WCL solution composition, Toner et al. (2014b) estimated that salts formed during freezing hold about 1.3 wt.% water using a chemical divide model. Freezing results in a greater degree of salt hydration because water activities are higher during freezing than during evaporation. This suggests that soil salts on Mars were formed during freezing processes, and are not evaporite remnants formed during warmer/wetter conditions in the past.

$Ca(ClO_4)_2$-rich solutions did not form in our modeling, which is consistent with results from other equilibrium models (Hanley et al., 2012; Marion et al., 2009, 2010). This is because Ca^{2+} precipitates as gypsum or calcite during evaporation or freezing. In perchlorate-rich brines this effect is even stronger than in similar concentration chloride solutions owing to the high ion activity coefficient of Ca^{2+} in the presence of concentrated perchlorate, which leads to a strong 'salting out' effect for gypsum and calcite. If salts at the Phoenix site are in equilibrium through periodic contact with aqueous solutions, then $Ca(ClO_4)_2$ salts will not form due to the high concentrations of sulfate and alkalinity relative to Ca^{2+} measured in the Phoenix WCL experiment. On the other hand, if $Ca(ClO_4)_2$ salts are present at the Phoenix site, as suggested by Kounaves et al. (2014), then this argues for a strong disequilibrium and the virtual absence of aqueous activity at the Phoenix site. However, this interpretation conflicts with numerous inferences of past and present aqueous activity at the Phoenix site e.g. Boynton et al. (2009), as well as our own analysis of the WCL data (see Fig. 5).

Neither our evaporation model nor FREZCHEM's predicts calcite ($CaCO_3$) formation; instead, Ca^{2+} precipitates as gypsum and alkalinity precipitates with Mg^{2+} as hydromagnesite. (Note that at low residual water contents, carbonate chemistries could not be evaluated because too many salt phases were precipitating, which causes convergence failures. We addressed this by removing alkalinity from the model, and preserving charge balance by assuming that all remaining alkalinity precipitates as hydromagnesite.) Using the same initial WCL solution composition, Toner et al. (2014b) found that FREZCHEM does predict calcite precipitation from solution during freezing. Given that there is strong evidence for $CaCO_3$ at the Phoenix site based on a high temperature CO_2 release in the Thermal and Evolved Gas Analyzer (TEGA) (Boynton et al., 2009), one interpretation of the absence of calcite in our 298.15 K model is that salts at the Phoenix site must have formed at lower temperatures. Alternatively, later studies on the TEGA instrument have found that the high temperature CO_2 release can also occur with mixed (Fe,Mg,Ca)CO_3 solid solutions (Sutter et al., 2012), such as dolomite, ankerite ($FeCa(CO_3)_2$), and huntite ($CaMg_3(CO_3)_4$), among other possibilities. The presence of (Fe,Mg,Ca)CO_3 solid solutions at the Phoenix site is supported by the mixed carbonate compositions commonly found in other locations on Mars and in martian meteorites (Niles et al., 2013). Given that FREZCHEM only contains end member carbonate phases, and does not include solid-solutions, it is possible that $CaCO_3$ would precipitate within a solid solution if such phases were included.

Our model also predicts that at low residual water contents, kieserite and anhydrite precipitate instead of the more hydrated phases epsomite and gypsum. Epsomite transitions first to hexahydrite ($MgSO_4{\cdot}6H_2O$) at $a_w = 0.56$ in our model, which then transitions to kieserite at $a_w = 0.52$. Gypsum transitions to anhydrite at $a_w = 0.68$ in our model. These dehydrated salt phases precipitate due to the low water activities in concentrated perchlorate solutions; for example, saturated $NaClO_4$ and $Mg(ClO_4)_2$ solutions at 298.15 K have water activities of 0.44 and 0.39 respectively. Kieserite and bassanite have been reported on Mars from spectral data (Murchie et al., 2009; Wray et al., 2010) and anhydrite has recently been found by in Gale Crater by MSL (Bish et al., 2013). Kieserite is typically considered to be a high temperature $MgSO_4$ phase, but our equilibrium modeling suggests a low temperature pathway for the formation of dehydrated sulfates by direct precipitation from aqueous salt solutions, or concentrated salt solutions may mediate the dehydration of hydrated sulfates. Possibly, dehydrated minerals may also form at low temperatures through exposure to low relative humidity; for example, kieserite could form by dehydration of epsomite or hexahydrite. However, Vaniman et al. (2004) and Chipera and Vaniman (2007) have observed that at low temperatures (<320 K), kieserite does not form by dehydration of more hydrated phases; instead, epsomite and hexahydrite dehydrate to an amorphous hydrated $MgSO_4$ phase.

5. Conclusions

The identity of soluble salt phases in martian soils is critical for understanding the past aqueous history and the potential for liquid water to form. In the absence of direct measurements of crystalline salts, equilibrium models provide valuable insights into what salt assemblages should form in soils under different temperature conditions during freezing or evaporation. Here we use solubility data at 298.15 K to better parameterize a Pitzer model for multicomponent perchlorate-rich brines, and then apply this model to the soil solution measured in the Phoenix WCL experiment. This model can be integrated into the existing geochemical program FREZCHEM. Our model is a significant improvement to the current FREZCHEM model, particularly for the important Na–Mg–Cl–ClO_4 and Na–SO_4–ClO_4 salt systems. However, some salt systems could not be modeled to the accuracy of the experimental solubility data, possibly due to extensive ion pairing in concentrated perchlorate solutions, such as in ternary systems involving potassium, the Mg–SO_4–ClO_4 system, and the Na–Mg–ClO_4 system. A model that explicitly accounts for ion pairing in these systems may improve the model fits, but this comes at the expense of considerably more complexity in the model.

We applied our model to a nominal WCL solution by modeling evaporation at 298.15 K. Results indicate that the WCL solution evaporates to a residual Mg–Na–Cl–ClO_4-rich brine and that kieserite (0.46 wt.%), hydromagnesite (0.33 wt.%), $Mg(ClO_4)_2{\cdot}6H_2O$ (0.26 wt.%), $NaClO_4{\cdot}H_2O$ (0.2 wt.%), $KClO_4$ (0.11 wt.%), anhydrite (0.06 wt.%), and halite (0.04 wt.%) form upon complete evaporation. $Ca(ClO_4)_2$ salts do not form in our model owing to the precipitation of Ca^{2+} as gypsum or calcite. Our model predicts that about 0.29 wt.% water is held in hydrated salts, which is considerably lower than minimum estimates between 1.5 and 2 wt.% H_2O from both orbital and in situ measurement of soil water content. In addition, our model does not predict calcite precipitation, which conflicts with in situ measurements of calcite in Phoenix soils. Instead, Ca^{2+} precipitates entirely as gypsum. This is in contrast to models of freezing WCL solutions by Toner et al. (2014b) and Marion et al. (2010), which indicate that calcite does precipitate from solution and that 1.3 wt.% H_2O is held in hydrated salts. This suggests that salts at the Phoenix site probably formed at low temperatures, and are not remnants of salts formed by evaporation during past, warmer climates.

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