Modeling aluminum–silicon chemistries and application to Australian acidic playa lakes as analogues for Mars

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Abstract

Recent Mars missions have stimulated considerable thinking about the surficial geochemical evolution of Mars. Among the major relevant findings are the presence in Meridiani Planum sediments of the mineral jarosite (a ferric sulfate salt) and related minerals that require formation from an acid–salt brine and oxidizing environment. Similar mineralogies have been observed in acidic saline lake sediments in Western Australia (WA), and these lakes have been proposed as analogues for acidic sedimentary environments on Mars. The prior version of the equilibrium chemical thermodynamic FREZCHEM model lacked Al and Si chemistries that are needed to appropriately model acidic aqueous geochemistries on Earth and Mars. The objectives of this work were to (1) add Al and Si chemistries to the FREZCHEM model, (2) extend these chemistries to low temperatures (<0 °C), if possible, and (3) use the reformulated model to investigate parallels in the mineral precipitation behavior of acidic Australian lakes and hypothetical Martian brines.

FREZCHEM is an equilibrium chemical thermodynamic model parameterized for concentrated electrolyte solutions using the Pitzer approach for the temperature range from < −70 to 25 °C and the pressure range from 1 to 1000 bars. Aluminum chloride and sulfate mineral parameterizations were based on experimental data. Aluminum hydroxide and silicon mineral parameterizations were based on Gibbs free energy and enthalpy data. New aluminum and silicon parameterizations added 12 new aluminum/silicon minerals to this Na–K–Mg–Fe(II)–Fe(III)–Al–H–Cl–Br–SO4–NO3–OH–HCO3–CO3–CO2–O2–CH4–Si–H2O system that now contain 95 solid phases.

There were similarities, differences, and uncertainties between Australian acidic, saline playa lakes and waters that likely led to the Burns formation salt accumulations on Mars. Both systems are similar in that they are dominated by (1) acidic, saline ground waters and sediments, (2) Ca and/or Mg sulfates, and (3) iron precipitates such as jarosite and hematite. Differences include: (1) the dominance of NaCl in many WA lakes, versus the dominance of Fe–Mg–Ca–SO4 in Meridiani Planum, (2) excessively low K+ concentrations in Meridiani Planum due to jarosite precipitation, (3) higher acid production in the presence of high iron concentrations in Meridiani Planum, and probably lower rates of acid neutralization and hence, higher acidities on Mars owing to colder temperatures, and (4) lateral salt patterns in WA lakes. The WA playa lakes display significant lateral variations in mineralogy and water chemistry over short distances, reflecting the interaction of acidic ground waters with neutral to alkaline lake waters derived from ponded surface runoff. Meridiani Planum observations indicate that...
such lateral variations are much less pronounced, pointing to the dominant influence of ground water chemistry, vertical ground water movements, and aeolian processes on the Martian surface mineralogy.

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1. INTRODUCTION

Recent Mars missions have stimulated considerable thinking about the surficial geochemical evolution on that planet and the links between aqueous chemical weathering and mineral precipitation with paleoecological evolution and other global issues (Lane et al., 2004; Morris et al., 2004, 2006; Squyres et al., 2004, 2006; Kargel, 2004a,b; Bibring et al., 2005, 2006; Clark et al., 2005; Gendrin et al., 2005; Glotch and Christensen, 2005; Langenau et al., 2005; McLennan et al., 2005; Navrotsky et al., 2005; Tosca et al., 2005; Tosca and McLennan, 2006; McSween, 2006; Ming et al., 2006; Glotch and Rogers, 2007). The reworking of our understanding of Mars is so deep that people are asking how planets so similar in many ways as Earth and Mars can be so different. Indeed, from the broadest global perspective, Mars is geochemically and petrologically very similar to Earth (Kargel and Lewis, 1993; Kargel, 2004a); considered at finer scales, Mars and Earth exhibit many of the same types of landforms, and chemically both have been deeply altered and processed by water. However, the quickest glance at global color images of Mars and most arid regions of Earth’s continents show them to be very different at every level. An important exception is that much of Western Australia (WA) bears a strong color resemblance to Mars. They are both very red lands, marked by the ubiquitous signature of hematite and other ferric iron compounds.

Among the major recent Mars mission findings are the presence of the mineral jarosite (a ferric sulfate salt), which requires formation from an acid–salt brine in oxidizing environments (Bishop et al., 2004; Klingelhöfer et al., 2004; Kargel, 2004b; Kargel and Marion, 2004; Clark et al., 2005; Golden et al., 2005; Navrotsky et al., 2005; Tosca et al., 2005; Fernandez-Romolar et al., in 2008). Alternative mechanisms for acidification include pyrite oxidation (Long et al., 1992b; Bishop et al., 2003, 2004; Zolotov and Shock, 2005), ferrolysis (McArthur et al., 1991; Long et al., 1992a,b; Papike et al., 2006), and acidic volatiles emitted by volcanoes (Banin et al., 1997; McCollom and Hynek, 2005). Earth analogues for Meridiani Planum surface geochemistries include: (1) acid mine drainages (AMD) (Fernandez-Romolar et al., 2003, 2004, 2005; Bishop et al., 2004), (2) Antarctic deserts (Wierzchos and Ascaso, 2002; Bishop et al., 2003; Kreslawsky and Head, 2008), and (3) acidic saline lakes (Benison and LaClair, 2003; Benison and Bowen, 2006; Benison et al., 2007; Bowen and Benison, 2008). Potential geochemistries of Meridiani Planum have also been explored using laboratory studies (Banin et al., 1997; Tosca et al., 2004; Golden et al., 2005) and modeling (Schaefer 1990, 1993; Morse and Marion, 1999; King et al., 2004; Tosca et al., 2005; Marion and Kargel, 2008; Marion et al., 2008b). In a recent paper, Benison and Bowen (2006) made a strong case for why WA acidic, saline lakes are especially sound as analogues for the Burns formation in the Meridiani Planum region of Mars. Given the mineralogical and sedimentary similarities between these two environments, our goal in this study was to further our understanding of potential acidic aqueous systems on Mars by modeling the aqueous geochemistry of selected Australian acidic, saline playa lakes.

The prior version of the equilibrium chemical thermodynamic FREZCHEM model was parameterized for the Na–K–Mg–Ca–Fe(II)–Fe(III)–H–Cl–Br–SO4–NO3–OH–HCO3–CO3–CO2–O2–CH4–H2O system. Lacking from the model were Al and Si chemistries and minerals needed to deal with acid ground waters on both Earth and Mars. While Al and Si concentrations are minor components in most aqueous solutions, they can become major components (along with Fe) in the acidic, saline waters that we will examine in this study. Therefore, the specific objectives of this work were to (1) add Al and Si chemistries to the FREZCHEM model, (2) extend these chemistries to low temperatures (<0 °C), if possible, and (3) use the reformulated model to explore Australian acidic saline playa lakes as terrestrial analogues for Mars. In particular, we seek a quantitative measure, through modeling, of the similarity between WA acidic saline lakes and Martian aqueous systems, so the former can be assessed as a suitable analogue for the latter.

2. METHODS AND MATERIALS

2.1. FREZCHEM model

2.1.1. Overview of FREZCHEM

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 total pressure range from 1 to 1000 bars (Marion and Farren, 1999; Marion, 2001, 2002; Marion et al., 2003, 2005, 2006, 2008b; Marion and Kargel, 2008). The previous version of the model was parameterized for the Na–K–Mg–Ca–Fe(II)–Fe(III)–H–Cl–Br–SO4–NO3–OH–HCO3–CO3–CO2–O2–CH4–H2O system and included 83 solid phases including ice, 14 chloride minerals, 30 sulfate minerals, 15 carbonate minerals, five solid phase acids, three nitrate minerals, six acid–salts, five iron oxides, two gas hydrates, and two bromide sinks. (see above references for these model parameters). Other solution constituents, such as Sr, Mn, Cu, Ni, and Sb that are not present in FREZCHEM, are only present at extremely low concentrations in the playa lakes of this paper (McArthur et al., 1989, 1991; Bowen and Benison, 2008). These minor constituents do not affect the major element chemistry and can be safely ignored. An objective of this work was to develop aluminum–silicon parameterizations based on classical chemical thermodynamic principles that can be incorporated seamlessly into FREZCHEM. This involved the incorporation
of 12 new solid phases into FREZCHEM. A FORTRAN version of the resulting model is available upon request from the senior author (giles.marion@dri.edu).

2.1.2. 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 (A), and neutral aqueous species (N), such as CO$_2$(aq) or CH$_4$(aq), are given by

$$\ln(\gamma_\text{M}) = \frac{\sum m_n \Psi_{\text{M}} + \sum m_n \Psi_{\text{M,N}} + z_M}{\sum m_n \Psi_{\text{M}} + \sum m_n \Psi_{\text{M,N}} + z_M} \times \sum m_a \lambda_{\text{M}} + 2 \sum m_a \lambda_{\text{M,N}} + 2 \sum m_a \lambda_{\text{M,N}}$$

(1)

$$\ln(\gamma_\text{N}) = \frac{\sum m_n \Psi_{\text{N}} + \sum m_n \Psi_{\text{N,M}} + z_N}{\sum m_n \Psi_{\text{N}} + \sum m_n \Psi_{\text{N,M}} + z_N} \times \sum m_a \lambda_{\text{N}} + 2 \sum m_a \lambda_{\text{N,M}} + 2 \sum m_a \lambda_{\text{N,M}}$$

(2)

$$\ln(\gamma_\text{A}) = \frac{\sum m_n \Psi_{\text{A}} + \sum m_n \Psi_{\text{A,N}} + z_A}{\sum m_n \Psi_{\text{A}} + \sum m_n \Psi_{\text{A,N}} + z_A} \times \sum m_a \lambda_{\text{A}} + 2 \sum m_a \lambda_{\text{A,N}} + 2 \sum m_a \lambda_{\text{A,N}}$$

(3)

where, $B$, $C$, $\Psi$, $\lambda$, and $\zeta$ are Pitzer-equation interaction parameters, $m$ is the molal concentration, and $F$ and $Z$ are function equations. 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 $d$ 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

$$a_w = \exp\left(-\phi \sum m_n \right)$$

(4)

where $\phi$ is the osmotic coefficient, which is given by

$$\phi = \frac{-A_1^{1/2}}{\sum m_n} + \frac{A_2^{1/2}}{1 + a_n^{1/2}} + \frac{A_3^{1/2}}{1 + a_n^{1/2}} + \sum m_n \Psi_{\text{M,N}} + \sum m_n \Psi_{\text{M,N}} + z_M$$

(5)

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

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

$$P = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T + a_6 \ln(T)$$

(6)

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

2.1.3. Aluminum–silicon data sets and solubility products

The leading source of older data ($\leq$1958) for Al–Cl and Al–SO$_4$ chemistries was from compilations in Linke (1958). In several cases, a specific “Linke” compilation is based on multiple published datasets. The assumptions involved in accepting or rejecting data are discussed in Linke (1958). Also, the Linke (1958) publication is more easily accessible compared to most of the earlier publications. For these reasons, we will cite Linke (1958) as the source of these data, rather than the original datasets. Some assumption examples are discussed in this paper.

A thermodynamic approach to estimate the solubility product ($K$) for a given mineral is as follows

$$\text{Al(OH)}_3(c) + 3H^+ \leftrightarrow \text{Al}^{3+} + 3\text{H}_2\text{O}$$

(7)

and

$$K = \frac{(a_{\text{Al}^{3+}})(a_{\text{H}^+})^3}{(a_{\text{Al}^{3+}})(a_{\text{H}^+})^3} = \frac{(\gamma_{\text{Al}^{3+}})(m_{\text{Al}^{3+}})(a_{\text{H}^+})}{(\gamma_{\text{H}^+})(m_{\text{H}^+})^3}$$

(8)

where $a$ is the activity of the subscripted component, $\gamma$ is the activity coefficient, and $m$ is the molality [mol kg$^{-1}$]. Given experimental measurements of the molalities (m) and an equilibrium model that can calculate $\gamma$ and the activity of water, $a_w$ (Eq. (1)–(5)), one can directly estimate $K$ (Eq. 8).

In many cases, especially for insoluble aluminum minerals, experimental molalities are lacking, so we need to use an alternative thermodynamic approach to estimate equilibrium constants. $K$ is related to the Gibbs free energy ($G$) as follows (Nordstrom and Munoz, 1994)

$$\ln(K) = -\frac{\Delta G^0}{RT}$$

(9)

where $\Delta G^0$ is the change in the Gibbs free energies of formation for the components of a given reaction (Eq. 7).

$$\Delta G^0 = \Delta G^0_{\text{Al}^{3+}} + 3 \Delta G^0_{\text{H}^+} - \Delta G^0_{\text{Al(OH)}_3} - 3 \Delta G^0_{\text{H}_2\text{O}}$$

(10)

In what follows, several of the equilibrium constants were estimated based on Eq. 9.

Experimental estimates of molalities as a function of temperature allow one to directly estimate the temperature dependence of $K$, which is how we estimated this temperature dependence whenever such data were available. Where such temperature data were lacking, we used the van’t Hoff equation to estimate the temperature dependence:

$$\ln(K_T) = \ln(K_{T_1}) + \frac{\Delta H^0}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

(11)

We used both $\Delta G^0$ (Eq. 9) and $\Delta H^0$ (Eq. 11) from the literature to estimate the temperature dependence of these solubility products. The accuracy of these extrapolations to lower temperatures is difficult to judge. But Plummer et al. (1988) claim that the temperature range for their PHRQPITZ model is generally 273–333 K, if $\Delta H^0$ is known at 298 K. And Pitzer (1995) has pointed out that $\Delta H^0$ is often nearly constant over a limited temperature range.
2.1.4. FREZCHEM Al–Si–pH model options

Especially critical in this playa lake application are controls on system pH and the capability of FREZCHEM to quantitatively model pH. Previously published FREZCHEM papers dealt with pH under alkaline conditions dominated by carbonate geochemistry (Marion, 2001) and pH under acidic conditions dominated by both strong acids (HCl, HNO₃, H₂SO₄; Marion, 2002) and ferric iron geochemistry (Marion et al., 2008b). The strong acid paper confirmed the applicability of FREZCHEM into the negative pH range (to –2.0), which extends well below the known pH values of these playa lakes, which generally have pH values that are >2.0 (McArthur et al., 1989, 1991; Alpers et al., 1992; Gray, 2001; Benison and Bowen, 2006; Benison et al., 2007; Bowen and Benison, 2008).

Several reactions deal with aluminum hydroxide minerals that produce (or consume) H⁺ ions (e.g., see Eq. 7). If we ignored H⁺ ion production (or consumption) for these reactions, the aqueous solutions will become charge imbalanced (Nordstrom et al., 2008), and as a consequence, the calculated properties of these aqueous solutions would be erroneous. In the modified FREZCHEM model for aluminum–silicon chemistries, we created four user-selectable options for handling these H⁺ ion (pH) calculations. These choices are identical to options in a published iron paper (Marion et al., 2008b).

In Option 1, we ignore pH entirely. This is probably only valid for some laboratory experimental data [e.g., AlCl₃ or Al₂(SO₄)₃ data]. Fig. 1 depicts the distribution of Al⁺³ and hydroxyl complexes. At pH 3.0, 99.6% of the Al⁺³ is present as Al(OH)⁺²⁺. A 0.1 m AlCl₃ salt solution would have a pH ≈ 3.0 due to the reaction of water with Al⁺³. Virtually all the Al⁺³ will be present as Al(OH)⁺²⁺ (99.6%, see above). As the AlCl₃ molality increases, the pH and % of the Al(OH) complexes decreases (see several Al⁺³ examples in Christov et al., 2007, and a similar Fe⁺³ example in Marion et al., 2008b). The Al experimental data used in this paper were almost entirely from systems with concentrations greater than 0.1 m; so Al complexes should be minimal. In the use of experimental data in this paper (see Sections 3.1 and 3.2), we ignored pH, except in cases where the H⁺ ion was a component of the experimental data.

In Option 2, we fix the pH at a user-designated value (e.g., pH 2.0). In applying the FREZCHEM model to natural environments, it is necessary to recognize explicitly reactions such as Eq. 7. Whenever such a reaction such as Eq. 7 takes place, we assume that the H⁺ ions will be neutralized by reaction with minerals releasing cations into the solution. We partitioned the excess H⁺ charge by increasing the aqueous cations proportionally to their existing charges. Allowing the produced H⁺ ions to accumulate as H⁺ ions, instead of other cations, can cause a precipitous drop in pH, which is outside the desired range of the simulation. We can use the change in cation contents (equivalents) as a measure of H⁺ ion production, which is useful to know.

Both Options 3 and 4 have explicit equations for controlling charge balance and H⁺ ion concentrations and activities. Option 3 is the “acidity” option where acidity is controlled by total H⁺ input. In this option, we partitioned aluminum hydroxide produced acidity charge among the solution cations as was done in Option 2. Option 4 is the “alkalinity” option where acidity is controlled by alkalinity reactions with solution phase species such as HCO₃⁻ and CO₃²⁻ and solid phases such as calcite (CaCO₃). Whenever, a reaction such as Eq. 7 takes place, we assume that the H⁺ ions are neutralized by reactions with carbonate minerals releasing cations into the solution.

2.2. Australian acidic playa lakes

There are abundant acidic playa lakes in Australia (McArthur et al., 1989, 1991; Alpers et al., 1992; Long et al., 1992a,b; Gray, 2001; Benison et al., 2007; Bowen and Benison, 2008) that could serve as analogues for acidic environments on Mars (e.g., Benison and Bowen, 2006; Marion et al., 2008a). In this paper, we chose Lakes Gilmore and Swann as our working acidic lakes because of existing high quality chemical data on the water chemistry and descriptive mineralogical data available for these lakes (McArthur et al., 1989, 1991). The specific lake samples used in our simulations were collected in June 1987 during and after some autumn rainfall (see Table 1 in McArthur et al., 1991). In autumn, water tables are at their lowest. During winter with heavy rainfall, standing water can occur in these playa lakes. In the McArthur et al. studies, brine samples were collected from ground waters that were within 50–100 cm of the playa surface along a transect from the edge of the dry lake to as far as 380 m into the lake. These transect samples allowed us to examine lateral chemistry patterns in these playa lakes. The Lake Gilmore samples were numbered from 0 to 14 in order from the edge of the lake to the furthest samples from shore. These sample designations were used in our study for the same localities. The Lake Swann samples were designated from A to S; in our study, we redesigned these sample data, which they labeled A, C, D, F2, 6, 11, and S, as 0, 1, 2, 3, 4, 5, and 6, respectively. This will simplify the text discussions. For additional details on sample collection and analyses, see McArthur et al. (1989, 1991).
There were no ice equilibrium data except at the eutectic point. The model ice-line is anchored at 273.15 K where AlCl₃ = 0.0 \( (a_s = 1.00) \) and at the eutectic \( (a_s = 0.5918) \); data between these two points are derived from our model predictions, but with no experimental data for comparative purposes.

Parameterization of Al–Cl binary interactions to 218.15 K allowed us to estimate a temperature-dependent solubility product for chloraluminate \((\text{AlCl}_3 \cdot 6\text{H}_2\text{O})\) (Table 3) based on solubility data (Linke, 1958). The model calculated eutectic temperature for this system occurred at 218.65 K with \( \text{AlCl}_3 = 2.53 \) m, which is in good agreement with the literature values of 218.15 K with \( \text{AlCl}_3 = 2.54 \) m (Linke, 1958).

There is also a scattering of data in the literature that allowed us to estimate ternary parameters for Al–Cl interactions with K, H, Mg, and Fe(III) (Linke, 1958; Christov, 2001; Christov et al., 2007). For ternary interactions other than the latter four ions, we used surrogates (see Table 2 footnotes).

The ternary \( \psi_{\text{K,Al,Cl}} \) and \( \theta_{\text{K,Al}} \) parameters over the temperature range from 273.15 to 298.15 K were taken from Christov et al. (2007) (Table 2). The ternary \( \psi_{\text{H,Al,Cl}} \) and \( \theta_{\text{H,Al}} \) parameters over the temperature range from 273.15 to 298.15 K were also taken from Christov et al. (2007) (Table 2).

There were two datasets for Fe(III)–Al–Cl chemistries at 273.15 and 298.15 K (Fig. 4) (Linke, 1958). At the time that we estimated \( \psi_{\text{AlFeCl}} \) from these datasets, we already knew the solubility products for FeCl₃–6H₂O (Marion et al., 2008b) and AlCl₃–6H₂O (Fig. 2), both of which were precipitates in the experiments. Therefore, in principle, we should have been able to use both of these solubility products to calculate \( \psi_{\text{AlFeCl}} \). But it was impossible to estimate a \( \psi_{\text{AlFeCl}} \) that would fit both the AlCl₃–6H₂O and the FeCl₃–6H₂O equilibria; optimally the AlCl₃–6H₂O equilibrium required a positive value for \( \psi_{\text{AlFeCl}} \) while the FeCl₃–6H₂O equilibrium constant required a negative value.

3. AL–SI MODELING RESULTS

Table 1 includes all the aluminum and silicon minerals that are now part of the FREZCHEM model. These new chemistries will be presented in five sections representing: aluminum chlorides, aluminum sulfates, aluminum hydroxides, silicon minerals, and density and pressure parameterization.

### 3.1. Aluminum chlorides

The Pitzer parameters for Al–Cl interactions at 298.15 K were taken from Christov (2001); this osmotic coefficient database extended to 3.3 m AlCl₃ (ionic strength \( I = 19.8 \) m). Unfortunately, the databases for lower temperatures were very limited. The AlCl₃–H₂O system (Fig. 2) has a datum at the eutectic temperature of 218.15 K (Linke, 1958) that has a fixed \( a_w = 0.5918 \) due to the presence of ice at that temperature. This single datum allowed us to extend the \( B_{\text{AlCl}}^0 \) Pitzer parameter to 218.15 K by fixing \( B_{\text{AlCl}}^0 \) and \( c_{\text{AlCl}} \) at their 298.15 K values (Table 2). Note in Fig. 2 that

![Fig. 2. Equilibria for AlCl₃ chemistry down to subzero temperatures. Symbols are experimental data; lines are model estimates.](image-url)
Table 2
Binary, ternary, and volumetric Pitzer-equation parameters derived in this work or taken from the literature (numbers are in computer
scientific notation where ±xx stands for 10±xx).

<table>
<thead>
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<th>Pitzer-equation parameters</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$a_5$</th>
<th>$a_6$</th>
<th>Temperature range (K)</th>
<th>Source</th>
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<td>218–298</td>
<td>Christov (2001); this work</td>
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Volumetric parameters

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Table 2 (continued)

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</table>

1 Assumed the same as Mg analogue.
2 Assumed the same as Fe(III) analogue (Marion et al., 2008b).
3 Based on Al–O2(aq) equilibrium as analogues for Al–Gas, where soluble gas is O2(aq), CO2(aq), or CH4(aq).
4 Assumed the same as Bi(OH)4 analogue (Millero, 2001).

Table 3

| Equilibrium constants [as \( \ln(K) \)] derived in this work or taken from the literature (footnoted) (numbers are in computer scientific notation where e±xx stands for 10±xx). |
|-----------------------------------|----|----|----|----|----|---------------------------------|
| a1                                | a2 | a3 | a5 |    |    | Temperature Source range (K)   |
| Solution-solid phase equilibria   |    |    |    |    |    | 218–303                        |
| AlCl3·6H2O \( \rightleftharpoons \) Al3+ + 3Cl+ + 6H2O | -1.084571e2 | 6.75193e-1 | -8.626394e-4 |    |    | 273–298                        |
| Al2(SO4)3·17H2O \( \rightleftharpoons \) 2Al3+ + 3SO42- + 17H2O | -5.343639e1 | 2.91648e-1 | -5.359448e-4 |    |    | 261–298                        |
| NaAl(SO4)2·12H2O \( \rightleftharpoons \) Na+ + Al3+ + 2SO42- + 12H2O | -1.75150e-1 | 2.59544e-2 |    |    |    | 273–298                        |
| KAl(SO4)2·12H2O \( \rightleftharpoons \) K+ + Al3+ + 2SO42- + 12H2O | -3.98684e-1 | 8.6936e-2 |    |    |    | 273–298                        |
| MgSO4·Al2(SO4)3·2H2O \( \rightleftharpoons \) Mg2+ + 2Al3+ + 4SO42- + 2H2O | -1.84542e1 |    |    |    |    | 298                             |
| FeSO4·Al2(SO4)3·2H2O \( \rightleftharpoons \) Fe2+ + 2Al3+ + 4SO42- + 2H2O | -1.9706e1 |    |    |    |    | 298                             |
| Al(OH)3 + 3H+ \( \rightleftharpoons \) Al3+ + 3H2O | 1.26598e4 |    |    |    |    | 273–298                        |
| NaAl(SO4)2·OH4 + 6H+ \( \rightleftharpoons \) Na+ + 3Al3+ + 2SO42- + 6H2O | 3.09584e-4 |    |    |    |    | 273–298                        |
| KAl(SO4)2·OH4 + 6H+ \( \rightleftharpoons \) K+ + 3Al3+ + 2SO42- + 6H2O | -9.23367e1 | 2.77587e4 |    |    |    | 273–298                        |
| SiO2(quartz) + 2H2O \( \rightleftharpoons \) Si(OH)40 | 9.682e-1 | -3.0718e3 |    |    |    | 273–298                        |
| SiO2(amorphous) + 2H2O \( \rightleftharpoons \) Si(OH)40 | -6.051e-1 | -1.6838e3 |    |    |    | 273–298                        |
| Al2Si2O5(OH)4 + 6H+ \( \rightleftharpoons \) 2Al3+ + 2Si(OH)40 + H2O | -5.25218e1 | 1.96764e4 |    |    |    | 273–298                        |
| Solution phase equilibria         |    |    |    |    |    | 273–298                        |
| Al3+ + H2O \( \rightleftharpoons \) Al(OH)+ + H+ | 7.8904e9 | -5.7851e3 |    |    |    | 273–298                        |
| Al3+ + 2H2O \( \rightleftharpoons \) Al(OH)+ + 2H+ | 2.23287e1 | -1.35797e4 |    |    |    | 273–298                        |
| Al3+ + 3H2O \( \rightleftharpoons \) Al(OH)+ + 3H+ | 2.86813e1 | -2.0085e4 |    |    |    | 273–298                        |
| Al3+ + 4H2O \( \rightleftharpoons \) Al(OH)+ + 4H+ | 2.69466e1 | -2.3621e4 |    |    |    | 273–298                        |
| Si(OH)40 \( \rightleftharpoons \) Si3O4(OH)3 + H+ | -1.6234e1 | -3.0790e3 |    |    |    | 273–298                        |

1 Derived using Eqs. (9) and (11) with DG0 and AHf0 from Nordstrom and Munoz (1994).
2 Derived using Eqs. (9)–(11) with DG0 and AHf0 from Table 4.

1958). Therefore, to simulate AlCl3·6H2O precipitation with the FREZCHEM model parameterization, one would have to remove FeCl3·6H2O (and FeCl3·10H2O at temperatures below 273 K) from the mineral database. This is however only a problem where Fe(III) concentrations are exceptionally high (e.g., Fig. 4). A similar problem exists for Al–Gas, where soluble gas is O2(aq), CO2(aq), or CH4(aq).

### 3.2. Aluminum sulfates

Binary Pitzer parameters for Al–SO4 at 298 K were taken from Christov (2001) and extended to lower temperatures with ice-equilibrium data (Linke, 1958) (Fig. 5). This is similar to how we handled Al–Cl binaries; but in the case of Al–SO4, we had seven ice data (Fig. 5), rather than just one for Al–Cl (Fig. 2). The binaries for Al–SO4 (Table 2) were exactly the same as previously used for Fe(III)–SO4 (Marion et al., 2008b) because in the latter case we used Al–SO4 parameters as surrogates for Fe(III)–SO4.

The degree of hydration for alunogen [Al2(SO4)3·17H2O] varies in the literature from 16 to 18 (Linke, 1958). In this paper, we assigned a hydration of 17 for all cases examined regardless of how the original papers designated the degree of hydration. Given Al–SO4 binaries, we were able to estimate the temperature dependence of Al2(SO4)3·17H2O (Table 3) (Fig. 5). Our model estimate of the eutectic was Al2(SO4)3 = 1.092 m at 260.65 K, which is in good agreement with literature values of Al2(SO4)3 = 1.092 m at 261.15 K (Linke, 1958).

There was a scattering of data in the literature that allowed us to estimate ternary parameters for Al–SO4 interactions with Na, K, H, Mg, Fe(II) and Fe(III). For ternary interactions other than the latter six ions, we used surrogates (see Table 2 footnotes). There were two datasets for Al2(SO4)3–Na2SO4 at 273.15 K and one at 298.15 K com-
As was the case for some figures below, the experimental data for these systems were not in complete agreement with our model. For example, at \( \text{Na}_2\text{SO}_4 = 0.0 \) at 298.15 K, our model predicts that \( \text{Al}_2(\text{SO}_4)_3\cdot17\text{H}_2\text{O} \) is equal to 1.126 m (Fig. 5), while the experimental datum gave a measured value of 1.211 m (Fig. 6). Linke (1958) stated that the latter value was higher than reported by other investigators. Similarly, our model predicts that the \( \text{Na}_2\text{SO}_4 \) concentration at \( \text{Al}_2(\text{SO}_4)_3 = 0.0 \) at 273.15 K is equal to 0.319 m, but the experimental datum is 0.485 m (Fig. 6). Our model estimate was based on an extensive temperature-dependent dataset (Marion and Farren, 1999), which we believe is more accurate than the experimental data in Fig. 6. However, because the shapes of the experimental and model curves are similar, we ignored these discrepancies. The solubility data for \( \text{Al}_2(\text{SO}_4)_3\cdot17\text{H}_2\text{O} \) and \( \text{Na}_2\text{SO}_4\cdot10\text{H}_2\text{O} \) were used to estimate \( W_{\text{Na,Al,SO}_4} \) (Table 2). With the new \( W_{\text{Na,Al,SO}_4} \) parameter, we derived a solubility product for sodium alum \( [\text{NaAl}(\text{SO}_4)_2\cdot12\text{H}_2\text{O}] \) (Table 3).

The model-calculation peritectics for mineral equilibria along the two temperature lines in Fig. 6 are in reasonable agreement, given the previously discussed discrepancies. Fig. 7 depicts the relationship of \( K_2\text{SO}_4 \) and \( \text{Al}_2(\text{SO}_4)_3 \). The experimental data were used to estimate \( W_{\text{K,Al,SO}_4} \) (Table 2) and the solubility product for potassium alum \( [\text{KAl}(\text{SO}_4)_2\cdot12\text{H}_2\text{O}] \) (Table 3). The model-calculated peritectics for mineral equilibria along the two temperature lines in Fig. 6 are in reasonable agreement, given the previously discussed discrepancies.

There was a single dataset depicting the solubility of alunogen \( [\text{Al}_2(\text{SO}_4)_3\cdot17\text{H}_2\text{O}] \) in \( \text{H}_2\text{SO}_4 \) at 298.15 K (Linke, 1958) (Fig. 8). The upper limit of the FREZCHEM model \( \text{H}_2\text{SO}_4 \) molality is 8.0 m (Fig. 8; Marion, 2002). This data-
set was used to estimate $B(0)_{\text{Al;HSO}_4}$, $B(1)_{\text{Al;HSO}_4}$, $C_{\text{Al;HSO}_4}$, and $W_{\text{H,Al,SO}_4}$. Other parameters needed for these chemistries ($\Theta_{\text{H,Al,HSO}_4}$, $\Psi_{\text{SO}_4,\text{HSO}_4,\text{Al}}$, and $B_{\text{Al;HSO}_4}$) were taken from the literature or assigned values of 0.0 (Table 2). The data fit is reasonably good (Fig. 8).

There was one dataset for MgSO$_4$–Al$_2$(SO$_4$)$_3$ equilibria at 298.15 K (Linke, 1958) (Fig. 9). We used the MgSO$_4$–7H$_2$O sector of this curve to estimate $\Psi_{\text{Me,Al,SO}_4}$ (with $\Theta_{\text{Me,Al}} = 0.0$) (Table 2). Then with these parameters, we estimated the equilibrium constant for pickeringite [MgSO$_4$·Al$_3$(SO$_4$)$_3$·22H$_2$O]. The resulting model fit the experimental data is good. Also included in Fig. 9 are extrapolations of the model to 273.15 K. This curve is anchored accurately at each end where either Al$_3$(SO$_4$)$_3$ or MgSO$_4$ = 0.0 m. But between these two anchors, it is difficult to assess accuracy. For example, pickeringite is not predicted to precipitate at 273.15 K, but that may simply reflect that the model assumed a fixed solubility product for pickeringite that is independent of temperature (Table 3), which is highly unlikely. This extrapolation of the model is similar to the “ice line” in Fig. 2.

A dataset similar to that used for pickeringite (Fig. 9) was used for halotrichite [FeSO$_4$·Al$_3$(SO$_4$)$_3$·22H$_2$O] (Fig. 10). The fit at 298.15 K was excellent. Again, assuming a constant equilibrium constant for halotrichite did not allow this solid phase to precipitate at 273.15 K (Fig. 10) based on a temperature extrapolation. It is not unusual for double salts such as pickeringite (Fig. 9) or halotrichite (Fig. 10) to become less prevalent at colder temperatures (Marion and Farren, 1999). Only future experimental work will clearly solve the uncertainty associated with the temperature dependence of these two double salt minerals.

There were two datasets for Al–Fe(III)–SO$_4$ chemistries at 293.15 and 298.15 K (Fig. 11) (Linke, 1958). As was the case for Al–Fe(III)–Cl (Fig. 4), we had to truncate the Fe “X” axis at Fe$_2$(SO$_4$)$_3$ = 1.0 because of the high $I$ values associated with Fe$_2$(SO$_4$)$_3$ chemistries ($I = 31.6$ m for Fe$_2$(SO$_4$)$_3$·9H$_2$O at 298.15 K, Marion et al., 2008b). The data used to estimate $\Psi_{\text{Fe(III),Al,SO}_4}$ were only in equilibrium
with Al₂(SO₄)₃·17H₂O. Note the sharp drop in the solubility of Al₂(SO₄)₃·17H₂O between 298 and 293 K (Fig. 11). The estimated $\Psi_{\text{Fe(III)AlSO₄}}$ values were very different between 293 (0.3064) and 298 K (−0.0827), which fits the data adequately (Fig. 11), but not well. Extending the $\Psi_{\text{Fe(III)AlSO₄}}$ equation (Table 2) to even lower temperatures will cause a sharp drop in the solubility of Al₂(SO₄)₃·17H₂O. So some caution is necessary for extrapolating chemistries such as these to lower temperatures. This is why we specify the temperature ranges for our model parameters (Tables 2 and 3). Also, as was the case for FeCl₃–AlCl₃, one should remove Fe₂(SO₄)₃ salts from the mineral database as they sometimes cause problems by precipitating when they should not. This, however, is only a problem where Fe(III) concentrations are exceptionally high (e.g., Figs. 4 and 11).

3.3. Aluminum hydroxides and silicon minerals

In contrast to the previously discussed parameterizations of aluminum chlorides and sulfates that were based on experimental solubility measurements, all the solubility products for aluminum hydroxides and silicon minerals (Table 1) were based on application of Eqs. (9)–(11) using the $\Delta G^0_i$ and $\Delta H^0_i$ data of Table 4. In addition to the calculated solubility products for these solid phases, Table 3 also includes Al solution phase complexes with the hydroxide ion (OH⁻). All of the $\Delta G^0_i$ and $\Delta H^0_i$ data for these complex reactions were taken from Nordstrom and Munoz (1994). Fig. 1 depicts the distribution of these complexes. Below pH 3.0, virtually all the aluminum ions are present as Al⁻³ (−99.6%); above pH 3.0, aluminum chemistry necessitates an explicit recognition of hydroxyl complexes (Fig. 1). The soluble aluminum hydroxide species [Al(OH)₃⁺, Al(OH)₂⁺, Al(OH)⁺, Al(OH)²⁻] and soluble silicon species [SiO(OH)₃, Si(OH)₁⁰⁻] were assigned activity coefficients of 1.00, FeOH⁺, and Fe²⁺ for neutral, ±1, and +2 charges, respectively. Unfortunately, the single-charged parameters are only defined for FeOH–Cl binaries.

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3.4. Density and pressure parameterization

The FREZCHEM model is structured to predict the effects of pressure on equilibrium constants, activity coefficients, the activity of water, and solution density (Marion et al., 2005, 2008b; Marion and Kargel, 2008). Implementation of the pressure equations requires a specification of the partial molar volume ($V^0_i$) and compressibility ($K^0_i$) of individual species [e.g., Al³⁺ and Si(OH)₄⁰⁻ and binary Pitzer equation volumetric parameters (e.g., $B^*_{\text{ACCl}}$), except for equilibrium constants, which only require $V^0_i$ and $K^0_i$].

The aluminum density data needed to estimate these Pitzer volumetric parameters are scarce (see Linke, 1958). We used Fe(III) surrogates from Marion et al. (2008b) for Al–Cl binary volumetric parameters and mixed Na(or K)Al(SO₄) solutions (Linke, 1958) to estimate these parameters for Al–SO₄ (Table 2). The Pitzer ion interaction parameters for SiO(OH)₄⁻ ions are only developed for Na–SiO(OH)₃ ions (Pitzer, 1987; Felmy et al., 2001). This scarcity makes it impossible to develop a broad chemical composition for SiO(OH)₃⁻ chemistries, which is not a major concern because SiO(OH)₃⁻ ions are relatively minor constituents in aqueous solution. Application of the model to predict the pressure dependence of equilibrium constants requires estimates of molar volumes and compressibilities of solution phase species and solid phases (Marion et al., 2005, 2008b; Marion and Kargel, 2008). The molar volumes of the aluminum and silicon solid phases are included in Table 1. The molar volumes and compressibilities of most solution phase species are included in Marion et al. (2005, 2008b), and Marion and Kargel (2008), except for the Al³⁺ ion and Si(OH)₄⁰⁻. We used the molar volume and compressibil-
ility of the B(OH)$_4^-$ species (Millero, 2001) as a surrogate for Si(OH)$_4^0$ (Table 2), which allows one to determine the pres-
sure dependence of reactions involving Si(OH)$_4^0$ (e.g.,
quartz and kaolinite precipitation, Table 3). We assumed a
linear fit to Na$^+$ and Mg$^{2+}$ molar volumes and compressibil-
ity data over the 273–298 K temperature range (Millero,
2001) would extrapolate reasonably well for Al$^{3+}$. This is
exactly how we calculated similar parameters for the Fe$^{3+}$
ion (Marion et al., 2008b). The temperature-dependent equa-
tions are in Table 2. Our model estimates at 298.15 K are $V_{Al^{3+}} = -41.09$ cm$^3$ mol$^{-1}$ and $K_{2}^{Al^{3+}} = -12.14e$-3 cm$^3$
 mol$^{-1}$ bar$^{-1}$, which are close to values for Fe$^{3+}$ of
$-35.99$ cm$^3$ mol$^{-1}$ and $-11.85e$-3 cm$^3$ mol$^{-1}$ bar$^{-1}$ (Marion
et al., 2008b) and values for PO$_4^{3-}$ of $-50.46$ cm$^3$ mol$^{-1}$ and
$-16.71e$-3 cm$^3$ mol$^{-1}$ bar$^{-1}$ (Millero, 2001).

The model-estimated $V_{Al^{3+}}$ and binary Al–SO$_4$ volumet-
ric parameters can be used, along with other previously
defined parameters (Marion et al., 2005), to estimate the
density of the mixed Na(or K)Al(SO$_4$)$_2$ solutions (Linke,
1958) that were used to develop the binary Al–SO$_4$ volumet-
ric parameters. How accurate was this parameterization?
The KAl(SO$_4$)$_2$ solutions ($n = 4$) have model values ranging
from 1.025 to 1.065 g cm$^{-3}$ over the temperature range from
0 to 25 °C, respectively, that compares favorably with the
experimental values of 1.028 to 1.059 g cm$^{-3}$. Similarly,
the NaAl(SO$_4$)$_2$ solutions ($n = 5$) have model values ranging
from 1.269 to 1.319 g cm$^{-3}$ over the temperature range from
0 to 25 °C that also compares favorably with the
experimental values of 1.264 to 1.313 g cm$^{-3}$. Overall the
standard error for these nine comparisons was 0.42%.

4. MODEL VALIDATION AND LIMITATIONS

The paucity of aluminum and silicon data and problems
related to frequent metastable appearance and persistence of
phases makes it difficult to fully validate the model. While
model fits to experimental data are encouraging and point
out the self-consistency of the model and data inputs (Figs.
2–11, and the density comparisons in Section 3.4), they are
not a substitute for validation, which requires comparison
to independent data for multicomponent solutions.

Comparing model predictions of mineral stabilities in
acidic systems can be used to at least qualitatively validate the
model. For example, minerals found in Lakes Gilmore
and Swann include jarosite, Fe-oxides, alunite, kaolinite,
quartz, halite, and gypsum (McArthur et al., 1989, 1991;
Long et al., 1992a,b; Benson et al., 2007; Bowen and Ben-
sion, 2008). These findings are consistent with our model SI
calculations that indicate supersaturation, saturation, and
near-saturation for all of these minerals (see Figs. 14
and 15 in Section 5).

In Table 5, we compare our model estimates of alumi-
nium equilibrium constants [$ln(K)$] at 25 °C with Christov
references. These equilibrium constants are in good agree-
ment. This is true despite the differences in how we extended
the temperature ranges (Figs. 2 and 5), and complications and
assumptions inherent in other cases (Figs. 6 and 7).

The paucity of aluminum and silicon data is a severe
limitation for accurately parameterizing these chemistries.

There are only limited chloride and sulfate databases
across limited temperature ranges. In many cases, the
parameters are only defined for 298 K (Tables 2 and 3).
Applications of the FREZCHEM model using these
298 K parameters assume constant parameters value
across all temperatures. Applications of temperature-
dependent equations to temperatures lower than their
database temperatures (listed in Tables 2 and 3) are based
on simple mathematical extrapolations of these equations,
which is often necessary for reactions at subzero tempera-
tures (Marion, 2001, 2002; Marion et al., 2003, 2006,
2008b). A good example of the paucity of data is the single
data at 218 K for AlCl$_3$ (Fig. 2) that was used to ex-
tend the 298 K binary parameters to 218 K, which, in
turn, were used to define the AlCl$_3$–H$_2$O (chloraluminite)
equilibrium constants from 298 to 218 K.

In some cases, the existing experimental data show obvi-
ous room for improvement. For example, the Al$_2$SO$_4$–
Na$_2$SO$_4$ data in Fig. 6 date back to 1927–1954 (Linke,
1958). In these cases, the salt solubilities along the $Y$ or $X$
axis, where the other axis molality is 0.0, are out of line with
the generally accepted solubilities (see discussion with
respect to Fig. 6).

There are also problems related to ionic strength ($I$). For
example, the $I$ of pure FeCl$_3$–H$_2$O at 298 K is 36.6 m. The
maximum $I$ for saturated AlCl$_3$–H$_2$O was 20.4 m (Figs.
2 and 4). So applying binaries for AlCl$_3$ to this ternary system
(Al–Fe–Cl) is an extension beyond the range of AlCl$_3$ bin-
ary parameterization. A similar case exists for Fe$_2$SO$_4$–
Al$_2$SO$_4$ (Fig. 11) where the $I$ of pure Fe$_2$(SO$_4$)$_3$–H$_2$O at
298 K is 31.6 m at saturation and the $I$ of Al$_2$(SO$_4$)$_3$–17H$_2$O
used for binaries was only 16.8 m. A third similar and persistent case deals with K$_2$SO$_4$. The binary
parameterization of K$_2$SO$_4$ was based on data up to
K$_2$SO$_4$ saturation ($I = 2.1$ m) (Marion and Farren, 1999).
Application of these binary K$_2$SO$_4$ parameters to a
K$_2$SO$_4$–H$_2$SO$_4$ system ($I$(max) ≈ 10 m) led to a poor fit
(Marion, 2002). Application of these binary K$_2$SO$_4$ parame-
ters to a K$_2$SO$_4$–Fe$_2$(SO$_4$)$_3$ system ($I$(max) ≈ 15 m) led
to a poor fit (Marion et al., 2008b). And in this paper,
application of binary K$_2$SO$_4$ parameters to a K$_2$SO$_4$–Al$_2$(SO$_4$)$_3$
system (Fig. 7) also led to a poor fit at 25 °C. Poor binaries
will always lead to poor ternaries, and subsequently poor
over-all fits. Earlier (Marion, 2002) we extended Na$_2$SO$_4$
binary parameters to $I$ values beyond the solubility of mirabilite (Na$_2$
SO$_4$·10H$_2$O). So in principle, these limiting binaries can be
extended to higher $I$ values if adequate data exist, which
currently is the problem.

Another problem in applying the FREZCHEM model has
to do with the state of chemical equilibrium for alumi-
num and silicon minerals. Often these minerals are super-
saturated in natural environments (see Figs. 14 and 15
in Section 5). In contrast, quartz, halite, and gypsum
approach mineral saturation (SI = 0), which greatly simpli-
fies system simulation. This state of gross supersaturation
with respect to minerals that are known to be precipitating
is also the case for Fe(III) solid phases (see Figs. 14 and 15
in Section 5; Marion et al., 2008b). Nordstrom and Munoz
(1994) compared gypsum and jarosite precipitation from
acid sulfate soil waters and found that gypsum solubilities
approached saturation (but not supersaturation), while jarosite was generally supersaturated by orders of magnitude (see their Figs. 9.15 and 9.16). These findings are similar to our results (see Figs. 14 and 15 in Section 5). Nordstrom and Munoz (1994) attributed jarosite supersaturation, compared to gypsum, to a strong kinetic barrier to saturation equilibrium. A similar example exists for Earth seawater that is supersaturated with respect to CaCO$_3$ minerals (Morse and He, 1993), which is attributed to crystal formation inhibitors such as Mg$^{2+}$, orthophosphate, and organic matter (Pytkowicz, 1973; Bischoff et al., 1993; Morse et al., 2007). Interestingly, we just found a theoretical approach for modeling seawater CaCO$_3$ supersaturation (Marion et al., 2008c). But this, to date, is an exception on how to cope with mineral supersaturation. Generally speaking, one cannot assume, as was done in previous applications of the FREZCHEM model, that the solution and mineral phases are simultaneously in thermodynamic equilibrium, especially for Fe(III), Al, and Si minerals.

5. AUSTRALIAN ACIDIC PLAYA LAKES

Fig. 12 shows the molal concentrations and pH of brine samples collected by McArthur et al. (1989, 1991) moving from the edge towards the center of Lake Gilmore. Note how soluble Na, K, Mg, Ca, Cl, and SO$_4$ ions increase in concentration between Samples 0 and 8 (Fig. 12). Between Samples 8 and 14 (further out into the basin), the latter ions are relatively constant. Al, Fe, and Si, on the other hand, tend to be highest at the low sample numbers and decrease with distance into the playa lake. These differences between ions were likely caused by pH, which varied between 2.9 and 3.4 in Samples 0–6, and then rose to 5.3 by Sample 14 (Figs. 12). Note the sharp drops in Al and Si concentration between Samples 6 and 8.

Fig. 13 shows the molal concentrations and pH of brine samples collected by McArthur et al. (1989, 1991) near the edge of Lake Swann (Samples 0–4). As in Lake Gilmore, the soluble ions Na, K, Mg, Ca, Cl, and SO$_4$ ions increase in concentration between Samples 0 and 5 (Fig. 13). Between Samples 5 and 6 (further out into the basin), the latter ions are relatively constant. Al, Fe, and Si, on the other hand, tend to be highest at the low sample numbers and decrease with distance into the playa lake. These differences between ions were likely caused by pH, which varied between 3.0 and 3.4 in Samples 0–4, and then rose to 5.2–6.4 in Samples 5 and 6 (Fig. 13). Note the sharp drops in Al and Si concentrations between Samples 4 and 5.

Lakes Gilmore and Swann have very similar chemical features, except for a few minor issues. Both lakes increase in soluble ion concentrations nearshore and decrease in Al, Fe, and Si further offshore. The pH breakpoint for Lake Gilmore occurred between Samples 6 and 8 (75–110 m into the lake) (Fig. 12), while the pH breakpoint for Lake Swann occurred between Samples 4 and 5 (25–61 m into the lake) (Fig. 13). Also at the higher pH values of Lake Swann, bicarbonate began to accumulate (Fig. 13). In both lakes, pH and Al concentrations were related as we will demonstrate by considering mineral saturation indices.

Saturation indices (SI) for minerals are defined by

\[
SI = \log(IAP/K_{sp}) 
\]

where IAP is the model-calculated ion activity product and $K_{sp}$ is the solubility product. SI = 0.0 implies mineral equilibrium; SI < 0.0 implies mineral undersaturation; and SI > 0.0 implies mineral supersaturation. In applying the FREZCHEM model to estimate SI values, we ran the simulations at 25 °C, which is within the average air temperature range for these Australian lakes (10–27 °C, Benison et al., 2007). We also used Option 2 (see Section 2.1.4) to constrain pH values at experimentally measured values (see Table 1 in McArthur et al., 1991). The Lake Gilmore and Lake Swann chemical data were out of charge balance by average errors of –2.9 and –2.2%, respectively. We forced a charge balance for individual samples in our sim-

![Fig. 12. The concentrations of solution species and pH in Lake Gilmore, Australia. Sample designations (McArthur et al., 1991) range from near-shore (0–6, 20–75 m) to off-shore playa waters (8–14, 110–380 m).](image)
ulations by minor adjustments of the Cl (dominant anion) concentration.

**Table 5**
A comparison of equilibrium constants \([\ln(K)]\) for aluminum minerals at 25 °C.

<table>
<thead>
<tr>
<th>Minerals</th>
<th>This study</th>
<th>Reference studies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlora-luminite (AlCl(_3)·6H(_2)O)</td>
<td>16.16</td>
<td>16.05 (Christov, 2001)</td>
</tr>
<tr>
<td>Sodium alum [NaAl(SO(_4))(_2)·12H(_2)O]</td>
<td>-9.77</td>
<td>-9.95 (Christov, 2002)</td>
</tr>
<tr>
<td>Potassium alum [KAl(SO(_4))(_2)·12H(_2)O]</td>
<td>-13.9</td>
<td>-13.7 (Christov, 2001)</td>
</tr>
<tr>
<td>Pickeringite [MgSO(_4)·Al(_2)(SO(_4))(_3)·22H(_2)O]</td>
<td>-18.45</td>
<td>-18.01 (Christov, 2001)</td>
</tr>
</tbody>
</table>

Fig. 14 depicts the SI values for Fe(III) [jarosite (KFe\(_3\)(SO\(_4\))\(_2\)(OH)\(_6\)) and hematite (Fe\(_2\)O\(_3\))], Al (alunite, gibbsite and kaolinite), quartz, halite (NaCl), and gypsum (CaSO\(_4\)·2H\(_2\)O) minerals that precipitate in the Lake Gilmore region (McArthur et al., 1989, 1991). The Fe(III) minerals were supersaturated throughout the entire sampling range (Fig. 14); on the other hand, Al minerals, except for kaolinite, were undersaturated where pH values were 2.9–3.6, but became supersaturated where pH increased above 4 (Fig. 14). The only minerals that approached chemical thermodynamic equilibrium (SI = 0.0) were gypsum and quartz (Fig. 14). Since gypsum components of the solution (Ca\(^{2+}\) and SO\(_{4}^{2-}\)) are orders of magnitude more abundant than silica, it is not surprising that coarse gypsum blades and rosettes are commonly observed to be abundant both on the playa surface and in the subsurface muds of Lake Gilmore, whereas amorphous silica and other silicate phases are not obvious (McArthur et al., 1989, 1991).

Fig. 14. The concentrations of solution species and pH in Lake Swann, Australia. Sample designations (McArthur et al., 1991) range from near-shore (0–4, 0–28 m) to off-shore playa waters (5–6, 61–70 m).

Fig. 14. The saturation indices for minerals and pH in Lake Gilmore, Australia at 25 °C. Sample designations (McArthur et al., 1991) range from near-shore (0–6, 20–75 m) to off-shore playa waters (8–14, 110–380 m).
Fig. 15 depicts the SI values for Fe(III) (jarosite and hematite), Al (alunite, gibbsite and kaolinite), quartz, halite, and gypsum minerals that precipitate in the Lake Swann region (McArthur et al., 1989, 1991). The Fe(III) minerals were generally supersaturated throughout the entire sampling range (Fig. 15); on the other hand, Al minerals, except for kaolinite, were undersaturated where pH values were 3.0–3.4, but became supersaturated where pH increased to 5.2–6.4 (Fig. 15). The only minerals that approached chemical thermodynamic equilibrium (SI = 0.0) were gypsum, quartz, and halite (Fig. 15).

As was the case in comparing solution concentrations (Figs. 12 and 13), the mineral SI patterns were similar between Lakes Gilmore and Swann (Figs. 14 and 15). Iron minerals and kaolinite were generally supersaturated across the entire range of sample collections. The Al minerals, alunite and gibbsite, only became supersaturated when the pH increased to >4.0, further out into the lake. Halite and gypsum were undersaturated nearshore, and approached saturation (SI = 0) offshore. McArthur et al. (1991) found gypsum precipitating offshore in Lake Gilmore at and beyond Sample #7; our model analyses have gypsum close to saturation offshore in Samples #8, 11, 12, and 14 (Fig. 14), but undersaturated near shore (Samples 0, 1, 3, 4, 5, and 6). Similarly, McArthur et al. (1991) found gypsum precipitating in the area of Samples 5 and 6 in Lake Swann (Fig. 15), but not precipitating near shore, which agrees with our model calculations. Halite calculations remain undersaturated in these playa lakes (Figs. 14 and 15), which is consistent with McArthur et al. (1991) field observations. Quartz was supersaturated nearshore and approached saturation offshore.

6. COMPARISONS BETWEEN WA LAKES AND MARS

Benison and Bowen (2006) made a strong case for why WA acidic, saline lakes may be especially sound as mineral-geochemical, and physical analogues for the Burns formation in the Meridiani Planum region of Mars: the minerals that precipitate in these WA lakes include Ca and Mg sulfate, jarosite, hematite, and chlorides; and the WA sedimentary textures/structures include siliciclastic components, fine-medium sand grains, planar laminations, cross-bedding, hematite concretions, displacive crystals, ripple marks, and mudcracks (see their Table 1). All of these WA acidic, saline lake properties are also characteristic of the Burns formation (Clark et al., 2005; Grotzinger et al., 2005; McLennan et al., 2005). In what follows, we will examine aqueous chemistry differences and related mineralogical implications for hypothetical Mars and WA acidic ground waters.

Table 6 compares the composition of a hypothetical Martian brine and Lake Gilmore-Sample 0 (Figs. 12 and 14) that we used in model simulations. The Mars brine is based on the composition of an acid-weathered basalt (with olivine) (Tosca et al., 2005; Marion et al., 2008b). This Martian brine represents an immature weathering product, while the Lake Gilmore brine has a more complex history reflecting a variety of processes discussed more fully below (Gray, 2001; McArthur et al., 1989, 1991). Evidence suggests that wet periods on Mars were relatively short-lived (Kerr, 2008) so that relatively simple, single stage weathering interactions may be typical for Mars, although this is obviously a topic of great uncertainty. The temperature used in our simulations was 15 °C, which is in the range of average air temperatures at the WA sites (10–27 °C, Benison et al., 2007). We assigned both of the modeling cases a fixed pH of 3.0. This was deemed reasonable for the Martian brine, based on the observed acidic mineral assemblages already known to exist; the actual pH of the Lake Gilmore-Sample 0 was 3.3 (McArthur et al., 1991). Fixing the pH value at 3.0 is Option 2 discussed in Section 2.1.4, which replaces H+ ions produced by reactions such as Eqs. 7, (13)–(15) with other cations. This option is useful because it allows one to estimate total H+ production by comparing the initial and final
cation abundances (in moles). Finally, all 95 solid phases that are currently in the FREZCHEM model were included in our simulations. We did not remove any minerals from our mineral database, as we have done in many simulations in the past. Therefore, only the most stable minerals will precipitate (e.g., hematite, and not goethite). The simulations were done based on fractional crystallization, which does not allow minerals that have precipitated to dissolve and reprecipitate.

These two water samples are clearly different with respect to their dominant chemistries (Table 6). The Martian brine is dominated by Mg–Ca–Fe–SO₄, reflecting its formation from basalt (Tosca et al., 2005), and the Lake Gilmore sample is dominated by Na–Cl, which is largely derived from marine aerosols (Alpers et al., 1992).

Table 6
A comparison of a Mars and a Lake Gilmore solution phase composition used in our simulations (Fig. 16 and 17). Temperature and pH were arbitrarily set.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Mars¹</th>
<th>Lake Gilmore²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0.000316 m</td>
<td>0.6590 m</td>
</tr>
<tr>
<td>K</td>
<td>0.000105 m</td>
<td>0.0046 m</td>
</tr>
<tr>
<td>Mg</td>
<td>0.00558 m</td>
<td>0.0520 m</td>
</tr>
<tr>
<td>Ca</td>
<td>0.00285 m</td>
<td>0.0038 m</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>0.00279 m</td>
<td></td>
</tr>
<tr>
<td>Fe(III)</td>
<td>0.00279 m</td>
<td>0.000085 m</td>
</tr>
<tr>
<td>Al</td>
<td>0.00020 m</td>
<td>0.0031 m</td>
</tr>
<tr>
<td>Cl</td>
<td>0.00420 m</td>
<td>0.7458 m³</td>
</tr>
<tr>
<td>SO₄</td>
<td>0.1268 m²</td>
<td>0.0195 m</td>
</tr>
<tr>
<td>Si(OH)₄</td>
<td>0.02300 m</td>
<td>0.0013 m</td>
</tr>
<tr>
<td>Temperature</td>
<td>15 ºC</td>
<td>15 ºC</td>
</tr>
<tr>
<td>pH</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Ionic Strength</td>
<td>0.5555 m</td>
<td>0.8686 m³</td>
</tr>
</tbody>
</table>

¹ From Marion et al., 2008b.
² From McArthur et al., 1991, Sample 0.
³ Dominant anion that was adjusted to lead to a perfect charge balance.

Evaporation of this Cl-dominated solution eventually led to significant precipitation of Cl salts (halite, carnallite, and bischofite) along with various sulfate salts (gypsum, anhydrite, epsomite, and kieserite). Because jarosite did not precipitate in this simulation, the K⁺ ion concentrations were maintained at moderate values, ultimately causing precipitation of the K⁺ salts: alunite [KAl₃(SO₄)₂(OH)₆] and carnallite (KMgCl₃·6H₂O). Also the prevalence of Cl⁻ ions in this solution led to a high ionic strength (I) of 17.2 m at the end of the simulation, which is why low-hydrate salts such as anhydrite (CaSO₄) and kieserite (MgSO₄·H₂O) formed. This did not occur in the Mars simulation (Fig. 16) because the final I was only 12.2 m. However, if we had driven the Mars simulation to the point where Cl salts would precipitate, then I values would have increased sufficiently for low-hydrate salts to precipitate.

Fig. 16. The molal concentrations of a hypothetical Martian brine during evaporation at 15 ºC. Arrows indicate where solid phases start to precipitate.
Because we used Option 2 to maintain a constant pH value in our simulations, we can estimate H⁺ production by counting the change in cation contents (mol) between the start and finish of the simulations (see Section 2.1.4 for a fuller explanation). H⁺ production for the Mars case (Fig. 16) was 0.23406 mol/kg (H₂O), while the Lake Gilmore case (Fig. 17) was only 0.00649 mol/kg (H₂O), a 36-fold difference. Most of this difference reflects the much higher initial concentration of Fe(III) for the Mars case (32.8-fold) than for the Lake Gilmore case (Table 5). Much more hematite, jarosite, and natrojarosite formed in the Mars simulation (Fig. 16) than was the case for Lake Gilmore where lesser amounts of hematite and alunite formed (Fig. 17). All of these solid phases produce H⁺ ions through reactions such as

\[
\text{Fe}_2\text{O}_3(\text{cr}) + 6\text{H}^+ \Leftrightarrow 2\text{Fe}^{3+} + 3\text{H}_2\text{O} \quad \text{(hematite)}
\]

\[
\text{KFe}_3(\text{SO}_4)_{2}(\text{OH})_6(\text{cr}) + 6\text{H}^+ \Leftrightarrow \text{K}^+ + 3\text{Fe}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O} \quad \text{(jarosite)}
\]

\[
\text{KAl}_3(\text{SO}_4)_{2}(\text{OH})_6(\text{cr}) + 6\text{H}^+ \Leftrightarrow \text{K}^+ + 3\text{Al}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O} \quad \text{(alunite)}
\]

Had we not replaced these H⁺ ions with other cations in order to maintain pH 3.0, then the final H⁺ concentrations would have resulted in approximate pH values of 0.63 [−log(0.23406)] and 2.19 [−log(0.00649)] for the Mars and Lake Gilmore cases, respectively.

### 7. DISCUSSION AND CONCLUSIONS

Various studies of Australian acidic saline lakes have reported jarosite, Fe-oxides, alunite, kaolinite, gypsum, halite, and silica formation in the lake sediments (McArthur et al., 1989, 1991; Long et al., 1992a,b; Benison et al., 2007; Bowen and Benison, 2008). These findings are generally consistent with our model SI calculations (Figs. 14 and 15). Gray (2001) investigated regional variations in the composition of WA ground waters, and found that strongly elevated acidity was mainly characteristic of the upper part of the ground water mass in the Lake Gilmore and Lake Swann region. Gray’s data indicated that deep ground waters in these areas were relatively reduced and enriched in Fe(II), consistent with the expectations of McArthur et al. (1989, 1991) who invoked Fe(II) oxidation and associated iron oxide precipitation as a key source of acidity. Gray (2001) further offers the suggestion that these acidic waters also caused dissolution of kaolinite, the most reactive phase remaining in the intensely weathered upper regolith, in turn, leading to high concentrations of dissolved Al and Si (Figs. 12–15). The emergence of these acidic ground waters in and around playa margins results in the precipitation of the mineral suite listed above, generating additional acidity via reactions such as (Eqs. (13)–(15)) until the brine becomes depleted in Al and Fe, and the pH rises. These brines in various stages of depletion (Figs. 14 and 15) mix with near neutral saline lake brines, which fluctuate in concentration depending on precipitation amounts, associated surface water inflow, and subsequent evaporation (McArthur et al., 1989, 1991; Gray, 2001; Benison et al., 2007; Bowen and Benison, 2008).

Key aspects of the WA ground water and lake geochemistry therefore are (1) an intensely weathered regolith, (2) low hydraulic gradients, (3) the development of dense, saline ground waters, which are anoxic at depth and slowly recharged via density flow, (4) the interaction of these deep ground waters with regolith causing release of Fe(II), (5) the development of acidity in the subsurface, either by ferrication, pyrite oxidation, or other means; this acid production commonly “runs away” as waters near the surface, and additional acid-generating phases precipitate, and finally (6) mixing of the remaining ground water-derived solutes with solutes derived from meteoric surface waters that pond within the lakes, without first percolating deeply and interacting with the regional ground waters (Gray, 2001).

There were similarities, differences, and uncertainties between acidic saline playa lakes on Earth and waters that...
formed salt accumulations in the Burns formation on Mars. Both systems were dominated by (1) acidic saline ground waters and sediments, (2) Ca and Mg sulfates, and (3) iron precipitates such as jarosite and/or hematite (cf., Figs. 16 and 17). Major differences included: (1) the dominance of NaCl (and halite precipitation) on Earth, and the dominance of Fe–Mg–Ca–SO₄ (and low halite precipitation) on Mars, (2) extremely low K⁺ concentrations on Mars due to jarosite precipitation (cf., Figs. 16 and 17), and (3) higher acid production in the presence of high iron concentrations on Mars.

Terrestrial playa lakes that receive a substantial influx of both ground and surface waters, such as the lakes in WA, display lateral chemical variations in areas where the waters from these different sources mix and interact (Figs. 12 and 13). In contrast, Mars studies suggest that rainfall and surface water movements were greatly limited compared to the Earth (Kerr, 2008), and that broad, continental scale, ground water movements may have been a very important hydrologic process that shaped the surface mineralogy (Andrews-Hanna et al., 2007). There is little evidence for lateral compositional variation in Meridiani Planum (Clark et al., 2005), where observations show mixed saline evaporite and non-evaporite mineral components that have been re-worked and modified by both aeolian and ground water diagenetic processes (Clark et al., 2005; Grotzinger et al., 2005; McLennan et al., 2005; Tosca et al., 2005). Thus, marked, lateral variations in mineralogy (and brine chemistry) like that seen in WA acid playa settings, may not provide a close Martian analogue. Instead, Mars sediments may reflect the dominance of broader variations in ground water chemistry, vertical ground water movements, and aeolian processes.

In summary, both the WA acid lake setting and Mars Meridiani Planum setting have mineral assemblages that can be modeled as the products of acid-saline brines. Some of the mineral products formed in the two cases are closely similar (i.e., calcium and magnesium sulfates, and iron minerals); however large differences in the initial brine chemistries also lead to important mineralogical differences. In particular, the WA playa mineral assemblages are dominated by NaCl and other chloride mineral phases (Fig. 17), while the modeled Meridiani Planum brine is dominated by Mg–Ca–Fe-sulfates (Fig. 16). These geochemical differences lead to significant differences in H⁺ production (Eqs. (13)–(15)) related to the likely higher initial iron concentrations in the hypothetical Martian versus terrestrial ground waters. Owing to the absence or extremely limited occurrence of precipitation on Mars, chemical sediments there are also likely to display less lateral chemical variation than the Australian lake deposits. Thus, the playa lakes of WA are a good, but not perfect, geochemical analogue for Meridiani Planum on Mars.

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REFERENCES


Clark B. C., Morris R. V., McLennan S. M., Gellert R., Jolliff B., Knoll A. H., Squires S. W., Lowenstein T. K., Ming D. W.,


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