**ACIDIC AUSTRALIAN PLAYA LAKES AS ANALOGUES FOR MARS.** G.M. Marion[1], J.K. Crowley[2], B. J. Thomson[3], S.J. Hook[3], N.T. Bridges[3], A.J. Brown[4], J.S. Kargel[5], and C.R. de Souza Filho[6], [1]Desert Research Institute, 2215 Raggio Parkway, Reno, NV 89512, giles.marion@dri.edu.  [2]USGS,  [3]NASA JPL, Caltech,  [4]NASA Ames, [5]Univ. of Arizona, [6]Univ. of Campinas, Brazil.

**Introduction:** There is abundant evidence for the presence of jarosite on Mars [1-5], which requires an acidic environment for formation.  Earth analogues for acidic environments such as acidic lakes in Australia [6-9] could help elucidate these processes for Mars. The objectives of this paper were to (1) add new chemistries (Al and Si) to an existing acid chemical thermodynamic model (FREZCHEM), (2) use the model to characterize acidic Australian playa lakes (Gilmore and Swann) [6], and (3) extend these Earth analogues to Martian environments.

**Methods and Materials:**  The FREZCHEM model is an equilibrium chemical thermodynamic model parameterized for concentrated electrolyte solutions using the Pitzer approach [10] for the temperature range from $<-70$ to 25°C and the pressure range from 1 to 1000 bars [5, 11].  The previous version of the model was parameterized for the Na-K-Mg-Ca-Fe(II)-Fe(III)-H-Cl-SO$_4$-NO$_3$-OH-HCO$_3$-CO$_3$-CO$_2$-O$_2$-CH$_4$-H$_2$O system and includes 81 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 oxide/hydroxide minerals, and two gas hydrates [5, 11].  Currently, we are adding Br, Al, and Si chemistries to this model.  Our focus in this paper will be on Al and Si chemistries.

We chose Lakes Gilmore and Swann in Australia as our working acidic lakes because of the extensive chemical analyses available for these lakes [6].  Furthermore, these are playa lakes, which have been suggested as the source of salts for the Meridiani Planum region of Mars [12].  Playa lakes are only seasonally wet at the surface.

**Results:**      The Pitzer approach requires parameterization of solution phase species and the solubility of solid phases.  Figure 1 shows how Al-SO$_4$ solutions equilibrate from 25°C to the model-calculated eutectic temperature at -12.5°C, which is in reasonable agreement with the experimental eutectic temperature of -12.0°C.  Similar relationships were developed for Al-Cl chemistries.  New Al solid phases added to the FREZCHEM model include:  gibbsite [Al(OH)$_3$], alunite [KAl$_3$(SO$_4$)$_2$(OH)$_6$], natroalunite [NaAl$_3$(SO$_4$)$_2$(OH)$_6$], alunogen  [Al$_2$(SO$_4$)$_3$·16H$_2$O], and AlCl$_3$·6H$_2$O.  This model also added solution phase Al-OH complexes.  New Si chemistries include solution phase species, Si(OH)$_4^0$ and SiO(OH)$_3^-$, and solid phase species, quartz (SiO$_2$) and amorphous silica (SiO$_2$).
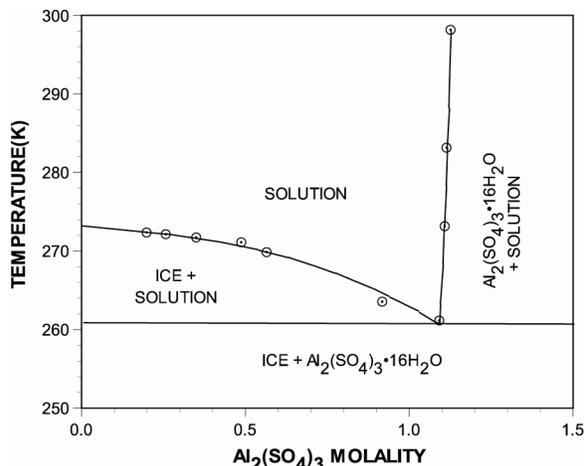


Figure 1. Equilibria for aluminum sulfate chemistry to subzero temperatures. Symbols are experimental data; lines are model estimates.

**Earth Acidic Playa Lakes:**  Figure 2 shows the molal concentrations and pH of brine samples collected from the edge of Lake Gilmore (Samples 0-6) where fresh ground waters flowing into this saline basin act as a diluent.  Note how soluble Na, K, Mg, Ca, Cl, and SO$_4$ ions increase in concentration between Samples 0 and 8 (Fig. 2).  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.  This difference between ions was 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. 2-3).  Note the especially sharp drop in Al concentration between Samples 6 and 8 (Fig. 2). pH and Al concentrations were related as we will demonstrate by considering mineral saturation indices.

Saturation indices (SI) for minerals are defined by

$$SI = \log (IAP/K_{sp}) \qquad (1)$$

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. Figure 3 depicts the SI values for several Fe(III) [jarosite (KFe$_3$(SO$_4$)$_2$(OH)$_6$ and hematite (Fe$_2$O$_3$)], Al (alunite and gibbsite), quartz, halite (NaCl), and gypsum (CaSO$_4$·2H$_2$O) minerals that precipitate in the Lake Gilmore region [6].  The Fe(III) minerals were

supersaturated throughout the entire sampling range (Fig. 3); on the other hand, Al minerals were under-saturated where pH values were 2.9-3.6, but became supersaturated where pH increased above 4 (Fig. 3). The only minerals that approached chemical thermo-dynamic equilibrium (SI = 0.0) were gypsum and quartz (Fig. 3).
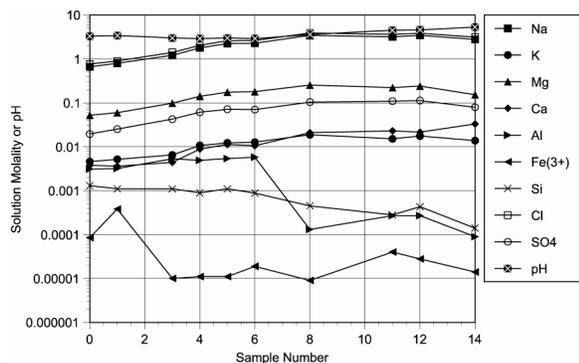


Figure 2. The concentrations of solution species and pH in Lake Gilmore, Australia. Sample numbers range from near-shore (0-6) where ground water discharge is mixing with lake water to off-shore waters (8-14) with less mixing.
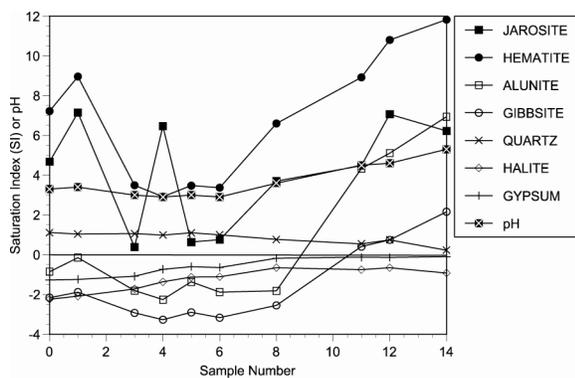


Figure 3. The saturation index for minerals and pH in Lake Gilmore, Australia. The sample numbers range from near-shore (0-6) where ground water discharge is mixing with lake water to off-shore waters (8-14) with less mixing.

**Mars Implications:** There are, at least, four reasons why these Earth analogues are relevant to Mars: ferrolysis, mineral supersaturation, playa environments, and lake salt variability. McArthur et al. [6] attributed acidification of these southwestern Australia

playa lakes to ferrolysis, which is described by the reaction:

$$4Fe^{2+} + O_2(g) + 10H_2O \iff 4Fe(OH)_3(cr) + 8H^+ \ (2)$$
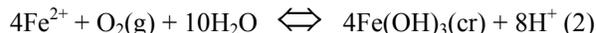
Ferrous iron is weathered from local rocks, reacts with $O_2(g)$, and precipitates as a ferric iron mineral producing acidity. Given that Mars surfaces have high iron concentrations [1-5, 11-13], it is highly likely that ferrolysis played an important role for acidification on Mars [11]. Supersaturation with respect to precipitated iron minerals is a common observation on Earth [5], and therefore requires consideration when simulating Martian environments. These acidic playa lakes in Australia are similar, but not identical, to acidic playa lakes on Mars, which may be the source of salts for the Burns Formation on Mars [2, 12-13]. For example, the anions in Lake Gilmore are dominated by Cl (Fig. 2), while the anions on Mars are dominated by $SO_4$ [2, 4, 5, 13]. And finally, nonuniform distributions of playa lake salts (Figs. 2-3) may need to be explicitly recognized in simulating Mars salt accumulations.

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