

**MODELING HYDROTHERMAL SYSTEMS ON MARS.** G.M. Marion<sup>1</sup>, J.S. Kargel<sup>2</sup>, J.K. Crowley<sup>3</sup>, and D.C. Catling<sup>4</sup>,  
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**Introduction:** In recent years, there have been abundant studies suggesting that hydrothermal systems have existed on Mars, especially for massive silica deposits in the Gusev Crater region [1-3]. During the past decade, the FREZCHEM model has been used to simulate chemistries on Mars including carbonates, sulfates, chlorides, perchlorates, iron, aluminum, and silicon [4-7]. But the FREZCHEM model was limited to a high temperature of 25°C, which is too low to simulate hydrothermal systems. The specific objective of this study was to create a FREZCHEM-like chemical thermodynamic model that would raise the upper temperature range to 100°C.

**Approach:** FREZCHEM is an equilibrium chemical thermodynamic model parameterized for concentrated electrolyte solutions (to  $I > 20$  m) using the Pitzer approach [8] for the temperature range from  $< -70$  to 25°C and the pressure range from  $< 1$  to 1000 bars [4-7]. The current version of the FREZCHEM model is parameterized for the Na-K-Mg-Ca-Fe(II)-Fe(III)-Al-H-Cl-ClO<sub>4</sub>-Br-SO<sub>4</sub>-NO<sub>3</sub>-OH-HCO<sub>3</sub>-CO<sub>3</sub>-CO<sub>2</sub>-O<sub>2</sub>-CH<sub>4</sub>-Si-H<sub>2</sub>O system and contains 101 solid phases. The new hydrothermal model, which is built on the FREZCHEM foundation, is called CHEMCHAU (CHEMistry CHAUd, where chaud means “hot” in French). This model will be initially limited to the Na-K-Mg-Ca-H-Cl-ClO<sub>4</sub>-SO<sub>4</sub>-OH-HCO<sub>3</sub>-CO<sub>3</sub>-CO<sub>2</sub>-O<sub>2</sub>-CH<sub>4</sub>-Si-H<sub>2</sub>O system. The chloride and carbonate chemistries within FREZCHEM were based in part on temperatures to 90°C [9,10]. So these chemistries were easy to develop for CHEMCHAU. Extending perchlorate, sulfate, and silicon chemistries largely relied on existing models that included these chemistries in many cases to temperatures  $> 100^\circ\text{C}$  [11-13]. But to maintain an accurate model, it was necessary in most cases to re-estimate the equilibrium constants. Figure 1 is an example for CaSO<sub>4</sub> chemistries. Our model estimate of the peritectic for CaSO<sub>4</sub>-CaSO<sub>4</sub>·2H<sub>2</sub>O occurs at 325 K (52°C), which is in the range for most estimates of this poorly defined peritectic (40-60°C) [14].

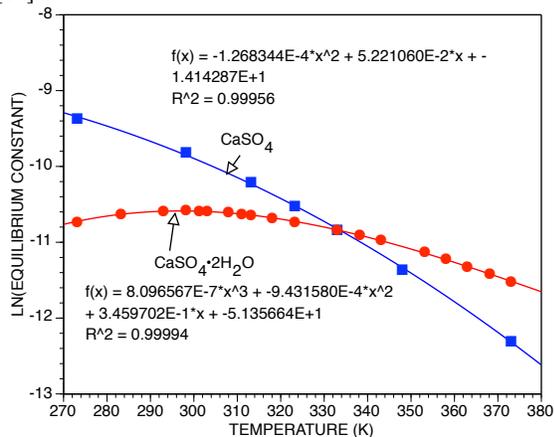


Figure 1. The natural log of the equilibrium constants for anhydrite (CaSO<sub>4</sub>) and gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) over the temperature range from 273 to 373 K.

**Applications to Mars:** Two Mars chemistries that are highly temperature dependent are equilibrium for calcite (CaCO<sub>3</sub>) and amorphous silica (SiO<sub>2</sub>); calcite is believed to

be an important mineral at the Phoenix site [15] and amorphous silica is believed to be an important mineral at the Home Plate site [1-3]. We ran a simulation from 273(0°C) to 373(100°C) K with a baseline composition of NaCl = 0.1 m with P<sub>CO2</sub> = 0.1 bars. An early Mars atmospheric CO<sub>2</sub> concentration may have been in the range of 0.05-0.25 bars [16]. Levels of CaCO<sub>3</sub> and Si(OH)<sub>4</sub> in these simulations were sufficient for mineral saturation and precipitation across this temperature range.

Si is much more soluble at high temperatures, and Ca is much more soluble at low temperatures (Fig. 2).

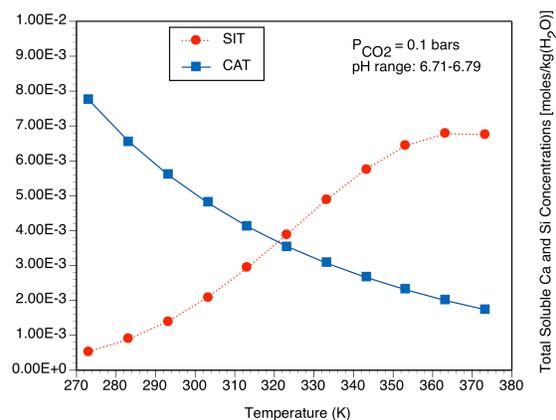
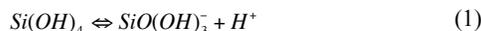


Figure 2. The soluble Ca and Si concentrations for systems in equilibrium with calcite and amorphous silica.

At high temperatures, primary volcanic silicates react with circulating hydrothermal fluids, releasing silica into solution. When the fluids reach the cool surface of Mars, rapid precipitation of amorphous silica would be expected, consistent with our model (Fig. 2). The high solubility of CaCO<sub>3</sub> at low temperatures could be partly responsible for few accumulations of carbonate minerals on Mars [15].

The simulation in Figure 2 is somewhat limited with respect to pH (6.71-6.79) because we fixed P<sub>CO2</sub> = 0.1 bars. In Figure 3, we estimated the pH associated with the reaction:



as a function of temperature along with amorphous Si precipitation. Si is most soluble at high temperatures and high pH. Below a pH of  $\approx 7$ , there is virtually no SiO(OH)<sub>3</sub><sup>-</sup>, which fixes the soluble Si as Si(OH)<sub>4</sub> (Eq. 1). At a low temperature of 273 K, there is no significant soluble Si variation with pH, simply because of the low mineral solubility at that temperature (Figs. 2-3).

For the calcite pH case, we assumed equilibrium for calcite with variable P<sub>CO2</sub> values (1.0e-4 to 1.0 bars), which led to soluble Ca equilibrium values over the pH range from 6 to 9 (Fig. 3). Calcite shows decreasing solubility with increasing temperatures at a given pH, which is the opposite of the case for amorphous Si (Fig. 3). While silica can form at pH values  $< 6$ , this is unlikely for CaCO<sub>3</sub> because it dissolves at low pH (Fig. 3).

**Conclusions:** These figures (1-3) illustrate how variable equilibrium cases can be for different chemistries and their temperature and pH dependencies likely found on Mars, which may help explain why mineral locations and assemblages are so highly variable on Mars, as they also are on Earth in hydrothermal deposits. In the near future, we will have the CHEMCHAU equilibrium model available at the Internet site (<http://frezchem.dri.edu>) for planetary applications.

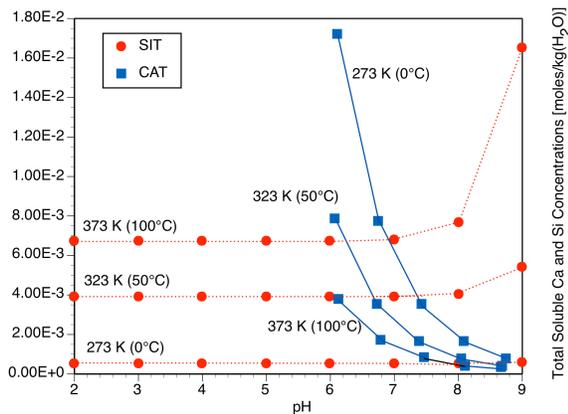


Figure 3. The soluble Ca and Si concentrations for systems in equilibrium with calcite or amorphous silica as a function of temperature and pH.

**References:** [1] Morris, R.V. et al., (2008) LPSC XXXIX, Abstract 2208. [2] Ruff, S.W. et al., (2008) LPSC XXXIX, Abstract 2213. [3] Squyres, S.W. et al., (2008) *Sci.* 320, 1063-1067. [4] Marion, G.M. and Kargel, J.S. (2008) *Cold Aqueous Planet. Geochem. with FREZCHEM*, Springer. [5] Marion, G.M. et al. (2008) *GCA*, 72, 242-266. [6] Marion, G.M. et al. (2009) *GCA*, 73, 3493-3511. [7] Marion, G.M. et al. (in press) *Icarus*. [8] Pitzer, K.S., (1995) *Thermodynamics*, McGraw-Hill. [9] He, S. and Morse, J.W., (1993) *GCA*, 57, 3533-3555. [10] Spencer, R.J. et al., (1990) *GCA*, 54, 575-590. [11] Greenberg, J.P. and Moller, N. (1989) *GCA*, 53, 2503-2518. [12] Millero, F.J. and Pierrot, D. (1998) *Aqueatic Geochem.* 4, 153-199. [13] Moller, N., (1988) *GCA*, 52, 821-837. [14] Raju, K.U.G. and Atkinson, G. (1990) *J. Chem. Eng. Data*, 35, 361-367. [15] Boynton, W.V., (2009) *Sci.* 325, 61-64. [16] Bridges, J.C. et al., (2001) *Space Sci. Rev.* 96, 365-392.