Sulfite-Sulfide-Carbonic Equilibria on Earth and Mars.

G.M. Marion[1], D.C. Catling[2], J.K. Crowley[3], J.S. Kargel[4]. [1]Desert Research Institute, 2215 Raggio Parkway, NV 89512, Giles.Marion@dri.edu, [2]University of Washington, Seattle, WA 98195, [3]USGS, Reston, VA 20192, [4]University of Arizona, Tucson, AZ 85721,

Introduction: Volcanic emitted SO_2 and H_2S gases and associated sulfite and sulfide salts are thought to play complex roles in sulfur chemistries on Earth and Mars [1-3]. In particular, sulfur-bearing gases in the early martian atmosphere (>3.8 Ga) have been proposed to maintain moderate surface temperatures via a thermostatic mechanism involving silicate weathering and sulfite precipitation, analogous to the role played by chemical weathering and carbonate precipitation processes on Earth [2]. On the other hand, others have shown that sulfur-containing gases oxidize in plausible atmospheres to make sulfate aerosols (along with S_8 aerosols in reducing atmospheres) [4]. Such aerosols cool the climate by reflecting sunlight, which is undoubtedly what happens with volcanic sulfate on Earth [4]. Thus, the climatic influence of sulfur may have been opposite to that proposed on Mars [2].

Objectives: FREZCHEM [5] allows geochemical modeling over a wide range of temperatures (-100 to +100°C) and pressures (1-1000 bars.) By adding reduced sulfur gas and salt chemistries to the model, we can better examine Mars surface and atmospheric processes throughout a range of conditions relevant to early Mars.

Results: Figure 1 is an example of how we parameterized a sulfite salt, $Na_2SO_3 \cdot 7H_2O$, which relied on a Pitzer parameter at 298 K [6] that was then tied to the ice line for lower temperature Pitzer parameters, which were then used to estimate the equilibrium constant for $Na_2SO_3 \cdot 7H_2O$. The model eutectic (solid lines) is 0.593 m at 269.68 K, compared to an experimental eutectic (symbol) at 0.568 m at 269.70 K [7].

Figure 2 illustrates the distribution of aqueous sulfite, sulfide, and carbonic species over the pH range from 0 to 11.

Standout differences between sulfite, sulfide, and carbonic species are clearly evident. For example, between pH 3.0 and 6.0, the dominant sulfite species is HSO_3^-, the dominant sulfide species is H_2S^0, and the dominant carbonic species is CO_2^0. Similarly, between pH 7 and 10, the dominant sulfite species is SO_3^{2-}, the dominant sulfide species is HS^-, and the dominant carbonic species is HCO_3^-. The ionic compositions of sulfite, sulfide and carbonic species are highly pH dependent. Below, we will illustrate the temperature dependence.
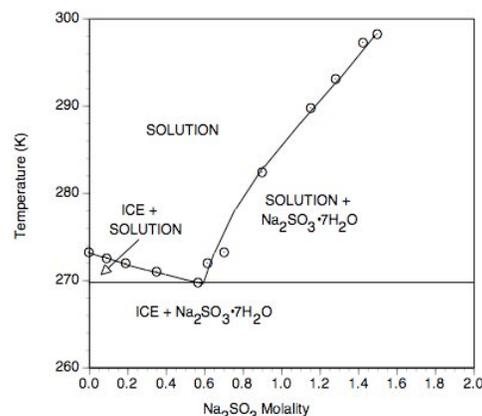

Figure 1. Equilibrium of sodium sulfite in the 270-298 K temperature range. Symbols are experimental data; solid lines are model estimates.
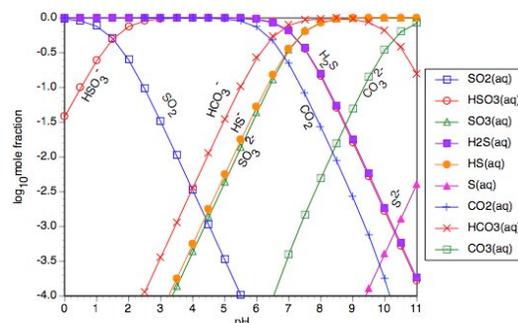

Figure 2. The relative distribution of aqueous sulfite, sulfide, and carbonic ions and neutrals in the pH range from 0 to 11.

Figure 2 clearly shows a different distribution among aqueous sulfites, sulfides, and carbonic species. But also important are differences among SO_2, H_2S,

and CO_2 gas distributions. Halevy et al. [2,3] demonstrated how solubilities of sulfite and carbonate salts differed at 298 K; for example, $CaSO_3 \cdot 0.5H_2O = CaCO_3$ where $\log_{10}(pSO_2/pCO_2) = -7.31$. Running FREZCHEM model for similar chemistries led to $CaSO_3 \cdot 0.5H_2O = CaCO_3$ at $\log_{10}(pSO_2/pCO_2) = -7.33$ at 298 K (Fig. 3), in excellent agreement with the Halevy et al. model. If the pSO_2 value becomes higher than the value at 298 K ($pSO_2 = 4.7e-12$ bars), (Fig. 3, the blue line) or pCO_2 becomes lower than the value at 298 K ($pCO_2 = 1.0e-4$ bars), then $CaSO_3 \cdot 0.5 H_2O$ becomes the dominant solid phase, and if pSO_2 becomes lower or pCO_2 becomes higher, then $CaCO_3$ becomes the dominant phase. Despite the much lower pSO_2 value (4.7e-12 bars) compared to the pCO_2 (1.0e-4 bars), the SO_3^{2-} value (5.3e-3 m) is higher than the CO_3^{2-} value (3.3e-5 m) because SO_2 is much more water soluble than CO_2.

The "blue line" ($CaCO_3 = CaSO_3 \cdot 0.5H_2O$) and "green line" ($MgCO_3 = MgSO_3 \cdot 6H_2O$) (Fig. 3) decrease with decreasing temperature, which is due to the higher solubility of $CaCO_3$ and $MgCO_3$ at low temperatures, and the lower solubility of $MgSO_3 \cdot 6H_2O$ and the slightly higher solubility of $CaSO_3 \cdot 0.5H_2O$ at low temperatures. At least for these Ca and Mg salts over the 253-298 K temperature range, lower temperatures favor higher precipitation of the sulfite salts.

Despite an early CO_2-rich atmosphere on Mars, Halevy et al. [2,3] attributed the prevalence of sulfur in Martian surfaces as due to the role of SO_2 and H_2S gases, which is a result consistent with our model (Fig. 3). Small quantities of SO_2 in a CO_2-rich atmosphere suppresses formation of carbonates (Fig. 3), which may be a major reason why sulfates are much more common on Mars. Also, perhaps equally, important is temperature that favors $CaSO_3 \cdot 0.5H_2O$ and $MgSO_3 \cdot 6H_2O$ precipitation at lower temperatures (Fig. 3). Volcanism on a cold Mars may be the primary causes of high sulfur minerals on Mars, compared to

volcanism on a warm Earth that led to high carbonate minerals. Much more sulfur-rich volcanic gases on Mars than on Earth [8] would strengthen this difference.

References: [1] Zimbelman, D.R. et al. (2005) Chem. Geol., 215, 37-60. [2] Halevy, I. et al. (2007) Science, 318, 1903-1907. [3]Halevy, I. et al. (2008) LPSC XXXIX, Abstract # 2287. [4] Tian et al. (2010) EPSL, 295, 412-418. [5] Marion, G.M., Kargel, J.S. (2008) Cold aqueous planetary geochemistry with FREZCHEM, Springer. [6] Rosenblatt, G.M. (1981) AIChEJ, 27, 619-626. [7] Linke, W.F. (1965) Solubilities (Vol. II), Am. Chem. Soc. [8] Gaillard, F., Scaillet, B. (2009) EPSL, 279, 34-43.
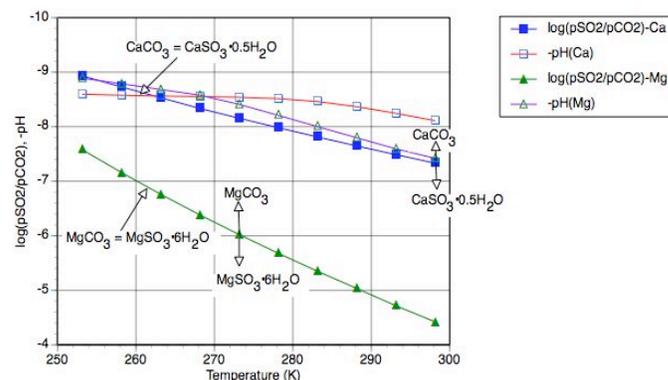

Figure 3. The distribution of Ca and Mg carbonate and sulfite minerals as functions of pCO2 and pSO2 gas concentrations and temperature.