

**CONSTRAINTS ON EVAPORATION PROCESSES AT MERIDIANI PLANUM: COMBINING THEORETICAL AND EXPERIMENTAL DATA.** N. J. Tosca<sup>1</sup> and S. M. McLennan<sup>1</sup>, <sup>1</sup>Department of Geosciences, State University of New York, Stony Brook, NY 11794-2100 (ntosca@ic.sunysb.edu).

**Introduction:** The identification of sulfate minerals at Meridiani Planum and other regions identified by the OMEGA instrument has clearly demonstrated the importance of evaporation processes at the martian surface. The formation of saline mineral assemblages found at Meridiani Planum has been approached by both theoretical and experimental means. Such approaches serve to provide an independent test of the hypothesis that chemical weathering has generated dilute fluid compositions and evaporation has led to the formation of soluble materials found in re-worked sediments. Theoretical approaches to evaporation often exploit the fact that equilibrium is typically reached between fluid and mineral phases over the course of evaporation. In addition, robust models have been built that adequately calculate thermodynamic concentrations (activities) in high ionic strength fluids. However, limitations of theoretical approaches to evaporation can be significant, especially in the unique and somewhat unfamiliar geochemical system typified by Meridiani Planum sediments [1]. Such limitations can indeed be responsible for the presence or absence of particular minerals of a modeled saline assemblage. Experimental data, however, can be used to improve and test existing geochemical models and strengthen their predictions by highlighting discrepancies between theoretical and experimental phenomena. The goal of this study is to combine experimental and theoretical results obtained from the evaporation of basaltic weathering derived fluids and provide more detailed knowledge of the controls on saline mineral formation at the martian surface. The results discussed below relate to the first portion of this effort – understanding the Meridiani Planum geochemical system.

**Theoretical Model, Methods and Input data:** The theoretical model employed in this study is described in detail in [1]. The model traces reaction paths of a given system by iteratively calculating its equilibrium state. Pitzer's equations are used for activity coefficient calculations and include the components Ca, Mg, Na, K, Fe(II), Fe(III), Al, SO<sub>4</sub>, Cl and H<sub>2</sub>O for temperatures at 25°C and pH less than or equal to 4. Al was added to the database presented in [1], largely using interaction parameters from [2] and solubility constants for Al-minerals from [2, 3].

Experimental data were obtained by conducting evaporation experiments with a fluid derived from weathering olivine-bearing basalt at pH ~2. The experimental approach and details of the data are discussed in [4]. Over 50 complete fluid analyses were obtained for the experiment and all major chemical components were analyzed [4]. As a check on the quality of the solution analyses, calculations indicate that all analyses are within 10% charge imbalance, suggesting that they are suitable for use in geochemical modeling. The experimental system is well characterized,

with major mineral precipitates confirmed by two analytical methods and their formation tied to solute fractionation apparent from solution data [4].

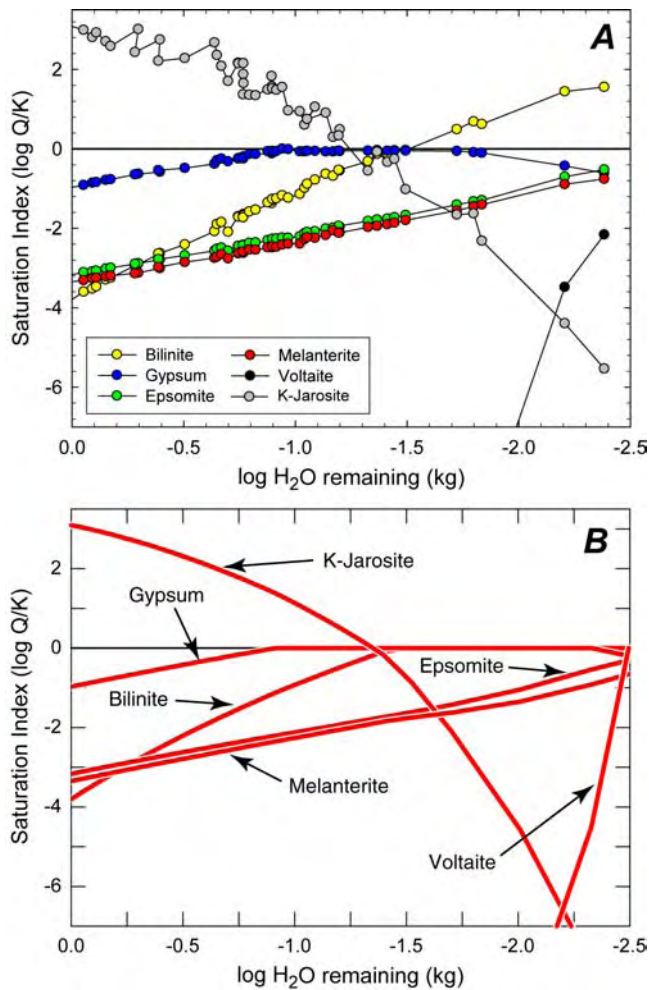
The geochemical model is used here in two ways: (1) to calculate the equilibrium state of each individual solution analysis and allow comparison of calculated mineral saturation states with observed precipitation points, and (2) to simulate the entire evaporation process by tracing the reaction path during the evaporation of only the starting solution. This approach facilitates comparison of solution compositions, mineral saturation states and resulting precipitates, and assesses the overall accuracy of predictions made with the geochemical model.

**Results:** Tosca et al. [1] noted that complete solution analyses of acid solutions with Fe<sup>2+</sup>, Fe<sup>3+</sup> and Eh determinations provide ideal tests of Fe activity calculation at high ionic strength – an added capability of the model. As an additional test to the model, measured Eh values throughout the experiment were compared with those calculated by the model. The agreement is excellent and all calculated and experimental values agree to within 10 mV, compared to 30 mV agreement reported in [1].

The equilibrium modeling results for each solution analysis are shown in Figure 1A. The saturation indices (SI, or the tendency of a mineral to precipitate) of relevant minerals were recorded. As discussed in [4], the points of precipitation of gypsum, bilinite and voltaite were observed from solution data and the precipitates identified by XRD and SEM. Therefore, at these points, calculated saturation indices should reach zero at precipitation and level off as the mineral is precipitated and the fluid reaches equilibrium. In Fig. 1A, the SI for gypsum is tabulated and agrees with the point of precipitation indicated in [4]. Gypsum saturation is reached at an SI of 0.0029 and then levels off as gypsum is precipitated, maintaining a SI which is slightly below saturation, at approximately -0.05.

The tabulated SI values for bilinite are also shown in Fig. 1A. Unlike gypsum, bilinite increases in saturation beyond the point where precipitation is indicated from experiments (-1.7 log kg H<sub>2</sub>O). Bilinite was observed, but calculated SI values (Fig. 1A) indicate that the fluid did not reach equilibrium with bilinite during the experiment.

The SI data tabulated for voltaite do not appear to capture the point of precipitation in the experiment, as voltaite was also identified. Voltaite saturation was likely reached between the last two data points, as the last data point reflects a value where K<sup>+</sup> has already been fractionated [4]. Epsomite and melanterite saturation were not captured in the solution data and this is confirmed with SI values in Fig. 1A. Interestingly, SI values for K-jarosite indicate that it is supersaturated until about -1.3 log kg H<sub>2</sub>O remaining.



**Figure 1.** A. Tabulated SI values from experimental solution data. B. SI values generated from an evaporation simulation using only the initial fluid composition.

However, there is no indication that K-jarosite actually formed in the experiment from either solid or solution analysis. The initial 5 data points indicate that a poorly crystalline material may have formed, but if this occurred, it was only brief and is not clear if the precipitate was a form of jarosite or another insoluble material [4]. Nevertheless, it is likely that jarosite never formed in equilibrium with the fluid from both SI data and a lack of solute fractionation during the experiment.

Figure 1B shows the results of simulating the evaporation process by modeling evaporation of only the initial fluid composition. In this reaction model, jarosite was not allowed to form at the beginning of the experiment, in accordance with solution and SI data. Back reaction was allowed however, as no minerals appeared to fractionate during the experiment. The agreement between calculated and experimental SI values is generally excellent with the exception of bilinite. The model predicts that bilinite immediately precipitates in equilibrium with the fluid and this is not observed. Instead, bilinite precipitation is likely slug-

gish producing some bilinite, but not reaching equilibrium with the fluid. In the model, it is the back-reaction of bilinite that releases available Fe<sup>2+</sup> and Fe<sup>3+</sup> for subsequent voltaite precipitation. However, in the experiment, it was likely the sluggish precipitation of bilinite that kept Fe<sup>2+</sup> and Fe<sup>3+</sup> concentrations high enough for voltaite to form.

Comparing the bulk mineralogy produced in the experiment to that inferred from Meridiani Planum results, it is clear that both are dominated with Mg- and Ca- sulfates. However, it is the Fe redox chemistry that presents a complicated set of formation pathways for the observed jarosite, hematite and oct-Fe<sup>3+</sup> bearing materials identified in Meridiani Planum sediments. The experiment discussed above focuses on Fe behavior during evaporation of basaltic weathering derived fluids and places constraints on this aspect of the Meridiani Planum system. For example, the results presented here indicate that the precipitation kinetics of jarosite are indeed slow. SI values indicate that jarosite was supersaturated until -1.3 log kg of water remained. Interestingly, 26 days elapsed from the start of the experiment until jarosite was no longer saturated and yet no jarosite was found from solution data or solid analysis. This observation has important implications for interpretation of Meridiani Planum results, suggesting that jarosite likely formed either before evaporation or during diagenesis of other Fe-bearing sulfate minerals.

The results discussed above also carry implications for geochemical modeling. The model used here and described in [1] uses estimates of solubility products for several Fe-bearing sulfates and incorporates Fe-redox disequilibrium into Pitzer's equations under acidic conditions. Geochemical models assume equilibrium relationships when in actuality, many processes do not reach equilibrium. However, it is the combination of theoretical and experimental or field data that allow discrepancies to be easily identified. Identifying what these processes are will significantly increase the reliability of geochemical modeling predictions. If it is understood that a reaction may not proceed to equilibrium over the time scale of interest, more realistic metastable conditions can be considered.

Finally, the excellent agreement between experimental data and modeling evaporation of only the initial fluid composition indeed shows that the outcome of the evaporation process, from brine evolution to saline mineral formation, is sealed at the time dilute waters have acquired their solutes. It is this principle that the "chemical divide" concept is based upon – slight variation in the composition of basaltic weathering fluids on Mars can lead to significant variation in evaporite mineralogy [5].

**References:** [1] Tosca, N. et al. (2005) *EPSL*, 240, 122. [2] Reardon, E. (1988) *J. Phys. Chem.*, 92, 6426. [3] Hemingway, B. & Sposito, G., in *Envir. Chem. of Aluminum*, CRC, pp. 81-116. [4] Tosca, N. & McLennan, S. (2006) *LPS XXXVII, this conference*. [5] Tosca N. & McLennan, S. (2006) *EPSL*, 241, 21.