

GEOCHEMICAL MODELING OF EVAPORITES ON MARS: INSIGHT FROM MERIDIANI PLANUM.

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Introduction: New data returned from the MER mission have revealed abundant evaporites in the sedimentary record at Meridiani Planum. A working hypothesis for the formation of these materials involves the evaporation of fluids derived from the weathering of Martian basalt and subsequent diagenesis [1]. On Earth, evaporite formation in exclusively basaltic settings is rare. Also, because of the complex physical and chemical nature of the sedimentary rocks at Meridiani Planum, fluid chemistry prior to evaporation is difficult to derive by inverse modeling. An alternative approach taken here is to investigate mineral precipitation during the evaporation of fluids derived by weathering of typical basalts. Data obtained in the laboratory from the weathering of synthetic Martian basalt provides a starting point for the investigation of evaporation processes at Meridiani Planum.

Methods: In this study, we employ Pitzer's ion interaction approach to predict mineral solubility in evaporating basaltic weathering solutions [2]. The treatment of Fe is of particular importance when modeling geochemical processes on Mars. In aqueous environments on Earth, Fe(II)/Fe(III) disequilibrium with respect to imposing redox conditions is the rule, not the exception [3]. As a result, both Fe²⁺ and Fe³⁺ are expected to be important components in the Meridiani system, especially in an evaporitic setting. Therefore, we have expanded the Pitzer parameter database published in [4] to include Fe²⁺, Fe³⁺, and several related minerals [5]. *The Geochemist's Workbench*[®] software was used to calculate reaction paths during fluid evaporation [6]. The modeling code is currently limited to 25°C as a result of thermodynamic data added from the literature. Because of these limited data, Al³⁺, SiO₂ (aq), and CO₂ are not included in this model. Conclusive evidence for carbonates at Meridiani is lacking and SO₄ appears to have been the primary anion and source of acidity (as H₂SO₄) in the system. In addition, carbonate precipitation (even under high pCO₂) is not expected to occur in this system until pH ~8, when siderite (FeCO₃) precipitates [7].

To assess the accuracy at which Fe²⁺ and Fe³⁺ activities can be calculated in high ionic strength, multi-component solutions, the equilibrium state of several concentrated acid mine waters (analyzed in the field by [8]) was calculated. The resulting Fe activities were used to calculate Eh and comparison was made to Eh measured in the field. In general, the agreement is excellent with deviation of no more than 30 mV between calculated and measured Eh.

Input solution analyses used for evaporation calculations are largely from the dataset reported by [9]. These solutions were generated by experimentally weathering synthetic basalt and glass of martian composition. Thus, we consider this dataset to be among the most relevant to the study of fluid evaporation at the martian surface.

Discussion: Major differences in predicted evaporite assemblages result from differences in fluid chemistry prior to evaporation. On Mars, where surface lithologies are largely basaltic, surface and sub-surface fluids will bear a chemistry controlled by basaltic weathering.

One of the most important differences shown in the modeling is comparison of evaporite assemblages produced from olivine basalt and basalt containing no olivine. In aqueous environments where the amount of time available for weathering is limited by fluid evaporation, the most rapidly dissolving mineral will make the largest contribution to the fluid chemistry [9]. Upon evaporation of fluids generated by the weathering of olivine-bearing basalt, dominant evaporite phases are: Mg-sulfates, Fe²⁺-sulfates and lesser, but significant amounts of both Ca-sulfates and Fe³⁺-sulfates (Fig. 1). Evaporation of fluids

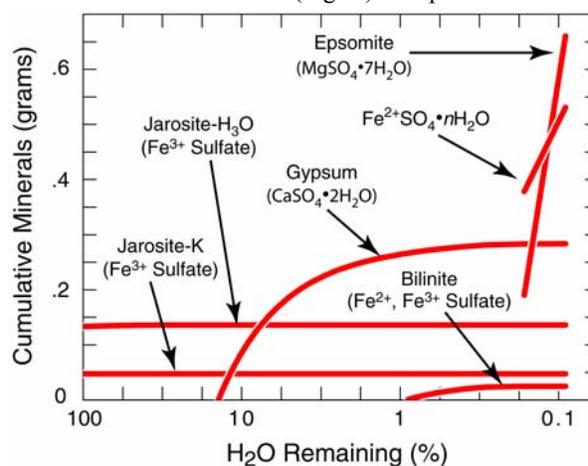


Figure 1 – Example of mineral precipitation upon basaltic weathering fluid evaporation (from L to R).

derived from olivine-free basalt precipitates no Mg-sulfates, inconsistent with evidence returned by the *Opportunity* rover suggesting Mg-sulfates are an important component of evaporite mineralogy [10]. Thus, the presence of olivine is crucial in supplying the Mg to solution in order to form substantial amounts of Mg-sulfates upon evaporation [11].

Because both Fe^{2+} and Fe^{3+} are included in the model, the degree of Fe redox disequilibrium can be expressed by the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in solution. This ratio was varied to assess the importance of both Fe^{2+} and Fe^{3+} in evaporitic settings. At high levels of $\text{Fe}^{2+}(\text{aq})$, the Fe-bearing evaporite mineralogy is dominated by $\text{Fe}^{2+}\text{SO}_4 \cdot n\text{H}_2\text{O}$ salts such as melanterite ($n=7$). At increasing levels of $\text{Fe}^{3+}(\text{aq})$, such phases decrease in abundance and the most insoluble sulfate, jarosite, increases in abundance. Additional Fe^{3+} -bearing sulfates, such as copiapite, precipitate at high levels of $\text{Fe}^{3+}(\text{aq})$. Calculations always predict jarosite to form at the beginning of evaporation even with small amounts of $\text{Fe}^{3+}(\text{aq})$. Also, the limiting K and Na content of basaltic weathering fluids requires most of the jarosite in the calculations to be composed of the H_3O endmember. The prediction of jarosite saturation at the outset of most calculations suggests that basaltic weathering fluids relevant to Mars may be saturated with respect to jarosite. Similarly, in many aqueous environments on Earth, waters are often saturated or supersaturated with respect to jarosite [12]. This is caused by kinetic limitations in jarosite precipitation and these factors may be operable at the Martian surface, as well. As a result, jarosite formation at Meridiani may occur either by initial weathering processes or by evaporative concentration, forcing jarosite precipitation.

Diagenetic reactions are also modeled in this study by assessing the stability of evaporite mineral assemblages upon reaction with later fluids. Such situations are representative of fluid infiltration into sediment layers (Fig. 2).

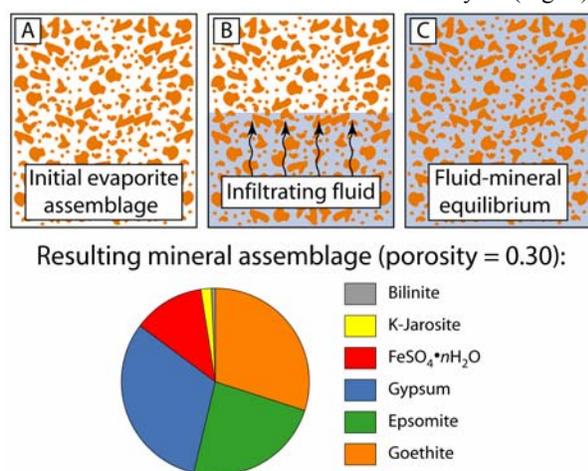


Figure 2 – Physical representation of diagenesis modeling (top) and product of example calculation (bottom).

In these calculations, the ratio of rock to infiltrating fluid (modeled as porosity) is a crucial factor. With modeled porosity values of less than 0.30, the fluid (initially pure water in this case) quickly reaches saturation with respect to soluble phases such as Mg- and Fe^{2+} -sulfate salts. A finite amount of these materials dissolve until the reaction is suppressed by saturation. In terms of pore fluid flushing

events, if the fluid is transported away from the sediment layers, model results suggest that at a rock porosity of 0.30, only 3 events are required to completely dissolve Mg- and Fe^{2+} -bearing sulfates, whereas several hundred events are required to dissolve more insoluble gypsum. Analysis of concretion geometry suggests that fluid flow was negligible during diagenesis events, making gypsum an unlikely candidate for a mineral which has occupied crystal molds observed in the outcrop [13].

Another important reaction predicted by the diagenesis calculations is the transformation of jarosite to goethite, which is thermodynamically favored in all calculations. This provides one possible mechanism for hematite concretion formation if they were formed by goethite aging.

Conclusions: The evaporation and diagenesis results are consistent with several geochemical data obtained at Meridiani Planum. For example, Mg-sulfates are likely an important component of the evaporite mineralogy at Meridiani from the general correlation of Mg with SO_3 in APXS data obtained from the outcrop [10]. The requirement of acidic olivine weathering to produce the observed abundances of Mg-sulfates also requires the liberation of significant Fe^{2+} and $\text{SiO}_2(\text{aq})$. Therefore, these components played a significant role in the geochemical evolution of Meridiani outcrop material, likely in the form of Fe^{2+} -sulfates and siliceous alteration phases. The formation of gypsum in all calculations is consistent with mass balance calculations suggesting that Ca-sulfates are present in the outcrop [13, 14]. Also, Fe^{2+} -bearing sulfates are predicted to be an important component of initial evaporite mineralogy, if redox conditions permit. The lack of observable Fe^{2+} -bearing sulfates (by Mössbauer spectroscopy) either suggests that these phases never formed, or that they were oxidized or dissolved, providing several possible mechanisms for ferric sulfate and Fe-oxide mineral formation. The modeling results discussed above provide a foundation for understanding evaporite formation in exclusively basaltic environments. Although it is one of several possibilities, a simple scenario has been found to be consistent with much of the available data related to the Meridiani outcrop.

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