

AN EXPERIMENTAL APPROACH TO EVAPORATION PROCESSES AT THE MARTIAN SURFACE.

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Introduction: Evaporite minerals record detailed information on the aqueous environments in which they form. On Mars, areas containing saline minerals have the most potential to yield information on ancient surface environments. The interpretation of detailed analyses of such materials by various exploration missions requires that equilibrium relationships in evaporating systems be fully understood. The distinct geochemistry that appears to be typical of evaporite assemblages on Mars is quite rare on Earth. Accordingly, much work is needed to develop a comprehensive understanding of such systems to extract detailed information on ancient surface environments.

In this study, we use an experimental apparatus to investigate equilibrium relationships during the formation of saline minerals from evaporating basaltic waters. The apparatus allows the identification of saturation points in solution where saline minerals precipitate. The detailed and comprehensive analysis of the solution compositions at the point of precipitation and of corresponding minerals allows thermodynamic data to be estimated which can be used to improve theoretical modeling capabilities and identify kinetic effects present in this multicomponent system.

Methods and Analyses: The apparatus used here is a jacketed 5L borosilicate glass reaction vessel with a 50 μ m glass fritted disk and zero-dead space bottom-sampling valve. The vessel is evacuated to ~20-30 mbar with a PTFE vacuum pump and continuously stirred with a vacuum-sealed PTFE stirrer. Temperature is maintained at 25°C \pm 0.1 by circulating water through the outer vessel jacket. Relative humidity and headspace temperature are monitored continuously. Solution is regularly sampled over the course of evaporation through the bottom valve. All solutions are doubly filtered with a 0.22 μ m filter or centrifuged and diluted appropriately with 4% HNO₃.

For each solution, Eh was measured using a Pt electrode calibrated against ZoBell's solution and pH measurements used a combination gel electrode. Because the H⁺ concentration reached extremely high values during the experiments, un-scaled individual ion activity coefficients for H⁺ were used to calculate pH. The values were derived from H₂SO₄ standards and an appropriate Pitzer ion interaction model [1]. Major cation concentrations (Na, Mg, Al, K, Ca, Fe_T) were measured using a DCP-AES. Fe²⁺, Fe_{Total}, SO_{4Total} and Cl were measured using a Hach DR/2000 spectrophotometer.

Residual solids were extracted and in some cases, large individual crystals were collected and isolated in parent brine (Fig. 1). These crystals were coated in oil

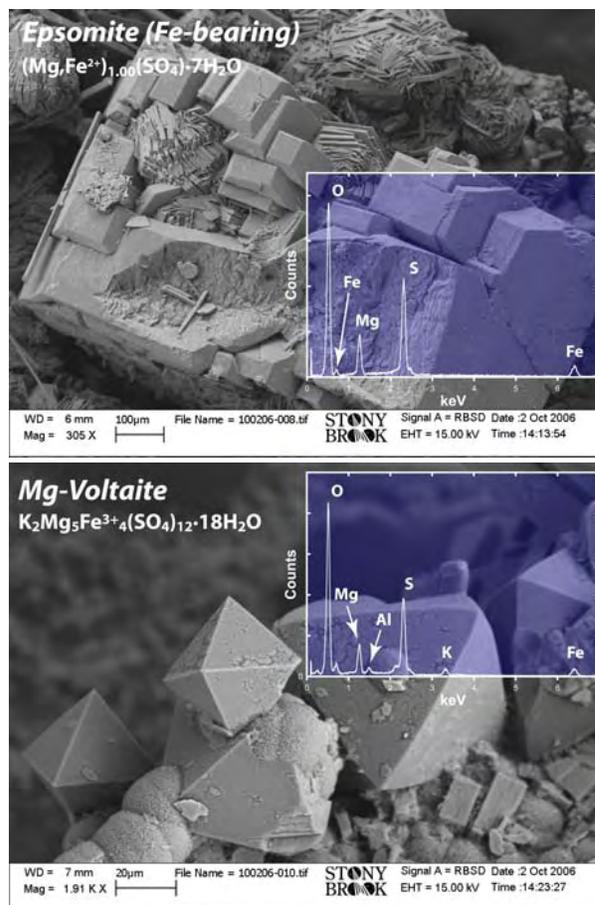


Fig. 1: SEM images of some experiment precipitates.

and analyzed by single-crystal X-ray diffraction to allow unambiguous identification and structure refinement. Bulk precipitates mounted in silicone grease were analyzed by powder XRD to identify major components. SEM-EDS was used to aid in identification and semi-quantitative analysis. Selected mineral samples were prepared for electron microprobe analysis by mounting crystals in fast-setting epoxy at room temperature. The technique resulted in minimal sample disturbance, although analysis under high vacuum resulted in some water loss.

Solution chemistry during evaporation: The experiments described here are first aimed at a systematic investigation of the extent of Fe oxidation ($\text{Fe}^{2+}/\text{Fe}_T$) on evaporation processes at the martian surface. We begin by using a fluid composition reported by [2] obtained by experimental weathering of synthetic martian basalt. The initial pH value upon evaporation was approximately 2.0.

When component concentrations are plotted against the amount of H₂O removed (determined by comparison to the most conservative elements), points of solute fractionation indicate the precipitation of saline minerals. During an experiment using a Fe²⁺/Fe_T of 0.5, fractionation in Ca and late fractionation in K, Fe²⁺, Fe³⁺, Mg and SO₄ were apparent. With adequate data coverage, it becomes possible to extrapolate back to the point of mineral saturation. This data point is taken as an “equilibrium saturation” point with which accompanying solid analysis and multicomponent thermodynamic modeling can be used to estimate equilibrium constants for several new mineral phases.

Evaporite precipitates: The experiments thus far have been equilibrium systems. The evaporite precipitates are allowed to back-react with a fluid of changing composition and largely maintain contact with the solution. The mineral phases identified from the Fe²⁺/Fe_T = 0.5 experiment include (in order of precipitation): gypsum, Mg-voltaite, Fe-bearing epsomite and rhomboclase. The Fe-bearing epsomite phase was identified in the vessel by the presence of large crystal “rafts” which precipitated on the surface of the fluid and were held in place by surface tension.

Sulfate mineral solubility data: Once solution compositions are tied to well-characterized mineral precipitates, we calculate component activities for the entire solution analysis. The fluid analysis must agree to within 10 relative % of charge balance. This is model dependent because the amount of SO₄²⁻ and HSO₄⁻ are determined through chemical equilibrium calculations. However, we may input an “as is” fluid composition to our multicomponent thermodynamic model to estimate charge balance.

The analyses for which saturation points are calculated may not be in true equilibrium because the solid phase may recrystallize at its surface and change composition in response to prolonged contact with the parent brine [3]. Thus, we refer to the inflection points present in solution data as *primary saturation* as discussed in [3].

Because the evaporite precipitates display extensive solid solution between several components, the estimates of equilibrium products derived from this study can also be used to estimate thermodynamic mixing parameters of solid solution sulfate salts.

Implications for evaporation processes on Mars:

The results collected so far show that there are significant differences between what precipitates in the experiment and what is predicted to precipitate with a thermodynamic model.

One example of solid solution effects on evaporite mineral assemblages is in the experiment using a Fe²⁺/Fe_T ratio equal to 0.5. An equilibrium model using the starting composition of the experiment predicts discrete melanterite and epsomite phases upon evaporation. However, because of some degree of Fe substi-

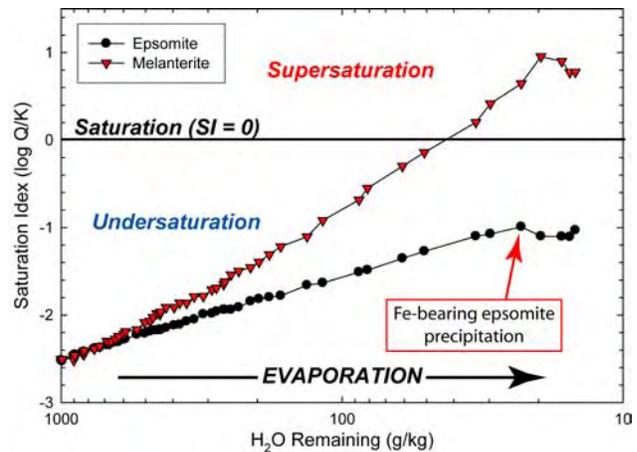


Fig. 2: Saturation indices for epsomite and melanterite during experimental evaporation.

substitution in the epsomite structure, the precipitation of Fe-bearing epsomite has prevented the precipitation of melanterite. In addition, the voltaite predicted by the thermodynamic model is pure voltaite whereas Mg-voltaite was precipitated in the experiments (Fig. 1). This voltaite phase also contained Al substitution in place of Fe³⁺ (see Fig. 1, EDS inset).

This effect can be shown quantitatively by plotting mineral saturation indices for each solution analysis. Fig. 2 shows that at the inflection point indicating Fe-bearing epsomite precipitation, melanterite is supersaturated and epsomite is undersaturated. The discrepancy is controlled by the excess free energy as a function of solid solution composition between the two components.

To conclude, several sulfate mineral phases display significant substitution and solid solution properties as a result of their relatively large crystal structures and high solubility. Although there are differences between predicted and laboratory-derived results, the data extracted in this study for solid solution compositions may be incorporated into thermodynamic models. This may help to provide a more accurate representation of the distribution of sulfate mineral species at the martian surface. Also, the solid solution compositions resulting from a basaltic-weathering derived system will shed light on analytical ambiguities that result from *in-situ* or remote analyses. For example, when interpreting compositional data returned on martian sulfate assemblages, elements such as Al, K, Na and Cl may be partitioned as minor components into dominant minerals which would prevent the formation of a discrete Al, K, Na or Cl-bearing phase. A better understanding of mineral composition in these systems will help provide a more rigorous interpretation of such measurements at the martian surface.

References: [1] Nordstrom, D. et al. (2000) *Env. Sci. Tech.*, 34, 254. [2] Tosca, N. et al. (2004) *JGR*, 109, E05003. [3] Glynn, P. & Reardon, E. (1990) *Am. J. Sci.* 278, 164.