THE FORMATION AND STABILITY OF SALINE MINERALS AT THE MARTIAN SURFACE.
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Saline minerals in the martian sedimentary record: Through recent orbital and landed exploration of the martian surface, it is clear that the martian crust contains an intricate sedimentary record. If terrestrial sedimentary geology is any indication, a wealth of information stands to be extracted from a sedimentary record that may indeed be as expansive and as complex as the Earth’s. An exciting result of more recent exploration however, is the observation that evaporite salts likely constitute a larger fraction of the sedimentary budget on Mars than on Earth. Because evaporites and other secondary precipitates can record detailed information of the aqueous fluids from which they have formed, they are priority targets for future exploration. Indeed, a detailed understanding of the ancient martian climate, surficial geochemistry, and habitability of this system remain one of the most important goals for Mars exploration. Our approaches toward this goal have revealed that the dominantly basaltic lithology on Mars gives rise to a distinct geochemical system that is rarely observed at the Earth’s surface. Here, we discuss results from both theoretical and experimental approaches to understanding the formation of saline minerals in this system and discuss steps toward extracting detailed paleo-environmental information from their detection and characterization on Mars. More specifically, we focus on: (1) geochemical controls on saline mineral formation, (2) variation in saline mineralogy at the martian surface, (3) the behavior of Fe in evaporative systems on Mars, (4) improving predictive capabilities for saline mineral formation on Mars, and (5) the stability of sulfate minerals (especially Fe-bearing) in response to changing climatic conditions. In the following discussion, we include our perspectives on the level of understanding in these areas and identify some priorities for future research.

Distinct surficial geochemistry: The influence of basaltic weathering: Evaporite minerals on Earth are controlled mainly by ocean chemistry and dilute fluids weathering the continental crust [1]. As a result, the dominant minerals found in terrestrial evaporite settings most commonly include halite, calcite, gypsum/anhydrite and various K- and Na-containing chlorides and sulfates. Because the martian upper crust is dominated by basalt, fluids weathering ferromagnesian minerals will be dominated by Mg, Fe, Ca and SiO2 [2]. It is the relative proportions of these constituents in martian surface waters compared to terrestrial surface waters that result in two completely different saline mineral distributions. For example, Figure 1 compares the relative proportions of chemical components in average terrestrial seawater and a fluid derived by weathering synthetic martian basalt under acidic conditions. Compared to terrestrial seawater, basaltic weathering-derived fluids are poor in K and Na, but enriched in Mg, and even more so in SiO2 (resulting in large part from the terrestrial silica cycle). However, the largest difference by far - and one of the most important - is the presence of Fe in fluids weathering the martian crust. Compared to other elements, Fe in terrestrial seawater is kept to a scant amount owing to slightly basic pH and oxidizing conditions [3]. On Mars, if Fe is not completely oxidized and/or pH levels are kept below solubility minima with respect to goethite and similar phases, aqueous Fe will be present in significant amounts. Fe mobility and the presence of Fe in evaporating waters on Mars are responsible for the distribution of Fe-bearing evaporite salts identified at the martian surface and may account in part for the distribution of much less soluble “ochreous” phases at the martian surface such as schwertmannite, jarosite, goethite and hematite [4-5]. One is left with the question of how this unique system gives rise to such distinct evaporite mineral assemblages and more specifically, what additional information can be extracted from the inclusion of Fe in the system.

Insight from theoretical studies: For terrestrial evaporites, the prediction of mineral precipitation sequences is a useful tool in understanding the origin and evolution of saline mineral deposits. Harvie et al. [6] were among the first to apply thermodynamics of high ionic strength (i.e., evaporating) solutions to geologic
systems of interest. They demonstrated excellent agreement between predicted and observed evaporite mineral assemblages – generally a result of such minerals rapidly attaining solubility equilibrium. Their method of calculating solution properties (i.e., component activities) relative to mineral phases was based on the Pitzer ion interaction model [7]. For geochemical systems on Mars, Fe$^{2+}$ and Fe$^{3+}$ are abundant components and application of this predictive model to martian systems require that Fe be included. With the recent availability of thermodynamic properties in the Fe$_2$(SO$_4$)$_3$-H$_2$SO$_4$-H$_2$O system, solubility data and new thermodynamic measurements of Fe-sulfate minerals [8-9], Fe can be considered as a geochemical component in the prediction of mineral precipitation sequences from evaporating martian waters.

From geochemical modeling, we conclude that the variation in evaporite mineralogy on Mars is controlled to a large degree by volatile-anion input – a variable intimately tied to pH [10]. Specifically, during the basaltic weathering process, if pH rises to the point where atmospheric CO$_2$ becomes chemically available to precipitate carbonates (pH~5-6), the overall evaporite assemblage will be composed of largely carbonate minerals, and depending on input from SO$_4$, a mixture of carbonates and sulfates [10]. Conversely, if acid-generating processes (e.g., volatile input, Fe-oxidation, sulfate mineral recycling) outweigh the acid-buffering potential of basaltic weathering, then the evaporite assemblage will be dominated with sulfate minerals indicating an acidic origin [10].

This simple model for the surface water composition on Mars will be manifested by several different possibilities for evaporite mineral assemblages on Mars. Using the “chemical divide” concept, where evaporite mineral assemblages can be used to unravel characteristics of the aqueous fluid, evaporite minerals at the martian surface can be used as sensitive probes of pH, atmospheric composition, volatile input and cation proportion in solution [10]. When applying this approach to evaporite assemblages characterized in the Nakhli meteorites as well as evaporite components in Meridiani Planum sediments, two geochemical systems result, each characterized by different pH and consequently, anion input to solution. [10] The physical setting of the two end-members is less clear, but such chemical differences can easily result, for example, from surficial compared to sub-surface geochemical environments.

A complicating factor, but one that may yield a different and important set of chemical characteristics is the extent of Fe$^{2+}$-oxidation at the outset of saline mineral formation. Identification of siderite in several SNC meteorites, as well as models for atmospheric O$_2$ evolution for Mars and the importance of acidic conditions at the surface all demand that incomplete Fe$^{2+}$-oxidation (redox disequilibrium) be evaluated [5, 10].

Evaluating the predicted saline mineral assemblage as a function of the degree of Fe oxidation (expressed as Fe$^{2+}$/Fe$^{3+}$) indicates a trend among the Fe-sulfate portion of the assemblage that progresses from Fe$^{2+}$-bearing, Fe$^{2+}$-Fe$^{3+}$-bearing and Fe$^{3+}$-bearing sulfates [5]. This progression is intuitive and even agrees with pyrite oxidation sequences in areas on Earth affected by acid mine drainage (AMD) [11]. Because the Fe-sulfates are sensitive to pH, the degree of Fe oxidation and relative humidity, understanding phase relationships in greater detail will ultimately exploit the presence of complex Fe-sulfates at the martian surface as a different set of geochemical probes.

The presence of Fe in evaporative systems is clearly the source of much of the complexity in understanding saline minerals on Mars. However, the behavior of Fe has been studied in detail in AMD areas on Earth. One of the most important lessons learned from such terrestrial examples is that the Fe system is complicated by a number of factors which make the departure from equilibrium of these natural examples difficult to describe and even more difficult to study and characterize [8-9]. Thus, these complications spread to geochemical modeling studies, which provide the foundation for understanding the equilibrium “end-point”. However, terrestrial AMD geochemistry shows us that comparison to natural environments that have not reached the end-point allows the controlling processes to be identified. Below, we focus on two important factors that contribute to the complexity of predicting equilibrium behavior for Fe-containing systems: (1) purity and solid solution behavior of evaporite phases and (2) stability of Fe-sulfate minerals with respect to oxidizing conditions and the numerous kinetic pathways by which equilibrium is normally achieved.

**Testing saline mineral predictions with experiment:** In addition to chemical analog systems, experimental investigations of the evaporation process can identify some of the complicating factors mentioned above and their potential importance at the martian surface. With an experimental design focused on monitoring mineral-water equilibrium and mineral solubility in the geochemical system most relevant to martian evaporites, the aggregate effect of solid solution behavior and precipitation kinetics on the whole system can be identified and specific problems studied in greater detail [12].

Using the experimental approach described in [12], the effects of solid solution behavior in sulfate minerals can be identified. In particular, the Fe-sulfate minerals appear to accommodate the most extensive substitutional impurities - in some cases on multiple crystallographic sites. This extensive substitution in these minerals (particularly Fe-sulfates) is mainly a result of the relatively large crystal structures and the amount of polyhedral distortion that can usually be accommodated [13]. Although the problem of solid-solution
behavior in geochemical modeling has been acknowledged as a complication, laboratory experiments on the geochemical system most relevant to martian saline environments suggest that the problem has a much greater effect than anticipated [12].

For example, experiments conducted on increasing degrees of Fe-oxidation (i.e., decreasing Fe$_2^+$/Fe$_T$) in the evaporating fluid show complex evaporite mineralogy due to the Fe-system [12]. Beginning with a basaltic weathering-derived solution where Fe$_2^+$/Fe$_T$ = 1.0, the mineralogy is dominated by epsomite, melanterite and gypsum. The epsomite and melanterite each contain a small amount of Fe$^{2+}$ and Mg, respectively, at levels less than 15 mol %. Increasing the amount of Fe$^{3+}$ in the evaporating solution results in the presence of mixed-valence Fe-sulfates such as volraine and copiapite-group minerals. These minerals are stable only at the very low pH (<0-1) typically reached by evaporating slightly acidic fluids and are very soluble. However, using identical chemistry of the evaporating solution, but with all of the Fe as Fe$^{3+}$, no Mg-sulfates are precipitated and the final products consist only of Mg-copiapite ([MgFe$^{3+}$)$_6$(SO$_4$)$_6$(OH)$_2$·22H$_2$O]) and gypsum [12].

This rather anomalous saline assemblage results because Mg-copiapite precipitation consumes the majority of available Mg$^{2+}$ and Fe$^{3+}$, leaving Ca$^{2+}$ and comparatively minor amounts of K$^+$ and Na$^+$ in solution. As Mg$^{2+}$ and SO$_4^{2-}$ are consumed during Mg-copiapite precipitation, Mg-SO$_4$ minerals such as epsomite become quickly undersaturated and are prevented from forming in any appreciable amount. This behavior has also been seen with volraine, another mixed-valence Fe-sulfate mineral where the Fe$^{2+}$ site is almost completely filled with Mg$^{2+}$.

Solid solution behavior of this kind, in particular Mg$^{2+}$ substitution, can be expected to be an important process occurring in martian evaporative environments because Mg$^{2+}$ is abundant in solutions weathering the martian crust. The implications are potentially interesting, in that if Mg-copiapite minerals were identified at the martian surface, possible constraints could be placed on the Fe$^{2+}$/Fe$_T$ ratio required to form such assemblages from laboratory results of this type.

Identifying the important solid solution compositions in this system and deriving information on their stability is useful for several additional reasons. First, the solubility, dehydration behavior and general chemical properties of solid solutions can be quite different from end-members [14]. Also, stability relationships of these compositions may be used to construct more accurate models of saline mineralogy derived from bulk compositional analysis at the martian surface. The Mg-copiapite example described above is relevant when using this approach for Paso Robles materials identified at Gusev Crater. The soils are rich in Mg, Fe (almost entirely ferric), SO$_4$ and PO$_4$. Mössbauer spectra are dominated by Fe$^{3+}$-sulfates (not jarosite), of which copiapite-group minerals may be candidates [15]. If these materials were formed from fluids rich in Mg and Fe$^{3+}$, then it is possible that no discrete Mg-SO$_4$ phase actually exists at these locations and the Mg is partitioned into Fe-sulfates. Independent methods to identify Mg-SO$_4$ phases at this site may help to discriminate the mechanism of formation and also whether the materials precipitated from the same fluid or have been mixed by sedimentary processes. It is desirable to be able to draw upon phase relationships in multi-component geochemical systems to help discriminate possible mineral phases present at a given location. Some of the most important factors controlling the formation of saline minerals in this system can only be identified by considering the system as a whole.

**Linking observation with prediction: the stability of saline minerals on Mars:** The most important link between prediction and observation comes from investigations of mineral stability under changing environmental conditions. Of particular relevance are factors such as oxidation conditions (affecting Fe$^{3+}$-containing saline minerals) and relative humidity. As Mars has certainly undergone large-scale climatic variability throughout its history, such investigations are a necessary compliment to those described above.

An observation to consider is that Fe$^{2+}$-bearing saline minerals are sensitive to oxidation which, depending on pH conditions, may result in a variety of oxidized mineral products. This instability is at odds with suggestions that the martian climate became progressively more oxidizing over geologic time in response to decreased volcanic activity which serves to buffer photochemically-produced atmospheric oxygen [16].

One of the most conspicuous pieces of evidence for a shift in climatic conditions is at Meridians Planum.
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where essentially all of the sedimentary Fe occurs in the Fe$^{3+}$ state [17]. This observation, coupled with evidence for multiple episodes of groundwater infiltration and diagenetic alteration [18], leaves open the possibility of oxidation reactions among Fe$^{2+}$-bearing salts that may have been formed during the evaporation process. The hypothesis that much of the Fe$^{2+}$-bearing mineralogy at Meridiani Planum occurred in response to diagenesis may be a viable one to consider. If the Fe$^{2+}$ that was released from basaltic weathering and partitioned into Fe$^{3+}$-bearing evaporite minerals was not completely oxidized, then some subsequent oxidation reactions would be expected to occur in order to arrive at the present condition.

Experimental tests of a diagenesis hypothesis yield interesting results. Under high ionic strength, Fe$^{2+}$ oxidation begins with the initial precipitation of schwertmannite from Fe-bearing basaltic brines (Fig. 2) [4]. Schwertmannite is metastable with respect to jarosite and goethite. Oxidation experiments have shown that the initial pH has a significant effect on the transformation of schwertmannite. Ageing of schwertmannite at pH values between 4 and 2 produces assemblages that are composed of mixtures of goethite and jarosite [4]. Values of pH close to 4 produce mainly goethite and values closer to 2 produce mainly jarosite. Under acid sulfate conditions, goethite occurs as a nano-crystalline phase owing to slow growth kinetics. Interestingly, nano-phase goethite is unstable with respect to hematite at most near surface geological conditions in liquid water over a range in pH [19]. Further, at high ionic strength conditions expected to be characteristic of diagenesis at Meridiani Planum (see [18]) and the corresponding low water activity ($a$$_{H2O}$), dehydration of goethite to hematite is favored – a transformation that may also be catalyzed by the presence of residual Fe$^{3+}$ in the aqueous phase [20]. Initial results support the presence of nano-phase hematite, but resolving the stability of nano-phase goethite at high ionic strength is currently under separate investigation.

Phase transformations among saline minerals also occur in response to changing relative humidity. For example, phase transitions among the Mg-SO$_4$ hydrates have been investigated in some detail and have provided a foundation through which the kinetic behavior of dehydration, re-hydration, amorphization and other reactions can be understood at the martian surface [21]. As Vaniman et al. [21] point out, the range in relative humidity at the martian surface varies significantly, leaving open the possibility for a large number of possible phase changes among hydrous minerals. The Fe-sulfates are less understood, due in part to the comparative lack of new crystal structure models for the large number of Fe-sulfate phases and also because of difficulties in obtaining thermodynamic data for such materials.

Conclusions: Thus far, evaporite mineral occurrences in the sedimentary record indicate that surface environments were strongly influenced by acidic conditions. This appears to contrast with assemblages identified in the SNC meteorites, which are a mixture of carbonates and sulfates – requiring higher pH, but demonstrating the likely influence of CO$_2$ on early Mars. Appreciable carbonates have yet to be detected, but they may be more common at the subsurface. Acidic conditions can be most easily distinguished from conditions under which basaltic weathering has largely buffered acidity by two means: (1) the proportion of carbonate to sulfate minerals and co-existing Fe-mineralogy. The latter is much more difficult to assess because of numerous pathways for oxidation and precipitation, but understanding this aspect will yield even more detailed constraints on saline mineral formation on Mars.

Saline minerals appear to occupy a substantial portion of the martian sedimentary record, which implies that the action of liquid water has significantly weathered basaltic materials on Mars. Basaltic weathering of ferromagnesian minerals, to a large degree, appears to have controlled the cation proportions of saline minerals, as phases such as Mg-sulfates, Fe-sulfates (and oxides), and Ca-sulfates dominate observed evaporite mineralogy at the martian surface. Fe-sulfate minerals in particular act as probes of oxidation conditions, pH and relative humidity. Our understanding of mineral stability in this geochemical system remains fragmentary and many data on fundamental stability and formation are still lacking. In particular, low-temperature investigations of mineral stability, solid solution behavior of sulfate minerals and saline mineral precipitation kinetics under relevant conditions are only a few examples where there is a need for continued study.