

COMPARISON OF PREDICTED SALT PRECIPITATION SEQUENCES WITH MARS EXPLORATION ROVER DATA. P. L. King, D. T. Lescinsky and H.W. Nesbitt, Dept. Earth Sciences, The University of Western Ontario, London ON N6A 5B7 Canada.

Introduction: We compare predicted salt sequences for Mars [1-3] with Mars Exploration Rover (MER) data to place constraints on martian waters.

Model background and assumptions: On Mars, geomorphic and geochronologic evidence [e.g. 4, 5] suggest that surface solutions occurred episodically, and chemical evidence suggests limited weathering of the basaltic crust [6]. Saline solutions are produced via leaching of *bulk* martian surface materials (martian and impactor materials) containing sulfides, olivine, pyroxene, plagioclase \pm glass. The resulting *bulk* solution would contain Mg-Ca-Na-(K-Fe)-C-O-H-S-(N-P)-halogen species, with abundant Mg, Na, SO_4 and Cl [e.g. 6]. Local compositional variations are likely.

On Mars, sulfate stays in solution, unlike on Earth where sulfate is reduced to sulfide either via biologic processes or hydrothermally at mid-ocean ridges. We model the martian solution compositions as they are concentrated (via freezing or evaporation) using salt solubility and phase equilibria, assuming: 1) thermodynamic modeling is appropriate; 2) 25 °C and $\sim 10^5$ Pa phase diagrams are valid at martian conditions; and, 3) activity coefficients are unity (details in [3]).

Predicted salt sequence: When martian basaltic surface materials are leached insoluble Fe-phases and an Mg-rich, $\text{SO}_4/(\text{SO}_4 + \text{Cl} + \text{HCO}_3)$ -rich solution are produced. If the solution is concentrated the following sequence of salts forms: phosphates; carbonates; gypsum; epsomite; bloedite; halite; hexahydrate; and, finally bischofite, with some minor variations [3].

1. *Carbonates:* Our model suggests that any carbonates precipitate out of solution early as Fe-Mg-Ca-carbonates, depleting the solution in Fe and Ca. The $\text{Mg}/(\text{Mg}+\text{Ca})$ is likely >0.6 [3] and the amount of carbonate is unknown, but correlates with the partial pressure of CO_2 (P_{CO_2}) [e.g. 7]. In high- and low- HCO_3 -solutions the salt sequence in the Ca-Mg- HCO_3 - SO_4 system (Fig. 1) is: calcite (zoned Ca- to Mg-rich: Cc to Mg-Cc), then Mg-Cc+Ca-protodolomite (Ca-Pr), joined by gypsum (Gy) at P1. If the salts are isolated from solution then the solution follows the Gy+Ca-Pr join and those salts are joined by magnesite (Mag) at P2, then Mag-Gy-epsomite (Ep) form at E.

2. *Sulfates & chlorides:* Because the modeled bulk composition is Mg- SO_4 -rich, it plots in the epsomite (Ep) field (e.g., *a* in Fig. 2). The solution will precipitate Ep first if concentrated, then precipitate Ep-Bloedite (Bl) until halite (Ha) precipitates at P1. If the solution is isolated from the salts it will continue to evolve to P2 (Ep+hexahydrate (Hx)+Ha), and finally to

the eutectic (E) where Ha+Hx+bischofite (Bi) crystallize. Ep may lose H_2O to form Hx or kieserite (Ki).

If Mg-bearing salts crystallize readily (e.g., Mg-Cc or Mg-phosphate), the solution will decrease in $\text{Mg}/(\text{Na}_2 + \text{Mg})$ (points *b* – *c* or lower, Fig. 2). If sulfate crystallization starts at *b*, Bl will crystallize followed by Ep+Bl, with final crystallization at P1. If sulfate salt crystallization starts at *c*, the solution will first precipitate Bl, then Ha+Bl and final salts at P1. If $\text{Mg}/(\text{Na}_2 + \text{Mg})$ is lower than *c* then Na-rich sulfates will precipitate. Precipitation of gypsum (Gy vector) or Na-carbonate (Na vector) will not significantly change the starting composition, *a*. In all cases the chlorides and other halogen salts will precipitate last.

Fe-bearing minerals: Figure 3 shows a phase diagram for the martian surface [following 7, 10-12], with thermodynamic data [10,13], and minerals and compositions from the martian missions [6, 14, 15] and martian meteorites [2]. We use the readily altered mineral pyrite as a proxy for Fe-bearing minerals and a S-source. Hematite is stable at log partial pressures of oxygen (P_{O_2}) > -69 , indicating that HS^- is unlikely in solution on Mars. Siderite stability depends on P_{CO_2} , with a lower limit of $\text{pH} \sim 3.9$ for $P_{\text{CO}_2} = 2$ and $\text{pH} \sim 4.7$ for $P_{\text{CO}_2} = 0.05$ [also see 7]. The stability of Fe-sulfate (jarosite) and Fe-hydroxide minerals (modeled as ferrihydrite following [12]) are strongly dependent on the ion activities [16-18], mineral stoichiometry [18], grain size [19], and photochemical reactions [19]. Thus the data on stability of sulfate and hydroxide phases are poorly constrained [18, 20, Fig. 3 inset].

Comparison of the predicted salt sequence with MER data: We predict few carbonates, in agreement with levels less than 5% based on Miniature Thermal Emission Spectrometer (Mini-TES) spectra. The infrared spectra from the Mini-TES is best fit by Mg- and Ca-sulfates [21] and Na-bearing salts have also been proposed [15], as our model predicts. The Cl abundances [14] support the possibility of late crystallizing Ha \pm Bi, and it is likely that bromides formed late cements, causing variable Br [14].

The occurrence of fine-grained hematite and other Fe^{3+} -rich minerals [22 23], in particular concentrated on inferred concretions, is also consistent with precipitation from an aqueous solution that has weathered basaltic material. Figure 3 shows that Fe^{3+} -rich minerals such as hematite and ferrihydrite may precipitate with S in solution as SO_4^{2-} . Such a solution could precipitate Ca-Mg-Na-sulfates and Fe-phases, thus chemical processes may cause the poor correlation between Fe and S, in addition to physical processes [24].

The MER Mössbauer data [23] and bulk compositions [14] suggest that the jarosite is K-poor. If the composition of jarosite and Fe-hydroxides and grain size and ion activities are varied then the phase stabilities may change dramatically (inset, Fig. 3, discussed above). This system would benefit from more analytical and thermodynamic studies to better constrain the sulfate formation, particularly with respect to the high levels of Ni and Zn reported [14].

MER evidence for multiple salt cementation events: MER observations of variable cementation [15] and variable chemical composition [14] are consistent with remobilization and (re)deposition of salts presented in our model. The MER data include geomorphic and chemical evidence that relatively soluble mineral(s) precipitated, followed by Fe-concretions, followed by dissolution of the first soluble mineral, resulting in crystal-mold porosity or vugs [15]. This sequence is consistent with our model: although it is possible that the Fe-oxides precipitation and salt dissolution events may have been near coincident. Such events most likely occurred during volcanic/hydrothermal events, dust storms, outflow channel events, seasonal sublimation events, or where solutions percolated along mineral surfaces by capillary action due to ice melting or groundwater transport.

Occurrence of "primary minerals" with salts: Our model is consistent with the Mini-TES finding that basaltic minerals (olivine, pyroxene and feldspar) are found in all spectra [21], these minerals are found throughout Meridiani [22] and that the overall silicate composition is basaltic [14]. Aeolian processes provide a physical mechanism for combining basaltic minerals and salts in one outcrop; however, our model for limited chemical weathering also explains this observation. We propose that the martian solutions that precipitated the salts may have been dominated by small, episodic amounts of water focused along grain boundaries of basaltic minerals.

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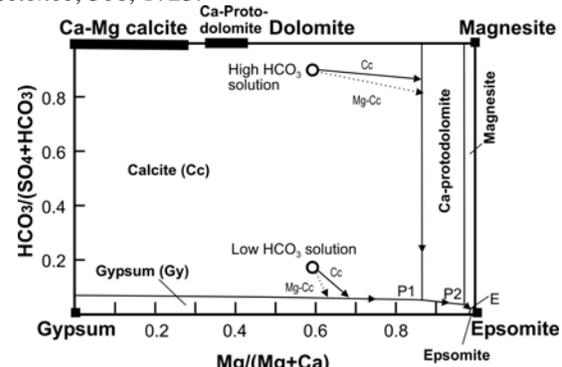


Fig. 1: $\text{HCO}_3/(\text{HCO}_3 + \text{SO}_4) - \text{Mg}/(\text{Mg} + \text{Ca})$ phase diagram with the epsomite field expanded for clarity [after 3, 8].

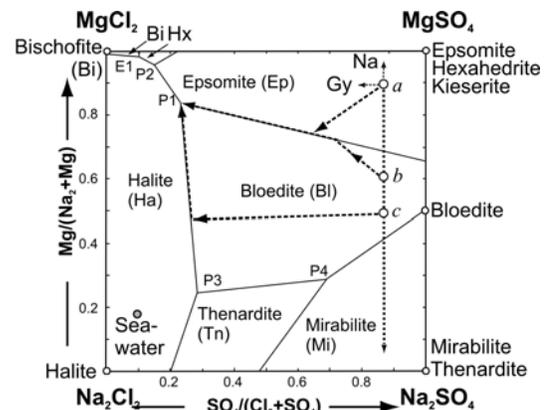


Fig. 2: Phase diagram for the Mg-Na-SO₄-Cl system with salt assemblages and solution compositions [after 3, 9].

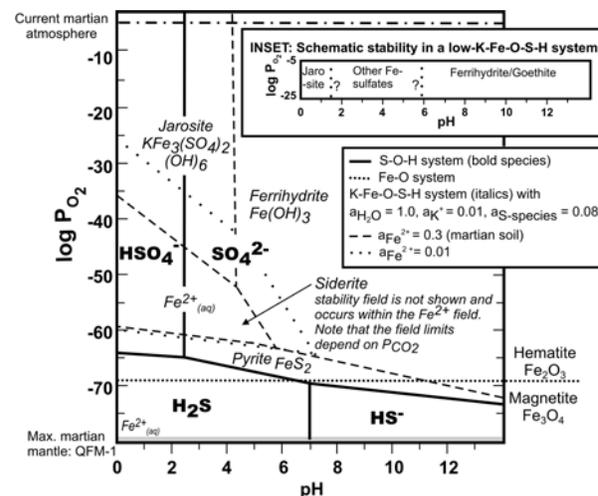


Fig. 3: Stability of Fe-phases in the K-Fe-O-S-H system [after 2].