Evaporation of Fe(II)/Fe(III) sulfate brines under CO_2 and ultraviolet light: Implications for Mars

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Fe(III)-sulfates were detected in the sedimentary records at Meridiani Planum and Gale Crater [1,2], and Fe^{2+}/Fe^{3+} redox is suggested to be critical controlling brine evolution and mineral assemblages on Mars, and may hold keys to the ancient climate and habitability of the red planet [e.g., 3,4].

We experimentally investigated Fe-sulfate brine evolution and final products during evaporation at 25°C. Five sulfate brines with varied oxidation states (molar Fe^{2+}/Fe_T = 0, 0.25, 0.5, 0.75, 1; Fe_T = 500 mM) and three irradiation/atmosphere combinations (i.e., ambient light/CO_2; UV_{254nm}/CO_2, UV_{254nm}/ Earth atmosphere) were systematically examined to identify possible influences on the final Fe assemblages.

Varied Fe^{2+}/Fe^{3+} ratios of initial brine resulted in systematic changes in crystalline phases of final evaporites (ambient light/CO_2). The ferrous-only experiment precipitated melanterite ($FeSO_4{\cdot}7H_2O$), and the ferric-only brine precipitated rhomboclase plus ferricopiapite ($(H_5O_2)Fe(SO_4)_2{\cdot}2H_2O$ and $Fe_{0.69}Fe_4(SO_4)_6(OH)_2{\cdot}20H_2O$ respectively). In Fe^{2+}/Fe^{3+} mixing brines, rozenite ($FeSO_4{\cdot}4H_2O$) was the major Fe^{2+} phase. Rhomboclase was the Fe^{3+} phase for Fe^{II}-25% and Fe^{II}-75% experiments, but amarantite ($Fe_2(SO_4)_2O{\cdot}7H_2O$) was the Fe^{3+} phase for Fe^{II}-50% experiment. XRD analysis also showed presence of minor amorphous phases, enriched in O (or OH/H_2O) and depleted in S in general, likely resulted from Fe^{3+} hydrolysis.

Under UV irradiation and CO_2, ferric-only experiment produced solidified gel (other brines under UV with CO_2 or Earth atmosphere are ongoing). Such gel was XRD-amorphous but SEM/TEM/EDS identified presence of nano-sized ferricopiapite in the gel matrix. Plus, the gel matrix was equivalent to rhomboclase in composition. We will report comprehensive results and implications at the conference.

[1] Klingelhofer *et al.* (2004) *Science* **306**, 1740-1745. [2] Rampe *et al.* (2017) *EPSL* **471**, 172-185. [3] Hurowitz *et al.* (2017) *Science* 356 (6341). [4] Tosca *et al.* (2018) *Nat.Geoscience* 11(9).