

**MODELING FERROUS/FERRIC IRON CHEMISTRY WITH APPLICATION TO MARTIAN SURFACE GEOCHEMISTRY.** G.M. Marion<sup>1</sup>, J.S. Kargel<sup>2</sup>, and D.C. Catling<sup>3</sup>, <sup>1</sup>Desert Research Institute, 2215 Raggio Parkway, Reno, NV 89512, giles.marion@dri.edu. <sup>2</sup>University of Arizona, kargel@hwr.arizona.edu. <sup>3</sup>University of Bristol, david.catling@bristol.ac.uk.

**Introduction:** The Mars Exploration Rover (MER) missions have stimulated considerable thinking about the surficial geochemical evolution of Mars [1-4]. Among the major MER findings is the presence of the mineral, jarosite (a ferric sulfate salt), which suggests formation from an acid-sulfate brine. The objectives of this work were to (1) add ferric iron chemistry to an existing ferrous iron model (FREZCHEM), (2) extend ferrous/ferric iron geochemical models to lower temperatures (< 0 °C), and (3) use the reformulated model to explore ferrous/ferric iron geochemistries on Mars.

**Methods and Materials:** The FREZCHEM model is an equilibrium chemical thermodynamic model parameterized for concentrated electrolyte solutions using the Pitzer equations [5] for the temperature range from <-70 to 25°C and the pressure range from 1 to 1000 bars [6-10]. The model is parameterized for the Na-K-Mg-Ca-Fe-H-Cl-SO<sub>4</sub>-NO<sub>3</sub>-OH-HCO<sub>3</sub>-CO<sub>3</sub>-CO<sub>2</sub>-CH<sub>4</sub>-H<sub>2</sub>O system, which includes 81 solid phases.

**Results:** One of our prime objectives was to extend existing Pitzer-approach ferric iron parameterizations to lower temperatures. Freezing-point-depression data for FeCl<sub>3</sub> solutions [11] were used to extend Fe(III)-Cl parameterization to the eutectic temperature at 238 K (-35°C). A similar approach was used to extend Fe(III)-SO<sub>4</sub> parameterization to 261 K (-12°C). But, in this particular case, we used Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> data as an analogue for Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> data because the latter cold temperature data are lacking.

Table 1 is a listing of ferrous and ferric iron solid phases that are currently in the model. Extending the solubility products to temperatures < 25°C was based on experimental measurements whenever possible. Lacking such experimental data, we relied on the van't Hoff equation

$$\ln(K_{T_2}) = \ln(K_{T_1}) + \frac{\Delta H_r}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (1)$$

to extend the solubility products to lower temperatures.

Evidence to date strongly suggests that iron minerals on Mars have likely gone through paragenesis (mineral transformations over time) [3,4]. In Table 2 are examples of iron transformations from pyrite to jarosite on Earth. Overall, paragenesis of iron minerals on Earth [12] follows the weathering sequence:

rock ⇒ ferrous sulfates ⇒ ferrous/ferric sulfates ⇒ ferric sulfates ⇒ ferric hydroxides ⇒ ferric oxides (2)

On Earth, the dominant process leading to acid sulfate brines is oxidation of sulfide minerals such as pyrite (Table 2), which produces sulfuric acid as a byproduct; on Mars, it appears more likely that acids were added to surfaces via atmospheric deposition. The first iron sulfate minerals to precipitate are ferrous sulfates which follow a clearcut hydration pattern from melanterite (FeSO<sub>4</sub>•7H<sub>2</sub>O) to rozenite (FeSO<sub>4</sub>•4H<sub>2</sub>O) to szomolnokite (FeSO<sub>4</sub>•H<sub>2</sub>O) (Table 2). This pattern occurs because of dehydration that is likely caused by kinetic factors, ionic strength, evaporation, or freezing. Such dehydration is likely responsible for the prevalence of the mineral kieserite (MgSO<sub>4</sub>•H<sub>2</sub>O) on Mars [3,13]. Over time, these ferrous sulfate minerals are transformed into mixed ferrous/ferric sulfates, then into ferric sulfates, followed by ferric hydroxides, and finally ferric oxides (Eqn. 2).

We developed simulations for evaporation of a hypothetical Martian fluid based on a composition resulting from acid weathering of basalt [4]. The initial composition of this solution was: Na = 3.16e-4 m, K = 1.05e-4 m, Ca = 2.85e-3 m, Mg = 5.58e-2 m, Fe(II) = 2.79e-2 m, Fe(III) = 2.79e-2 m, Cl = 4.20e-3 m, and SO<sub>4</sub> = 0.1265 m. We ran these simulations at T = 0°C, P = 1.01 bars, and at pH = 1.0, 2.0, and 3.0. In these simulations, precipitated salts were not allowed to re-equilibrate with the solution phase (fractional crystallization).

Using the full suite of iron minerals and salts (Table 1) for model simulations at pH = 2.0 resulted in the precipitation of ferric iron as a mixture of jarosite and hematite, which is in excellent agreement with the Meridiani Planum findings [3,4]. However, it is unlikely that insoluble ferric oxides (or hydroxides) are primary precipitates based on paragenetic processes on Earth (Table 2, Eqn. 2). Therefore, we reran the simulations at pH = 2.0 after removing hematite, goethite, and lepidocrocite from the mineral database. In this case, the initial solution was supersaturated with bilinite and jarosite (Fig. 1). Jarosite was clearly limited by the presence of K, which dropped from 1.0e-4 to 1.0e-8 m (Fig. 1). Other minerals that precipitated as the water was reduced from 1000 to 1 g through evaporation included gypsum, epsomite, and melanterite (Fig. 1).

Running this simulation at pH = 1.0 led to the same suite of minerals, except that jarosite did not precipitate at this low pH. At pH = 3.0, gypsum, epsomite, melanterite, mirabilite, MgSO<sub>4</sub>•12H<sub>2</sub>O, jarosite, natrojarosite, and schwertmannite were predicted to precipi-

tate. It is clear from the results of this study (Fig. 1) and other studies (Table 2; [4]) that the paragenesis of iron minerals is complex.

Note in Fig. 1 that what began as a predominantly Mg-Fe-SO<sub>4</sub> solution ended as a predominately Mg-Cl solution. The last salt to precipitate at this temperature (0°C) is likely MgCl<sub>2</sub>•12H<sub>2</sub>O, a highly soluble salt that could be responsible for vugs (cavities) in the sedimentary rocks at Meridiani Planum [3,4].

**Current and Future Work:** Most of the minerals suggested from Earth-based paragenesis of iron minerals [12] are now components of our model (cf., Tables 1 and 2). The simulation discussed in Fig. 1 is just the beginning of our exploration of the processes that led to the geochemical evolution of the iron-based Martian surface.

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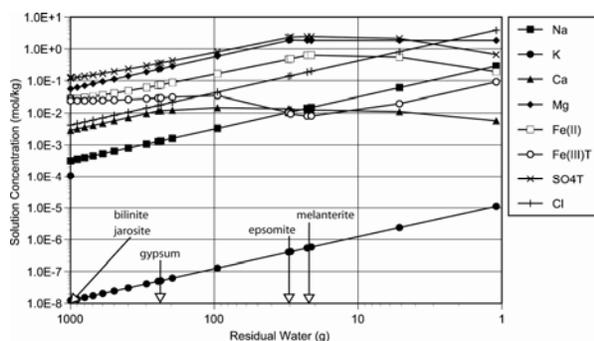


Figure 1. The change in ion concentrations as a hypothetical martian brine evaporates at 0°C with pH = 2.0. Arrows show where specific minerals start to precipitate.

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Table 1. Iron minerals and salts currently in the FREZCHEM model.

#### A. Ferrous Minerals

Mineral Name	Chemical Formula
	FeCl <sub>2</sub> •4H <sub>2</sub> O
	FeCl <sub>2</sub> •6H <sub>2</sub> O
szomolnokite	FeSO <sub>4</sub> •H <sub>2</sub> O
rozenite	FeSO <sub>4</sub> •4H <sub>2</sub> O
melanterite	FeSO <sub>4</sub> •7H <sub>2</sub> O
	FeSO <sub>4</sub> •Na <sub>2</sub> SO <sub>4</sub> •4H <sub>2</sub> O
mereiterite	FeSO <sub>4</sub> •K <sub>2</sub> SO <sub>4</sub> •4H <sub>2</sub> O
siderite	FeCO <sub>3</sub>

#### B. Ferrous/Ferric Minerals

Mineral Name	Chemical Formula
römerite	Fe(II)Fe(III) <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> •14H <sub>2</sub> O
bilinite	Fe(II)Fe(III) <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> •22H <sub>2</sub> O
copiapite	Fe(II)Fe(III) <sub>4</sub> (SO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub> •20H <sub>2</sub> O
voltaite	K <sub>2</sub> Fe(II) <sub>3</sub> Fe(III) <sub>4</sub> (SO <sub>4</sub> ) <sub>12</sub> •18H <sub>2</sub> O

#### C. Ferric Minerals

Mineral Name	Chemical Formula
hydromolysite	FeCl <sub>3</sub> •6H <sub>2</sub> O
	FeCl <sub>3</sub> •10H <sub>2</sub> O
erythrosiderite	FeCl <sub>3</sub> •2KCl•H <sub>2</sub> O
mikasaite	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>
kornelite	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> •7H <sub>2</sub> O
coquimbite	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> •9H <sub>2</sub> O
ferricopiapite	Fe <sub>3</sub> (SO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub> •20H <sub>2</sub> O
	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> •2K <sub>2</sub> SO <sub>4</sub> •14H <sub>2</sub> O
rhomboclase	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> •H <sub>2</sub> SO <sub>4</sub> •8H <sub>2</sub> O
jarosite	KFe <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
natrojarosite	NaFe <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
hydronium jarosite	(H <sub>3</sub> O)Fe <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
schwertmannite	FeO(OH) <sub>0.75</sub> (SO <sub>4</sub> ) <sub>0.125</sub>
ferrhydrite	Fe(OH) <sub>3</sub>
lepidocrocite	γ-FeO(OH)
goethite	α-FeO(OH)
hematite	α-Fe <sub>2</sub> O <sub>3</sub>

Table 2. Paragenetic sequences of Fe-sulfate minerals from pyrite oxidation (adapted from [12]).

time	Chile	Laboratory	Iron Mt., California
early	pyrite	pyrite	pyrite
		melanterite	melanterite
		siderotil	
		rozenite	rozenite
	szomolnokite	szomolnokite	szomolnokite
	römerite	rhomboclase	copiapite
	quenstedtite		römerite
	coquimbite	coquimbite	coquimbite
	pickeringite	römerite	kornelite
	copiapite		rhomboclase
	parabutlerite	voltaite	voltaite
late	jarosite		halotrichite-bilinite