

EXPERIMENTAL CONSTRAINTS ON TRACE ELEMENT BEHAVIOR IN MARTIAN EVAPORITE MINERALS. B. C. Hahn¹, S. M. McLennan¹, N. J. Tosca², and R. J. Reeder¹, ¹Department of Geosciences, Stony Brook University, Stony Brook, NY 11794-2100 (bhahn@mantle.geo.sunysb.edu; scott.mclennan@sunysb.edu; rjreeder@stonybrook.edu), ²Department of Organismic & Evolutionary Biology, Harvard University, 26 Oxford St., Cambridge, MA 02138 (ntosca@fas.harvard.edu).

Introduction: The Mars Exploration Rovers have detected a distinctive suite of evaporite minerals at the Martian surface precipitated from fluids derived from basaltic weathering under low pH conditions. Orbital spectroscopic methods have confirmed global distributions of these materials. The formation and stability of evaporite assemblages have been well modeled at Meridiani Planum for major element chemistry. However, in addition to providing major element abundances of Martian surface materials, the APXS (Alpha-Proton X-Ray Spectrometer) instruments onboard the Mars Exploration Rovers have returned a selection of trace element abundances in soils and rocks including Ni, Zn, and Cr. These measurements have shown considerable trace element abundance variability that is not well-understood (see **Table 1**, below). Accordingly, it is of interest to constrain the trace element partitioning behavior for the distinctive evaporite minerals that likely exist at Meridiani Planum, including gypsum, Mg- and Fe-sulfates.

Background: Although relatively uncommon in terrestrial environments, acidic weathering of basaltic rock is likely the primary chemical weathering regime for the Martian surface [3, 4]. Acidic, sulfur-rich brines evaporate along a particular pathway producing the specific set of evaporite mineral assemblages (**Fig. 1**, right) observed or implied throughout Meridiani Planum. These evaporite minerals have then been modified, reworked, and mixed with altered siliciclastic debris to form sulfur-rich, layered sandstone outcrops (most notably observed at the Burns Formation). Periods of diagenetic modification have further altered these deposits [5]. Trace element behavior during the formation and evolution of these specific mineralogies has not previously been studied experimentally in any detail.

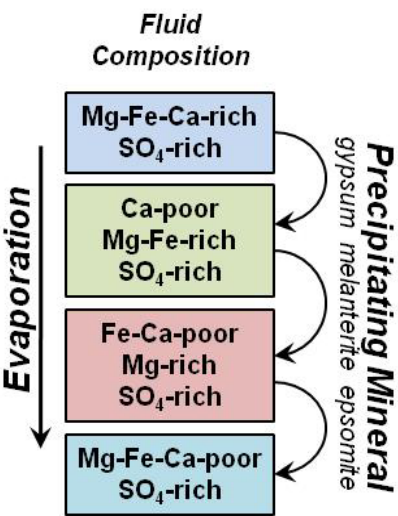


Fig. 1: The pathway of evaporating, early-stage, sulfate-rich, acidic fluids like those modeled for Meridiani Planum. Adapted from Tosca and McLennan, 2006 [6].

Method & Results: To fully characterize the partitioning of a trace element throughout an evolving evaporating system, one must first characterize the trace element behavior into each precipitating mineral phase, starting with the earliest precipitated (**Fig. 1**, above). Here we describe an experimental approach and preliminary results of trace element incorporation into gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) – which precipitates early in an evolving evaporation system and for which the precipitation process is well-understood. Determining trace element partitioning during the formation of evaporites is difficult through experimental means due to various kinetic effects and complicating factors. Also, analysis of trace element abundances in the final precipitated mineral can be further complicated by the presence of ubiquitous fluid inclusions [7].

Table 1: Averages, standard deviations, and ranges of Ni, Zn, and Cr abundances detected at MER landing sites from APXS for soils and rock targets [1,2]. Note, the standard deviations and ranges show that these trace and minor elements show considerable variability in abundance (through Sols 720).

		MER-A Spirit ^[1]			MER-B Opportunity ^[2]	
		All	Soils	Rocks	Soils	Rocks
Ni	average(±1s.d.):	505±268 ppm	475±159 ppm	423±335 ppm	625±254 ppm	576±181 ppm
	range:	24-2086 ppm	109-997 ppm	24-2086 ppm	233-1292 ppm	81-1639 ppm
Zn	average(±1s.d.):	270±146 ppm	257±95 ppm	157±103 ppm	320±72 ppm	406±114 ppm
	range:	38-667 ppm	98-460 ppm	54-667 ppm	178-452 ppm	38-634 ppm
Cr	average(±1s.d.):	0.20-0.19 wt%	0.22±0.06 wt%	0.23±0.30 wt%	0.24±0.05 wt%	0.14±0.04 wt%
	range:	0-1.95 wt%	0.03-0.34 wt%	0-1.95 wt%	0.17-0.33 wt%	0.07-0.34 wt%

Due to kinetic effects, sensitivity to changing pH conditions, oxidation effects, and other variables, we will use a Chemo-Stat and/or pH-Stat titration experimental setup to reliably characterize the trace element partitioning coefficients into a precipitating evaporite mineral. However, it is useful to first perform a series of initial evaporation drift experiments that can broadly define the nature of the evaporating system as a particular mineral phase forms, and thus provide experimental constraints for the more rigorous titration method.

Solutions of calcium sulfate are allowed to evaporate in stirred, open-vessels under a fume hood – each with different initial concentrations of Ni, Zn, or Cr. A small amount of H_2SO_4 (stock sulfuric acid) is also added to provide some initial solution acidity and a

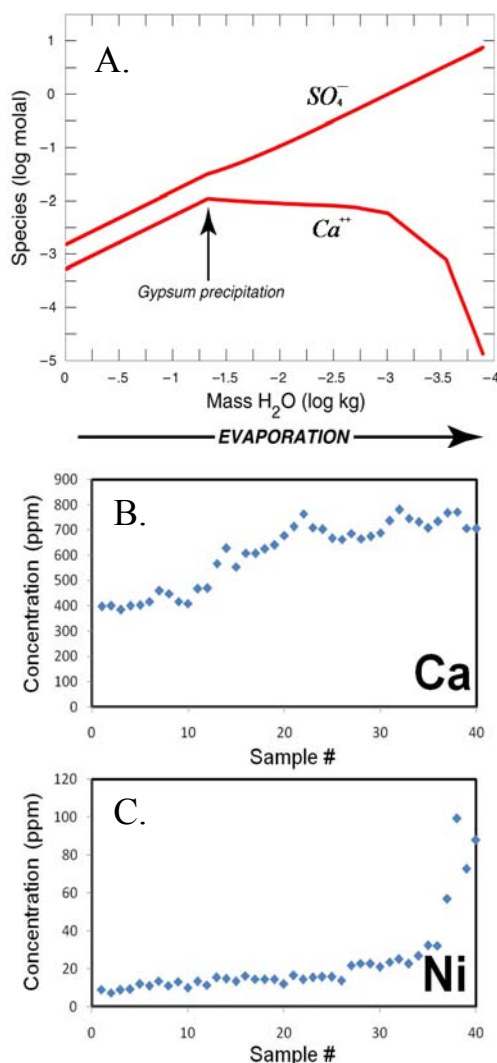


Fig. 2: A. Modeled solution behavior for Ca in an evaporating sulfate-rich fluid. Ca concentrations are expected to increase until start of gypsum precipitation, then begin to decrease; B. Measured Ca concentrations for an evaporation experiment with 10ppm added Ni; C. Measured Ni concentrations for the same experiment.

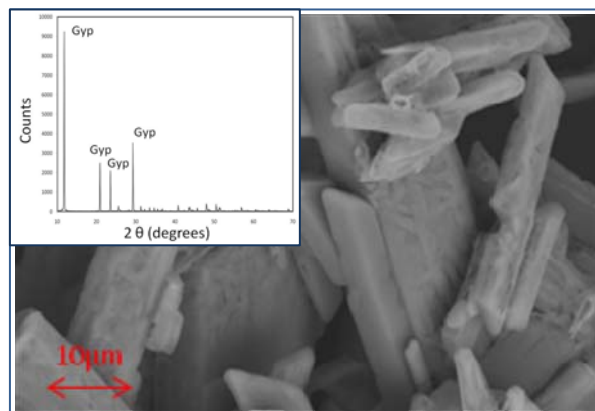


Fig. 3: Residual materials of a $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ evaporation experiment with 10ppm added Ni. Solids are characterized with SEM and XRD (inset).

source of excess sulfate. The solution is sampled and filtered throughout the evaporation process and the fluid samples and residual materials are thoroughly analyzed by a variety of methods. For example, Fig. 2 (left) shows modeled behavior for an evaporating calcium sulfate solution and the preliminary DCP determined (DC-Plasma Emission Spectrometer) chemical results for one such evaporation experiment (400 ppm Ca and 10 ppm Ni starting solution). Note that, as expected, Ca concentrations in solution begin to level off with the onset of gypsum formation (Fig. 2ab, left). However, the dramatic increase in Ni concentration (Fig. 2c, left) toward the end of the experimental run indicates that Ni is highly incompatible and remains in solution during gypsum precipitation. Fig. 3 (above) shows the SEM (Scanning Electron Microscope) and XRD (X-Ray Diffraction) analyses of residual materials for this experiment, confirming gypsum formation.

After characterizing the partitioning behavior of Ni, Zn, and Cr in gypsum, we will begin similar experiments with the other evaporite minerals in the Meridiani Planum sulfates suite. These include: A. *melanterite* [$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$]; B. *epsomite* [$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$]; and C. *jarosite* [$(\text{H}_3\text{O}, \text{Na}, \text{K})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$]. Note, that while gypsum formation is mostly insensitive to complicating variables such as pH and oxidation effects, the formation of these later minerals is more complex and experimental setups will be modified to optimize synthesis and analysis.

References: [1] Gellert R. et al. (2004) *Science*, 305, 829-832. [2] Rieder R. et al. (2004) *Science*, 306, 1746-1749. [3] Tosca N. J. et al. (2005) *EPSL*, 240, 122-148. [4] Hurowitz J. A. et al. (2006) *JGR*, 111, 10.1029/2005JE002515. [5] McLennan S. M. et al. (2005) *EPSL*, 240, 95-121. [6] Tosca N. J. and McLennan S. M. (2006) *EPSL*, 241, 21-31. [7] Schreiber and Tabakh (2000) *Sedimentology*, 47, 215-238.