TRACE ELEMENT BEHAVIOR IN MARTIAN EVAPORITE MINERALS: EXPERIMENTAL CONSTRAINTS.

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Introduction: The Mars Exploration Rovers have detected distinctive suites of evaporite minerals at the Martian surface precipitated from fluids derived from basaltic weathering under low pH conditions. Orbital spectroscopic observations have confirmed the global distributions of these materials. The formation and stability of evaporite assemblages have been well modeled at Meridiani Planum for major element chemistry. In addition to providing major element abundances of Martian surface materials, the APXS (Alpha-Particle 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 [1, 2]. 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 much of 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 and surrounding terrains). Periods of diagenic modification have further altered these deposits [6]. Trace element behavior during the formation and evolution of these specific mineralogies has not previously been studied experimentally in any detail.
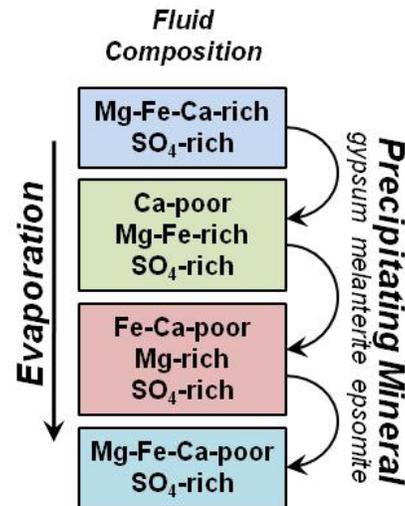

Fig. 1: The pathway of evaporating, early-stage, sulfate-rich, acidic fluids like those modeled for Meridiani Planum. Adapted from Tosca and McLennan, 2006 [5].

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*). 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].

We use a Chemo-Stat and/or pH-Stat titration experimental setup to reliably characterize the trace element partitioning coefficients into a precipitating evaporite mineral. These experiments are ongoing and

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%

provide partition coefficients of more use to geo-chemical modeling. However, it is useful to first per-form 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.

Three sulfate evaporites are studied - gypsum ($CaSO_4\cdot2H_2O$), epsomite ($MgSO_4\cdot7H_2O$), and melanterite ($Fe^{2+}SO_4\cdot7H_2O$). For each, three sets of solutions are prepared with a different trace element (Ni, Zn, and Cr). Each solution set consists of three separate ex-periments with different initial concentrations of a particular trace element (~2 ppm, ~10 ppm, ~50 ppm) – i.e., 27 separate solutions with different combina-tions of dissolved sulfate, trace element, and initial trace element concentration.

Sulfate solutions are prepared at concentrations close to but before the saturation point for each respec-tive mineral. Ni and Zn are added to the solution as dissolved Ni- and Zn-sulfates; while Cr was added as a commercially available standard. These solutions are allowed to evaporate in stirred, open-vessels, at room temperature, under a fume hood. A small amount of H_2SO_4 (stock sulfuric acid) is also added to provide some initial solution acidity and a source of excess sulfate. Over the course of 1-2 weeks, the solution is sampled, filtered, and monitored throughout the evapo-ration process and during the precipitation of the sul-fate mineral. The fluid samples and residual materials are thoroughly analyzed by a variety of methods.

Fluid samples are analyzed by DCP (**Fig. 2**, *right*) and measured for pH. After complete evaporation of the solution, the residual materials were collected and analyzed under optical microscope and SEM for mor-phology and their composition was confirmed with XRD and EDS (see examples in **Fig. 3**, *right*).

Generally, all three trace elements studied showed incompatible behavior during the mineral formation – tending to remain in solution rather than become in-corporated into the precipitating minerals. For exam-ple, preliminary estimates of partition coefficients for Ni, Zn, and Cr in gypsum formation range from 0.02-0.08.

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] Tosca N. J. and McLen-nan S. M. (2006) *EPSL, 241*, 21-31. [6] McLennan S. M. et al. (2005) *EPSL, 240*, 95-121. [7] Schreiber and Tabakh (2000) *Sedimentology, 47*, 215-238.
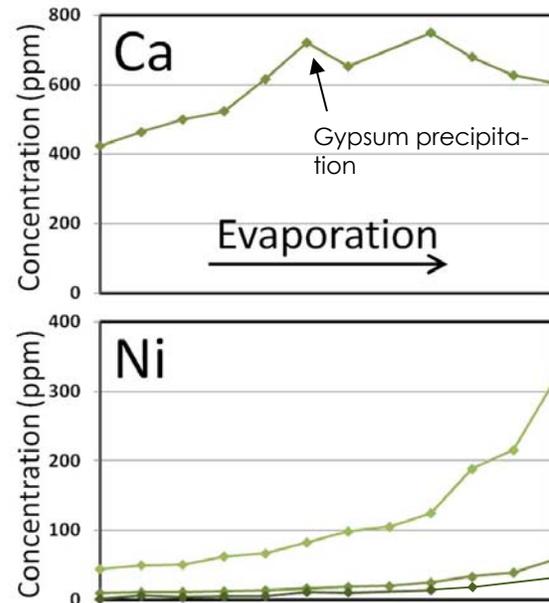

Fig. 2: *Example DCP analyses for a set of three solutions with the same initial concentration of dissolved gypsum ($CaSO_4\cdot2H_2O$) and varied concentrations of included Ni (50 ppm [light green, top], 10 ppm [green, middle], 2 ppm [dark green, bottom]).*
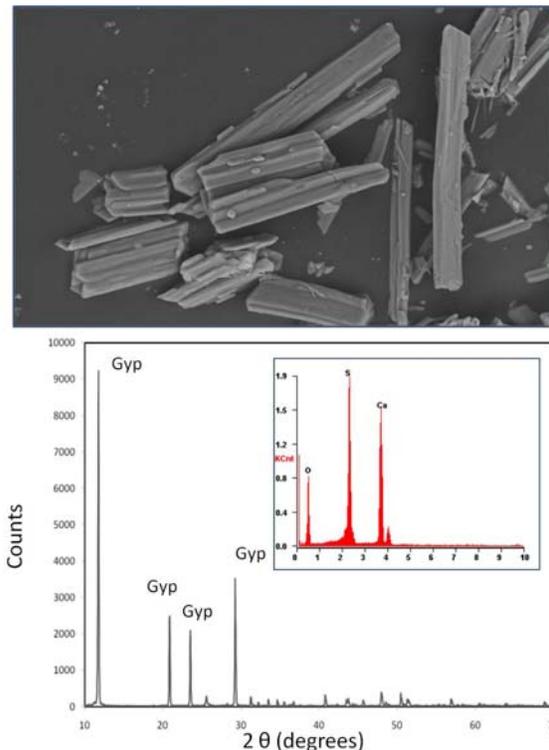

Fig. 3: *Residual materials were also analyzed for mor-phology with SEM (**top** – a typical sample of precipitated gypsum) and optical microscope and with XRD (sample spectra from the same experiment, shown **bottom**) and EDS (**bottom, inset**).*