

**EXPERIMENTAL CONSTRAINTS ON TRACE ELEMENT MOBILITY IN MARTIAN BASALT.**

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**Introduction:** It is widely believed that aqueous alteration on Mars has been strongly influenced by low pH conditions. Experimental work has shown that these low pH environments result in the mobility of elements, such as Fe (III) and Al, that are relatively insoluble under most near surface conditions on Earth. Although these studies have increased our understanding of major element behavior, little is known about the mobility of trace elements under Martian conditions. The Mars Exploration Rovers have provided and continue to provide analyses of Ni, Zn, and Cr at both the Spirit and Opportunity landing sites. In situ rock and soil analyses show that these trace elements are highly variable (Figure 1), which generates many questions about the processes that control their distribution. Among the issues that need to be considered are the roles of meteoritic contributions, aqueous alteration, residual enrichments, evaporative concentrations, and so forth. A central question to addressing these issues is the nature of the mobility of Ni, Zn, and Cr during aqueous alteration under Martian conditions. Accordingly, we have begun a series of aqueous alteration experiments on synthesized Martian basalt in an attempt to better understand the mobility of Ni, Zn, and Cr on the Martian surface.

**Basalt Analog Synthesis:** Basalt analog compositions are the same as those used in previous studies from our lab [1] and are based on average S- and Cl-free Pathfinder soil, with trace elements of Ni, Zn, and Cr added (Table 1). Oxide components are homogenized and placed into a platinum container.

After the capsule has been sealed under vacuum it is placed into a furnace and raised above its liquidus. Once the mixture has been melted, the capsule is quenched resulting in glass with a basaltic composition. The container can also be cooled slowly to control the crystallization of the sample for future batch experiments (see future work). The composition of the glass is analyzed by electron microprobe.

Table 1: Target basalt composition [1], average of electron microprobe analyses normalized to 100%, and the composition of RATED Adirondack basalt for comparison.

	PFS Target	PFS Average	Adirondack
SiO <sub>2</sub>	48.42	49.83	47.07
TiO <sub>2</sub>	1.17	1.18	0.49
Al <sub>2</sub> O <sub>3</sub>	10.29	10.22	11.20
FeO <sub>T</sub>	19.10	18.23	19.36
MnO	0.49	0.30	0.42
MgO	8.00	7.70	11.15
CaO	7.15	6.88	6.55
Na <sub>2</sub> O	3.55	3.69	2.48
K <sub>2</sub> O	0.65	0.66	0.07
P <sub>2</sub> O <sub>5</sub>	1.18	1.24	0.54
Cr <sub>2</sub> O <sub>3</sub>	0.10	0.10*	0.63
Ni (ppm)	785.00	785.00*	200.00
Zn (ppm)	800.00	800.00*	100.00
Total	100.00	100.00	100.00

\* Estimated; to be analyzed

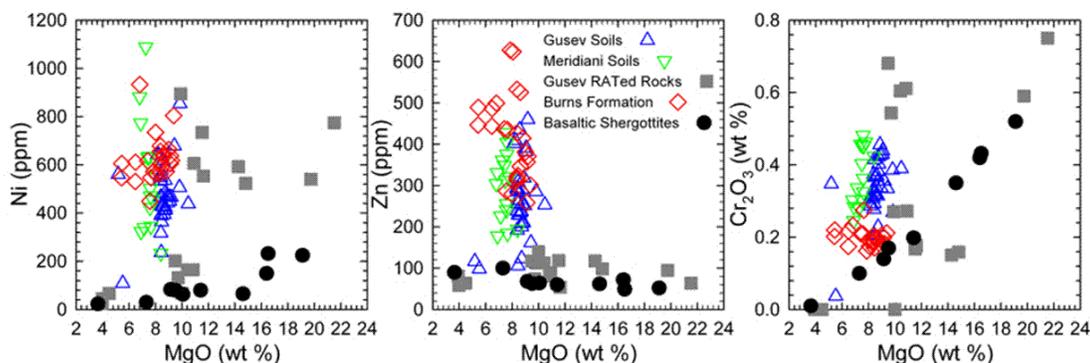


Figure 1: Plots of Ni, Zn, and Cr versus MgO for Gusev and Meridiani soils, Gusev RATED rocks, RATED Meridiani outcrop, and basaltic shergottites. Note that the trace elements show considerable variability in their abundance.

**Batch Experiments:** After synthesis, the glass is extracted from the platinum capsule and then crushed and sieved to constrain the particle size between 710 and 63  $\mu\text{m}$ . The basalt is then ultrasonically rinsed in acetone to remove ultrafine particles and dried overnight. The material is divided up and placed into Teflon<sup>®</sup> beakers that contain varying concentrations of sulfuric and hydrochloric acids in order to achieve a water-to-rock ratio of 10. Acid mixture concentrations range from a 1M  $\text{H}_2\text{SO}_4$ /0.25M HCl mix to 100  $\mu\text{M}$   $\text{H}_2\text{SO}_4$ /25  $\mu\text{M}$  HCl, each with a S:Cl molar ratio of 4 which is comparable to typical Martian soils (Table 2). The fluid-rock mixture is kept at 25  $^\circ\text{C}$  and allowed to react for a period of 14 days. During this time the fluid is periodically sampled for analysis by atomic emission spectroscopy (DCP-AES) so that the total amount removed does not exceed 4% of the initial volume. At the end of this 14 day period, residual solids and secondary phases are characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM), which also includes energy dispersive X-ray microanalysis (EDS).

Acid Mixture	$\text{H}_2\text{SO}_4$ mol/L	HCl mol/L	pH
A	$1.0 \times 10^0$	$2.5 \times 10^{-1}$	0
B	$1.0 \times 10^{-1}$	$2.5 \times 10^{-2}$	1
C	$1.0 \times 10^{-2}$	$2.5 \times 10^{-3}$	2
D	$1.0 \times 10^{-3}$	$2.5 \times 10^{-4}$	3
E	$1.0 \times 10^{-4}$	$2.5 \times 10^{-5}$	4

Table 2: Acid mixtures used in alteration experiments

**Preliminary Results:** PFS glass reacted with solution A resulted in almost complete dissolution of the glass in less than 48 hours. After evaporating remaining fluids from the beakers, Sample A appeared as green transparent grains. Figure 2 shows the relative abundance and nature of secondary phases formed during experiment A. Experiment B formed large gypsum crystals, some up to 3 mm in length, covering the surface of most of the basalt grains. Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) was also identified by XRD in experiment A and B, and by SEM in D. Other secondary minerals were identified including alunogen ( $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$ ) and melanterite ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) in experiments A, B and C, anhydrite ( $\text{CaSO}_4$ ) and tamarugite ( $\text{NaAl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ) in experiments A and B, and hexahydrite ( $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ) in experiment A. No secondary minerals have been identified in experiment E.

**Discussion and Future Work:** Secondary phases identified thus far in this study are almost identical to those found in the previous study [1], with one exception. Fe oxides identified by SEM/EDS in

experiments D and E by Tosca et al. (2004) are absent in our experiments. The reason for this discrepancy, and whether or not trace elements play a role, has yet to be determined. Thus far, no evidence for residual minerals, such as clays, has been found and alteration appears to be dominated by dissolution processes. Analyses of the fluids (which are pending) will inform us about whether trace elements are also being released solely by bulk dissolution processes. Future work consists of DCP analyses of all aqueous samples to determine the concentration of Ni, Cr, and Zn. We will perform more batch experiments with crystalline basalt of the same composition to evaluate what phases control the trace element mass balance.

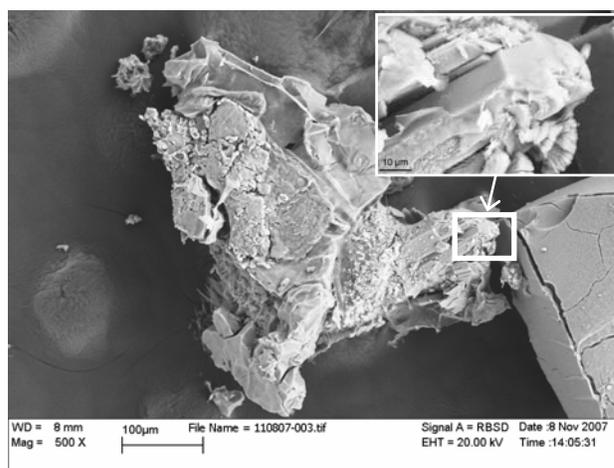


Figure 2: Scanning electron micrograph of basaltic glass reacted with solution A (Inset: gypsum).

**References:** [1] Tosca, N. J. et al. (2004) JGR, 109, E05003.