

EXPERIMENTAL CONSTRAINTS ON TRACE ELEMENT MOBILITY IN MARTIAN BASALT: PROGRESS REPORT. L. J. Beavon¹, D. H. Lindsley¹, S. M. McLennan¹, N. J. Tosca², ¹Department of Geosciences, Stony Brook University, Stony Brook, NY 11794-2100 (lbeavon@ic.sunysb.edu; scott.mclennan@sunysb.edu; dlindsley@notes.cc.sunysb.edu), ²Department of Organismic & Evolutionary Biology, Harvard University, 26 Oxford St., Cambridge, MA 02138 (ntosca@fas.harvard.edu).

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, 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. We are conducting a series of aqueous alteration experiments on synthesized Martian basalt in an attempt to better understand the potential 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). Trace element concentrations were chosen being mindful of instrumental detection limits and the stability of related minerals. Oxide components are homogenized and placed into a gold-palladium (Au₈₀Pd₂₀) capsule. 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 can be quenched to obtain glass with a basaltic composition, or cooled slowly to control the crystallization of the sample. The composition of the glass is analyzed by electron microprobe. Similar experiments were performed at higher temperatures in platinum capsules. Although these experiments resulted in a chromite free glass, electron microprobe analysis determined the resulting levels of Ni and Zn were minimal. These two elements have a high affinity for platinum, which might explain their low levels in the melt. Results from batch alteration experiments performed on these samples can be found below.

Basalt Synthesis Complications: During our basalt synthesis we encountered a number of problems.

	PFS Target	PFS Average	Adirondack
SiO ₂	48.42	48.35	47.07
TiO ₂	1.17	1.16	0.49
Al ₂ O ₃	10.29	9.92	11.20
FeO _T	19.10	18.72	19.36
MnO	0.49	0.47	0.42
MgO	8.00	7.91	11.15
CaO	7.15	6.69	6.55
Na ₂ O	3.55	3.53	2.48
K ₂ O	0.65	0.56	0.07
P ₂ O ₅	1.18	1.10	0.54
Cr ₂ O ₃	0.10	0.06	0.63
Ni (ppm)	1570.00	2129.00	200.00
Zn (ppm)	1600.00	1598.00	100.00

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

These difficulties have been resolved with one major exception: the persistence of chromite at the calculated liquidus. Attempts to eliminate the spinel phase have included using a different oxide as the source of chromium and reducing the initial amount of chromium added to the mix. According to studies on the solubility of chromite in basaltic melts, the chromium content in a melt increases with decreasing oxygen fugacity, at constant temperature. The increased content of chromium in the melt reflects the increase in the Cr²⁺/Cr³⁺ ratio with decreasing oxygen fugacity [2, 3]. Since Cr²⁺ prefers the melt relative to Cr³⁺ [4], and studies have shown that Cr²⁺ is not readily incorporated into the spinel structure [5, 6], the stability of chromite is reduced. Other spinel phases would also be destabilized as Fe³⁺ concentrations also decrease with decreasing oxygen fugacity. We are in the process of synthesizing a Martian analog at lower oxygen fugacity (See future work).

Batch Experiments: After synthesis, the glass is crushed and sieved to obtain the particle size between 710 and 63 μm. The material is divided up and placed into Teflon[®] 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 H₂SO₄/0.25M HCl mix to 100 μM H₂SO₄/25 μM HCl, each with a S:Cl a molar ratio of 4 which is comparable to typical Martian soils

Acid Mixture	H ₂ SO ₄ mol/L	HCl mol/L	pH
A	1.0 x 10 ⁰	2.5 x 10 ⁻¹	0
B	1.0 x 10 ⁻¹	2.5 x 10 ⁻²	1
C	1.0 x 10 ⁻²	2.5 x 10 ⁻³	2
D	1.0 x 10 ⁻³	2.5 x 10 ⁻⁴	3
E	1.0 x 10 ⁻⁴	2.5 x 10 ⁻⁵	4

Table 2: Acid mixtures used in alteration experiments

(Table 2). The fluid-rock mixture is kept at 25 °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).

Preliminary Results: The following results are for those experiments performed in platinum capsules at higher temperatures (see above). PFS glass reacted with solution A resulted in almost complete dissolution of the glass in less than 48 hours. Figure 1 shows the relative abundance and nature of secondary phases formed during experiment A. Gypsum (CaSO₄·2H₂O) was identified by XRD in experiments A and B, and by SEM in D. Other secondary minerals were identified including alunogen (Al₂(SO₄)₃·17H₂O) and melanterite (FeSO₄·7H₂O) in experiments A, B and C, anhydrite (CaSO₄) and tamarugite (NaAl(SO₄)₂·6H₂O) in experiments A and B, and hexahydrate (MgSO₄·6H₂O) in experiment A. No secondary minerals have been identified in experiment E.

In experiments A, B and C, the glass dissolved in near-stoichiometric proportions with respect to major elements. In contrast, experiments D, and E dissolved

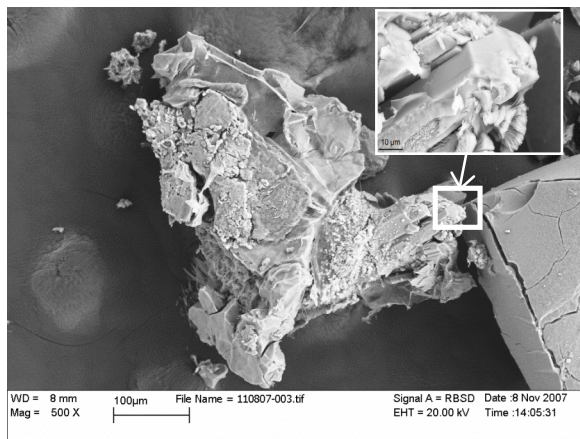


Fig. 1: Scanning electron micrograph of basaltic glass reacted with solution A (Inset: gypsum).

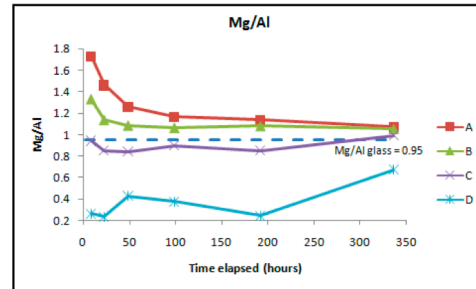


Figure 2: Mg/Al ratio vs. time in PFS glass, solutions A-D.

in a non-stoichiometric manner that appears to be preferentially releasing univalent network-modifying elements (Fig. 2). Figure 3 shows that Cr and Al, two trivalent elements, were released in close to stoichiometric proportions in experiments A and B. Experiments C-E are not shown because trace element concentrations were below detection limits.

Discussion and Future Work: Secondary phases identified in this study are almost identical to those found in the previous study [1]. Thus far, no evidence for residual minerals, such as clays, has been found and alteration appears to be dominated by dissolution processes. Currently we are performing experiments on our Martian analog at lower oxygen fugacity in the attempt to synthesize chromite free glass with detectable amounts of Ni and Zn. Once this complication has been resolved we will perform batch experiments to better understand the mobility of Ni and Zn under low pH conditions. We will also synthesize crystalline basalt of the same composition to find out what phases control the trace element mass balance.

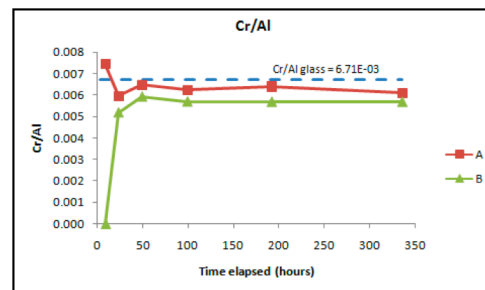


Fig. 3. Cr/Al ratio vs. time in PFS glass, solutions A & B.

References: [1] Tosca, N. J. et al. (2004) JGR, 109, E05003. [2] Murck, B.W. and Campbell, I.H. (1986) Geochim. Cosmochim. Acta 50, 1871-1887. [3] Roeder, P.L. and Reynolds, I. (1991) J. Petrol., 32, 909-934. [4] Papike, J.J. et al. (2005) Am. Mineral., 90, 277-290. [5] Schreiber, H.D. and Haskin, L.A. (1976) Proc. Lunar Sci. Conf. 7, 1221-1259. [6] Hanson, B. and Jones, J.H. (1998) Am. Mineral., 83, 669-684.