

**TRACE ELEMENT (Cr, Ni, Zn) GEOCHEMISTRY OF SURFICIAL PROCESSES ON MARS: INSIGHTS FROM EXPERIMENTS AND IMPLICATIONS FOR *IN SITU* MEASUREMENTS.** S. M. McLennan<sup>1</sup> and Y.-Y. S. Zhao<sup>1</sup>, <sup>1</sup>Department of Geosciences, State University of New York at Stony Brook, Stony Brook, NY, 11794-2100, USA ([Scott.McLennan@sunysb.edu](mailto:Scott.McLennan@sunysb.edu); [yuyan.zhao@stonybrook.edu](mailto:yuyan.zhao@stonybrook.edu)).

**Introduction:** APXS contact instruments on rovers to Mars have provided measurements for several trace elements, including Cr, Ni and Zn, in rocks and soils on the Martian surface. Interpretations of these elements for Martian igneous rocks are well founded in a wealth of experimental and analytical data. However, interpreting trace elements in terms of surficial processes, such as weathering/alteration, sedimentary deposition and diagenesis, is less well understood for a variety of reasons, such as the lack of adequate analogs on Earth and the lack of relevant experimental data.

For several years, our laboratory has been engaged in experimental studies evaluating trace element behavior on the surface of Mars. Included are experiments related to acid alteration of Martian basalt [e.g., 1,2], evaporative processes of Martian brines [3] and oxidative diagenetic processes of Fe-sulfate and Fe-oxide minerals [4,5]. Here we describe how results from such experiments can be used to help interpret Cr, Ni and Zn data obtained by Martian rovers.

**Importance of Provenance:** A critical issue in evaluating trace element behavior is that Martian crust exposed to aqueous processes is basaltic and thus of fundamentally different composition than Earth's upper continental crust, the main source of terrestrial sediment and dissolved components in weathering fluids [6]. For Cr, Ni and Zn, Martian crust is enriched by factors of ~5-30 and this is expected to translate into comparably enriched aqueous solutions and derived sediments (Table 1), especially if prevailing conditions of aqueous alteration are at low pH.

**Table 1.** Trace elements in Martian crust and terrestrial upper continental crust [7].

	<i>Mars</i>	<i>Earth</i>	<i>Mars/Earth</i>
Cr (ppm)	2600	83	31
Ni (ppm)	337	44	7.7
Zn (ppm)	320	71	4.5

**Basalt Alteration Experiments:** During acid alteration of Martian basaltic rock and glass the overall order of relative mobility is Ni > Cr > Zn, although details depend on pH and exact mineralogy. All are mobile enough to be important constituents in aqueous fluids and thus available for partitioning into chemically precipitated minerals. In basalt glass, all are released stoichiometrically at low pH (0-2) but non-stoichiometrically for higher pH with order of release

being Ni > Cr > Zn. For crystalline basalt, Ni (mainly in olivine), releases stoichiometrically whereas Cr (mainly in oxides) releases non-stoichiometrically causing a fractionation in Cr/Ni ratio. Depending on whether plagioclase is stable, order of release can be Ni > Zn > Cr (no plag) or Ni > Cr > Zn (plag; due to increased Cr content in olivine at the lower  $f_{O_2}$ ) [1,2].

**Evaporation Experiments:** Preliminary mineral – solution free-drift experiments suggest Cr, Ni and Zn are incompatible during evaporative crystallization of gypsum and epsomite from low pH brines [3]. However, partition coefficients are high enough ( $K_D^{gyp} \sim 0.05$ ;  $K_D^{epsom} \sim 0.1$ ) that significant substitution into sulfates could occur from concentrated brines during Martian evaporite formation. Ferrous sulfates (e.g., melanterite) form Fe-Ni and Fe-Zn solid solutions (e.g., morensite, goslarite), and substantial partitioning of Ni and Zn into iron-bearing sulfate evaporite suites likely occurs. Ni and Zn would preferentially replace  $Fe^{2+}$  in ferrous sulfates (e.g., melanterite) and Cr preferentially replace  $Fe^{3+}$  in ferric sulfates (e.g., jarosite) in more oxidized evaporating fluids.

**Oxidative Diagenesis Experiments:** Experiments indicate ferrous sulfates (e.g., melanterite) diagenetically oxidize, under acid aqueous conditions, to hematite through three pathways, depending on conditions (mainly pH): (1) melanterite  $\Rightarrow$  jarosite  $\Rightarrow$  hematite; (2) melanterite  $\Rightarrow$  schwertmannite  $\Rightarrow$  goethite ( $\Rightarrow$ hematite) and (3) melanterite  $\Rightarrow$  schwertmannite  $\Rightarrow$  goethite+jarosite ( $\Rightarrow$ hematite). Such processes could result in formation of hematitic spherules at Meridiani (see below) and in spatial correlations between sulfates and iron oxides seen from orbit. Uptake of Cr, Ni and Zn was evaluated and all three elements partition into schwertmannite, goethite(?) and jarosite with  $Cr^{3+}$  substituting into the structures (for  $Fe^{3+}$ ) and  $Ni^{2+}$  and  $Zn^{2+}$  being adsorbed onto surfaces and possibly incorporated into structures through coupled substitutions. Overall order of preferred uptake into hematite for Path (1) was  $Cr \gg Zn > Ni$ , for Path (2)  $Cr \gg Ni > Zn$  and for Path (3) intermediate with relative uptake of Ni and Zn depending on the relative amounts of goethite and jarosite.

**Implications for Interpreting Trace Element Results from Mars:** Below, we describe two examples where such experimental results help to constrain the nature of surficial processes on the Martian surface.

**Surface alteration.** Aqueous alteration of Martian rocks was studied by comparing RATed (relatively fresh) and brushed (relatively altered) surfaces [7], and suggests that acidic fluids interacting with rocks at low water/rock ratio caused the alteration. For Adirondack Class rocks (olivine-bearing; Adirondack, Humphrey), alteration is dominated by olivine dissolution, whereas in Clovis Class rocks (olivine-free; Clovis, Ebenezer) alteration is dominated by basalt glass or pyroxene dissolution. Experimental results now allow for these models to be tested with trace elements.

Experiments indicate olivine dissolves stoichiometrically from crystalline basalt under acidic conditions, such that Ni/Mg ratios remain constant. Resulting altered rock has elevated Cr/Mg because Cr is preferentially held in minerals that dissolve slower than olivine (e.g., chromite). However, at low pH ( $\leq 3$ ) Mg, Cr and Ni all dissolve stoichiometrically from basalt glass, and Cr/Mg and Ni/Mg ratios remain constant. The models of [7] thus predict that alteration of Adirondack Class should result in elevated Cr/Mg (due to Mg loss) in weathered rinds but constant Ni/Mg whereas alteration of Clovis Class should result in both Cr/Mg and Ni/Mg being unchanged, and this is observed in APXS data (Fig. 1). For Clovis Class rock Ebenezer, the Ni/Mg ratio is lower in altered material, possibly suggesting a phase other than glass was involved in the alteration.

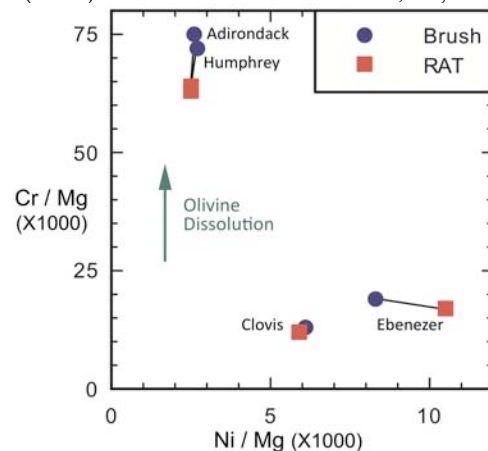
**Hematitic spherules.** Hematitic spherules in sedimentary rocks of the Burns Fm. have been the object of great interest. One argument against the spherules being concretions is their high Ni content, considered by some to be inconsistent with substitution into an Fe(III) mineral (hematite) [8]. Are trace element experiments consistent with spherules being concretions? Mass balances suggest hematitic spherules have approximately Cr  $\leq 1,000$  ppm; Ni  $\geq 2,000$  ppm; Zn  $\sim 500$ -600 ppm [5] and compared to crustal abundances (Table 2) are enriched by factors of  $<0.4$  (Cr),  $>6$  (Ni) and  $\sim 1.5$ -2 (Zn). Accordingly, trace element features that need to be explained are high Ni content, high Ni/Zn ratios and low Cr/Ni ratios.

Experimental studies of acid alteration of crystalline olivine basalt, likely a dominant process on Mars [9], indicate relative release rates of Ni  $>$  Cr  $>$  Zn thus providing for aqueous fluids having lower Cr/Ni and higher Ni/Zn than average crustal abundances. Trace elements in diagenetic fluids, although ultimately coming from basalt alteration, could be derived from evaporitic minerals within the sediment providing an additional stage for trace element fractionation, however, insufficient experimental data exist to provide quantitative constraints. An important factor would be the oxidation state during evaporation, which would

influence  $\text{Fe}^{3+}/\text{Fe}^{2+}$  [10] and thus Cr/Zn and Cr/Ni ratios. In any case, experiments clearly are consistent with diagenetic fluids that could be elevated in trace elements and, compared to crustal abundances, have low Cr/Ni and high Ni/Zn.

Experiments examining oxidative diagenesis of melanterite provide some final constraints. Of the three pathways described above, Path 2 (melanterite  $\Rightarrow$  schwertmannite  $\Rightarrow$  goethite  $\Rightarrow$  hematite), provides for both significant partitioning of Ni into hematite and an elevated Ni/Zn ratio compared to the starting fluid. (Other diagenetic pathways are permitted but only with an additional source (e.g., meteoritic) of Ni to elevate Ni/Zn.) Accordingly, experimental data provide clear evidence that the trace element content of hematitic spherules are consistent with an origin as sedimentary concretions without any additional processes being needed to explain high Ni, high Ni/Zn and low Cr/Ni.

**References:** [1] Beavon L. J. et al. (2009) *LPS XL*, Abstract #1879. [2] Beavon L. J. et al. (2013) in prep. for *JGR-Planets*. [3] Hahn B. C. et al. (2009) *LPS XL*, Abstract #1194. [4] Zhao Y. et al. (2009) *LPS XL*, Abstract #1978. [5] Zhao, Y.-Y. S. and McLennan S. M. (2013) *Geochim. Cosmochim. Acta* (submitted). [6] Taylor S. R. and McLennan S. M. (2009) *Planetary Crusts: Their Composition, Origin and Evolution* (Cambridge). [7] Hurowitz J. A. et al. (2006) *JGR-Planets*, 111, E02S19. [8] Knauth L. P. et al. (2005) *Nature*, 438, 1123. [10] Tosca N. J. et al. (2004) *JGR-Planets*, 109, E05003. [9] Tosca N. J. and McLennan S. M. (2009) *Geochim. Cosmochim. Acta*, 73, 1205.



**Figure 1.** Plot of Cr/Mg vs Ni/Mg for brushed (altered) and abraded (unaltered) surfaces of Adirondack and Clovis rock classes from Gusev Crater. Olivine dissolution results in elevation of Cr/Mg but no change in Ni/Mg because Mg and Ni are released stoichiometrically from olivine-bearing basalt whereas Cr is preferentially held back. For basalt glass dissolution at  $\text{pH} \leq 3$ , near stoichiometric release of Mg, Cr and Ni results and so neither ratio should change. Lowering of Ni/Mg in Ebenezer may result from phases other than glass being involved in alteration.