EXPERIMENTAL CONSTRAINTS ON TRACE ELEMENT BEHAVIOR DURING MARTIAN FE-OXIDATION PROCESSES AT MERIDIANI PLANUM.

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Introduction: The APXS (Alpha-Particle X-Ray Spectrometer) onboard the Mars Exploration Rovers (MER) has returned element abundances of over 200 soil and rock samples at both the Opportunity and Spirit landing sites [1]. Besides major elements, a selection of trace element concentrations including Ni, Cr, and Zn are also available. These data demonstrate that the trace element abundances of Meridiani outcrop material are variable (Table 1) and their behavior is very poorly understood [2]. Accordingly, it is of interest to set up a series experiments to investigate controls and behaviors of these key trace elements during Martian surficial processes. Tosca et al.[3] have proposed a mechanism that diagenetic oxidation and maturation of initially formed Fe^{2+} sulfate minerals (such as melanterite) may account for the presence of jarosite and hematite in Meridiani Planum outcrop. In this model, the trace element behavior during low pH aqueous-mediated diagenesis processes may be partially responsible for their distribution observed by MER in situ analyses. Therefore, in this study, a series of Fe-oxidation experiments with added Ni, Cr, and Zn were conducted to investigate their behavior during oxidation and reaction with precipitation products.

		Meridiani Planum (MER-Opportunity)	
		Soils	Rocks
Ni	average (±1s.d.): range:	625 ± 254 ppm 233 ~ 1292 ppm	576 ± 181 ppm 81 ~ 1639 ppm
Zn	average (±1s.d.): range:	320 ± 72 ppm 178 ~ 452 ppm	406 ± 114 ppm 38 ~ 634 ppm
Cr	average (±1s.d.): range:	0.24 ± 0.05 wt% 0.17 ~ 0.33 wt%	0.14 ± 0.04 wt% 0.07 ~ 0.34 wt%

Table 1: Averages, standard deviations, and ranges of Ni, Zn and Cr abundances detected at the Opportunity landing site from APXS for soil and rock targets [1, 2].

Method: Detailed experimental and analytical methods were described by Tosca et al. [3], with Ni^{2+}, Cr^{3+}, and Zn^{2+} added respectively. In each experiment, 500ml epsomite-saturated solution was placed in pyrex beakers as a high ionic strength matrix (I = 12 molal).

Trace elements were added at levels of 400-500 ppm initially in each experiment. Ni^{2+} and Cr^{3+} were added from commercially available standard solution containing 5% HNO_3 and Zn^{2+} was added as $ZnSO_4$ solid. In addition, 1~2 grams of KCl solid was added to provide K^+ for K-Jarosite precipitation. Various amounts of reagent-grade $FeSO_4 \cdot 7H_2O$ (melanterite) was then added to the beakers (10 g/L, 50 g/L, 200 g/L and 400g/L). All beakers were covered but allowed to maintain contact with ambient atmosphere ($pO_2 = 0.21$ atm), and continuously stirred at 25 ℃. During the experiments, pH was monitored with a pH electrode. Suspension samples were periodically collected and centrifuged at 5,000 rpm at 25 ℃ for 40 minutes. The supernatant was analyzed for Mg, Fe_T, Fe^{2+}, SO_{4T}, K, Ni, Cr and Zn. The extracted solid samples were washed with de-ionized water (to remove residual Mg-sulfate) and air dried. Solids were analyzed with X-ray Diffraction (XRD), FT-IR spectroscopy, and Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Microanalysis (EDS). Experiments were allowed to run for approximately 40~80 days.

Results and Future Work:

pH ranges in experiment. Due to Fe^{2+}, Fe^{3+} hydrolysis and 5% HNO_3 in the Ni^{2+}, Cr^{3+} standard solutions, the pH value in each experiment started low and continuously decreased. The pH ranges over the course of individual experiments were: Ni experiment 2.1 to 1.45; Cr experiment 3.9 to 3.25 (10 g/L melanterite) and 3.3 to 1.7 (200 g/L melanterite); Zn experiment, 4 to 2.8 (10 g/L melanterite), 3 to 1.67 (200 g/L melanterite).

Precipitate phases. The experiments that started with the high amounts of melanterite (200 g/L or 400 g/L) precipitated only jarosite from the first day through to the end of experiment. On the other hand, experiments beginning with low amounts of melanterite (10 g/L or 50 g/L) yielded mixed phases. For instance, in the Zn experiment with low melanterite (10 g/L), an orange precipitate was observed on the first day, and then orange to yellow precipitates occurred on the 5th days and persisted until the end of experiment at 48 days. XRD and SEM-EDS confirmed the orange precipitate was schwertmannite and the yellow colored phase was crystallized jarosite (Figure 1). Breakdown of schwertmannite and growth of jarosite

particles can be observed (Figure 1), consistent with schwertmannite transformation into jarosite observed in other studies [3, 4]. Furthermore, where (H_3O, K)-jarosite precipitated, H_3O-Jarosite is the dominant component even when considerable free K^+ remained in the residual solution. Goethite, though expected, was undetected by XRD, FT-IR and SEM-EDS in all the experiments; the reason is yet to be determined.
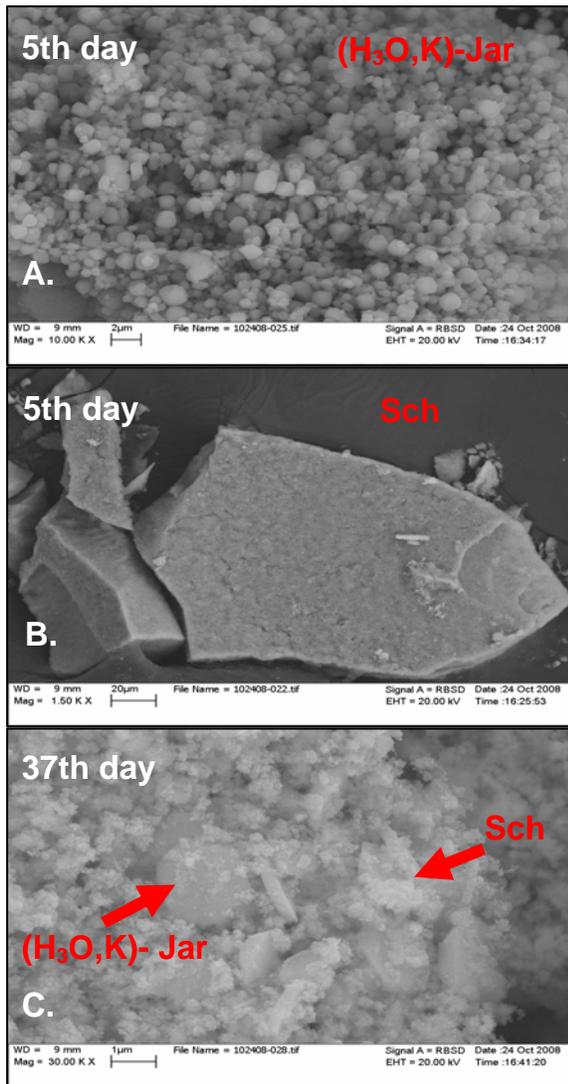

Figure 1. A. (H_3O, K)-jarosite particles on the 5th day; B. Chunk of schwertmannite on the 5th day; C. (H_3O, K)-jarosite coating with amorphous schwertmannite on the 37th day. From the 5th to 37th day, crystallized particle size grew(A,C), and schwertmannite broke down(B,C).
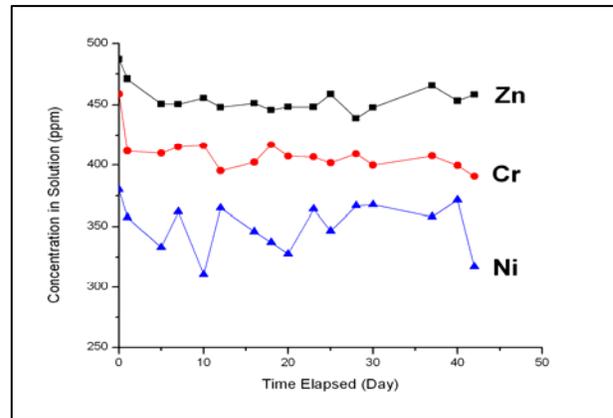

Figure 2. Zn, Cr and Ni concentration varies in solution in jarosite-only precipitation experiments.

Ni, Cr, Zn behavior with jarosite precipitation. Based on the experiments of jarosite-only precipitation, Figure 2 shows Ni, Cr, and Zn concentration in solution during the experiment. Ni concentration varies erratically during the experiment while Zn and Cr are relatively stable after a sharp decrease at the beginning. Assuming that 100% of the Fe removed from solution precipitated into jarosite, calculations suggest a constant mole ratio of Cr(III)/Fe and Zn(II)/Fe in the formed precipitate, which may indicate the elements were incorporated into the jarosite structure. The variation of Ni(II) concentration and lack of stable mole ratio with Fe suggests the dominant control of Ni behavior in the solution is adsorption-desorption processes on the jarosite surface. The changing surface area during jarosite precipitation also may influence the concentration variation. SEM-EDS confirmed the presence of Cr-bearing jarosite, Mg-bearing jarosite and pure (Cr- and Mg-free) jarosite all in one sample. This finding indicates the substitution of Fe with Cr is non-uniform and would not affect all precipitated jarosite. The formula of substituted jarosite can be written as $(H_3O,K)Fe_{3-x}Cr_x(SO_4)_2(OH)_6$. The coefficient x will be determined in future work. Zn-bearing jarosite is yet to be confirmed by SEM-EDS. The trace element behavior in mixed precipitation experiments and during schwertmannite-goethite-jarosite phase transformation needs to be further investigated.

References: [1] Hahn B. C. (2008) LPS XXXIX, Abstract #1845. [2] Rieder R. et al. (2004) Science, 306, 1746-1749. [3] Tosca, N. J. et al. (2008) JGR, 113, E05005. [4] Acero P. et al. (2006) GCA, 70, 4130-4139.