

PHYLLOSILICATE FORMATION AND TRACE ELEMENT PARTITIONING DURING ISOCHEMICAL HYDROTHERMAL BASALT ALTERATION. R. D. Nickerson¹, S. M. Chemtob¹, and J. G. Catalano¹,
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Introduction: Detection of a suite of secondary minerals provides strong evidence for widespread aqueous alteration of the Martian basaltic crust [1,2]. Phyllosilicates are hypothesized to have formed through isochemical alteration in the subsurface, possibly under hydrothermal conditions [3,4,5]. While such alteration may be associated with fluid-flow driven compositional changes, such alteration may be near-isochemical in some settings [6,7]. Smectites forming in such settings are predicted to be magnesium and iron-bearing trioctahedral phases [8,9,10]. In addition MSL Curiosity recently discovered what has been initially identified as a trioctahedral smectite just below an oxidized surface in the Sheepbed Mudstone of Gale Crater [11].

These observations indicate that abundant trioctahedral Fe/Mg smectites have formed through alteration of basaltic crystal materials on such. Using Martian phyllosilicates to establish conditions at the time of their emplacement or deposition thus requires an understanding of their formation processes. Tracking the fate of iron is of importance because this is sensitive to redox conditions during formation or later alteration. Understanding trace element repartitioning during mafic rock alteration to smectites, which appears to have occurred in units at Endeavor Crater [12], may provide additional insight into formation conditions and allow an additional method to trace extent of alteration. We have thus investigated mineral formation and trace element fate during the hydrothermal isochemical alteration of a series of mafic rocks.

Methods: For this study two terrestrial USGS igneous rock standards (BIR-1a, Icelandic basalt; and DNC-1a, North Carolina dolerite) were chosen for their compositional similarity to basalt rocks examined at Gusev Crater by the Spirit Rover [13]. A dunite (DTS-2b, Twin Sisters dunite) was also studied to investigate an ultramafic rock that may produce serpentine during alteration.

The rock standards were first ground in a micronizing mill to a particle size range of 1-5 μm . Once ground they were loaded with pure deionized water into PTFE-lined hydrothermal reaction vessels and reacted for 3 weeks at 200°C in an anoxic nitrogen environment. The altered basalts were then brought into an anoxic glovebox where they were dried for characterization. Additional samples were prepared using similar methods on unground materials to provide courser particles more optimal for imaging.

Mineralogy of the initial materials and alteration products was determined via XRD using a Bruker D8 Advance powder diffractometer and a JEOL JXA-8200 electron microprobe. Imaging of particle size and secondary mineralization was accomplished using a JEOL 7001LVF SEM. In addition, Fe K-edge X-ray absorption fine structure (XAFS) spectra were collected at the Advanced Photon Source on beamline 12-BM in transmission mode for all rock samples and at 5-BM for mineral samples. Additionally Mn and Zn K-edge spectra were collected in fluorescence mode. This technique quantifies oxidation state and characterizes local coordination environment around a target element which together indicate how these elements partition into secondary minerals during alteration.

Results: The bulk compositions of both BIR and DNC are similar and XRD shows that they are both dominated by plagioclase feldspar and pyroxene with lesser olivine. DNC has a minor chlorite component as indicated by a 14.4 Å reflection at low angles (Fig. 1). EPMA spot analysis revealed that while the pyroxene is fairly iron poor the olivine is correspondingly iron rich, containing most of the iron available for mobilization. It was also found that Zn resided primarily in spinel phases while Mn was highly correlated with Fe. Upon alteration substantial smectite was formed in DNC and some small amount of smectite in BIR (Fig. 1). This smectite is visible on the surface of primary grains in SEM (Fig 2.). DTS differs in mineralogy from the mafic rocks and is composed primarily of olivine with trace chromite and minor serpentine. Upon alteration, DTS formed substantial serpentine with disordered layer stacking.

The XAFS spectra of the unaltered basaltic materials are similar to that of pure olivine, reflecting the large proportion of iron in olivine, in agreement with EMP data. The XAFS spectra of altered BIR and DNC match closely with a synthetic trioctahedral ferrous smectite (Fig. 3) [14]. The Fe XAFS spectrum of unaltered DTS closely matches that of pure olivine. Upon alteration the edge position shifts to higher energies indicating partial oxidation of iron (Fig. 3). The reproducibility of oxidation in DTS and the lack of oxidation in the mafic samples suggest this is not an experimental artifact. A possible reaction is iron oxidation coupled to water reduction producing magnetite. The final assemblage of Fe-bearing secondary minerals is likely complex, possibly being a mix of serpentine, magnetite, chlorite, and other phases.

Trace metals show distinct behaviors during alteration. Zn does not appear to be as there are no changes in Zn XAFS spectra following alteration. This indicates that it is in a resistant phase. Mn appears to be more mobile with the development of a new peak in XANES spectrum and a change in the EXAFS spectrum that is similar to that seen for iron in the same altered sample (Fig. 4). This indicates that the degree of Mn depletion and Zn enrichment could be potential markers for the extent of aqueous alteration.

References:

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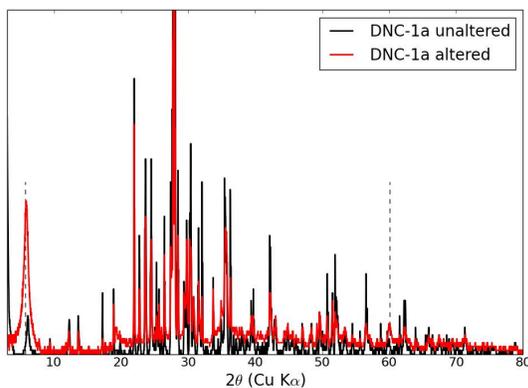


Figure 1. Comparison of unaltered and altered DNC-1a in XRD. Note the considerable smectite peak present at low angles in the altered sample. It is shifted slightly from the chlorite peak visible in the unaltered sample.

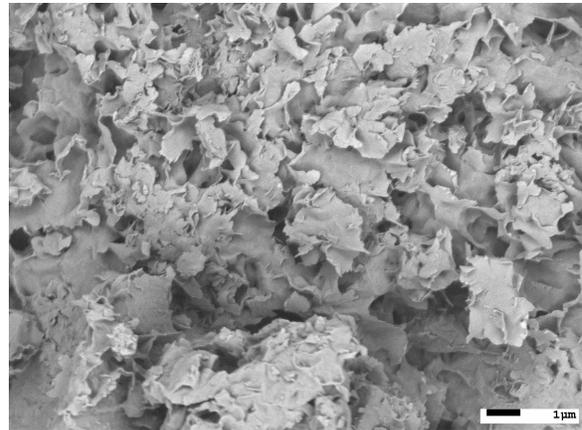


Figure 2. Secondary mineralization visible in DNC-1a.

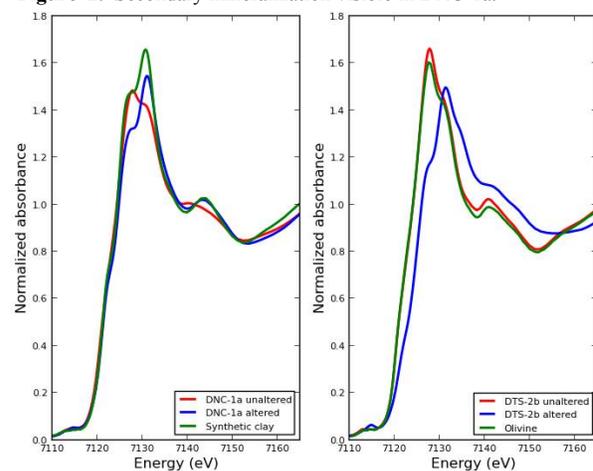


Figure 3. (left) Fe XANES spectra of DNC-1a samples compared to a synthetic ferrous saponite of composition $\text{Ca}_{0.24}\text{N-a}_{0.02}(\text{Fe}_{0.93}\text{Mg}_{0.87}\text{Al}_{0.82})(\text{Si}_{3.47}\text{Al}_{0.53})\text{O}_{10}(\text{OH})_2$. (right) Fe XANES spectra of DTS-2b samples compared to an olivine standard.

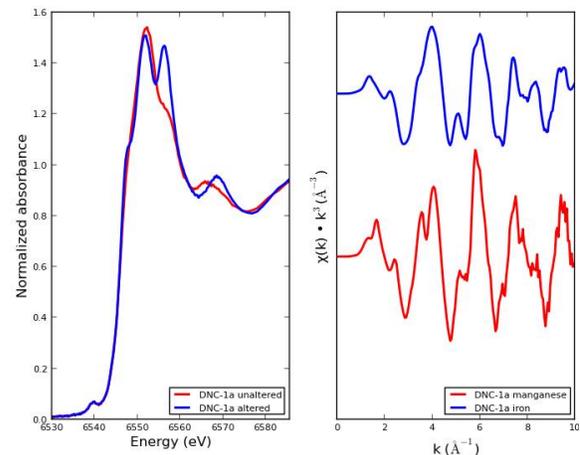


Figure 4. (left) Mn XANES spectra of DNC-1a samples. (right) Mn and Fe EXAFS spectra of altered DNC-1a.