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AMAZONIAN HYDROTHERMAL ALTERATION: COMPARING NAKHLITE SECONDARY MINERALOGY TO WATER-ROCK REACTION EXPERIMENTS. J. C. Bridges¹, L. J. Hicks¹, M. A. Miller², S. P. Schwenzer³, U. Ott^{4,5}, J. Filiberto^{3,6}, C. Chavez⁷, H. Smith⁷, A. H. Treiman⁸, S. P. Kelley², J. M. Moore⁷, T. D. Swindle⁹, M. A. Bullock¹⁰, R. A. McIntosh² and P. Craig¹¹. ¹Space Research Centre, University of Leicester, UK (j.bridges@le.ac.uk); ²SwRI, San Antonio, Texas 78228; ³The Open University, UK; ⁴ATOMKI, Debrecen, Hungary, ⁵MPI, Mainz, Germany ⁶Southern Illinois University, Carbondale, IL, USA; ⁷NASA Ames Research Center, Moffett Field, CA USA; ⁸Lunar and Planetary Institute, USRA, Houston, TX, USA; ⁹Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ, USA; ¹⁰SwRI, Boulder, CO USA., ¹¹Planetary Sciences Institute, Tucson AZ.

Introduction: The 9 nakhlites offer a unique opportunity to characterise water-rock reaction in the Amazonian martian crust. On the basis of their secondary mineralogy it has been established that H₂O-CO₂-rich fluids preferentially dissolved olivines and feldspathic mesostasis in the nakhlite parent rocks [1-4]. Up to 4 vol% Fe-rich carbonates crystallised [1] followed by crystalline saponite and Al-rich ferric serpentine, and then a poorly crystalline gel and soluble salts [2-4]. This detailed mineralogical record gives the opportunity to design water-rock reaction experiments with analog minerals in order to determine duration of the nakhlite alteration, temperature, pH, redox, and fluid chemistry, and to complement previous modelling-based studies [5]. As part of a consortium study the fluid chemistry and surface Raman Spectroscopy of reaction products, from a set of water-rock reaction runs at the Aqueous Simulation Facility at NASA Ames designed to mimic the nakhlite alteration, have been analysed [6]. Here we report on the SEM, TEM, and X-ray Absorption based mineralogy of the reaction products and compare the alteration mineralogy to our ongoing nakhlite mineralogical analyses.

Methods: We have characterised reaction products from 1 and 9 month duration experimental runs of analog mineral mixes (Mg-olivine, andesine, augite, nakhlite glass composition, blasting sand as an analog for Fe-rich olivine) [6]. The reaction took place under 1 bar CO₂-pressure at 35 °C. The starting fluid was carbonated (oxygen-depleted) water. In total we have analysed 10 samples from the one month duration runs, and 11 samples from the nine month duration experiments. In both the samples from the one and nine month we have selected a representative range of mineral mixtures from pure olivine to 25% andesine, 25% augite, 10% Mg-olivine, 40% blasting sand, and a variety of mixtures in between (numbered M1-27). We conducted SEM-EDX, followed by FIB-SEM preparation of micron-scale wafers for HRTEM. Clay lattice spacings from alteration veins were measured on a JEOL 2100 TEM. We used the I-18 Beamline, of the *Diamond* synchrotron, with a spatial resolution of ~2 x 2.5 μm. Measurements included the X-ray Absorption Near-Edge

Structure (Fe K XANES), which enables determination of Fe³⁺/ΣFe ratios [4].

Results: Nearly all alteration identified was associated with olivine grains, in veins varying in width up to 30 μm. The average chemical composition of the clay material identified within the olivines after 1 month is MgO 44.8, Al₂O₃ 0.9, SiO₂ 51.8, FeO 1.1, Fe₂O₃ 1.3 wt%. Typically the alteration material has a small increase in Mg/Mg+Fe_{tot} (Mg#) and Si/(Fe+Mg) at. ratios compared to the surrounding olivine (Table 1).

Fe K XANES analyses of nakhlite clay and amorphous gel shows a variable but generally high ferric content of Fe³⁺/ΣFe = 0.3 to 1.0 [4]. Similarly, a positive shift in the *1s*→*3d* centroid shows an increase in the Fe³⁺/ΣFe ≤ 0.5 for the 1-month alteration products, and up to Fe³⁺/ΣFe = 0.9 in the 9-month alteration (Fig. 2).

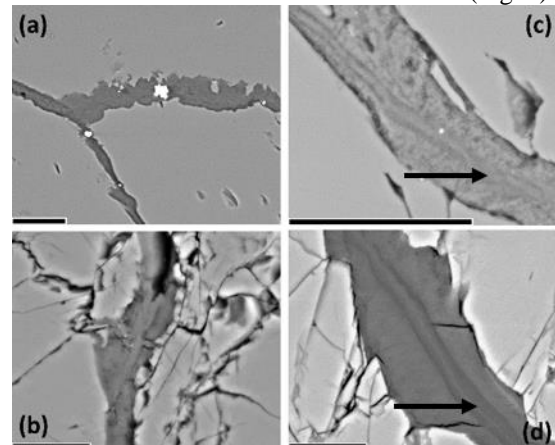


Fig. 1. From the 1-month experiment, alteration material in the fractures of M-15 olivine (a), which is shown as a representative example, and shows similarities to olivine fracture clay in nakhlite NWA 998 (b). From the 9-month experiment, alteration material in the fractures of M-5 olivine (c) also show similarities to the crystalline smectite in Lafayette olivine fractures (d), including a central band of amorphous Fe-silicate (arrowed). Scale 10 μm.

We found no significant variation in the geochemistry between the 1 and 9 month experiment samples, with the exception of material located in the veins near the edges of the olivine grains of run M-22 (9 months, pure

Fo92 olivine reactants) which contain an increase in the Mg# and Si/(Fe+Mg) ratio compared to that of the typical alteration material. This particular material in M-22 also has much larger alteration veins (>30 μm), compared to the smaller (<13 μm) fractures of the other samples. Other alteration material, found on the edges of the M-22 olivine grains, has little change in the geochemistry compared to the 1 month M-18 alteration, however it also has the highest ferric content ($\text{Fe}^{3+}/\Sigma\text{Fe} > 0.9$), which was typically <0.1 in others including the M-22 fractures. One exception is the alteration veins in the olivine of M-18 (1 month, pure Mg-olivine) with $\text{Fe}^{3+}/\Sigma\text{Fe} < 0.6$. The d -spacings - where present - are largely consistent across all samples, with T-O layering 0.72-0.76 nm, showing similarities to the ~ 0.70 nm T-O layering for serpentine alteration material found in the nakhlite samples (Fig. 3) [4]. However, the crystalline, ferric serpentine was intermixed with amorphous clay of the same composition, showing that much of the veining material is poorly crystalline.

Feldspar alteration. The complementary surface mineralogy analyses by Raman [6] revealed magnesite and calcite phases in some mixtures containing ol+andesine. The andesine shows some signs of corrosion in the SEM analyses, though any major element changes are minor.

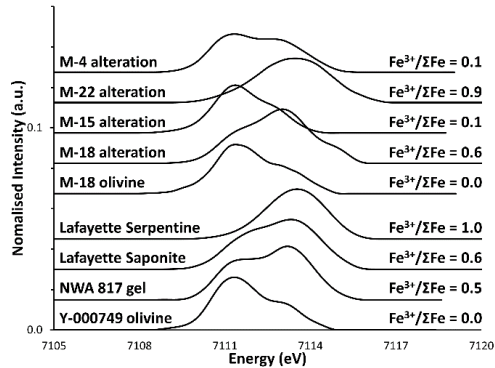


Fig. 2. $\text{Fe-K XANES } 1s \rightarrow 3d$ centroids for the alteration features observed in olivine fractures of samples M-15 and M-18 from the 1-month experiment, and M-4 and M-22 of the 9-month experiment. The ferric content ($\text{Fe}^{3+}/\Sigma\text{Fe}$) varies from 0.1-0.9. These are compared to the surrounding ferrous olivine of M-18. Also shown for comparison are ferrous nakhlite Y-000749 olivine, and ferric nakhlite alteration material, including NWA 817 Fe-silicate gel, and Lafayette saponite and serpentine [4].

Discussion: The mineralogy of the reaction products from our nakhlite analog mineral-fluid reaction experiments show important similarities to the nakhlites. For instance, olivine is the most reactive phase, but there are signs that andesine also reacts to a lesser extent. It

is striking that the poorly crystalline serpentine and the traces of carbonate formed rapidly, within 1 month of exposure to a 35 $^{\circ}\text{C}$, near neutral brine. Longer exposure to the fluid increased the volume of alteration veining in olivines, but the mineral assemblage remained the same. The increase in $\text{Fe}^{3+}/\Sigma\text{Fe}$ associated with this clay-dominated alteration is similar to that seen in the nakhlites [4].

The mineralogical results of our experiments suggest that an important type of fluid alteration in the Amazonian may be short duration (e.g. less than 1 year) events from near neutral, dilute brines, that were able to exchange CO_2 either directly, or via ice reservoirs, with the atmosphere.

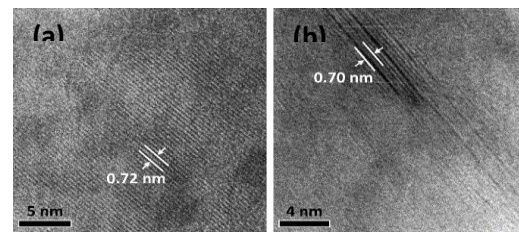


Fig. 3. (a) HR-TEM image showing crystalline d -spacings measuring ~ 0.72 nm in a 2-layer structure in M18, one month duration sample (b) Similar d -spacing measurements of ~ 0.70 nm in a 2-layer T-O structure observed in Lafayette crystalline serpentine clay [4].

Table 1. Comparison between 1 and 9-month experiments for the pure olivine and the ol-andesine (50-50 %) mixes.

	1-month		9-month	
	M-18	M-15	M-22	M-4
Composition:				
MgO	45.7	45.5	31.1	43.2
SiO ₂	51.1	50.9	68.3	52.3
FeO	1.2	3.1	0.6	3.9
Fe ₂ O ₃	2.0	0.4	0.1	0.5
Mg# at. %	95.9	95.1	98.9	94.9
Si/(Mg+Fe) at. %	0.72	0.72	1.46	0.77
Vein widths (μm)	<6	<13	<30	<13
TEM d -spacings (nm)	0.73	0.76	0.75	0.75
$\text{Fe}^{3+}/\Sigma\text{Fe}$	<0.6	<0.1	~ 0.1	<0.1

M-18 and M-22 = 100 % olivine (Mg# = 92.1), M-15 and M-4 = 50 % olivine, 50 % andesine.

References: [1] Piercy J. D. et al. (2018) LPSC #2020. [2] Changela H. G. and Bridges J. C. (2011) *Meteoritics & Planet. Sci.*, 45, 1847-1867. [3] Treiman A. H. et al. (1993) *Meteoritics*, 28, 86-97. [4] Hicks L. J. et al. (2014) *Geochim. Cosmochim. Acta*, 136, 194-210. [5] Bridges J. C. and Schwenzer S. P. (2012) *Earth Planet. Sc. Lett.*, 359-360, 117-123. [6] Miller M. A. et al. (2018) LPSC #1688.