MARTIAN PHYLLOSILICATES IN THE NAKHLITE METEORITES

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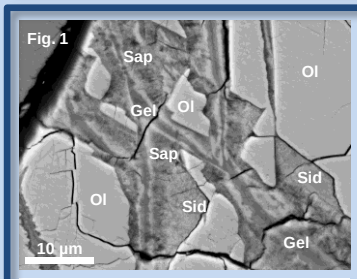
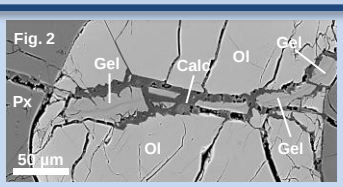
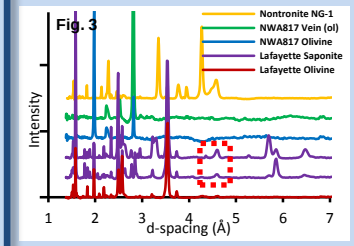
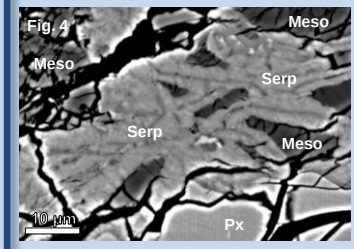
Introduction

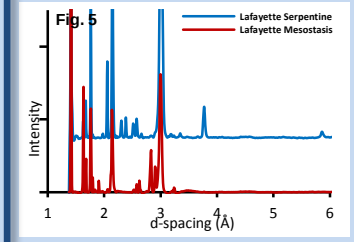
The identification of saponite and amorphous material in the Sheepbed mudstone of Gale Crater by *CheMin* XRD on *Mars Science Laboratory* [1] has highlighted the importance of understanding the nature of martian phyllosilicates and amorphous material, as they have the potential to reveal the fluid history of habitable terrains [2,3]. The nakhlite meteorites are the only martian samples on Earth which contain phyllosilicates and poorly crystalline or amorphous material [4-10], which we can study by new XRD and X-ray Absorption techniques and TEM to provide an accurate $Fe^{3+}/\Sigma Fe$ ratio, composition and structural comparison to the *in situ* analyses on Mars.











Scanning Electron Microscopy

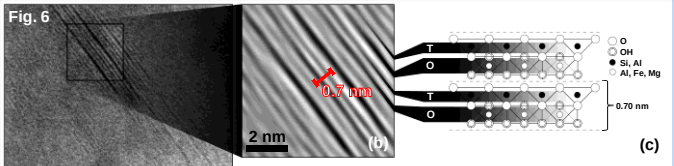
The nakhlites fracture deposits have been observed in BSE images and analysed: Fig. 1 shows crystalline phyllosilicates with a central amorphous (or poorly crystalline) gel features within a Lafayette olivine; Fig. 2 shows similar gel and terrestrial calcite in a NWA817 olivine; and Fig. 4 is crystalline phyllosilicates within Lafayette mesostasis. EPMA data has also been obtained.

Transmission X-ray Diffraction

Peaks in Lafayette saponite were identified at 6.46, 5.85, 5.70, 4.59, 2.846, 2.778, 2.636, 2.056, 1.886, 1.772, 1.580, 1.550, 1.471 Å that are not associated with the surrounding olivine grain (see Fig. 3). Lafayette serpentine has peaks at 5.86, 3.774, 3.348, 3.183, 2.661, 2.513, 2.384, 2.306, 2.146, 2.056, 1.978, 1.50 Å (see Fig. 5) that are not associated with the surrounding feldspathic mesostasis. The NWA817 gel has one detected peak, at 2.525 Å, that is not clearly associated with the surrounding olivine.

The Nontronite NG-1 trace on Fig. 3 shows a broadened and asymmetric diffraction peak at 4.57 Å (red dashes). The shape and breadth is indicative of turbostratic disorder which is present in almost all smectite minerals [11]. The Lafayette saponite traces have peaks at 4.59 Å which are very similar in shape and breadth, and it is assumed that the saponite also exhibits turbostratic disorder.

BSE image key: olivine (Ol); saponite (Sap); siderite (Sid); gel (Gel); pyroxene (Px); calcite (Calc); serpentine (Serp); mesostasis (Meso).



Transmission Electron Microscopy

High resolution imaging (HRTEM) was analysed using a *JEOL 2100* microscope, to observe the lattice d_{001}-spacings of crystalline deposits. Fig. 6 shows a HRTEM image of a section extracted from a Lafayette mesostasis fracture (a), which has been energy filtered to reveal the lattice spacings in layered groups measuring ~0.7 nm (b). This layering correlates with the 1:1 *T-O* structure of serpentine (c) [adapted from 12]. Similar HRTEM analysis of sections extracted from Lafayette olivine fractures reveals *d*-spacings measuring ~0.96 nm, correlating with the 2:1 *T-O-T* structure of smectite (saponite) [13].

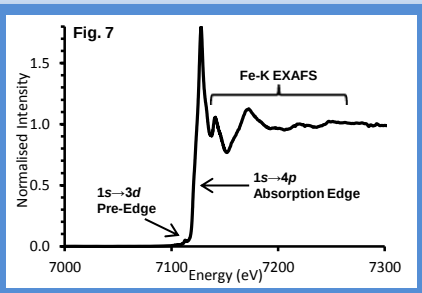
XRD and Fe-K XAS

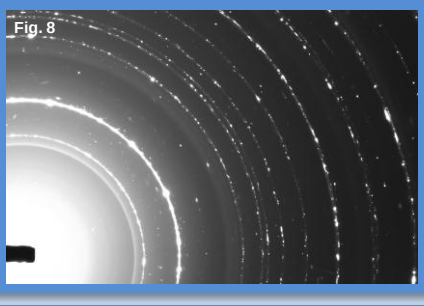
All measurements were taken at the *Diamond Light Source* Synchrotron, using Beamline I-18, capable of a beam spot size of 2.5 µm.

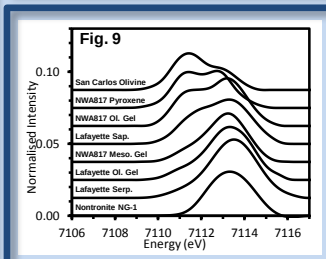
Fe-K XAS measurements range 6900-7500 eV at resolution 1.0-3.5 eV, with a resolution of 0.1 eV over the XANES region of 7090-7145 eV (see Fig. 7).

Transmission XRD measurements were taken at 13 keV, with observable *d*-spacings ranging 9-1.5 Å, corresponding to 2θ = 5.5° to 38.4°. Fig. 8 shows the XRD pattern for a powdered NG-1 nontronite standard.

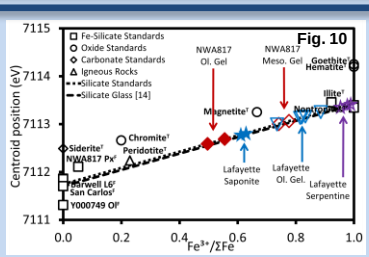
XRF maps have also been produced of regions of interest at a pixel resolution of 2 µm, observing elements of Z >20, in order to locate accurately points for Fe-K XAS measurements.







▲ Fe-K XANES 1*s*→3*d* pre-absorption edge positions of phyllosilicates, gels (within olivine fractures), and reference materials. Higher energy pre-edge centroids are characteristic of increasing ferric content.



▲ Fe-K XANES ferric calibration. The 1*s*→3*d* pre-absorption edge positions of nakhlite phyllosilicates and gel are superimposed on the calibration line determined from standards, to derive the proportion of ferric iron. (F) Fluorescence mode, (T) Transmission mode analysis. The dashed line is a silicate glass calibration [14].

Fe-K X-ray Absorption Near-Edge Structure

In order to calculate the $Fe^{3+}/\Sigma Fe$ ratio in the phyllosilicate, we measured the position, in eV, of the Fe-K pre-absorption edge centroids (see Fig. 9). By using a range of mineral standards of known ferric content, we then constructed a calibration plot of centroid position versus $Fe^{3+}/\Sigma Fe$ ratio (see Fig. 10). The regression line coincides nearly exactly with one determined previously by [14] for silicate glasses.

Using our calibration together with analyses of the major elements, we calculate that the average chemical formula of the saponite minerals within the Lafayette olivine fractures is a stoichiometric, trioctahedral ferric saponite with formula: $(Ca_{0.2}K_{0.1})_{\Sigma 0.3}(Mg_{2.6}Fe^{2+}_{1.3}Fe^{3+}_{1.7}Mn_{0.1})_{\Sigma 5.7}[(Si_{6.7}Al^{IV}_{0.9}Fe^{3+}_{0.4})_{\Sigma 8.0}O_{20}](OH)_4.nH_2O$. The highly ferric silicate gel at the centre of the veins has $Fe^{3+}/\Sigma Fe$ values of up to ~0.9. The Fe-rich serpentine mineral within the mesostasis fractures of Lafayette is completely ferric $(Ca_{0.1}Mg_{0.7}Fe^{3+}_{1.0}Al^{VI}_{0.4})_{\Sigma 2.2}[Si_2O_5]OH_4$.

Conclusion

The siderite-rich alteration assemblage in the nakhlites [6,7] is distinct from the carbonate- poor or -free Sheepbed assemblage [1-3]. However, the trioctahedral ferric-rich saponite component may be analogous to the trioctahedral smectite identified in the Yellowknife Bay assemblage by [1]. In addition to the similar composition and structure, both contain turbostratic disorder. Ferric serpentine present in the nakhlites has not yet been identified at Gale Crater. The detection of only one *d*-spacing in the NWA817 vein gel that was not clearly derived from the surrounding olivine grain, is in contrast to the Lafayette saponite but consistent with the poorly crystalline nature of this material. The amorphous material in Sheepbed has been compared to allophane from alteration of the surface of basalt [1]. The rapidly cooled, metastable fracture fill veins present in the nakhlites are another possible type of source material for amorphous grains analysed in Gale Crater [15,16].

References: [1] Vaniman, D. T. et al. (2013) *Science*, doi:10.1126/science.1243480. [2] Grotzinger J. P. et al. (2013) Science, 10.1126/science.1242777. [3] McLennan S. M. et al. (2013) *Science*, 10.1126/science.1244734. [4] Gooding J. L. et al. (1991) *Meteoritics 326*, 135-143. [5] Treiman A. H. et al. (1993) *Meteoritics 28*, 86-97. [6] Changela H. G. and Bridges J. C. (2010) *Meteorit. Planet. Sci. 45*, 1847-1867. [7] Bridges J. C. and Schwenzer S. P. (2012) *EPSL, 359-360*, 117-123. [8] Lee M. R. et al. (2013) *Meteorit. Planet. Sci. 48*, 224-240. [9] Gillet P. H. et al. (2002) *EPSL, 203*, 431-444. [10] Hicks L. J. et al. (2014) *GCA* (in rev.). [11] Moore, D. M. and Reynolds, R. C. (1997) X-ray Diffraction and the Identification and Analysis of Clay Minerals, OUP. [12] Mookherjee, M. and Stixrude, L. (2009) *Earth and Planetary Science Letters*, 53, 440-451. [13] Solin S. A. (1997) *Annual Review of Materials Science*, 27, 89-115. [14] Berry, A. J. et al. (2003) *Am. Mineral., 88*, 967-977. [15] Bish D. L., et al. (2013) *Science, 341*, doi:10.1126/science.1238932. [16] Dehouk E. et al. (2014) *LPS XXXXV*, (this conf.).