**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, as they have the potential to reveal the fluid history of habitable terrains [2,3]. The nakhlite meteorites are the only martian minerals on Earth which contain phyllosilicates and poorly crystalline amorphous materials [4-10], which we can study by new XRD and X-ray Absorption techniques and TEM to provide an accurate Fe*2+/Fe*3* ratio, composition and structural comparison to the in situ analyses on Mars.

**XRD and Fe-KXAS**

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 690-7500 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 Å, corresponding to 2θ = 5.5° to 33.4°. 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 X-ray Absorption Near-Edge Structure**

In order to calculate the Fe*2+/Fe*3* 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*2+/Fe*3* 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, triothedral ferric saponite formula with: (CaO·SiO₂·Fe₂O₃·Al₂O₃·ΣAl·ΣFe)₃·(H₂O)₄·(SiO₂·Al₂O₃·ΣFe·ΣAl·ΣMg), where Na+, K+, Mg²⁺ are interlayer cations. The highly ferric silicate gel at the centre of the veins has Fe*2+/Fe*3* values of up to ~0.9. The Fe-rich serpentine mineral within the mesostasis fractures of Lafayette is completely ferric (CaO·SiO₂·Fe₂O₃·Al₂O₃·ΣFe·ΣMg·ΣNa·ΣK·ΣMg·ΣCa·ΣNa·ΣK·ΣMg·ΣCa·ΣNa·ΣK·ΣMg·ΣCa).

**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 triothedral ferric- rich saponite component may be analogous to the triothedral smectite identified in the Yellowknife Bay assemblage by [1]. In addition to the similar composition and chemistry, both contain a similar ferric serpentine disorder. The Fe-rich saponite 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 allopiane 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 glasses found in Gale Crater [15,16].

**References**


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**Scanning Electron Microscopy**

The nakhlite 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 Electron Microscopy**

High resolution imaging (HRTEM) was analysed using a JEOL 2100 microscope to observe the lattice 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-T structure of serpentine (c) (adapted from [12]). High energy filtered TEM analysis of sections extracted from Lafayette olivine fractures reveals d-spacings measuring ~0.95 nm, correlating with the 2:1 T-O-T structure of smectite (saponite) [13].

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**Fig. 1** nontronite-NG-1 NWA817 vein (d) Lafayette Saponite Lafayette Olivine

**Fig. 2** Suggestive Indexes on back of Lafayette mesostasis

**Fig. 3** 10μm

**Fig. 4** Crystalline XRD spacings of Lafayette X-ray diffractogram

**Fig. 5** (a) Transmission electron image of a nevskite inclusion within a mesostasis inclusion. The nevskite inclusion is ~6 μm across. (b) High resolution transmission electron micrograph (HRTEM) of the nevskite inclusion. (c) Fast Fourier Transform (FFT) of the HRTEM image, showing the characteristic ‘neuflower’ pattern.

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**Fig. 6** Transmission Electron Microscopy

The 2:1 T-O-T structure of the clay mineral montmorillonite (a) was also observed in the Lafayette olivine fracture (b). The montmorillonite exhibited a lattice spacing of 1.1 Å in this sample. (c) A high resolution image of a crystal of montmorillonite within a Lafayette olivine fracture, showing the characteristic 1:1 T-O-T structure.

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**Fig. 7** Fe-K EXAFS

**Fig. 8** X-ray Diffraction Pattern

**Fig. 9** Fe-K XANES pre-edge maxima

**Fig. 10** Fe-K XANES pre-edge minima

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**Fig. 11** Transmission Electron Microscopy

**Fig. 12** Scanning Electron Microscopy