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Phyllosilicates and Amorphous Gel in the Nakhlites

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1. Introduction

Previous studies of the nakhlite martian meteorites have revealed hydrothermal minerals present within the fractures of the olivine minerals and the mesostasis. The olivine fractures of the Lafayette nakhlite reveal variations with initial deposits of siderite on the fracture walls, followed by crystalline phyllosilicates (smectite), and finishing with a rapidly cooled amorphous silicate gel within the central regions of the fractures. The mesostasis fractures of Lafayette also contain a crystalline phyllosilicate (serpentine). The amorphous gel is the most abundant secondary phase within the fractures of the other nakhlites [1, 2].

By studying nine nakhlite samples, including Lafayette, Governador Valadares, Nakhla, Y-000593, Y-000749, Miller-Range 03346, NWA 817, NWA 998, and NWA 5790, our aim is to constrain the identity of the phyllosilicate secondary phase minerals found throughout the nakhlite martian meteorites. This is achieved using methods including Electron Probe Micro-analysis (EPMA); X-ray Absorption Near-Edge Structure (Fe-K XANES) spectroscopy measured using Beamline I-18 at the *Diamond Light Source* synchrotron; and the use of Transmission Electron Microscopy (TEM) at the University of Leicester for High-Resolution (HR) imaging and Selected Area Electron Diffraction (SAED).

2. Results

2.1 Fe-K XANES

By measuring the energy position of the Fe-K XANES $1s\rightarrow 3d$ pre-edge transition centroid and correlating these measurements for a set of standards with known ferric-ferrous ratios (Fe³⁺/ Σ Fe), a positive shift in centroid position is related to an increase in ferric content. This trend is utilised as a semi-quantitative method for determining the ferric content of the secondary phase minerals within the

nakhlite meteorites. The crystalline phyllosilicates and amorphous gel of the hydrothermal deposits filling the olivine fractures are found to have variable $\mathrm{Fe^{3+}/\Sigma Fe}$ values ranging from ~0.4 to ~0.9. In Lafayette, the central silicate gel parts of the veins are more ferric than the phyllosilicates around it. The phyllosilicates within the mesostasis fractures of Lafayette and NWA 817 have a higher ferric content than the olivine fracture deposits, with $\mathrm{Fe^{3+}/\Sigma Fe}$ values of up to 0.99.

2.2 TEM

SAED and HR-TEM analyses have shown there to be three distinct variations in the silicate secondary These include two crystalline phase minerals. phyllosilicates found in Lafayette, as a 2:1 T-O-T layered smectite in the olivine fractures, and a 1:1 T-O phyllosilicate in the mesostasis fractures, with average d_{001} basal spacings measuring 0.96 nm and 0.7 nm respectively. The SAED observed for both types of phyllosilicates show a largely polycrystalline structure. The third secondary phase silicate is the amorphous gel found in the central regions of Lafayette veins and filling the fractures throughout the other nakhlites. This amorphous nature is confirmed by the diffuse ring pattern observed in SAED across the gel regions. Some minor T-O-T crystalline structure has been observed in HR-TEM to be present within the amorphous silicate gel of the NWA 817 olivine fracture veining, similar to that of Lafayette.

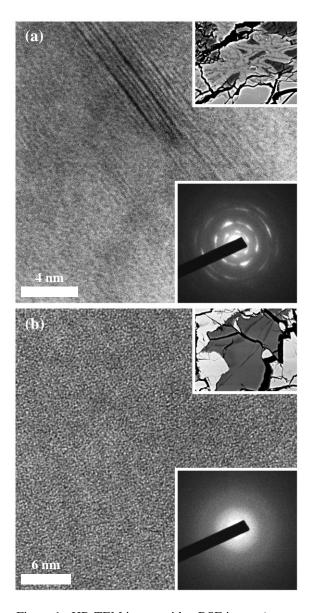


Figure 1: HR-TEM image with a BSE image (upper inset, image width $\sim\!80~\mu m$) and SAED (lower inset, at 200 kV and camera length 21.15 cm). (a) T-O crystalline phyllosilicate from a Lafayette mesostasis fracture. (b) Amorphous silicate gel from a NWA 817 olivine fracture.

3. Summary and Conclusions

Based on the HR-TEM analyses, the phyllosilicates of the olivine fractures in Lafayette and NWA 817, as a 2:1 layered smectite with a d-spacing measuring 0.96 nm, is likely representative of saponite in a collapsed dehydrated state [3]. Fe³⁺/ Σ Fe values of

~0.6 for these phyllosilicates lie within literature values for saponite mineralogy [4, 5]. In contrast, the phyllosilicates of the mesostasis fractures in Lafayette are found to be highly ferric and low in aluminium compared to the olivine fracture deposits and with its 1:1 layered structure measuring a *d*-spacing of 0.7 nm is characteristic of serpentine [6]. The amorphous gel found throughout the nakhlites is dominantly ferric, and in Lafayette is also observed to be more ferric than the phyllosilicates, suggesting that the alteration phases deposited by the secondary fluids flowing through the rocks were oxidizing relative to the surrounding ferrous olivine.

Our Fe-K XANES measurements have proved to be an effective method of determining the oxidation state of iron of various minerals, and complemented by TEM analyses, our data has suggested an identity for the fracture filling hydrothermal minerals within the nakhlites. The results of this study provide a detailed mineralogical analysis of the type of mineral assemblage, exposed on the surface of Mars, which are shown by CRISM (MRO) data to contain saponite and serpentine e.g. [7].

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