TEM STUDY OF ALTERATION ASSEMBLAGES IN THE NAKHLITES: VARIATION WITH BURIAL DEPTH ON MARS. H. G. Changela[1], and J. C. Bridges[1], [1]Space Research Centre Department of Physics & Astronomy, University of Leicester, University Road, LE1 7RH UK. E-mails: hgc3@le.ac.uk, jcb36@le.ac.uk

Introduction: The nakhlites are Martian meteorites which sample from different depths of their parent igneous parent body, with Lafayette from near the base and Miller Range and Y000593 from near the top [1,2]. A variety of secondary mineral assemblages are present within the rock's olivine and mesostasis. They have been identified as preterrestrial and can therefore inform about the type of aqueous environment which led to their formation on Mars [3,4]. Minerals include Fe-carbonate, sulphate, halite, phyllosilicate (e.g. smectite), amorphous gel, which precipitated rapidly from a low temperature ≤150 ^{o}C brine [2-6]. The composition of the secondary phases varies between the different nakhlites [5]. SEM-based studies have shown some of the textures to be submicron scale, necessitating the need for TEM. With the Focused Ion Beam (FIB) technique, we can extract these minerals *in situ* to electron transparency for subsequent TEM. From the 7 known nakhlites, Nakhla, Lafayette, Y000593 (and its pair Y000749) have been sampled in this study to compare their secondary alteration assemblages found within the olivine. Our TEM studies are revealing new detail about the type of alteration and the variation between different nakhlites related to different depth, cooling rate and varying water/rock ratio.

Methods: Polished sections of Nakhla, Lafayette, and Y000593/749 were initially analyzed by SEM to direct the TEM sectioning. We used an FEI Sirion FEG-SEM and Phillips XL30 ESEM. Energy Dispersive X-Ray Spectroscopy (EDX) was also performed across the veins or on different phases within the assemblages using the INCA EDX system. An FEI Quanta 3D FIB-SEM was used for milling and extraction. The automated FEI 'wizard' TEM runscript was used at 30 kV for milling an approximately 100-120 nm wafer with the focused Ga^+ ions. The runscript was aborted before the low polishing currents (<100 pA) in order to keep the soft phases intact within the wafer. Prior to application of the run script, the sample was capped with a 5 x 30 µm Pt layer of approximately 150 nm thickness. This layer was deposited via electron beam deposition (GIS). Manual thinning was applied post extraction for optimal electron transparency of the grain. The wafers were extracted *in situ* using the Omniprobe lift out mechanism, and attached to a copper grid. A Jeol 2100 TEM was used with a LaB_6 source, at 200kV and 109 µA emission current. Bright field imaging and TEM- EDX (PGT analyzer) was performed on the particle followed by SA electron diffraction.

Y000593/749: The vein material is amorphous as electron diffraction does not occur within these regions (Fig.1). The amorphous vein material contains Al although in small amounts relative to silica. They can also contain amorphous Fe-Mg silicate inclusions (Fig.1c). Sulphur seems to be concentrated along the edges of the veins. In the Y000749 sample there are also veins of sulphate-based alteration which cross cut the fusion crust. These are probably terrestrial in origin. SA diffraction and EDS suggest some veins consist of jarosite, consistent with [7].

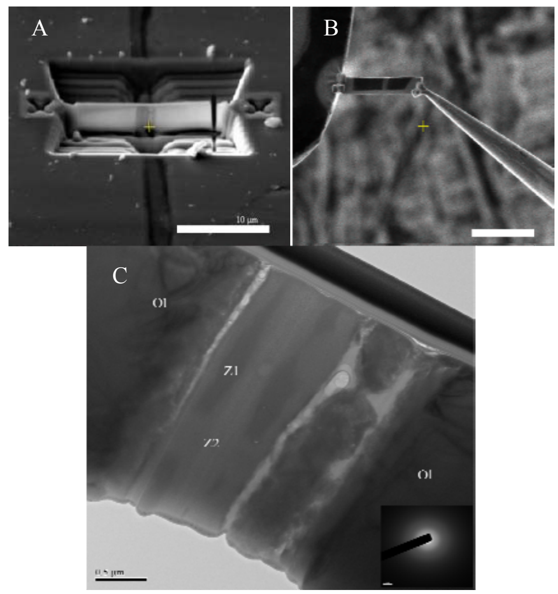

Fig 1: (a) FIB wafer after ion beam milling. Secondary vein is in middle of wafer (yellow cross) **(b)** Lift out onto copper grid (Omniprobe needle is on right side of image). **(c)** Bright field TEM of Y000593 vein. Z1= Amorphous Mg-Fe silicate. Z2 = Amorphous Fe-Mg-Al silicate. Ol olivine. Inset shows SA diffractogram. Scale bars 10, 10 and 0.2 µm respectively.

Nakhla: Compared to Y000593/749, secondary mineral veins are generally larger and are more clearly related to fracturing (impact-related) of the nakhlites. Veins are also distinguished from Y000593/749 in that they can contain crystalline carbonate along their margins with the amorphous Al-bearing silicate gel along the centres of the veins. The host olivine grains have a patchy texture related to weathering and partial break down Fig 2(b).

Lafayette: Secondary mineral grains up to approximately 50 µm width can be found, occupying up to a quarter of some olivine grains. Large areas of carbonate (Ca-Mn-Mg siderite) surrounding the central veinlets consisting of the silica-rich amorphous core are present. Along the margins of the central zones, or in circular sprays [6], are fibrous phyllosilicates - identified from EDX and SA electron diffraction (Fig. 3b). This zone merges inwards into a zone of what seems to be finer grained phyllosilicate intergrown with a dark, currently unidentified phase, and then leads to the amorphous core.

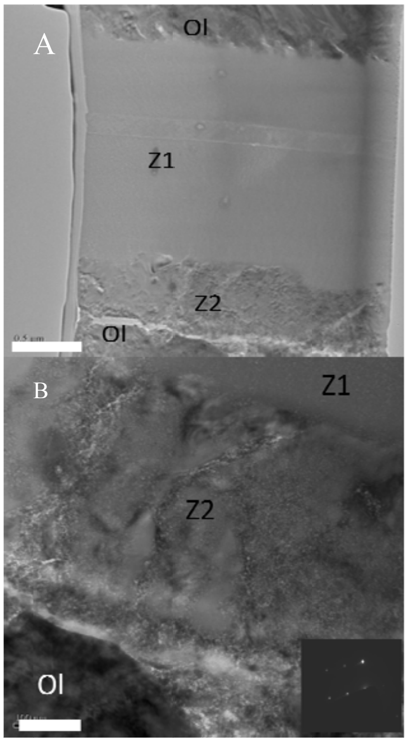

Fig 2: (a) Bright field TEM of vein from Nakhla. **(b)** Higher magnification of Z2 zone from (a). Z1 = amorphous Fe-Mg-Al Silicate. Z2 = Fe-Mg-Mn-Ca carbonate). Inset shows diffractogram of carbonate. Scale bars are 0.5 and 0.1 µm respectively.

Discussion: The core of nearly all secondary veins in the nakhlites is an amorphous (or very weakly crystalline) gel of Fe-Mg-Al silicate. The relative proportion of this phase is greatest in Y000593/Y000749 where crystalline phyllosilicates appear to be absent. The amorphous cores may have resulted from rapid crystallization near the surface of the nakhlite parent rocks on Mars with a low water/rock ratio. An order of crystallization is apparent: siderite crystallized at the margins of impact-induced fractures followed by fibrous phyllosilicate and then finally the amorphous gel. The crystalline secondary minerals are most clearly represented in Lafayette. Some Y000593 sections only contain veins of amorphous silicate gel. Mikouchi *et al* [2] determined the relative burial depths of the nakhlites based, for instance, on their olivine equilibration. It is apparent that the secondary mineral assemblages of the nakhlites also show a compositional and textural fractionation with the relatively coarse crystalline Lafayette assemblages having precipitated more slowly and with a higher water/rock ratio than the Nakhla or Y000593 secondary phases that were nearer to the Mars surface [8].

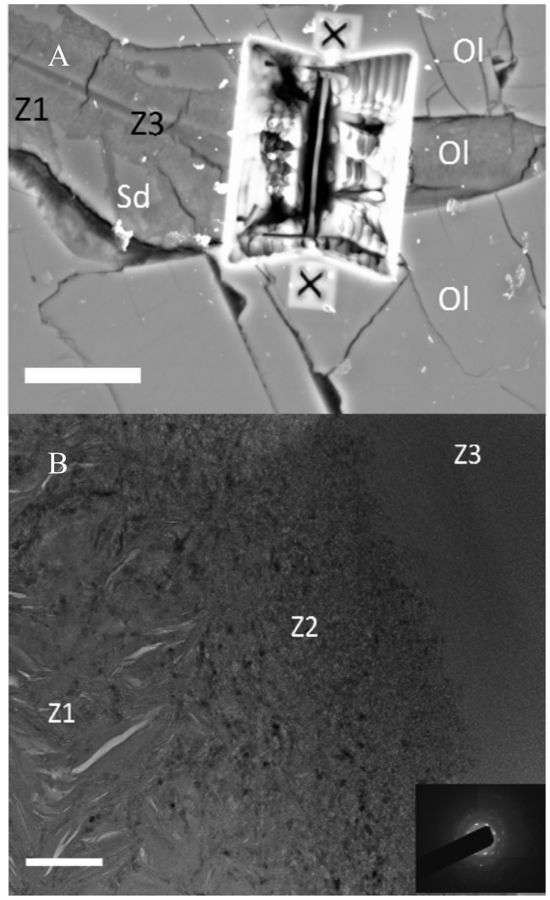

Fig 3: (a) BSE of secondary assemblage in Lafayette. **(b)** Bright field TEM image of wafer from (a). Z1 = Fibrous phyllosilicate. sd = Ca-Mn-Mg siderite. Ol olivine Z2 = fine grained phyllosilicate. Z3 = amorphous Fe-Mg-Al silicate core to the vein. Inset is Z2 diffractogram. Scale bars 10 & 0.2 µm.

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References: [1] Bridges J. C. & P. H. Warren *Journal of the Geological Society, London* (2006) *163,* 229-251. [2] Mikouchi *et al* (2003) LPS XXXIV #1944. [3] Gooding J. H., Wentworth S. J. and Zolensky M. E. *Meteoritics* (1991) *26,* 135-143. [4] Bridges J. C. *et al* (2001) *Space Science Reviews 96,* 365-392 [5] Treiman A. H. *Chemie der Erde - Geochemistry* (2005) 65, 203-270. [6] Vicenzi E. P. and Heaney P. J (1999) *LPS XXX*, #2005. [7] Kuebler K, Jolliff B. L. & Treiman A. H. (2004) *LPS XXXV* #2228. [8] Bridges J. C. and Grady M. M. *EPSL* (2000) *176*, 267-279.