

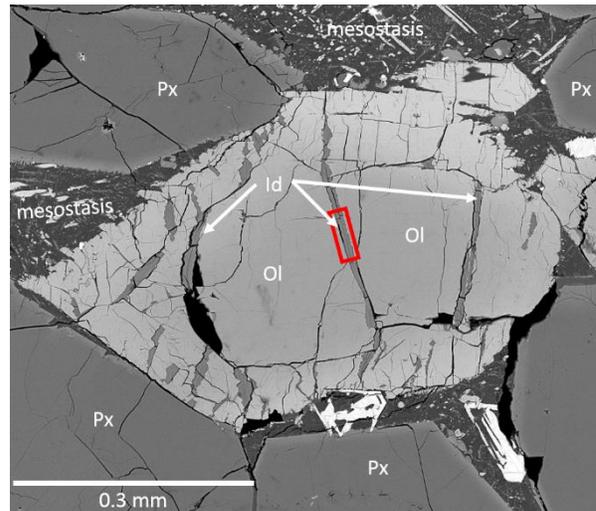
**INSIGHTS INTO MARTIAN FLUID-ROCK REACTIONS BY ATOM PROBE TOMOGRAPHY OF THE INTERFACE BETWEEN NAKHLITE OLIVINE AND IDDINGSITE.** L. Daly<sup>1</sup>, M. R. Lee<sup>1</sup>, P. A. J. Bagot<sup>2</sup>, L. J. Hallis<sup>1</sup>, J. Halpin<sup>3</sup>, W. Smith<sup>3</sup>, S. McFadzean<sup>3</sup>, <sup>1</sup>School of Geographical and Earth Sciences, University of Glasgow, Glasgow, G12 8QQ, UK. ([luke.daly@glasgow.ac.uk](mailto:luke.daly@glasgow.ac.uk)). <sup>2</sup>Department of Materials, University of Oxford, Oxford, OX1 3PH, UK. <sup>3</sup>Materials and Condensed Matter Physics, School of Physics and Astronomy, University of Glasgow, Glasgow, G12 8QQ, UK.

**Introduction:** The nakhlite meteorites are porphyritic mafic igneous rocks from Mars [1]. They are comprised predominantly of augite phenocrysts with some rarer olivine grains suspended in a fine grained mesostasis [1]. The nakhlites crystallised in at least four temporally distinct magmatic events between 1.3-1.4 Ga [2]. Their source rocks are likely to be spatially correlated on Mars as these meteorites all have ~11 Ma ejection ages [3] and low degrees of shock metamorphism (<15 GPa)[1].

An interesting feature of the nakhlite meteorite suite is that they preserve evidence for the action of liquid water in the shallow subsurface of the Martian crust [4]. These aqueous fluids altered olivine phenocrysts and some isolated portions of mesostasis under oxidizing conditions at low temperatures <140° to form veins of clay mineral assemblages collectively termed ‘iddingsite’ [4,5]. This aqueous alteration occurred on Mars at ~633 Ma [6]. The heat source to mobilise these fluids is not currently known. The two primary hypotheses are impact generated hydrothermal cells [7] and magmatic activity [6].

In this study, we apply atom probe tomography (APT) to observe the nanoscale atomic structure and geochemical gradients across the interface between olivine and iddingsite in two nakhlite meteorites (Lafayette and North West Africa (NWA) 817), to provide new insights into the nature of Martian fluids.

**Methods:** Olivine-iddingsite interfaces were identified and characterised in the Lafayette and NWA 817 nakhlite meteorites by scanning electron microscopy (SEM) imaging (e.g. Figure 1), energy dispersive X-ray spectroscopy (EDS) and electron backscatter diffraction (EBSD), on the Zeiss Sigma variable pressure field emission scanning electron microscope (VP-FE-SEM) at the Imaging Spectroscopy and Analysis Centre, at the University of Glasgow. EDS and EBSD analysis were conducted at 20 kV. EDS and EBSD data were collected using the Aztec 3.3 software package from Oxford Instruments and the EBSD data were processed using the Channel 5 Software package from Oxford Instruments. The orientation of the olivine-iddingsite interface was established by making a small trench across the interface using the FEI Ga and Xe source focused ion beam (FIB)-SEMs at the Kelvin Nanocharacterisation Centre at the University of Glasgow. The samples were prepared for APT following the ‘button’ method for interface targeting



*Figure 1. A backscattered electron (BSE) image of an olivine phenocryst with crystallographically controlled iddingsite veins cutting across the crystal in NWA 817. The red box indicates where APT samples were extracted using the FIB. Ol=Olivine, Id= Iddingsite, Px=Pyroxene.*

developed in Rickard et al., [8] whereby the interface was decorated with e-beam deposited Pt ‘buttons’ prior to the main Pt protective layer to ensure accurate targeting of the interface during the annular milling stage [8]. The samples were thinned until the iddingsite-olivine interface was close to the apex of the needle. Five APT needles were prepared from a single interface in both NWA 817 and Lafayette. The APT samples were analysed on the CAMECA LEAP 5000XR at the University of Oxford. Data were reconstructed and analysed and using the IVAS software package.

**Results:** Of the samples that were prepared, two data sets successfully ran through the iddingsite into the olivine (1 from NWA 817 and 1 from Lafayette). In addition, we obtained one data set comprised of only olivine and one data set comprised of only iddingsite from NWA 817. The APT data that contained only olivine were chemically homogeneous throughout. The iddingsite sample was heterogeneous in density but homogeneous in chemistry. The Lafayette and NWA 817 samples containing the iddingsite-olivine interface reveal that this boundary is gradational at the nanoscale. Towards the interface over a distance of 30-20 nm steady depletions in the major cations such as Mg are observed (Figure 2). These depletions are

complemented by an apparent steady enrichment in H towards the interface (Figure 2). EBSD analysis of NWA 817 indicate that the iddingsite vein is parallel to the {021} plane of the olivine consistent with previous petrographic descriptions of crystal orientation relationships in these meteorites [1].

**Discussion and conclusion:** APT datasets from iddingsite indicate that it is chemically homogenous and, as such, likely contains only clay minerals. No oxides, carbonates, sulphates or halides [4] or nanoscale chemical domains were identified. The variations in density within the iddingsite are interpreted to represent the preferential ionisation of individual phyllosilicate platelets (high density) followed by ‘bursting’ removing the clay mineral to leave a void (low density).

Previous studies of the Deuterium/Hydrogen (D/H) ratio of nakhlite iddingsite suggests that the water from which it formed was derived from the Martian atmosphere or crust [9]. However, the hydrogen isotopic composition of iddingsite can be strongly perturbed by terrestrial weathering [9, 10]. Therefore, measured D/H ratios of iddingsite are likely to be a mixture of signals derived from the Martian fluid, crust, atmosphere as well as some terrestrial sources. Our APT datasets suggest that H species may be enriched in the outer 20 nm of the olivine in contact with iddingsite (Figure 2). This 20 nm layer may store H more securely than clay. As such directly measuring the D/H ratio of hydrogen

contained within this interface may reveal the D/H ratio of the original fluid, and thereby constrain its source (e.g., Martian crust vs atmosphere).

Finally, the observation that the iddingsite-olivine interface is diffuse over 20 nm rather than a sharp boundary (Figure 2) is inconsistent with recent models of fluid alteration of glasses, such as interfacial dissolution-reprecipitation [11]. Our APT data agree better with a diffusion coupled hydration model whereby inward diffusion of hydrogen species is coupled with outward diffusion of cations [12]. Therefore, further APT analysis of weathered mineral surfaces from both terrestrial and extraterrestrial environments can provide new insights into the mechanisms that produce alteration assemblages.

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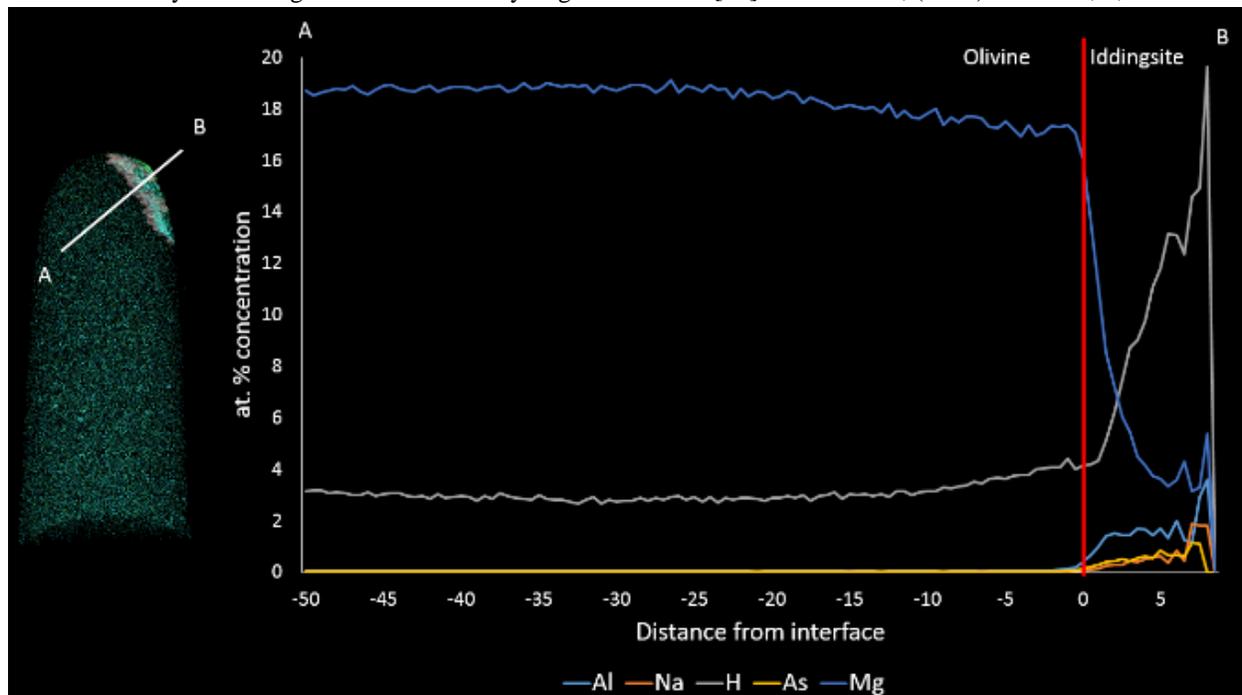


Figure 2. An atom probe needle through an olivine-iddingsite interface in NWA 817. The atom map (left hand side) represented by Al (blue dots) and Na (green dots) atoms defines the interface (grey iso-concentration surface). The graph is a proxigram of elemental abundance relative to the position of the interface (red line). These data indicate that the iddingsite is enriched relative to olivine in H, As, Na and Al while the olivine is enriched in Mg. Mg in the olivine exhibits a steady depletion over 20-30 nm towards the interface associated with a comparable rise in H.