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Please cite this article as: Piercy, J.D., Bridges, J.C., Hicks, L.J., MacArthur, J.L., Greenwood, R.C., Franchi, I.A., Terrestrial Alteration Mineral Assemblages in the NWA 10416 Olivine Phyric Shergottite, *Geochimica et Cosmochimica Acta* (2020), doi: https://doi.org/10.1016/j.gca.2020.03.026

Terrestrial Alteration Mineral Assemblages in the NWA 10416 Olivine Phyric Shergottite

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0. ABSTRACT

We report on the alteration history of the olivine-phyric, highly depleted (HD) shergottite, Northwest Africa (NWA) 10416, paying particular attention to the origin of the aqueous alteration seen affecting the meteorite's olivine megacrysts. The rock's interior displays 1 mm, zoned, altered olivine megacrysts set in a groundmass of clinopyroxene, unzoned olivine, and interstitial plagioclase and maskelynite. Synchrotron micro X-ray diffraction (μ-XRD) and transmission electron microscopy (TEM) show that plagioclase and maskelynite have been partially replaced by kaolinite. The relict olivine megacryst cores display a unique concentric colouration for Martian meteorites, having central amber-coloured zones surrounded by a brown mantle zone, with the rims remaining clear and unaltered. This colouration is a result of fluid alteration and partial replacement, with hydration. TEM analysis revealed the ~200 nm scale banded and largely amorphous nature of the alteration, but with some (~ 20%) relict crystalline olivine patches. Although the coloured olivine zones show cation and anion site vacancies compared to stoichiometric olivine, a relict igneous compositional trend is preserved in the megacrysts, from Mg-rich altered cores (Mg# = 76) to unaltered stoichiometric rims (Fo_{53}). Synchrotron Fe-K X-ray absorption near-edge structure (XANES) analysis revealed that the coloured zones of the megacryst have different Fe oxidation values. High ferric contents are present in the brown mantle zones ($Fe^{3+}/\Sigma Fe \leq 0.92$) and the amber zones ($Fe^{3+}/\Sigma Fe \leq 0.30$), whereas the clear rims are ferrous. This suggests alteration occurred in an oxidising environment and that the sharp contrast in colour of the megacryst (brown to clear) is a record of a relict fluid reaction front.

In order to test the terrestrial or extraterrestrial origin of the alteration, olivine material from a shock-melt vein was analysed by TEM. The analysis revealed 0.952 nm curved *d*-spacing's from clay alteration undisturbed by any shock effects, strongly suggesting a terrestrial origin. The d-spacing values most likely represent a collapsed saponite or vermiculite, showing that in some places olivine has been replaced by crystalline clay.

Oxygen isotope analysis of bulk ($\Delta^{17}O = 0.309 \pm 0.009$ (2σ) ‰) and amber-coloured megacryst material (= 0.271 ± 0.002 (2σ) ‰), are also consistent with terrestrial alteration. We propose a model in which, during the meteorite's time in Northwest Africa, low-temperature, likely acidic, groundwater exploited fractures. The fluid altered the olivine megacrysts in a way that was controlled by the pre-existing, igneous compositional zonation, with Mg-rich olivine being more susceptible to alteration in this fluid environment. The plagioclase and maskelynite were also altered to a high degree. After the alteration event it is likely that NWA 10416 had a significant residence time in Northwest Africa, accounting for terrestrial calcite and the dehydration of some clay phases.

1. INTRODUCTION

Northwest Africa (NWA) 10416, weighing 964 g was found in Mali, 2015. It has been classified as a martian meteorite based on oxygen isotope ratios, Fe/Mn ratios within clinopyroxene and olivine, and the anorthite content of its plagioclase (Bouvier et al., 2017). Although it is classified as an olivine-phyric shergottite in mineralogy and texture, it has undergone a much smaller shock pressure than other olivine-phyric shergottites and in this respect is similar to the martian augite-rich shergottite, NWA 8159, having only 10% of its feldspar converted to maskelynite. It has also been noted that NWA 10416, with CI-normalized La/Yb ~ 0.1, shows significant depletion in its Light Rare Earth Element (LREE) abundances, comparable to NWA 8159 and Dar al Gani (DaG) 476 (Bouvier et al., 2017; Herd et al., 2016), suggesting a Highly Depleted geochemical classification (Bridges and Warren, 2006).

Olivine-phyric shergottites are defined by the presence of olivine megacrysts within a groundmass of olivine, clinopyroxene (and sometimes orthopyroxene), plagioclase and maskelynite. There is much debate as to the origin of these megacrysts, with 4 main theories.
   (1) Xenocrysts derived from a melt of different composition (possibly with strong affinity to the poikilitic shergottites) (Wadhwa et al., 2001; Goodrich, 2002; Rahib et al., 2019),
   (2) Phenocrysts that formed in the early stages of crystallisation within the same melt and thus reflect the shergottite's bulk composition (Usui et al., 2008; Basu Sarbadhikari et al., 2009),
   (3) Antecrysts which crystallised in an earlier melt that underwent less fractionation (Balta et al., 2015; Liu et al., 2013),
   (4) or as a combination of these during complex multistage growth (Ennis and McSween, 2014).
For this reason, throughout this paper we shall refer to the coarse olivine grains within NWA 10416 as megacrysts.

A striking aspect of NWA 10416 is the amount of alteration it has been subjected to, notably within the olivine megacrysts which have a concentric amber-brown colouration to them. Although brown olivine in olivine-phyric and poikilitic shergottites is often attributed to shock darkening (DaG 489, Folco et al., 2000; Sayh al Uhaymir (SaU) 094, Gnos et al., 2002; SaU 150, Walton et al., 2005; Larkman Nunatak (LAR) 06319, Basu Sarbadhikari et al., 2009), we have identified no other shergottites displaying the distinctive concentric colouration pattern of NWA 10416. The crystalline feldspar and maskelynite has also been subject to high degrees of alteration, another feature that distinguishes it from most shergottites, the least altered group of martian meteorites.

Until Mars Sample Return, the classified 247 martian meteorites (Meteoritical Bulletin, 2019), many of which are pairs, remain the only samples of Mars that we can investigate with a large range of sophisticated techniques in ground-based laboratories. Studying the secondary mineral

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assemblages in these meteorites allows us to characterise fluid-rock interactions on Mars and therefore the potential for habitability in their formation environments. NWA 10416 and other shergottites may offer such a scientific opportunity. However, it is essential when characterising secondary mineral assemblages in martian meteorites to determine whether the alteration event took place on Mars, or on Earth. Confirmation of the origin, martian or terrestrial, is obtained from a suite of evidence, particularly textural relationships, as well as mineral compositions and stable isotopic ratios (e.g. Hallis and Taylor, 2011; Hallis et al., 2012a; Hallis et al., 2014; and Velbel, 2016). Previous work performed by Herd et al. (2016) and Vaci (2017) suggested the olivine alteration in NWA 10416 is pre-terrestrial in origin, due to serrated boundaries between the clear and brown olivine, as well as an overlap in compositions (Fo_{52-53}) between the groundmass olivine and megacryst clear rims. However, oxygen isotope data reported by Bouvier et al. (2017) indicates that at least some terrestrial alteration has occurred.

The nakhlites and Allan Hills (ALH) 84001 display the importance of unambiguous textural evidence confirming the origin of fluid alteration and much has been learnt from these meteorites regarding martian fluid-rock interactions since we can be confident that the secondary phases analysed are martian. In the nakhlites Nakhla and Lafayette, clay-filled veins are truncated by the fusion crust, showing a definite extraterrestrial origin (Gooding et al., 1991; Treiman et al., 1993). Investigations into the alteration minerals have led to a model which suggests that CO_2-charged hydrothermal fluids percolated upwards throughout the fractured nakhlite igneous mass, perhaps during an impact-induced event, with limited compositional fractionation of the secondary mineralogy along the way (Changela and Bridges, 2011; Bridges and Schwenzer, 2012, Hicks et al., 2014). Geochemical modelling suggests that the hydrothermal fluid was neutral to weakly alkaline, enriched in the most soluble species (e.g. K and Na) and had temperature variations consistent with a potentially habitable fluid environment (Bridges and Schwenzer, 2012). It is not common to find this kind of definitive evidence which can prove the origin of alteration. For example, goethite and feldspathic veins found in the martian regolith breccia NWA 8114 (MacArthur et al., 2019) could be of martian origin, consistent with D/H ratios within the meteorite (Agee et al., 2013). However, unequivocal evidence for a preterrestrial origin has not yet been identified.

Here we present our research on the textural, mineralogical and oxygen isotope relationships between NWA 10416's igneous silicates and alteration features in order to understand the nature and origin of this meteorite's secondary phases, particularly the megacrysts' unique colouration. We aim to distinguish between shock and fluidic alteration effects as a cause of the colouration and whether any fluidic alteration is martian or terrestrial. Key textural features in this respect are the relative timing of fractures, shock veins and the alteration.

2. SAMPLES AND METHODS

Our 2.1 g bulk sample of the martian shergottite NWA 10416 was prepared as 3 thin sections at the University of Leicester. Lapping was performed with an abrasive mixture of ethandiol fluid and 15 μm Al_2O_3 powder; and polishing with a combination of 3 μm diamond paste and MetaDi fluid.

2.1. Electron Microscopy

The sections were initially characterised with Back Scattered Electron (BSE) imagery and Energy Dispersive Spectroscopy (EDS), using a FEI Quanta 650 Field Emission Gun – Scanning Electron Microscope (FEG-SEM) at the University of Leicester's Advanced Microscopy Centre. EDS spectra were measured using an accelerating voltage of 20 kV and a beam current of ~1.0 nA. Imaging was performed with a working distance of 6 mm and EDS at 10 mm.

Mineral Liberation Analysis (MLA) was utilised to produce modal mineralogy maps of the thin sections at the University of Nottingham's Nanoscale and Microscale Research Centre. A FEI Quanta 600 SEM was used in conjunction with BRUKER EDS software and JKTech/FEI MLA software to output results including modal mineralogy and grain size and shape. EDS spectra were taken across the thin section, classified and fitted to reference spectra and are automatically produced. The maps have a resolution of 3.5 nm per pixel, performed with an accelerating voltage of 30 kV.

Wavelength Dispersive Spectroscopy (WDS) was performed using a JEOL JXA-8200 SuperProbe Electron Probe Microanalyzer (EPMA) at the University of Nottingham's Nanoscale and Microscale Research Centre. Measurements on silicate materials were taken with a beam diameter of 5 μm, whereas secondary phase compositions were taken with a defocussed beam of 20 μm diameter. All data was performed with an accelerating voltage of 15 kV and a working distance of 11 mm. A 3-spectrometer setup was used with the analysing crystals; TAP (Na, Mg, Al and Si), PET-J (P, S, K and Ca), LiF-H (Ti, Cr, Fe and Ni).

Focussed Ion Beam (FIB) milling was utilised to extract 5 μm x 15 μm wafers with <100 nm thicknesses, suitable for Transmission Electron Microscopy (TEM). The procedure was performed on a FEI Quanta 200 3D Dual FIB-SEM at the University of Leicester. First a platinum coating is deposited on the area of interest via the Gas Injection System (GIS), this area is then milled using a 30 kV Ga^+ ion beam and extracted by joining the wafer with an *Omniprobe* needle using deposited carbon via the GIS. A 15 kV, 1.0 nA electron beam is used for long duration

viewing of the sample, as viewing with the ion beam does destroy the material depending on its emission current, they are; 10 pA for short viewing, 5 nA for the initial trench milling, 0.3 - 0.5 nA for subsequent, finer milling and 0.1 nA for thinning the extracted wafer.

Transmission Electron Microscopy (TEM) was performed with a JEOL 2100+ TEM at the University of Nottingham's Nanoscale and Microscale Research Centre. The instrument has a LaB_6 thermionic source operating at an accelerating voltage of 200 kV and a beam current of ~110 µA. EDS was done using an Oxford Instruments X-MaxN 80 TLE EDS detector. Bright Field (BF) and Dark Field (DF) High-Resolution TEM (HRTEM) images were taken using the *GATAN Digital Micrograph Camera* program at magnifications up to ×600k. *d*-spacing's were determined by producing a Fast Fourier Transfer (FFT) of ×400k - 600k magnification BF images within the GATAN program, masking lattice features in the FFT and inverting the masked image in order to view the lattice spacing's in greater detail.

2.2. Synchrotron Analysis

Fe-K X-ray Absorption Spectroscopy (XAS) and transmission micro-X-ray Diffraction (µXRD) were carried out using the 2.5 µm resolution I-18 Microfocus Spectroscopy beamline at the *Diamond Light Source* synchrotron, UK. XAS measurements were taken from 6900 eV to 7500 eV, with a higher resolution of 0.1 eV increments measured over the X-ray Absorption Near Edge Structure (Fe K XANES) region; 7100 to 7125 eV. The higher resolution over this region is necessary to accurately measure the small energy shifts that occur due to the $1s \rightarrow 3d$ transition appearing in the pre-edge features. XAS data was normalised using *Athena 0.9.24*. XANES data presented here was taken from two separate experiments performed at *Diamond*, the energy shift between these experiments was calculated from data on Fe metal foils and corrected for. $Fe^{3+}/\Sigma Fe$ ratios for unknown silicates was determined by comparing the pre-edge centroid energies (XANES position 1s → 3d) of standard silicates with their known $Fe^{3+}/\Sigma Fe$ and producing a linear fit, as seen in Hicks et al. (2014). A linear fit was drawn between San Carlos olivine ($Fe^{3+}/\Sigma Fe = 0$, ferrous) and Nontronite-NAu-2 ($Fe^{3+}/\Sigma Fe = 1$, ferric) standards (Geological Survey of Japan/AIST, 1995; The Clay Minerals Society, 2013).

Transmission µXRD data was taken between a 2θ range of 4° to 40° with a beam energy of 13 keV ($\lambda = 0.95$ Å); this corresponds to a detectable range of *d*-spacing's from 1.4 Å - 9.1 Å. Measurements were for a variety of integration times; 60 s, 120 s and 180 s and compared to appropriate standards. LaB_6 was used as the calibration material and the XRD images were processed using the *Diamond Light Source* software package *DAWN 2.7.0*. Transmission µXRD analysis of clays is used as an important complementary, rather than conclusive, evidence for identification. Samples were in the form of a thin section, not powdered, therefore each measurement represents a limited view of that mineral

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due to limited crystal faces, within a grain of a particular orientation, being exposed to the ~2.5 μm beam. Thus, unlike with a powder measurement, there is no guarantee that all diffraction peaks will be observed or are seen at their representative intensities. Added complications arise when identifying clays as they produce a large amount of peaks due to their large crystal structures, a number of which are shared between clay groups.

2.3. Oxygen Isotope Analysis

From the material left over from thin sectioning, samples were handpicked with tweezers based on their colour for oxygen isotope analysis. Roughly 2.5 mg of amber-coloured olivine grains and ~13 mg of green (pyroxene) and white (plagioclase and clay) material, for a bulk measurement, were selected. Oxygen isotopic analysis of NWA 10416 was undertaken at the Open University using an infrared laser fluorination system (Miller et al., 1999; Greenwood et al., 2017). The normal operating procedure involves loading ~ 2 mg aliquots of samples and standards into a Ni sample block containing 22 drilled wells. The sample block is then loaded into a two-part chamber, made vacuum tight using a compression seal with a copper gasket and quick-release KFX clamp (Miller et al., 1999). A 3 mm thick BaF_2 window at the top of the chamber allows simultaneous viewing and laser heating of samples. Following sample loading the cell is heated under vacuum for a minimum of 24 hours and to a temperature of at least 70 °C to remove any adsorbed atmospheric moisture. Prior to fluorination, the system blank was systematically reduced by flushing the chamber with aliquots of BrF_5, such that the final blank was less than 60 nmol O_2. Sample heating in the presence of BrF_5 was carried out using an integrated 50 W infrared CO_2 laser (10.6 μm) and video system mounted on an X-Y-Z gantry supplied by Photon Machines Inc. (Greenwood et al., 2017). After fluorination, the released O_2 was purified by passing it through two cryogenic (liquid nitrogen) traps and over a bed of heated KBr. The isotopic composition of the purified oxygen was analysed using a Thermo Fisher MAT 253 dual inlet mass spectrometer (mass resolving power 200). Interference at m/z = 33 by NF^+ was monitored by performing scans for NF_2^+ on the sample gas before analysing each sample; this was below interference levels during the analyses reported here. Our current system precision based on repeat analyses (N = 39) of our obsidian internal standard is: ± 0.052 ‰ for $\delta^{17}O$; ± 0.094 ‰ for $\delta^{18}O$; ± 0.017 ‰ for $\Delta^{17}O$ (2σ) (Starkey et al., 2016).

Oxygen isotopic analyses are reported in standard δ notation, where $\delta^{18}O$ has been calculated as: $\delta^{18}O = [(^{18}O/^{16}O_{sample}/^{18}O/^{16}O_{ref}) - 1] \times 1000$ (‰) and, similarly, for $\delta^{17}O$ using the $^{17}O/^{16}O$ ratio. In order to compare our results with other published laser fluorination analyses of martian samples we calculate $\Delta^{17}O$, which represents the deviation from the terrestrial fractionation line, as $\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$.

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3. RESULTS

3.1. Petrography

The NWA 10416 hand specimen displays an olivine-porphyritic texture consisting of large (~1 mm) amber-brown zoned olivine megacrysts set in a finer groundmass of green clinopyroxene, unzoned clear olivine, and white, interstitial plagioclase (Figure 1). Mineral modal abundances (±5 mod.% (Maloy and Treiman, 2007)) by area fractions are ~8% relict olivine megacrysts, ~4% groundmass olivine, ~65% clinopyroxene, ~19% plagioclase feldspar (of which ~40% has been altered into a secondary phase), ~2% maskelynite and ~2% minor minerals.

3.1.1. Olivine

Olivine occurs in two forms; the ~1 mm, coarse grained megacrysts bearing distinctive zoned colouration, and smaller, ~300 - 600 μm, groundmass grains. The olivine megacrysts display central amber-coloured zones surrounded by dark brown mantle zones rimmed by comparatively clear olivine (Figure 2). The concentric colourations are not consistently regular but on average have the following dimensions in percentage of radii: amber (0 - 0.5%), brown (0.5 - 0.75%) and clear rim (0.75 - 1%). The clear rims are the least regular, this can be seen in figure 2 by the olivine protrusion indicated in the upper half of the grain. Most of the altered olivine megacrysts, the amber cores and brown mantle zones, have not preserved stoichiometric olivine compositions. However, stoichiometric olivine rims are on average Fo_{53}.

Groundmass olivine grains appear subhedral to anhedral in the thin section. Like the megacryst rims, groundmass olivine is mostly clear, but some grains have a dark brown colouration. In groundmass olivine the colouration is patchy, as opposed to the regular concentric pattern seen in the megacrysts. Groundmass olivine grains show no signs of zonation and have a large compositional range, Fo_{39-58} (Figure 3). EPMA-WDS results shown in table 1 indicate they have stoichiometric compositions with ~100 wt.% oxide totals, similar to the clear rim of the megacrysts. A relatively high CaO content of ~0.3 wt.% was found across all olivine grains in both unaltered and altered zones. This is characteristic of olivine-phyric shergottites (Folco et al., 2000; Walton et al., 2005; Basu Sarbadhiraki et al., 2009; Peslier et al., 2010 and Howarth and Udry. 2017).

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There are secondary replacement features within the megacrysts in the thin section (Figure 4). They are roughly circular features, vary in diameter from ~5 μm up to ~50 μm and are opaque when viewed in polarised light. Exclusively found in the amber-brown altered zones of the megacrysts, they occupy ~ 5 area% of the megacrysts. SEM-EDS X-ray maps and point analyses show that these features differ in major cation composition to the surrounding altered olivine. Having on average MgO = 10.1 wt.% and FeO = 37.7 wt.% (based on 6 point analyses of the features), they show a depletion by ~8 wt.% and enrichment by ~13 wt.% respectively, as well as a depletion in SiO_2 (~4 wt.%) and enrichments in Al_2O_3 (~2 wt.%), CaO (~0.6 wt.%) and P_2O_5 (~1 wt.%) relative to the host grains.

EPMA-WDS results (Table 1) of the megacrysts' different coloured zones also reflect partial replacement by secondary phases, consistent with secondary replacement features described above. Neither the amber nor brown zones are stoichiometric olivine, having low WDS totals consistent with hydration. The amber zone is seemingly less altered than the brown zone, containing less water calculated by difference (2.2 H_2O wt.%, as opposed to 5.4 H_2O wt.%) and having a more stoichiometric olivine Si atomic content when calculated based on 4 oxygens (Table 1). When recalculated we show that both the anion and cation sites contain vacancies 'v' within the structure, brown olivine, $(v_{0.34}Mg^{2+}_{0.95}Fe^{2+}_{0.16}Fe^{3+}_{0.55})v_{0.13}Si_{0.87}O_4$; and amber olivine, $(v_{0.19}Mg^{2+}_{1.24}Fe^{2+}_{0.45}Fe^{3+}_{0.12})v_{0.05}Si_{0.95}O_4$, where v represents the vacancy. The brown altered olivine also has a much higher ferric component (see Section 3.3.1 for the ferric value measurements).

However, SEM-EDS results and the contrast in the BSE images show a gradual compositional variation across the megacrysts that does not match the sudden changes in colouration seen with optical microscopy (Figures 2). The megacrysts have Mg-rich non-stoichiometric cores and mantle zones, Mg# = 76 and 65 respectively (Mg# = Mg / Mg + Fe), and rims of almost equal MgO and FeO content, stoichiometric Fo53. These gradual changes in MgO and FeO indicate an origin from igneous zonation rather than replacement and remobilisation of elements. Similar compositional zonation is seen in other olivine-phyric shergottites: NWA 10170 (Howarth and Udry, 2017), LAR 06319 (Basu Sarbadhikari et al., 2009), NWA 6234 (Gross et al., 2013), SaU 150 (Walton et al., 2005). Figure 2 shows an optical and BSE comparison of a shear-fractured olivine grain with a shock-melt vein present in between the two halves of the grain. It is notable that the shock-melt vein cross cuts both olivine colouration and zonation. The significance of this for determining a martian versus terrestrial origin for the secondary mineral assemblage is discussed later (Section 4.4).

Melt inclusions and relict high temperature mineral inclusions exist within all the thin section's olivine grains, predominantly in groundmass olivine. They exist in two forms; the first are observed mostly in the groundmass olivine. They are rounded but irregular shaped inclusions of ~5 - 40 μm size. They have a non-stoichiometric, Al-bearing pigeonite-like (but non-stoichiometric) composition (on average, Mg# = 55) and

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include pyrite and Ti-chromite grains. The second are smaller, ~2 - 10 µm in size, oval shaped inclusions within the altered olivine zones. They have a similar Al-bearing pigeonite dominant mineralogy ($En_{68}Fs_{28}Wo_4$) but also include a Cr-Fe oxide symplectic intergrowth (Figure 4). Several sub-micron Cr-Fe oxide inclusions also occur within the olivine grains, and this is characteristic of other olivine-phyric shergottites: NWA 6234 (Gross et al., 2013), DaG 489 (Folco et al., 2000), Yamato (Y) 980459 (Usui et al., 2008). These inclusions are found both within the Mg-rich altered cores of the NWA 10146 megacrysts (Figure 4) and the groundmass olivine, though none were observed in the megacrysts' clear unaltered rims. The inclusions are mostly randomly scattered. However, some are seen forming linear trails across the megacrysts.

3.1.2. Pyroxene

The medium grained pyroxenes comprising ~65 area% of the sample are euhedral to subhedral. However, moderate to severe fracturing has disrupted some grains. Grains viewed lengthways in thin section show average lengths and widths of ~400 - 500 µm and ~200 µm respectively. All pyroxene observed was clinopyroxene and the majority of grains show signs of compositional zonation; they have Mg-rich pigeonite cores, $En_{62-81}Fs_{17-30}Wo_{0-9}$ and Ca-rich augite rims, $En_{39-56}Fs_{19-45}Wo_{11-36}$ (Figure 3 and Table 1). EPMA-WDS results (Table 1) show that the pyroxenes have stoichiometric, unaltered compositions. These compositions also display a consistent variation: TiO_2, Na_2O and Al_2O_3 increase from the core to the rim, correlating with the increasing CaO and decreasing MgO, this trend has been noted in many shergottites (Goodrich, 2003; Walton et al., 2005; Basu Sarbadhikari et al., 2009 and Combs et al., 2019). There are no signs of hydrous alteration affecting the pyroxene, unlike the olivine grains. However, similar to the olivine grains, fractures and shock-melt veins are seen cross cutting and displacing their igneous zonation shown in the BSE images.

3.1.3. Plagioclase Feldspar

Feldspar grains comprise ~19 area% of the thin section and are interstitial between olivine and clinopyroxene with anhedral morphologies; no tabular feldspar grains were observed. Roughly 10 area% of all plagioclase within the thin section has been shock converted (and preserved) as the diaplectic glass phase maskelynite, evident from its isotropic nature when viewed in cross polarised light. This agrees with measurements presented previously (Vaci, 2017). Maskelynite grains are adjacent to shock-melt veins and fractures.

EPMA-WDS results (Table 1) shows that compositions of crystalline feldspar reflect stoichiometric plagioclase $Ab_{28-44}An_{55-72}Or_{0-1}$ – mainly labradorite, with minor bytownite. This compositional range is similar to the olivine-phyric shergottites DaG 476, An_{52-72}, (Zipfel et al., 2000)

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and DaG 489, An_{56-67}, (Folco et al., 2000). No signs of zonation were observed across any NWA 10416 plagioclase grains. They are of homogenous composition with a relatively high FeO content of ~0.3 - 0.5 wt.%. This was also noted in DaG 489, 0.37 wt.%, (Folco et al., 2000), Dhofar 019, 0.4 - 1.0 wt.%, (Taylor et al., 2002) and SaU 150, 0.42 - 0.56 wt.%, (Walton et al., 2005).

3.1.4. Altered Plagioclase and Maskelynite

A large amount, ~40 area%, of all labradorite grains have been altered to a secondary phase, therefore making up ~6% of the sample. The amount of each individual grain affected varies depending on the grain's proximity to fractures or shock-melt veins, the more altered being closer to these areas. Isotropic grains that we have identified as maskelynite are also shown to have been altered to a secondary phase, this is notable as the maskelynite would have formed during the shock event that lofted the rock off Mars. Therefore, if it is affected by secondary alteration, the alteration probably post-dates that event, indicating a terrestrial origin (see Section 4.4).

EPMA-WDS analyses (Table 1) of the secondary phase in both labradorite and maskelynite reveal a substantial depletion in the major cations, CaO and Na_2O, relative to the host feldspathic composition. SiO_2 has been depleted whilst Al_2O_3 content has been enriched. The phase also has increased K_2O, MgO, FeO and P_2O_5 contents relative to the unaltered feldspar. H_2O calculated by difference reveals that ~12 wt.% is present within the secondary phase. Compositions are relatively stoichiometric when calculated on the basis of 18 O, OH, and this composition closely resembles a dehydrated kaolinite group mineral with an enriched CaO content.

3.1.5. Minor Phases in the Groundmass

Minor mineral phases comprise ~2 area% of the sample and are identified as Ti-bearing magnetite, ilmenite, Ti-bearing chromite, pyrite and apatite. These were found to be mainly present throughout the sample's groundmass, at silicate boundaries, in varying sizes and with euhedral to subhedral forms. Calcite, typical of terrestrial desert weathering (Hicks et al., 2014), was found in filling pre-existing fractures, cross-cutting and postdating most phases, including the olivine coloured zones and the altered plagioclase. A few Mn-rich alteration veins, characteristic of terrestrial desert weathering products were also observed (Dorn. 2009).

3.1.6. Shock Features

Shock features are prominent in NWA 10416. All the major silicate phases (olivine, pyroxene and feldspar) display fractures, visible in both BSE and polarized light (Figure 2). Under BSE it is noticeable that fracturing is situated near grain boundaries and shock-melt veins. In areas of olivine grains that show a high density of fractures compared to the rest of the grain, there is also a noticeable increase in opacity when viewed in polarised light. This correlation has also been noted by Takenouchi et al. (2018).

Figure 2 shows one of the olivine megacrysts that has been fractured and displaced due to shock. The result is a shock-melt vein that runs between the two halves of the megacryst and is at least 1.8 mm long but extends beyond the boundaries of the thin section. Its width is on average ~10 - 15 μm. Figure 5 shows a BSE image of a section of the shock-melt vein viewed in figure 2. It consists of a bulk pyroxene-like composition with a fine-grained matrix of oxides entrapping fine grained silicates. These recrystallised grains are predominantly pyroxenes ($En_{44-58}Fs_{22-46}Wo_{6-33}$) with lesser olivine ($Fo_{50-58}$). The sub-micron, fine grained, web-like matrix consists of Fe oxides, Fe sulphides and chromite grains based on the combined compositions. This material was too fine grained to determine accurate SEM-EDS compositions of discrete crystallites.

3.2. Transmission Electron Microscopy

FIB sections were extracted from dark brown mantle zone within an olivine megacryst (Section 3.1.1), olivine embedded within the shock-melt vein seen in figures 2 and 5 (Section 3.1.6), and the altered plagioclase (Section 3.1.4). This was done in order to investigate the alteration mineralogy in more detail.

3.2.1. Brown Olivine

Figure 6 shows brown olivine HRTEM images at different magnifications. It displays numerous thin subparallel bands, each on average 200 - 300 nm long and 5 - 10 nm wide (Figures 6a and b). Longer bands, up to 2 μm but of comparable width, are observed cross cutting the shorter ones (Figure 6a), these can be curved relative to the subparallel bands and are far fewer in quantity (3 observed in the entire wafer). All of these features occupy around 70% of the wafer and are interspersed throughout the relict olivine. They also have a brighter contrast compared to the main mass of the wafer when viewed in bright field, indicating a higher degree of electron transparency most likely consistent with a lower mass density area. When viewed at higher magnifications (×50 - 100k), both the longer and shorter bands consist of a central channel with many perpendicular 'off-shoots', ~5 - 10 nm in length, protruding out into the intermediate material between the bands (Figures 6c and d). When

viewed at ×400 - 600k magnification, these alteration textures are seen to be amorphous as no structure was detected from the Fast Fourier Transform (FFT) image. Void spaces (Figure 6d) that exist within the brown olivine wafer vary in size and shape but are mostly elongated, the smaller voids are ~20 - 30 nm across and exist within or at the end of a long crosscutting feature (Figure 6a). The larger voids are ~150 nm across and the material surrounding them is also amorphous (Figure 6c). No iron metal nanoparticles, indicative of shock browning (Treiman et al., 2007), were found under HRTEM.

STEM-EDS analysis revealed qualitatively that the linear features and amorphous regions surrounding them are depleted in MgO and enriched in FeO, relative to the surrounding olivine. This matches the trend seen from the SEM-EDS analysis (Section 3.1.1) of the partial replacement features seen in figure 4. Crystalline material found in between the bands in figure 6 display a lattice spacing at 0.388 nm, corresponding to the d_{021} forsterite spacing (Downs et al., 1996).

3.2.2. Olivine Within Shock Veins

Figure 5 shows a shock-melt vein (Section 3.1.6) where grains of recrystallised pyroxene and olivine reside in a matrix of pyroxene-like silicate and intergrown Fe-Ti-Cr oxide. A FIB wafer was taken of the alteration within the labelled olivine (Figure 5) in order to investigate the sequence of events between shock and fluid alteration, the hypothesis being that if fluid alteration features overprint the shock features then it is more probable that the water-rock interaction took place after the shock event and most likely on Earth.

The embedded olivine grain lacks the features seen in the TEM analysis of the brown mantle olivine (Section 3.2.1), no void spaces and only two ~200 nm long curved linear features were observed. The grain is predominantly but not wholly a homogenous crystalline olivine grain, TEM bright field images show varying patchy contrasts across the grain that appear plate-like. STEM-EDS of these areas showed that although they have different compositions, comparable trends (enrichments in FeO and depletions in MgO compositions) are seen in the TEM analysis of the brown olivine (Section 3.2.1). Table 1 shows the composition measured. With a large P_2O_5 content of ~2.5 wt.% oxide, assumed as a small phosphate grain, the composition was renormalized without P and a proportion (3/5) of Ca before mineral recalculation. The mineral recalculation, based on 22 O, shows that the composition is close to that of saponite and vermiculite. Areas of this composition occupy 5 - 10 area% of the olivine grain, and in some of them sporadic curved d-spacings occur (Figure 7), characteristic of a hydrated phyllosilicate structure. The spacing's have a trioctahedral pattern and were measured consistently as 0.95 nm, when analysed through the FFT. This value also supports a saponitic composition. None of the clay-like d-spacing's are affected by any shock features such as dislocations, and no Fe-nanoparticles

where observed within the olivine, both features predicted in shock-browned olivine. We discuss the significance of this determining the relative timing of alteration and shock in section 4.4.

3.2.3. Kaolinite

Figure 8 shows features from TEM analysis of the altered plagioclase. Plagioclase occurs with a secondary phase forming veins throughout the wafer with planar features. When imaged in STEM mode (Figure 8a) and analysed by TEM-EDS, the plagioclase has a homogenous composition, whereas the altered zones show relative depletion in the major plagioclase cations, Na_2O (Figure 8c) and CaO (Figure 8d), comparable with WDS measurements shown in table 1.

When viewed in HRTEM we see that all observed secondary material has an amorphous nature (Figure 8b). The textures observed in the TEM wafer did not appear similar to silicates damaged by the Ga^+ beam during the FIB milling process, which produces a speckled-like patchy surface on the silicate material, and therefore the lack of structure on the FFT indicates an amorphous structure. However, although no lattice spacings were found throughout the wafer, some d-spacings were visible. These were of a similar curved nature to what was seen within the olivine alteration (see Section 3.2.2) having contorted fringes, again indicative of a hydrated phyllosilicate structure.

3.3. X-ray Microanalysis

3.3.1. X-ray Absorption Spectroscopy

Fe-K X-ray Absorption Spectroscopy was performed on the sample in order to gather information about the oxidation state of iron across the olivine megacrysts. The XAS spectra (Figure 9) and the calculated $Fe^{3+}/\Sigma Fe$ ratios (Table 2) reveal an oxidation variation across the sites indicated in figure 9. Table 2 also contains analyses from a separate synchrotron experiment, the minor energy shift between the two experiments has been corrected for and the data shows the same trend. The Fe-K XANES position of points B and D (dark brown olivine) differ from A, C and E in the fact that their pre absorption edge centroids are shifted to higher energies indicating a higher ferric content. The XANES position ($1s \rightarrow 3d$) and absorption edge energies are shown in table 2, in order from highest XANES position (± 0.05 eV) to lowest, and therefore highest oxidation state to lowest (represented by the ferric percentages, $Fe^{3+}/\Sigma Fe * 100$) they are; D (7113.74 eV; 92%), B (7113.25

eV; 61%), C (7112.56 eV; 17%), A (7112.35 eV; 3%) and E (7112.33 eV; 2%). Therefore, the darker the colouration, the more oxidised the olivine.

3.3.2. Transmission μ-XRD

Measurements were taken of plagioclase and altered plagioclase, the latter most likely a kaolinite-group clay from its WDS composition. XRD spectra of the altered plagioclase and unaltered labradorite were compared and the peaks that appeared solely in the altered plagioclase data set were selected for identification. These peaks have d-spacing values (in angstroms), in order of intensity, of 2.447, 2.293, 3.550, 2.495, 1.211, 2.340, 1.652 and 2.033. These values were compared to the ICDD (International Centre for Diffraction Data) database, with particular focus on matching with kaolinites, illites, smectites, micas and zeolites. The best returned match, matching four of the above eight peaks, was kaolinite-1A. If correct the four matched peaks correlate to d_{112} (2.495 Å), d_{-1-13} (2.340 Å), d_{131} (2.293 Å), d_{004} (1.788 Å) and d_{240} (1.652 Å). However, some of these peaks correlate to the mineral halloysite, a more hydrated version of kaolinite.

The fact that four diffraction peaks remain unidentified (3.550 Å, 2.447 Å, 2.033 Å and 1.211 Å)
, could be due to a mixture of phases within the plagioclase alteration. More investigation is needed to understand the origin of these peaks, but a kaolinitic affinity is clear. Some diffraction images show a thick diffuse ring and the equivalent spectra show a large amount of noise. This indicates an amorphous component, which reflects our TEM results where amorphous material was widespread.

3.4. Oxygen Isotope Analysis

Oxygen isotope analysis was carried out on bulk material and amber-coloured olivine separated from NWA 10416 (Table 3). Bulk material analyses are $\delta^{17}O$ = +2.99, +2.97 ‰, $\delta^{18}O$ = +5.16, +5.10 ‰, and $\Delta^{17}O$ = +0.306, +0.312 ‰, and amber-coloured olivine are $\delta^{17}O$ = +2.72, +2.63 ‰, $\delta^{18}O$ = +4.71, +4.55 ‰, and $\Delta^{17}O$ = +0.272, +0.271 ‰. Figure 10 shows that the bulk material, with an average $\Delta^{17}O$ value of 0.309 ± 0.009 (2σ) ‰, essentially plots on the Martian Fractionation Line (=0.307 ‰) (Franchi et al., 1999). The amber-coloured olivine, average $\Delta^{17}O$ value of 0.271 ± 0.002 (2σ) ‰, lies slightly closer to the Terrestrial Fractionation Line ($\Delta^{17}O$ = 0 ‰) and outside of the bulk measurements' error range. The two amber-coloured olivine analyses have $\Delta^{17}O$ displacements of 0.035, 0.036 ‰ away from the MFL. This indicates some terrestrial fluid contamination from the Northwest Africa desert find locality. The amber olivine also, with an average value of 4.63 ± 0.24(2σ)

‰, has a significantly lower $\delta^{18}O$ value than the bulk fraction, which has an average value of 5.13 ± 0.09 (2σ) ‰. This reflects the presence of $\delta^{18}O$ rich relict plagioclase and clay in the bulk.

4.   DISCUSSION

The petrography of NWA 10416 strongly resembles that of the other olivine-phyric shergottites. Zoned olivine megacrysts with Mg-rich cores and groundmass olivine with compositions that overlap with the megacryst rims (Figure 2) are a common feature within this group. However, what separates NWA 10416 from other olivine-phyric shergottites is the concentric texture of the olivine megacryst alteration and the degree of alteration seen in its plagioclase and olivine megacrysts. The shergottites are generally the least altered of martian meteorites, this may seem surprising given the shergottites are the largest family of martian meteorites, making up ~80%. However, they are the youngest subgroup having crystallisation ages largely between 150 - 596 Ma (Werner et al., 2014; Lapen et al., 2010) when the planet was extremely dry and much like today's Mars (Bibring et al., 2006). Two older shergottites have also been described recently; NWA 8159, 2.3 Ga (Herd et al., 2017) and NWA 7634, 2.4 Ga (Lapen et al., 2017). This makes identification and checking of any martian alteration assemblages in shergottites of significance for understanding the evolution of Mars' crust. However, the data surrounding secondary alteration in martian meteorites can be quite ambiguous, isolated mineralogical or isotopic data are insufficient to confirm an extraterrestrial origin. Only with the nakhlites and ALH 84001 can we be certain that the alteration is indeed martian, due to definitive textural relationships between the assemblages and fusion crust, or martian fractures respectively (Gooding et al., 1991; Treiman et al., 1993; Mittlefeldht, 1994; Hallis and Taylor, 2011; Hallis et al., 2012a; Hallis et al., 2014; and Velbel, 2016).

4.1. Plagioclase and Maskelynite Alteration

From our EPMA-WDS, TEM and µXRD results we have identified the secondary phase in both the plagioclase and maskelynite as a kaolinite clay mineral, a common product of low temperature alteration and weathering of feldspars on Earth. It is most likely kaolinite or halloysite based on µXRD analysis. Halloysite has a higher cation exchange capacity (~ 400 µeq/g as opposed to 10 - 100 µeq/g for kaolinite) which can better explain the major presence of Ca and P within the phase (Deer et al., 2013). The lack of *d*-spacing features found in TEM analysis and relatively noisy µXRD spectra indicate that this kaolinite-group phase is partially amorphous, suggesting a relatively quick formation. EPMA-WDS totals (indicating ~12 wt.% H_2O^+) (Table 1) show that the secondary phase affecting the plagioclase and maskelynite is not quite as hydrated as typical

kaolinite (~14 wt.% H_2O^+) or halloysite (~17 wt.% H_2O^+) (Deer et al., 2013). However, water content most likely varies within natural kaolinites. The lower water content inferred from EPMA totals, compared to those of natural kaolinite minerals can be explained by dehydration over a long exposure to a desert environment after the fluidic alteration had occurred. It is also possible that what we see is a mixture of secondary phases, possibly kaolinite and smectite clays, which could explain the unusual kaolinite-group cations, low H_2O^+ abundance and some unidentified diffraction peaks. TEM could potentially resolve this problem but due to the phases' predominantly amorphous nature, definitive analysis is a challenge.

4.2. Shock Olivine vs Altered Olivine

The distinctive concentric colouration seen within the olivine megacrysts: amber core, brown mantle zone and an encompassing rim of clear olivine, distinguishes NWA 10416 from other olivine-phyric shergottites. Many martian meteorites exhibit "brown olivine" (Treiman et al., 2007), particularly the shergottites. Although other SNC "brown olivine" is comparable in colour to some of what is seen in the NWA 10416 megacrysts, it is usually visible as patchy-homogenous areas of dark brown olivine and completely unlike the concentric pattern of NWA 10416.

Brown olivine in other martian meteorites is thought to form due to shock pressures, most likely caused by the extreme shock event needed to loft them off the surface of Mars (escape velocity of ~5 km s^{-1} (McSween and Treiman, 1998)). Treiman et al. (2007) suggested that the darkening was caused by Fe metal nanoparticles within the olivine, which form from olivine reduction (Fe^{2+} → Fe^0) during post shock heating. Van de Moortèle et al. (2007) and Bläß et al. (2010) suggested instead that the darkening was due to shock oxidation of olivine causing dislocations in the mineral lattice during the disproportionate reaction: $3Fe^{2+}_{olivine} \rightarrow Fe^0_{metal} + 2Fe^{3+}_{olivine} + V_{olivine}$ (where $V_{olivine}$ is a vacancy in olivine). Takenouchi et al. (2017) performed synchrotron radiation Fe-K XANES analysis on NWA 1950, a highly shocked (greater than 30 GPa) lherzolitic shergottite and found ferric contents of ~20% within brown olivine and an absence of a SiO$_2$-rich phase around iron metal nanoparticles. Their results supported the hypothesis of shock oxidation from Van de Moortèle et al. (2007) and Bläß et al. (2010) and suggested the higher the shock the greater the ferric content.

Work performed by Walton et al. (2016) indicates that NWA 10416's shock history is rather unique. It is not strongly shocked and together with NWA 8159, an augite-rich shergottite, is one of only two martian meteorites preserving crystalline plagioclase. Walton et al. (2016) suggested that NWA 10416 experienced a slightly higher but comparable shock pressure to NWA 8159 due to observations of isotropisation of feldspar in regions further from shock veins when compared to NWA 8159. NWA 8159 is reported to have experienced a shock pressure of ~16 GPa, based

on shock vein crystallization assemblages (Sharp et al., 2018). The value is consistent with the preservation of crystalline plagioclase in NWA 8159 (Fritz et al., 2005) and the prediction of 15 - 23 GPa (Herd et al., 2017), based on shock recovery experiments presented by Stöffler et al. (1986).

Our Fe-K XANES analysis of NWA 10416 relict olivine megacrysts (Figure 9; Table 2) show the pristine rims as essentially ferrous ($Fe^{3+}/\Sigma Fe$ = 0.02 to 0.04), the brown mantle zones to be predominantly ferric ($Fe^{3+}/\Sigma Fe$ = 0.61 to 0.92) and the amber cores having an intermediate ferric content ($Fe^{3+}/\Sigma Fe$ = 0.30 to 0.17). With a much lower hypothesised shock pressure but higher ferric content compared to many other shergottites, it is likely that the unique colouration and high ferric contents of NWA 10416 were not predominantly controlled by shock effects.

4.3. Olivine Alteration

Low EPMA-WDS totals (Table 1), partial replacement textures (Figure 4) and TEM analysis (Figures 6 and 7), all indicate aqueous alteration of igneous olivine. Replacement of olivine by a secondary phase is seen on multiple scales throughout our analyses. At the microscale we observe the partial replacement of olivine in thin section associated with MgO depletions and FeO enrichments (Figure 4). These areas show the incipient breakdown of igneous olivine to a secondary phase. At the nanoscale we observe relict crystalline olivine having been partially replaced by an amorphous phase with comparable compositional trends to what is seen at the microscale. HRTEM analysis shows a number of porous features in the brown mantle olivine: large voids, subparallel bands and larger crosscutting bands (Figure 6), all indicative of fluidic alteration. The linear features, both the 200 - 300 nm long sub-parallel features and the longer, up to 2 μm, linear features most likely represent past conduits for the fluid which grew during alteration. This is evident by the replacement of surrounding olivine by an amorphous phase. These features, given enough time would eventually manifest themselves as what is seen at the microscale (Figure 4).

Both micro and nanoscale partial replacement features correlate with the olivine's colouration. There is a higher abundance of these features in the brown olivine compared to the amber olivine, and none seen in the clear olivine rims, the same pattern that is seen with the hydration of the minerals. This is true for both SEM and TEM analyses. These trends, along with the previous results regarding ferric content and shocked olivine (Section 4.2), show that the distinctive, concentric pattern of colouration, is caused primarily by fluidic alteration.

Vaci et al. (2016 and 2017) performed μXRD and Raman spot analysis on the coloured, altered NWA 10416 olivine and suggested the presence of Mg-bearing laihunite in these areas. Laihunite is an opaque, oxidation product with the superstructure of olivine which can form either from

oxidation via hydrothermal alteration (Noguchi et al., 2009; Rost et al., 2006) or shock metamorphism (Tomioka et al., 2012; Blaß et al., 2010). A low-temperature (<150 °C) formation for laihunite has not previously been documented. The mineral has a general composition of $\nu_x Fe^{2+}_{2-3x}$ $Fe^{3+}_{2x} SiO_4$, where ν is the lattice vacancy (Kitamura et al., 1984; Shen et al., 1986). Just as shock effects can cause iron oxidation (Van de Moortèle et al., 2007; Bläß et al., 2010), described above, aqueous alteration at high oxygen fugacity (fO_2) conditions (i.e. more oxidising than the Fayalite-Magnetite-Quartz (FQM) buffer), and high temperature (400 - 800 °C), can also oxidise iron in olivine and destabilise its lattice (Tamada et al., 1983; Banfield et al., 1990 and Noguchi et al., 2009). Magnetite, hematite and amorphous silica are common products associated with this laihunite formation mechanism (Champness, 1970; Kondoh et al., 1985; Tomioka et al., 2012 and Martin et al., 2015).

Four laihunite-polytypes, which each have different ferric/ferrous ratios and structures, have been identified lying on a compositional spectrum between the two end-members fayalite and the theoretical ferrifayalite ($\nu_{2.0} Fe^{3+}_{4.0} (SiO_4)_3$). In increasing Fe^{3+}/Fe_{tot} they are; laihunite-2M, $\nu_{0.5}$ $Fe^{2+}_{2.5} Fe^{3+}_{1.0} (SiO_4)_2$ (Xu et al., 2014); laihunite-3Or, $\nu_{1.0} Fe^{2+}_{3.0} Fe^{3+}_{2.0} (SiO_4)_3$ (Xu et al., 2014); laihunite-3M, $\nu_{0.8} Fe^{2+}_{1.6} Fe^{3+}_{1.6} (SiO_4)_2$ (Shen et al., 1986) and laihunite-1M, $\nu_{0.5} Fe^{2+}_{0.5} Fe^{3+}_{1.0} (SiO_4)_2$ (Xu et al., 2014). From EPMA-WDS data (Table 1), we have recalculated the stoichiometries of NWA 10416 relict megacryst olivine to find; groundmass olivine, $(Mg^{2+}_{1.0} Fe^{2+}_{1.0}) SiO_4$; clear olivine, $(Mg^{2+}_{1.0} Fe^{2+}_{1.0}) SiO_4$; brown altered olivine, $(\nu_{0.34} Mg^{2+}_{0.95} Fe^{2+}_{0.16} Fe^{3+}_{0.55}) \nu_{0.13} Si_{0.87} O_4$; and amber altered olivine, $(\nu_{0.19} Mg^{2+}_{1.24} Fe^{2+}_{0.45} Fe^{3+}_{0.12}) \nu_{0.05} Si_{0.95} O_4$.

TEM analysis of reported terrestrial and martian laihunite all have a structure comprised of subparallel bands and precipitates oriented parallel to (001) (Kondoh et al., 1985; Noguchi et al., 2009; Bläß et al., 2010; Xu et al., 2014; Ejima et al., 2015 and Martin et al., 2015), and the presence of metal oxides and/or nano particles (Xu et al., 2014; Martin et al., 2015; Kondoh et al., 1985). Noguchi et al. (2009) detailed an analysis of laihunite alteration of a large olivine grain in the nakhlite Y-000593 and reported that when viewed with TEM it was composed of abundant subparallel bands, with "nano-tunnels" filled with a poorly crystalline material separating them.

Although at the TEM scale, NWA 10416 olivine bears some similar characteristics to previously reported laihunite (amorphous material, subparallel bands and "nano-tunnels"), they are not solely explained by laihunite formation and large differences remain, notably the lack of predicted oxides, magnetite and/or hematite. Kondoh et al. (1985) reports that a large change in stacking sequence of the closely packed oxygen layers is needed for the decomposition of fayalite into magnetite and silica, which probably wouldn't occur at low temperatures. Other differences, such as our large WDS MgO contents compared to other reported laihunite and the presence of silicon as well as cation vacancies all suggest that the coloured, ferric altered olivine phases observed are not stoichiometric laihunite. From the lack of oxides alone, it is likely that

neither shock effects nor high temperature aqueous alteration are responsible for the NWA 10416 olivine alteration. Laihunite is not well constrained in terms of formation temperature, making it difficult for us to estimate in a quantitative way, while the presence of kaolinite may give stronger constraints.

Due to the amorphous nature and mineral recalculation of the secondary phase affecting the olivine megacrysts, it is a challenge to give a definite identification of this phase. However, from amber to brown zones, the phases likely represent increasing stages of alteration to a low-temperature oxidation product of forsteritic olivine that shares some similarities to laihunite but a different formation mechanism. In places within NWA 10416, crystalline smectite has also formed, as seen in the shock vein olivine (see Section 4.4).

4.4. Evidence for a Terrestrial Origin of Secondary Minerals

Our main experiment to test the origin of alteration in NWA 10416 was TEM analysis of the olivine grain embedded within a shock-melt vein in order to answer whether the alteration affecting the meteorite's olivine occurred before or after the shock event that formed the shock-melt vein. The shock-melt vein in question is the one that lies in between the displaced olivine megacryst (Figures 2 and 5). The responsible shock event was probably the event that ejected the rock from Mars. If shock features (dislocations, metal nanoparticles, planar fractures, etc.) overprinted the clay then we could assume that they occurred after the alteration of olivine. No such features were found, however curved 9.5 Å d_{001}-spacings were found interspersed throughout the grain, indicating a phyllosilicate mineral with a flexible crystal lattice due to interlayer water molecules. This strongly indicates that the clay material formed after the shock event, and therefore in a terrestrial environment. A d_{001}-spacing of this value is most likely a collapsed (i.e. dehydrated) smectite. Saponite typically has a d_{001}-spacing of 10 - 15 Å which is dependent on the phases water content, however, it has been measured as low as 9.6 Å (Deer et al., 2013) and 9.7 Å (Hicks et al., 2014) in a dehydrated state.

The maskelynite within the meteorite is observed adjacent to shock-melt veins and fractures with some of the grains bearing EDS measurements representative of the secondary Ca-rich kaolinite phase, correlating with the cross-polarised light images of maskelynite. Since the maskelynite is almost certainly a result of the large shock event that lofted the parent rock off Mars, any alteration of this mineral is presumed to be terrestrial.

Bouvier et al. (2017), Herd et al. (2016) and Ziegler et al. (2016) reported oxygen isotopic analyses on the three distinctive colourations of the olivine megacrysts. They measured the altered amber core at ($\delta^{18}O$ = 13.417, 12.623‰, and $\Delta^{17}O$ = 0.026, -0.019‰), the brown mantle zone at ($\delta^{18}O$ = 8.553, 9.596‰ and $\Delta^{17}O$ = 0.102, 0.113‰) and the clear rim at ($\delta^{18}O$ = 4.937‰, $\Delta^{17}O$ = 0.253‰). These results show that the altered

coloured olivine's have a definite terrestrial component, strongly suggesting post-shock fluidic alteration of a terrestrial origin. Our results (Table 3) do not show the same extreme change in $\Delta^{17}O$ between the bulk and altered materials; perhaps some parts of the meteorite are more altered than others. The amber olivine has a slight shift towards the terrestrial fractionation line (TFL) compared to the bulk material but still lies close to the martian fractionation line (MFL). However, these slight shifts greater than the instrumental error, can only be explained by mixing with another oxygen reservoir, which in the context of this meteorite must be dissolution by and incorporation of terrestrial water. Furthermore, as martian hydrous fluids would be expected to have positive $\Delta^{17}O$ relative to the MFL (Karlsson et al., 1992) a martian origin for the fluids is not supported.

Extensive calcite veining, which is common in terrestrially weathered NWA meteorites, along with extensive olivine megacryst, plagioclase and maskelynite alteration indicates a significant residence time in Northwest Africa. The meteorites lack of a fusion crust also likely contributed to the extent of alteration. Although some studies have been able to estimate residence time based on the textures and extent of the alteration, these are not that common and are based on weathering patterns seen in discrete localities (e.g. Wlotzka et al. (1995) defined a five-step scale for meteorites found in Roosevelt County, New Mexico). The 'uniqueness' of NWA 10416's alteration and a lack of NWA residence time studies makes this texture-based estimate of residence time a challenge. Cosmogenic radionuclide decay measurements of ^{14}C and ^{36}Cl will be needed for a quantitative estimate of the residence time, particularly ^{14}C measurements for analysis of stony meteorites (Jull, 2001).

Further useful analysis, in order to constrain the origin of the alteration seen in NWA 10416 would be hydrogen isotope analysis. A large range of Deuterium/Hydrogen (D/H) has been measured in martian meteorites (δD = -111‰ - +6034‰; Usui et al., 2015; Boctor et al., 2003; Greenwood et al., 2008; Hallis et al., 2012a; Hu et al., 2014 and Usui et al., 2012) compared to the δD values for terrestrial water (δD = -350‰ - +50‰; Hoefs, 2009). The large range for Mars is generally thought to originate from two water reservoirs with distinctive D/H ratios; the martian mantle ($\delta D \sim$ -100‰; Filiberto et al., 2016; Chen et al., 2015 and Hallis et al., 2012b) and the martian atmosphere (δD = 4000‰ - 6000‰; Filiberto et al., 2016; Owen et al., 1988 and Webster et al., 2013). Intermediate D/H values between these two reservoirs are currently assumed to be mixing between the mantle and surficial water (representing the atmospheric reservoir). The loss of Mars' magnetic field and subsequent bombardment by solar wind is likely the reason for Mars' high D concentration in the atmosphere. Measurements of a low δD value for the alteration phases would be useful in providing further evidence towards a terrestrial origin, as it has been in other studies (Bucholz et al., 2013; Chen et al., 2011; Gaetani et al., 2012; Usui et al., 2015 and Hallis et al., 2012a).

4.5. Fluid Constraints

Many factors of the fluid and host olivine can affect the reactivity of olivine; eH, pH, dissolved carbonate (Pokrovsky and Schott, 2000; Wogelius and Walther, 1991), ionic strength, fayalite/forsterite ratio (Westrich et al., 1993), temperature (Oelkers, 2001; Rosso and Rimstidt, 2000), grain size and water activity (Olsen and Rimstidt, 2007). Hausrath and Brantley, (2010) carried out a series of investigations in which forsterite, fayalite and a basaltic glass were dissolved in a $CaCl_2$ and NaCl-bearing low temperature brine under a range of conditions; varying temperature, ionic strength, pH and oxidation. These experiments and others (Wogelius and Walther, 1992) showed that Fe-rich olivine dissolves more rapidly than Mg-rich olivine in anoxic conditions, conditions that would be more characteristically martian. There has not been a great deal of research on olivine reactivity under oxidising conditions and there is also a noted discrepancy between dissolution rates tested in the laboratory and those observed in the field that is unexplained (Velbel, 1986, 1993; White and Brantley, 2003). These studies compare silicate weathering rates from laboratory experiments with those calculated from natural watershed geochemical mass balances. They suggest that olivine reactivities measured in the laboratory might be as much as 2-4 orders of magnitude faster than those in the field (Schnoor, 1990; Brantley, 1992). These studies stated many possible reasons for this; temperature, effects on reactive surface areas, chemical affinity and energetically reactive sites.

If these uncertainties allow Mg-rich olivine to be more reactive than Fe-rich olivine in oxidising conditions when subjected to a low-temperature fluid, then it could explain why the Mg-rich olivine cores in NWA 10416 were preferentially replaced by a secondary phase. Our Fe K XANES analysis shows a definite ferric enrichment across the relict olivine megacrysts consistent with an oxidising environment.

Many studies have been carried out on feldspar dissolution over a range of conditions, but by far the most studied area is of albite end-member dissolution from acidic to alkaline conditions (Blum and Stillings, 1995; Brantley, 2003, 2008; Ganor et al., 2009). Gudbrandsson et al. (2014) carried out experiments to investigate the dissolution of plagioclase feldspars (An% = 1.6 - 88.8) from acidic to alkaline conditions at ambient temperature. They found that the dissolution rate increased in both acidic and alkaline conditions compared to neutral ones. Their results disagree with those of Amrhein and Suarez, (1992) who found that the dissolution rate, whilst being higher at acidic levels, continued to decrease through neutral conditions and into alkaline ones. Another finding of Gudbrandsson et al. (2014) was that at acidic conditions (pH $\leq$ 4) anorthite content plays a large part in the dissolution kinetics of the reaction. At pH $\sim$ 4 An-rich plagioclase dissolves approximately an order of magnitude faster than Ab-rich plagioclase. This was increased to two and a half orders of magnitude faster at pH $\sim$ 2. Blum and Lasaga, (1988) suggested that the dissolution mechanism of plagioclase changes around An% $\sim$ 70 due to an increased aluminium content within the tetrahedral lattice. At this An concentration it becomes possible to break the lattice without disturbing Si-O bonds (Blum and Lasaga, 1988; Oelkers and

Schott, 1995). Along with pH and An content at low pH, temperature is the factor that affects dissolution the most. Higher temperatures promote faster dissolution, however, low temperature dissolution experiments (down to 5 °C) of plagioclase have been performed successfully (Chen and Brantley, 1997; Welch and Ullman, 2000). Many studies (Neuhoff et al., 2000; Fridriksson et al., 2001; Neuhoff and Ruhl, 2006; and Arnorsson and Neuhoff, 2007) have shown that the dissolution mechanism and primary material composition controls the cations released in a reaction and therefore the formation of secondary phases. Since dissolution rates increase for An-rich plagioclase at acidic conditions, when these conditions are met Ca-rich secondary phases are expected.

Kaolinite has been shown in laboratory experiments to form at low temperatures (DeKimpe et al., 1964; Kittrick, 1970; Linares and Huertas, 1971) and the alteration from plagioclase to kaolinite is well documented (Jeong, 1998a, b; Papoulis et al., 2004; Inoue et al., 2012). Kaolinite formation is however, greatly affected by factors other than temperature (Borchardt, 1989; Wilson, 1999). Borchardt, (1989) found that fluids in acid conditions, with a moderate silica and alumina activity and the required base cations favoured the precipitation of kaolinite over a range of temperatures. This indicates that a high water/rock ratio is favourable in order to supply abundant fluid for the transportation of silica and alumina (Wilson, 1999). The significance of high water/rock ratios has also been documented by Huang et al., (1986), for this reason kaolinite is generally found in climates with more water in well-drained, porous soils (Borchardt, 1989).

Assuming that both the olivine and plagioclase alteration occurred in the same fluidic event in NWA 10416 and on Earth, it is more probable that a low temperature fluid affected the meteorite during its time in northwest Africa. This is supported by the positive identification of kaolinite, a common low temperature product of plagioclase alteration, as well as the lack of products often associated with increasing temperatures (hematite and magnetite) in the megacryst secondary phases. The low temperature fluid was most likely acidic, therefore promoting the high degree of alteration in the An-rich plagioclase and maskelynite. An acidic fluid also helps to explain the abundant ferric content in the unidentified olivine alteration phase, iron is easily oxidised in acidic conditions due to the presence of H^+ ions.

5.   CONCLUSIONS

A thin section of the olivine-phyric, highly depleted shergottite NWA 10416 has area fractions of ~8% olivine megacrysts, ~4% groundmass olivine, ~65% clinopyroxene, ~19% plagioclase feldspar, ~2% maskelynite and ~2%: minor minerals (Ti-bearing magnetite, ilmenite, Ti-bearing chromite, pyrite, apatite). Large amounts of the meteorite's igneous phases show evidence of aqueous alteration which is uncommon for the

shergottite group. Around 40% of the labradorite plagioclase grains have been replaced by a secondary phase and from EPMA-WDS, TEM and μXRD analysis, we have identified this phase as a partially amorphous, dehydrated kaolinite group mineral with significant CaO content.

NWA 10416's alteration and distinctive concentric colouration pattern in the relict olivine megacrysts is unique to the shergottites. The colour resembles 'brown olivine' seen in many martian meteorites. However, no others show the concentric pattern from amber to brown to clear that NWA 10416 does. EPMA-WDS totals and synchrotron Fe-K XANES analyses reveal a link between the hydration and ferric content associated with these zones. The darkest material, the brown mantle zones, display the highest degree of hydration and ferric content (up to $Fe^{3+}/\sum Fe$ = 91%), followed by the amber cores (up to $Fe^{3+}/\sum Fe$ = 30%) and finally the clear unaltered rims which show no hydration and up to only 4% $Fe^{3+}/\sum Fe$. The ferric content observed in the brown mantle zones is much greater than ferric contents recorded from shock browning alone, which is approximately ~20% (Takenouchi et al., 2017), leading us to conclude that the concentric pattern is primarily due to fluidic alteration, rather than shock processes. The relict megacrysts have cation deficiencies with some similarities to laihunite. However, the presence of amorphous regions at TEM scale (~70%, the remaining 30% being areas of crystalline relict olivine) and lack of clear laihunite stoichiometry argue against this as an accurate classification.

Oxygen isotope analyses show a slight terrestrial component within the altered cores of the olivine, consistent with a terrestrial origin for the alteration. However, TEM analyses of the shocked olivine from a shock-melt vein reveal clay d_{001}-spacings overprinting shock features within a shear zone of olivine, indicating secondary phase formation post shock. A shock event that can create such prominent shock-melt veins is presumed to be the event that lofted the rock off Mars, strongly suggesting a terrestrial formation for the secondary phases. This terrestrial alteration is also consistent with the alteration of the maskelynite phases.

We suggest that the fluid responsible for the alteration of NWA 10416's olivine, plagioclase and maskelynite was a terrestrial fluid, and a possible model in which the parent rock underwent igneous zonation as it cooled, creating the olivine's Mg-rich cores. Martian shock effects caused fracturing of the compositionally zoned olivine's and possibly some degree of browning (accompanied by an increase in ferric content). During its time in Northwest Africa, low-temperature, possibly acidic, groundwater exploited fractures and altered the olivine megacrysts in a way that was controlled by the pre-existing, igneous compositional zonation (i.e. preferentially Mg-rich olivine). This event created the colouration, reaction textures and oxidation zones across the megacrysts. After the alteration event, NWA 10416 probably had a long residence time in Northwest Africa before being found, accounting for terrestrial calcite veins crosscutting many phases and the dehydration of the clay phases.

6.   ACKNOWLEDGEMENTS

7.   REFERENCES

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Table Captions

Table 1 – EPMA-WDS (1-8) and normalised TEM-EDS (9) compositions of major silicates in NWA 10416. The groundmass olivine (1) and clear olivine rim (2) compositions are stoichiometric, however, the coloured olivine zones (3 and 4) are not - their v_{cation} and v_{anion} site vacancies, compared to stoichiometric olivine, are shown. Pyroxenes (5-6) and labradorite (7) are stoichiometric, and feldspar alteration (8), when based on 18 O, gives a good match to kaolinite. Although the phase's hydration and ferric content are unknown, the shock-melt olivine clay composition, when recalculated based on 22 O, is comparable to saponite and vermiculite. *A relatively large P_2O_5 values suggests we hit a small phosphate grain during analysis, for this reason the composition was renormalized without P and a proportion (3/5) of Ca before mineral recalculation. Detailed Fe^{3+} contents (1-4) based on Fe-K XANES analyses and calibration (Table 2 and Figure 9). Al^{IV} and Al^{VI} refer to tetrahedrally and octahedrally coordinated Al.

Table 2 – Fe-K XANES position (1s → 3d), absorption edge energies, and calculated $Fe^{3+}/\Sigma Fe$ ratios (Hicks et al., 2014) (Figure 9) of the different coloured regimes within the olivine megacrysts. Spectra from points shown in Figure 9 are labelled as such. Note: unlabelled points were taken during a separate experiment at Diamond Light Source and thus a correction for the energy shift between experiments has been applied.

Table 3 - Oxygen isotope analyses of bulk matrix material and amber megacryst material from NWA 10416.

Figure Captions

Figure 1 – Our 2.1 g bulk sample of NWA 10416 displaying coloured relict olivine megacrysts set in a groundmass of green clinopyroxene and white plagioclase. Dark shock-melt veins are present, shown by white arrows in both examples.

Figure 2 - Polarised light (a) and Back Scatter Electron (BSE) (b) image comparison of a fractured relict olivine megacryst in NWA 10416. The shock-melt vein (arrowed) runs between the two halves of this olivine grain and the boxed area is shown in more detail in figure 5. The megacryst grain boundary is drawn as a yellow line in the polarised light image, making it easier to see the extent of the clear rims and the protrusion to the grains top-left. The brown mantle - clear rim boundary is drawn as white line on BSE image. Minerals labelled: olivine (ol), pyroxene (Pyx), plagioclase (Plg) and maskelynite (Msk).

Figure 3 – Pyroxene quadrilateral showing combined compositional fields of NWA 7320 (Udry et al., 2017), NWA 5298 (Hui et al., 2011), Los Angeles (Warren et al., 2004), NWA 480 (Barrat et al., 2002) and Queen Alexandra Range (QUE) 9420 (McSween et al., 1996). NWA 10416 pyroxene data (N = 106), is overlaid. NWA 10416 Mg# data for groundmass olivine's and megacryst cores, mantles and rims is shown below.

Figure 4 – BSE image of microscale alteration features seen within the altered cores (both amber and brown zones) of the megacrysts, this site is indicated in figure 9. Arrow shows the pyroxene inclusions with a Cr-Fe oxide symplectic intergrowth referred to in section 3.1.1.

Figure 5 – BSE image of shock-melt vein within NWA 10416, it shows relict grains of pyroxene, olivine and a Ti-chromite. The site is from the same shock-melt vein highlighted in figure 3. The TEM wafer shown in figure 7, shown by the rectangle, was extracted from the olivine grain labelled in this image.

Figure 6 – HRTEM bright field images of the brown mantle olivine at varying magnifications. (a) ×20k, shows the widespread porous texture of the olivine, the small subparallel bands can be seen interspersed between the relict crystalline olivine, a longer channel can also be seen crosscutting the direction of the subparallel bands. (b) ×25k, highly porous area showing several void spaces. (c) ×50k, higher magnification view of the subparrallel band structures. The brighter areas of contrast indicate where there is either less material or a less dense phase, it is these areas that appear amorphous under higher magnifications. (d) ×100k higher magnification view of the amorphous components, on the left shows the degree of amorphisation surrounding some of the sub-parrallel bands whereas on the right of the image we see a more patchy amorphisation. These structures can also be seen in (c). Amorphous material makes up roughly 70% of the entire wafer.

Figure 7 – HRTEM image (×150k magnification) of alteration features seen in the TEM wafer of the shock-melt olivine grain labelled in figure 5. Curved d-spacing's, measured on average as 0.952 nm (9.52 Å), indicate the presence of phyllosilicates. Of the entire grain sampled in the TEM wafer, visible d-spacing's made up ~5-10%.

Figure 8 – TEM analysis of NWA 10416's kaolinite replacement of labradorite plagioclase. (a) STEM dark field image of a section of the wafer, relict unaltered plagioclase is present between alteration pathways. (b) HRTEM image displaying crystallinity of the labradorite and amorphous kaolinite. (c) CaO and (d) Na_2O STEM EDS X-ray maps of the area, the results indicate a depletion of the major cations, Na_2O and CaO in the kaolinite compared to the surrounding host labradorite.

Figure 9 – Fe-K XANES spectra highlighting the pre-edge features of measurements taken at sites A (Clear Rim), B (Altered Brown Mantle), C (Altered Amber Core), D (Altered Brown Mantle) and E (Clear Rim) on the altered olivine megacryst shown. The box is the location of the alteration features shown in figure 4 and the line indicates the olivine grain boundary. Table 2 displays the corresponding data.

Figure 10 – Oxygen isotope composition of bulk material and megacryst amber-coloured olivine materials from NWA 10416 shown in relation to a range of laser fluorination analysis of martian rocks from the literature (Franchi et al. (1999) and Meteoritical Bulletin Database oxygen isotope analyses for Tissint, DaG 478, DaG 670, Juddat al Harasis (JaH) 479, LAR 06319, NWA 1669, NWA 2737, NWA 4222, NWA 5718, NWA 5790, NWA 6162, NWA 7032, NWA 7042, SaU 094, Y-000027, Y-000047, Y-000097). The Martian Fractionation Line (MFL) is the mean $\Delta^{17}O$ of all the samples plotted in figure 10 with the exception of NWA 10416 and has a value of 0.307. The Terrestrial Fractionation Line (TFL) is the mean $\Delta^{17}O$ of a collection of terrestrial rocks analysed (Franchi et al., 1999). Table 3 displays the corresponding data.

	Groundmass Olivine (1)	Megacryst Clear Rim (2)	Megacryst Brown Mantle (3)	Megacryst Amber Core (4)	Pyroxene Pigeonite Core (5)	Pyroxene Augite Rim (6)	Labradorite (7)	Kaolinite (8)	Shock-melt Olivine Alteration (9)
SiO_2	35.3	34.9	34.2	36.9	55.6	51.7	52.3	44.6	31.7
TiO_2	0.01	0.02	-	0.02	0.07	0.3	0.04	0.04	1.01
Al_2O_3	0.02	0.07	0.90	0.48	0.60	1.57	29.7	35.3	18.9
Cr_2O_3	0.05	0.03	0.09	0.11	0.79	0.74	-	0.03	0.59
Fe_2O_3	-	-	25.8	6.45	-	-	-	-	-
FeO	41.3	43.0	8.14	21.0	13.1	14.8	0.5	0.83	41.3
MgO	23.1	21.4	24.9	32.4	28.3	15.1	0.13	0.50	1.04
CaO	0.30	0.31	0.38	0.29	1.47	14.8	13.4	4.83	2.82*
Na_2O	-	0.07	-	0.04	0.03	0.16	3.84	0.01	-
K_2O	-	-	-	-	-	-	0.04	0.42	0.15
P_2O_5	-	0.05	0.19	0.14	0.01	-	0.06	1.37	2.49*
H_2O^+	-	-	**5.40**	**2.17**	-	-	-	**12.07**	-
Total	100.08	99.85	100.00	100.00	99.97	99.17	100.01	100.00	100.00

Number of ions based on 4 O (1-4), 6 O (5-6), 32 O (7), 18 O, OH (8) and 22 O (9)

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Si	1.009	1.009	0.873	0.947	1.985 ⎱ 2.01	1.958 ⎱ 1.98	9.506 ⎱ 15.87
Al	0.001	0.002	0.027	0.015	0.025	0.022	6.367
Ti	-	-	-	-	0.002	0.070	0.006
Cr	0.001	0.001	0.002	0.002	0.022	0.009	-
Fe^{3+}	-	-	0.156	0.125	-	-	-
Fe^{2+}	0.986	1.041	0.550	0.451	0.392	0.469	0.076
Mg	0.983 ⎱ 1.98	0.922 ⎱ 1.98	0.947	1.241	1.505 ⎱ 1.98	0.852 ⎱ 2.01	0.035 ⎱ 4.09
Ca	0.009	0.010	0.010	0.008	0.056	0.602	2.611
Na	-	0.004	-	0.002	0.002	0.012	1.352
K	-	-	-	-	-	-	0.009
P	-	0.001	0.004	0.003	-	-	0.004
OH	-	-	0.919	0.372	-	-	-
v_{cation}	-	-	0.34	0.19			
v_{anion}	-	-	0.13	0.05			

Kaolinite (8)

Si	3.977	⎱ 4.00
Al^{IV}	0.023	
Al^{VI}	3.694	⎱ 3.83
Ti	0.003	
Cr	0.002	
Fe^{2+}	0.062	
Mg	0.067	
Ca	0.462	⎱ 0.61
Na	0.002	
K	0.048	
P	0.104	

Shock-melt Olivine Alteration (9)

Si	4.16	⎱ 8.00
Al^{IV}	3.84	
Al^{VI}	1.12	⎱ 6.00
Ti	0.13	
Cr	0.15	
Fe^{2+}	4.60	
Fe^{2+}	0.82	⎱ 1.15
Mg	0.14	
Ca	0.15	
K	0.04	
P	-*	

	(1)	(2)		(3)	(4)		(5)	(6)		(7)
Fo	50	47	Mg#$_{Fe,tot}$	57.3	68.3	En	77	44	Ab	34
Fa	50	53				Fs	20	25	An	66
						Wo	3	31	Or	0

Table 1

Analysed Points	XANES 1s → 3d Position (±0.05 eV)	Absorption Edge Position (±0.05 eV)	Fe³⁺/ΣFe (±0.03)
Megacryst	7112.37	7118.86	0.04
Clear Rim	7112.35 *(A)*	7118.85 *(A)*	0.03
	7112.33 *(E)*	7118.80 *(E)*	0.02
MEAN	**7112.35**	**7118.84**	**0.03**
Megacryst	7113.49	7121.01	0.76
Brown Mantle	7113.25 *(B)*	7119.90 *(B)*	0.61
	7113.74 *(D)*	7121.15 *(D)*	0.92
MEAN	**7113.49**	**7120.69**	**0.76**
Megacryst	7112.77	7119.51	0.30
Amber Core	7112.56 *(C)*	7119.25 *(C)*	0.17
MEAN	**7112.67**	**7119.38**	**0.24**

Table 2

Sample	$\delta^{17}O$‰	2σ	$\delta^{18}O$‰	2σ	$\Delta^{17}O$‰	2σ
Amber Megacryst Material	2.72		4.71		0.272	
Amber Megacryst Material	2.63		4.55		0.271	
MEAN	**2.68**	**0.13**	**4.63**	**0.24**	**0.271**	**0.002**
Bulk Material	2.99		5.16		0.306	
Bulk Material	2.97		5.10		0.312	
MEAN	**2.98**	**0.04**	**5.13**	**0.09**	**0.309**	**0.009**

Table 3

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: