Critically testing olivine-hosted putative Martian biosignatures in the Yamato 000593 meteorite - geobiological implications

Abstract:

On rocky planets such as Earth and Mars the serpentinization of olivine in ultramafic crust produces hydrogen that can act as a potential energy source for life. Direct evidence of fluid-rock interaction on Mars comes from iddingsite alteration veins found in Martian meteorites. In the Yamato 000593 meteorite putative biosignatures have been reported from altered olivines in the form of microtextures and associated organic material that have been compared to tubular bioalteration textures found in terrestrial sub-seafloor volcanic rocks. Here we use a suite of correlative, high-sensitivity, in-situ chemical and morphological analyses to characterize and re-evaluate these microalteration textures in Yamato 000593, a clinopyroxenite from the shallow sub-surface of Mars. We show that the altered olivine crystals have angular and micro-brecciated margins and are also highly strained due to impact induced fracturing. The shape of the olivine microalteration textures is in no way comparable to microtunnels of inferred biological origin found in terrestrial volcanic glasses and dunites, and rather we argue that the Yamato 000593 microtextures are abiotic in origin. Vein filling iddingsite extends into the olivine microalteration textures and contains amorphous organic carbon occurring as bands and sub-spherical concentrations <300 nm across. We propose that a Martian impact event produced the micro-brecciated olivine crystal margins that reacted with subsurface hydrothermal fluids to form iddingsite containing organic carbon derived from abiotic sources. These new data have implications for how we might seek potential biosignatures in ultramafic rocks and impact craters on both Mars and Earth.

Key words: biosignatures, serpentinization, impact events, hydrothermal-synthesis, organic carbon.

1. Introduction:

Ultramafic rocks containing olivine and pyroxenes are a major component of the lithosphere of early terrestrial planets and are altered in the presence of water to produce serpentine minerals (Muntener 2010). Hydrogen is released during serpentinization and is widely thought to be critical for the emergence of life, because it acts as an energy source for metabolism (e.g. Kelley et al. 2005; Russell, 2007). The subsurface of Mars has been postulated to provide a sizeable potential habitat for life supported by the interaction of liquid water with the mafic crust (Fisk and Giovannoni 1999, Schulte et al. 2006) and numerous candidate biosignatures have been suggested in these environments (e.g. Grosch et al. 2014). Rover missions and remote sensing surveys have documented abundant evidence for liquid water in near surface environments on Mars (Mustard 2008; Bishop et al. 2008; Squyres et al. 2012) and identified evidence for aqueous alteration of the crust, for example, in hydrothermal systems associated with impact craters (Ehlmann et al. 2011), and groundwater upwelling zones (Michalski et al. 2013). Direct evidence of the low-temperature aqueous alteration of the martian subsurface is found in the Nakhla group of meteorites that contain hydrous minerals such as carbonates, clays, opal-A and iron oxides, collectively referred to as iddingsite (Changela and Bridges 2011; Bridges and Schwenzer 2012; Lee et al. 2015). Evidence for life in the form of textural and chemical biosignatures in these meteorites is much more tentative, with putative reports coming from Nakhla (Fisk et al. 2006), Yamato 000593 (White et al. 2014) and Tissint (Lin et al. 2014) - although none of these have been widely accepted. Here we will further investigate the evidence found in Yamato 000593.

The alteration of terrestrial seafloor volcanic glass and ultramafic dunites has been explored as an analogue for identifying potential microbial alteration of the martain crust by several workers (e.g. Fisk et al. 2006; Grosch et al. 2014; McLoughlin and Grosch 2015; Turke et al. 2015). A study by Fisk et al. (2006) was the first to tentatively propose evidence of possible bioerosion in olivines of the Nakhla meteorite, in which they reported micron sized tunnels emanating from iddingsite filled fractures in the olivine (fig. 4 of Fisk et al. 2006), although these authors emphasize that a biogenic origin has not been conclusively demonstrated for either the terrestrial or martian microtunnels. More recently a study by White et al. (2014) reported putative indigenous organics in the meteorite Yamato 000593, comprising small spheres of carbon less than 500 nm across embedded in the iddingsite, which were tentatively suggested to be microbial in origin. The study also described microtextures at the interface between the olivine crystals and iddingsite alteration that were described as microtubular in shape and compared to microtunnels of inferred microbial origin found in terrestrial seafloor volcanic glasses. Here we will investigate these microtextures and associated organics at higher magnification and evaluate the biogenicity of these candidate martian biosignatures.

In this study we investigate the meteorite Yamato 000593 (henceforth Y000593) which is the largest fragment at 13.7 kg of a meteorite fall found near the Yamato Mountains in Antarctica that also includes the Yamato 000749 (1.28 kg) and Yamato 000802 (0.022 kg) meteorites. On the basis of mineralogical studies and noble gas analysis Y000593 has been classified as belonging to the Nakhlite subgroup of martian meteorites and is believed to be derived from a sill like body that formed <100m beneath the Martian surface (Mikouchi et al. 2003). Y000593 is a cumulate igneous rock termed a clinopyroxenite containing c. 80% coarse grained augite, c. 10% coarse grained olivine and c. 10% mesostasis (fine-grained interstitial material comprising plagioclase, pyrrhotite, apatite, fayalite, tridymite and magnetite). The meteorite contains a single generation of fractures cross cutting the igneous grains that are filled with iddingsite alteration, which are estimated to occupy 4% volume of the olivines (Changela and Bridges 2010) and give a brownish appearance to the olivines. Y000593 has a surface that is c. 60% covered by a black fusion crust formed during atmospheric entry that is observed to both truncate the veins of iddingsite alteration, and in some instances also melts these veins near the fusion crust (Treiman and Goodrich 2002). Based on these observations it has been argued that the iddingsite alteration formed prior to atmospheric entry and is pre-terrestrial in origin (Treiman and Goodrich 2002, White et al. 2014). Radiometric dating has found that Y000593 has an Amazonian crystallization age of 1310 ± 30 million years (Shih et al. 2002) and that the fracture filling iddingsite alteration yields Rb-Sr ages of 633 ± 23 Ma interpreted as the age of aqueous alteration on Mars (Borg and Drake 2005). Several studies of the composition and distribution of the aqueous alteration phases in the Nakhlites have argued for an origin from ephemeral subsurface hydrothermal alteration in impact craters on Mars (Changela and Bridges 2011; Bridges and Schwenzer 2012; Lee et al. 2015). Subsequently, Yamato and the co-magmatic Nakhlite meteorites were ejected from Mars by a large impact event that is estimated to have occurred c. 11 million years ago (Eugster et al. 2002).

Here we use focused ion beam (FIB) milling combined with transmission electron microscopy (TEM) enabling us to document at high-magnification the altered olivine crystals and associated alteration products in Y000593. In particular, we aim to document the morphology of the interface between the olivine and alteration products and to see if there is a progressive alteration front in the olivine crystals, thereby exploring the mechanism of olivine dissolution and alteration. In addition, we use a suite of high spatial resolution and high sensitivity spectroscopic techniques [TEM-EDS; electron energy loss spectroscopy (EELS); and nano-scale secondary ion mass spectrometry (NanoSIMS)] to characterize the distribution and ultrastructure of the organic carbon. We will use correlated C, N and Cl mapping to document if there is more than one generation of organic carbon, and to test for potential contamination derived from terrestrial sources, including sample preparation. TEM-EELS data will also allow us to characterize the bonding environment of the organic carbon and attached functional groups, to document for example, whether the carbon comprises crystalline graphite, or amorphous carbon and therefore explore possible sources for the organics. Our combined data will further test the origins of the olivine microalteration textures in Y000593, the source of the organic carbon, and whether either is relevant to seeking potential biosignatures on Mars.

2. Material and Methods:

2.1 Petrography and Scanning Electron Microscopy (SEM)

The Yamato meteorite sample was studied in a standard polished petrographic thin section (30µm thick) and as a polished chip using light microscopy and SEM to identify areas of interest (Fig. 1). This material is on loan from the Japanese polar institute. Optical images were obtained using a Nikon LV100Pol polarizing microscope and photographed using a DS-Fi1 color camera with 5.24-megapixel resolution coupled to NIS-Elements BR 2.30 software. A Zeiss Supra 55VP SEM at the University of Bergen, Norway was used to investigate the Ir coated samples in secondary electron (SE) and backscatter electron (BSE) mode. Elemental analysis was conducted using an attached Thermo Noran Six EDS system to obtain element spot analyses and qualitative maps of the elements of interest.

2.2 Focused Ion Beam (FIB) preparation and Transmission Electron Microscopy (TEM)

Ultra-thin lamellas for TEM analysis were prepared by FIB milling, using a dual-beam FEI Helios Nanolab 600. Electron beam imaging was used to identify target areas in the polished thin section, allowing site-specific TEM samples to be prepared. Two protection layers were always deposited on the sample surface prior to cutting out the TEM lamellas: A thin Pt layer was first deposited with electron beam assisted deposition to avoid any ion beam damage at the sample surface. A thicker Pt protection layer (ca. 2 µm thick) was deposition on top of the e-beam Pt by ion beam assisted deposition. The sizes of the TEM lamellas are ca. 8 × 10 µm across and 50-150 nm thick. They were lifted out and transferred to *Omniprobe* Cu TEM grids using an in-situ technique where a W lift-out needle is used to transfer the TEM lamella onto the grid, with ion-beam assisted Pt deposition used to weld the sample to the lift-out needle and to Cu posts on the TEM grid. Coarse thinning was performed at 30 kV ion beam acceleration voltage and with progressively lower beam current, finishing with 90 pA current. Further thinning was performed at 5 kV and 73 pA, before the final polishing at 2 kV and 17 pA.

Three lamellas were analyzed at the TEM Gemini Centre at NTNU by a double Cs corrected (probe- and image-corrected) cold-FEG JEOL ARM 200CF, operated at 200 kV. The ARM is equipped with a large solid angle (0.98 srad solid angle) Centurio SDD for X-ray Energy Dispersive Spectroscopy (EDS) and a fast Gatan Quantum ER with Dual-EELS (energy electron loss spectroscopy). Simultaneous EDS and EELS mapping was performed in STEM (scanning transmission electron microscopy) mode i.e. each pixel in every map contains one EDS and two EEL spectra. Based on the position of the zero loss peak, the low loss EEL spectrum was used to calibrate the energy scale in the core loss spectrum in every pixel. EEL spectra were collected with a 380 pA beam current and with semi-convergence and semi-collection angles of 27 and 66 mrad, respectively. Spectra taken to construct element maps were recorded with 1 eV/channel and 3 eV energy resolution. Mapping of the C peak was done with 0.1 eV/channel and 0.57 eV resolution (based on the FWHM of the zero loss peak), and the semi-collection angle was reduced from 66 to 33 mrad. Prior to inserting the FIB lamellas into the TEM, all samples were plasma cleaned using a gas mixture of 75% Ar and 25% O_2 for 2 min to remove all possible hydrocarbon contamination on the sample surfaces.

TEM image processing was conducted in the GATAN Digital Micrograph© software (64 bit DM 2.32.888.0). The intensities of the EDS and EELS bitmap files are qualitative and show relative variations inside the mapped regions. The selected area electron diffraction patterns were collected in TEM mode with a parallel beam. The diffraction patterns of unknowns were calibrated by diffraction patterns (taken under identical conditions) from a Si single crystal with known lattice parameters. The EEL spectra were also processed in Digital Micrograph©. The energy was calibrated from semi-simultaneously acquired low-loss spectra that included the zero loss peak. A standard power law function was used to subtract the background intensity.

2.3 Nano-scale secondary ion mass spectrometry (NanoSIMS)

NanoSIMS mapping of the polished chip embedded in a 25 mm epoxy ring was performed using a CAMECA NanoSIMS 50 at the Centre for Microscopy, Characterisation and Analysis (CMCA) at the University of Western Australia. A Cs^+ primary ion beam was rastered across analysis areas varying from 5 x 5 µm up to 20 x 20 µm, at a resolution of 256 x 256 pixels (each pixel measuring between 20 nm and 78 nm, depending on the size of the area imaged). Dwell times were 20 ms per pixel with a primary beam current of c. 2.8 pA (D1=2), 30 ms per pixel with a beam current of c. 1.3 pA (D1=3) and 45 ms per pixel in 'high resolution mode' using a c. 0.7 pA beam current (D1=4). Secondary ions mapped were $^{16}O^-$, $^{24}C_2^-$, $^{12}C^{14}N^-$, $^{32}S^-$ and $^{56}Fe^{16}O^-$, and charge compensation was achieved by using the electron flood gun. Nitrogen does not form secondary ions so the CN^- complex was used to map nitrogen distribution. In all cases, regions c. 2-5 µm larger than the intended analysis area were pre-sputtered with the primary ion beam (using c. 250 pA beam current; D1=1) to > 5 x 10^{16} ions/cm^2 in order to remove surface contamination, implant Cs^+ ions and reach a steady-state of ion emission. In order to discount any potential contribution from epoxy resin in our results we present ion maps from potential organic material as $^{12}C^{14}N^-/^{24}C_2^-$. Measurements of this ratio from the resin in which the rock chip was mounted resulted in a $^{12}C^{14}N^-/^{24}C_2^-$ of 0.5 +/- 0.1. In contrast, the $^{12}C^{14}N^-/^{24}C_2^-$ for organic material within the targeted alteration microtextures is at least an order of magnitude greater (mostly between c. 15 and 25). Hence, while resin is frequently present in fractures close to the microtextures of interest it cannot be responsible for the high $^{12}C^{14}N^-/^{24}C_2^-$ signals observed within specific microtextures. Analyses were performed on both the surface of a polished rock chip and on a TEM lamella extracted from below the surface of the rock chip. The TEM lamella for NanoSIMS was prepared using a FEI Helios G3CX dual beam instrument at CMCA following a similar procedure to that described above for the Nanolab 600 instrument.

3. Results:

The optical light microscopy images of Y000593 (Fig. 1 a-c) show curving fractures, especially around the margins of the olivine grains, filled with red-brown iddingsite alteration, which at higher magnification show apparent linear features propagating into the olivines (arrowed, Fig. 1c). The iddingsite shows an angular, “spikey” interface with the fresh olivine when observed by SEM (Fig. 1e and Fig. 2) and TEM (Fig 1f). There are two phases of alteration clearly seen in Fig 1d and Fig 2: a central more compact and amorphous phase (white arrows in Fig. 1d and f, termed iddingsite 1) that is more-dense and often shows a distinct central band, and an outer more porous and partially crystalline phase (black arrows in Fig. 1d and f, termed iddingsite 2) that rims the veins and penetrates along high-angle fractures into the olivines (Fig. 1d, arrowed). SEM-EDS mapping shows that the inner iddingsite phase is relatively Si enriched (black arrow in Si panel of Fig. 2) and the outer phase more Fe enriched (white arrow in Fe panel of Fig. 2), the iddingsite sometimes contracts due to dehydration during sample preparation and pulls away from the margins of the veins. TEM investigation reveals that the angular and micro-brecciated olivine crystal margins (Fig. 1 f-h) contain a high degree of strain and a significant defect density shown by the dark bands and complex contrast variation recorded in the bright field TEM images (Fig. 1g and h).

FIB milling was used to obtain electron transparent TEM lamellae orientated parallel, orthogonal and oblique to the margins of the iddingsite-filled veins at the locations shown in Fig. 3. During FIB milling a "saw tooth" interface was revealed between the olivine and the alteration products, both on the sample surface (Fig. 3c) and beneath (Fig. 3d arrow), again confirming the angular nature of these interfaces. Selected area electron diffraction (SAED) by TEM confirms that the olivines are single crystals (Fig. 3) and have lattice parameters (a=4.84 Å b=10.38 Å c=6.08 Å) close to the Fe-rich fayalite end member (a=4.82 Å b=10.47 Å c=6.10 Å), with very minor Mg also evident in chemical maps (Fig. 2). The vein-filling iddingsite phase is rather variable in composition. It is commonly amorphous but where it does show crystallinity the diffraction patterns plus the chemical mapping suggests the presence of smectitic clay (e.g., nontronite; Fig. 3) and small amounts of goethite (Fig. 3). The amorphous iddingsite is relatively Si enriched, whereas the outer more crystalline iddingsite is more Fe enriched (Fig. 2). Comparisons of the $^{32}S^-$, $^{56}Fe^{16}O^-$ and $^{16}O^-$ NanoSIMS maps (e.g. Figs. 4,5 and S1), plus some of the TEM-EDS maps (see below and Figs. 6-8) suggests the presence of a Fe-sulphate phase within the alteration products. In all cases the margins of the olivine crystals can be seen to break down into small fragments (Fig. 1e and h, 4,5) and the iddingsite phase penetrates into the olivine crystals along high-angle fractures (Fig. 3-8). This records a progressive alteration front between the olivines and iddingsite-filled veins that is angular in shape.

NanoSIMS ion mapping reveals elevated concentrations of organic material as sub-micron sized areas in the outer iddingsite phase close to the olivine interface (Figs. 4, 5 and S1). This organic material has a distinctive CN/C signal (> 10) that is at least an order of magnitude greater than the CN/C signal (< 1) from epoxy resin in which the sample is mounted (Fig. 4,5 and S1). This discounts resin as a source of the organics that are intimately associated with the olivine interface. The CN/C signal does not provide any information on the concentration of N in the organic material since we have no way of standardising this measurement, but rather as a relative comparison between the mounting resin and potentially indigenous organics. The location of the high CN/C organics close to and within the micro-brecciated olivine crystal margins suggest that they are related to micro-brecciation and early alteration of the olivine crystals and iddingsite formation. The organics appear unrelated to primary magmatic features such as inclusions and zoning in the olivines.

To further characterize the morphology, distribution and structure of the organic carbon that is intimately associated with the angular microalteration textures, TEM-EDS and EELS were employed. TEM images of FIB-milled cross sections through the alteration textures show that the organic carbon occurs as rare patches <300 nm across, especially in the outer vein-filling iddingsite phase 2 (Figs. 6-8). Area a shown in Fig. 6 shows bands of carbon along the margins of the iddingsite filled vein and occurring in fractures that penetrate deep into the host olivine crystals.

Area b (noted on Fig. 6 and shown at higher resolution in Fig. 7), also from the outer iddingsite phase, contains bands of carbon within the iddingsite plus smaller patches of carbon at the roots of the olivine-penetrating microfractures. Some of these patches suffer from FIB induced damage whereby differential rates of thinning particularly between organics and minerals results in small sub-spherical holes so potentially there were even greater volumes of carbon present prior to FIB-milling, e.g., Fig 8a. arrow. A further area mapped from a different FIB lamellae shown in Figure 8 reveals significant carbon located near to an angular olivine crystal margin. In all mapped regions the organic carbon distribution does not correlate with enrichments in Ca or O and is therefore not associated with a carbonate phase. There is no correlation of C with the Ga or Pt TEM-EDS maps, excluding contamination during FIB wafer preparation. We looked in several regions to check that the C and Cl EDS maps do not correlate (Fig. 6-8), also that no Cl peak is seen in the EDS or EELS spectra so that we can exclude possible glue/resin used in attaching the thin section to the glass slide as a source for the organics. In contrast, we found that in one FIB-lamella cut from the epoxy-embedded rock chip that was prepared for nanoSIMS ion mapping (and subsequently discarded), there was a correlation between the C and Cl in the TEM-EDS maps (Supplementary Fig. S2). In that case we interpret the C to be derived from the epoxy located in what was void space. We therefore conclude that the correlation between C and Cl TEM-EDS maps is an additional reliable way to check for possible contamination from epoxy during sample preparation, and that we thus have two robust methods (C and Cl correlation, plus CN/C ratio) to distinguish this from primary/indigenous sources of organic material. (Note, this NanoSIMS combined elemental mapping approach has previously been used to distinguish microbial organics found in fragments of seafloor volcanic glass from epoxy (McLoughlin et al. 2011), and the current study is the first to employ this approach to FIB lamellae mapped using both NanoSIMS and TEM-EDS.)

EELS spectra measured from organic bearing regions in Fig. 6 (red boxes) exhibit a carbon-K near edge structure very similar in shape to reference spectra derived from amorphous carbon (Fig. 9a), with a distinct but less intense π^* peak at ~285 eV and a broader more intense σ^* peak centered around 295 eV (Fig. 9b). The C-K near edge structure lacks the distinct $1s \rightarrow \sigma^*_1$ exciton at ~292 eV that characterizes crystalline graphite found in meteorites (Cody et al. 2008). The $1s \rightarrow \pi^*$ electronic transition at ~285 eV indicates a significant amount of C=C bonding, most likely polyaromatic domains (Bernard et al. 2010) while the broad, rather featureless σ^* peak centered around 295 eV indicates a lack of long range order in these domains (Garvie and Busek 2006). There appear to be small additional peaks in the 287-290 eV range that have been attributed in previous studies to either, stacking defects between the aromatic planes, or carboxylic functional groups due to partial oxidation of the sample (Bernard et al. 2010). Our samples do not show the sharp peaks at about 290 eV and 301 eV that indicate carbonate groups (Fig. 9a) and also lack the triplet of distinct peaks (at about 293, 298 and 305 eV) characteristic of high pressure phases such as diamond (Fig. 9a) that have previously been identified in meteorites (Garvie and Busek 2006) and lunar impact melts (Steele et al. 2010).

4. Discussion:

4.1 Nature and origin of the Y000593 microalteration textures.

The FIB-TEM data reported here enables us to examine at high magnification and in 3-dimensions the microalteration textures found in the olivines of the Y000593 meteorite. We find that the interface between the olivines and iddingsite alteration is angular and micro-brecciated in morphology (Fig. 1, 3) with a network of iddingsite filled fractures occurring between angular olivine fragments (Fig. 1-8). The altered olivines show a "saw tooth" interface between fragmented olivine crystal margins and the iddingsite alteration (Fig. 1-3). We find no tunnel-like features in our FIB-TEM images, neither in cross nor longitudinal section. We see no similarity in shape to microtunnels of inferred biological origin found in terrestrial volcanic glass and dunites. Summarising previous morphological studies of terrestrial bioalteration textures, the microtunnels are typically 1-6 µm wide, up to hundreds of micrometers long, and can be curving, twisted or even helical in shape (c.f. Fisk and McLoughlin 2013 and references therein). The terrestrial bioalteration tunnels occur in bands radiating at high angles from fractures in the glass, often co-occurring with spherical or so called granular alteration textures (Furnes et al. 2001). The Yamato microtextures are on average shorter in length, and rather than being microtunnel-shaped, are angular interconnected fractures that do not co-occur with spherical-etch pits or granular microtextures. We therefore reject the comparison to terrestrial bioalteration textures and a microbial origin for the microtexures found in olivine grains of Y000593 as suggested by White et al. (2014).

We highlight that the size, shape and distribution of the Y000593 olivine microalteration textures is also very different to etch pits produced by the terrestrial weathering of olivines (Velbel 2009, 2016). For example, a study of the nakhalite meteorite Miller Range (MIL) 03346 found notches and serrations along fractures in olivine grains, showing conical and biconical morphologies (figures 5-8 of Velbel 2016) that are concentrated within a few hundred microns of the meteorite's fusion-crust, supporting an origin from terrestrial weathering. These triangular or wedge shaped etch pits are up to 2µm long, can occur as diamond shaped pairs, or echelon arrays following dislocations in the olivines (figure 1 Velbel 2016). The smaller aspect ratio and triangular shape of these olivine terrestrial weathering textures distinguishes them from the much more elongate microtextures that we imaged in the olivines of Y000593 (Figs 1-5).

Our brightfield TEM images (Fig. 1g and h) show evidence of shock induced strain in the olivine crystals, recorded by the significant defect density shown by the dark bands and complex contrast variation (Fig. 1g and h). We therefore suggest that impact event(s) were responsible for creating the angular fracture network we observe in the Y000593 olivines that were subsequently aqueously altered. Previous studies have argued that the relatively low peak shock state of the nakhlites estimated at 20 GPa (Nyquist et al., 2001) is consistent with their location near the margins of a Martian impact crater, rather than being in the center of the crater.

4.2 Nature of the Y000593 iddingsite alteration and organics

The iddingsite alteration veins investigated here in Y000593 are pre-terrestrial in origin because they are truncated by the fusion crust (Treiman and Goodrich 2002). (In contrast a terrestrial weathering overprint is seen in Yamato Y000749 where small cracks and bubbles occur in the fusion crust (Treiman and Goodrich 2002) that is also cross-cut by terrestrial jarosite veins (Changela and Bridges 2010)). The Fe-rich fayalitic olivine compositions we measure (Fig. 3) are comparable to previous studies of the mineralogy of Yamato 000593 (Imae et al. 2003) and the Nakhlites more broadly (table 4 in Treiman 2005), and consistent with Fe-rich iddingsite alteration products found, as opposed to more Mg-rich clays/serpentinites. Several studies of the Nakhalites have shown that heat derived from an impact event caused melting of the Martian permafrost and formation of a hydrothermal system in an impact crater with aqueous alteration and iddingsite formation (e.g., Changela and Bridges 2011; Bridges and Schwenzer 2012; Chatzitheodoridis et al. 2014). Thermochemical modelling based on the mineral alteration assemblages observed suggests an initially CO_2-rich hydrothermal fluid at temperatures between 150 and 200 ^{o}C, with a water: rock ratio (W/R) $\leq$ 300, with a pH of 6–8 leading to Fe-carbonate precipitation, followed by a fluid that cooled to temperatures of 50 ºC, at a pH of 9 giving rise to Fe-rich phyllosilicate and serpentine precipitation, then formation of amorphous Si-rich gel (Bridges and Schwenzer 2012). Yamato being the shallowest of the Nakhla meteorites contains iddingsite that comprises largely a siderite-gel assemblage. The organic carbon found in Y000593 is thus located in the relatively low-temperature part of an impact generated hydrothermal system, with several potential sources for the organics.

The organic carbon we mapped in Y000593 occurs along the outer margins of the iddingsite alteration veins, and along fractures penetrating the micro-brecciated margins of the olivine crystals (Figs. 4-8). The location of the organics does not support an origin from primary magmatic inclusions in the olivines (c.f. Steele et al. 2016) because these would be concentrated in localized areas within the olivines and not around the margins of the olivine grains. The amorphous nature of the organics (Fig. 9) indicates that Y000593 has not experienced high pressures and temperatures that would produce crystalline graphitic carbon or diamonds, expected from intense impact-induced shock metamorphism (Garvie and Busek 2006, Steele et al. 2010). Nor is the Y000593 organic carbon hosted by shock-melt veins, as seen in recent studies of the martian meteorite Tissint for example (Lin et al. 2014). In addition, we exclude electrochemical reduction as a source for the organic carbon as recently proposed by Steele et al. (2018), for some of the reduced carbon found in the meteorites Tissint, Nakhla, and NWA 1950 where the carbon is intimately linked to titano-magnetite, sulfides, and their alteration products, which differs from the close association with iddingsite and olivine that we see in Y000593. Thus we propose that the organic carbon was either remobilized by, or perhaps sourced from early hydrothermal alteration processes that formed the iddingsite veins in an impact crater on Mars, and we will now explore this environment and associated alteration processes.

4.3 Model for the Y000593 microalteration textures and organics

Indigenous organic carbon has been found in several Martian meteorites and a variety of sources have been proposed, including: (i) high-pressure impact generation (Steele et al. 2010); (ii) primary igneous i.e. magmatic processes (e.g. Steele et al. 2012); (iii) electrochemical reduction (e.g. Steele et al. 2018); (iv) dead martian organisms (McKay et al. 1996); (v) reactions in rapidly cooling magmatic and, or impact generated gases (Zolotov and Shock 2000); (vi) subsurface hydrothermal fluids (Lin et al. 2014, Steele et al. 2014); and (vii) exogenous delivery to Mars (e.g. Sephton et al. 2002;). On the basis of the distribution and ultrastructure of the organics in Y00593 (see discussion of the TEM-EELS data in the previous section) we have excluded the first three potential sources. Now, considering source (iv) for the Y000593 organics, namely that they are derived from fossilized, perhaps hyperthermophilic martian micro-organisms we find this to be unlikely. The shape and distribution of the organics that occur in sub-micron bands and sub-spherical concentrations (Fig 6-8), does not provide morphological evidence for microfossil-like objects to support a biogenic origin. In addition, given that we have rejected a biological origin for the micro-alteration textures in the Y000593 olivines, we conclude that a biotic source for the organics is unsupported by the current data.

Considering abiotic synthesis of the organics, there are at least two possible pathways we need to explore, either reactions in rapidly cooling impact generated gases, source (v) above; or subsurface Fischer Tropsch-type (FTT) reactions, source (vi) above. Considering first, hydrocarbon synthesis from impact generated gases, this seems very probable given the setting of Yamato 000593 and this is a mechanism that was first proposed for the PAHs (polycyclic aromatic hydrocarbons) found in the martian meteorite ALH84001 (Zolotov and Shock 2000). It has been shown in experimental studies and thermodynamic calculations that impact heating events cause dissociation of ferrous carbonates in particular siderite, to yield fine grained magnetite, formation of a CO-rich local gas phase, and reduction of water vapor to form H_2. Rapid cooling and high-temperature quenching of the CO-, H_2-rich impact gases can lead to magnetite-catalyzed hydrocarbon synthesis (Zolotov and Shock 2000, McCollom 2003; Milesi et al. 2015). In addition, rapid cooling of trapped primary magmatic gases can generate organics (Zolotov and Shock 1999), especially if cooling was rapid enough to prevent reequilibration, and these early hydrocarbons can be aromatized by subsequent impact reheating (Zolotov and Shock 2000). Given the location of Y000593 in an impact crater and the occurrence of siderite in this meteorite, the aforementioned mechanisms for organic carbon synthesis seem probable.

Considering sub-surface hydrothermal processes, it has been found that the hydration of olivines and pyroxenes in serpentinizing mafic-ultramafic crust on earth and in laboratory experiments yields H_2 and CH_4 (Shock 1990; Berndt et al. 1996; McCollom and Seewald 2001, 2006). The CH_4 is considered to be produced by Fischer–Tropsch Type (FTT) reactions involving H_2 and a carbon-bearing molecule principally CO, or CO_2 in the gas phase, or in aqueous solution, catalyzed by magnetite, following the reaction(s):

$$(2n+1)\mathrm{H_2} + n\mathrm{CO} \quad \rightarrow \quad \mathrm{C_nH_{(2n+2)}} + n\mathrm{H_2O}$$

$$\mathrm{CO_2} + 4\mathrm{H_2} \quad \rightarrow \quad \mathrm{CH_4} + 2\mathrm{H_2O}$$

Short-chain hydrocarbons can also be produced by these reactions and have been identified in hydrothermal fluids discharged at mid-ocean ridge systems and in products from analog experiments (e.g. McCollom and Seewald 2001, Konn et al. 2009, Holm and Charlou 2001). Recent studies of natural serpentinites from the Mid-Atlantic Ridge (Ménez et al. 2012, 2018a) and a 90 Ma Tethyan ophiolite (Sforna et al. 2018) have documented reduced organic carbon associated with the alteration minerals (fig. 2 in Sforna et al. 2018). On Mars such reactions have been suggested as important contributors to the inventory of atmospheric CH_4 (Oze and Sharma 2005) and could also be a source of PAHs found in meteorites (Zolotov and Shock 1999). When considering the organics in Y000593 it is important to realise however, that the synthesis of organics by FT-type reactions is very slow at lower temperatures (McCollom and Donaldson, 2015) like those estimated by Bridges and Schwenzer (2012) for the Yamato hydrothermal system. Moreover, it now becoming apparent that whilst serpentinization reactions yield abundant H_2 the formation of methane and other hydrocarbons is kinetically inhibited during circulation of seawater through serpentinite-hosted hydrothermal systems, and that these compounds may be derived from elsewhere in terrestrial system (e.g., McDermott et al. 2015; Wang et al., 2018; McCollom, 2016). In short it seems unlikely that FT-type process may have synthesized significant amounts of organics in the Yamato impact crator, and that hydrothermal circulation may rather have been important for re-distributing organics derived from other abiotic sources.

Comparing the Carbon XANES (X-ray absorption near edge spectroscopy) measured on organic carbon found in terrestrial seafloor serpentinizing systems (e.g. figure 6 Ménez et al. 2018b) to our TEM-EELS data, reveals important spectral differences. For example, Ménez et al. (2018b) report C-K edge spectra with a well-defined peak at 288.6 eV attributed to carboxyl functional group, in contrast to our EELS spectra (Fig. 9b) that show two peaks, described in the results section above, and interpreted to reflect significant amounts of C=C bonding most likely in polyaromatic domains that lack long range order (Garvie and Busek 2006). The much higher aromatic carbon content of our organics from Yamato, is difficult to explain by purely FT-type processes, especially at the temperatures <200°C. Alternative sources for the organics in Y000593 may therefore be more consistent with our EELS spectra, involving abiotic processes in rapidly cooling impact gases as discussed above (source v), and/or hydrothermal re-heating of magmatically derived organic carbon that can cause aromatization.

A further potential source for the Y000593 organics is from the exogenous delivery of organics to the martian surface. Many organic molecules are known to be produced abiotically by astrochemistry in the interstellar medium and circumstellar regions (Herbst and van Dishoeck 2009), and become incorporated in the planet-forming disks of new star systems (Shaw 2007). Extraterrestrial delivery of such organics aboard (micro)meteorites, asteroids, and comets to Mars could be a significant contributor to the planets organic inventory (Pierazzo and Chyba 1999). It is therefore plausible that the organic carbon found in the iddingsite veins of Yamato 000593 was derived from exogenous organics condensed onto the Martian surface that were later redistributed into the subsurface by hydrothermal fluids circulating in the impact crater. It is also possible that the impacting bollide itself may have delivered the organics, particularly if it was a carbonaceous chondrite, or organic rich comet (Ehrenfreund and Charnley 2000). Such a scenario involving extra-Martian delivery of organics cannot be excluded on the basis of our data for the origin of the carbon we mapped in Y000593.

To summarise the microtextural history and potential sources for organic carbon in Yamato 00593 we have compiled a schematic diagram showing the sequence of events (Figure 10). There are three main stages: T1 shows the Nakhla family of meteorites located in the near subsurface of Mars, their magmatic crystallization age being 1310 ± 30 Ma (Borg and Drake 2005) with possible condensation of exogenous organics onto the Martian surface; T2 shows fracturing of the Martian crust due to an impact event that caused micro-brecciation of the Yamato olivines, with possible delivery of organics aboard the impacting bolloid, and or synthesis of organics from high-temperature impact gases, with melting of the permafrost leading to hydrothermal circulation; T3 shows subsurface hydrothermal circulation with aqueous alteration of the Martian crust and iddingsite formation at c. 633Ma (Borg and Drake 2005), re-distribution of organics into the subsurface carried by the hydrothermal fluids and possible, minor organic carbon synthesis by FT-type processes. These events were followed by a much later second impact event at c. 11 Ma that was responsible for ejection of the Nakhla family of meteorites from Mars (Imae et al. 2003) and delivery to Earth.

5. Implications for seeking biosignatures in ultramafic rocks and impact structures on Earth and Mars

In this study, we present abiotic mechanisms of generating both organic carbon and complex microalteration textures in altered olivines of the martian meteorite Y000593 that have implications for seeking textural and chemical biosignatures in ultramafic rocks on Earth. The Yamato microtextures were previously compared by White et al. (2014) to candidate biosignatures found in altered volcanic glasses, however, there is now a maturing body of work that has questioned the role of microbes in the formation of terrestrial "bioalteration" textures. Many early workers favoured a microbial origin for so called bioalteration textures found in seafloor glasses (e.g. Thorseth et al. 1992; Fisk 1998; Banerjee et al. 2003; Staudigel et al. 2008), but an increasing number of petrological and experimental studies have questioned the contribution of microbes to seafloor volcanic glass dissolution and suggested a range of possible abiotic mechanisms (e.g. Alt and Mata 2000; Knowles et al. 2012; Fisk et al. 2013; French and Blake 2016; Fisk et al. 2019), particularly for the granular microalteration textures (McCollom and Donaldson 2019), and also for microtextures found in ancient meta-volcanic glasses (Grosch and McLoughlin, 2014; Lepot et al. 2011). This study expands the range of known abiotic alteration processes recorded by olivine microalteration textures, and reports high-magnification imaging and chemical mapping data not yet reported from similar olivine microalteration textures found in terrestrial ultramafic rocks (Fisk et al. 2006).

We note that optical and SEM images of the Yamato microtextures (Fig 1-3 herein, also White et al. 2014) closely resemble features previously reported from olivines in the Nakhla meteorite, with apparently linear reddish-brown microtextures propagating at high angles to the iddingsite veins into the olivine crystals (see fig. 3c in Fisk et al. 2006, fig. 1c in Lee et al. 2015, and Gibson et al. 2006). We postulate that when these microtextures in the Nakhla meteorite are imaged using similar techniques to those employed here that a complex micro-brecciated interface between the olivine and iddingsite alteration may also be revealed. We suggest that previous lower-magnification imaging of the Y000593 olivine crystal margins may have given the appearance of apparent linear microtextures at high angles to the iddingsite veins, which were then compared to terrestrial bioalteration tunnels, but that when these are imaged at higher magnification and in 3-dimensions then their more complex morphology becomes apparent.

In this study, we argue that impact induced brecciation and fracturing in a martian impact crater is responsible for the microtextures found in olivines of Y000593, and this leads us to consider the prevalence of such processes in terrestrial impact sites. For example, in a previous discussion concerning enigmatic tubular microtextures found in impact glasses of the 14.6 Ma Reis impact structure, which were compared to terrestrial bioalteration textures of argued microbial origin by Sapers et al. (2014, 2014a, 2015), it was suggested that shock related processes needed to be more fully explored as an alternative origin for these microtextures and associated organics (McLoughlin and Grosch 2014, Sapers et al. 2014a). This current study reasserts that shock related processes can generate complex microalteration textures in impact rocks, albeit on Mars rather than Earth, and that there are a range of abiotic processes for generating and redistributing organics within rocks of the impact site. Taken together, our findings caution that although post-impact hydrothermal systems on Earth and Mars may be potential locations for the origins and emergence of life (e.g. Cockell 2006; Grosch et al. 2014), alteration textures and organics associated with iddingsite alteration are not necessarily biosignatures in these environments.

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Figure Captions:

Fig. 1. Morphology of alteration textures in olivine crystals of Martian meteorite Y000593. **(a)** Optical image of reddish brown iddingsite alteration along curving cracks in olivine (ol). **(b)** Iddingsite filled fractures on the margins of an olivine grain (arrowed). **(c)** Higher magnification image showing apparently linear features (arrowed) on the margins of the iddingsite filled fractures in an olivine grain. **(d)** BSE (back scatter electron) image of an olivine crystal containing fractures filled with banded iddingsite that shows a central band of more compact iddingsite (white arrows) and outer poorly crystalline iddingsite that shows a complex interface with the margins of the olivine crystal (black arrows). **(e)** Enlarged image showing the progressive alteration of an olivine

crystal (top left) to iddingsite (lower right). **(f)** HAADF STEM (high angle annular dark field scanning transmission electron microscopy) image of a FIB lamella cut across an iddingsite filled fracture showing the highly brecciated margin of the olivine (Ol) crystal and banded nature of the iddingsite. **(g)** Bright field TEM image showing angular brecciated margin of an olivine crystal. Complex contrast variations within the olivine are evidence of the highly defective and strained crystal. **(h)** Bright field TEM image showing angular fragments of olivine (Ol) with amorphous iddingsite alteration filling the fractures in between. Scale bar is 50 µm in (a and b), 10 µm in (c), and 2 µm in (d-f), 0.5 µm in (g-h).

Fig. 2. SEM-EDS maps of a fractured olivine grain (Ol) adjacent to a pyroxene grain (pyx). The fractures are filled with banded alteration products, collectively termed iddingsite that show a ramified interface with the host olivine. The Kα peak of the elements Si, Mg, Fe, O and Al were measured. The maps show a central fracture-filling alteration phase (iddingsite 1) that is relatively enriched in Si (black arrow), and an outer alteration phase (iddingsite 2) that is more enriched in Fe and O (white arrow). Note the dark area at the interface between the olivine and pyroxene grains is void space. Also the iddingsite in the lower fracture can be seen to have contracted and pulled away from the margin of the fracture. Scale bar is 5 µm, the intensity of the colour scale reflects the relative concentration of the individual elements.

Fig. 3. SEM images showing the location of the FIB lamellas cut from Y000593 and studied by TEM, plus examples of selected area electron diffraction patterns from olivine and alteration phases within Y000593. (**a**) FIB lamella 1 cut parallel to the margins of the iddingsite filled vein intersecting the ramified interface with the olivine (Ol) crystal, for TEM data see Fig. 8 (**b**) FIB

lamella 3 cut oblique to a vein in the olivine filled with banded iddingsite, for TEM data see Fig. 6; (**c**) FIB lamella 2 cut orthogonal to an iddingsite filled vein in the olivine; (**d**) the same FIB lamella mounted on a Cu TEM grid during thinning to reveal the "saw tooth" interface (arrowed) between the olivine and alteration products seen beneath the sample surface. (**e**) Diffraction pattern from a single olivine crystal with the beam parallel to the [001] axis, showing lattice parameters of a=4.84 Å and b=10.38 Å. (**f**) Diffraction pattern from another single olivine crystal with the beam parallel to [100], showing the lattice parameter of c=6.08 Å. Note that these are very close to the lattice parameters of the fayalite end member of the olivine solid solution series (a= 4.82 Å; b= 10.47 Å; c=6.10 Å). (**g**) Diffraction pattern from the iddingsite 1 phase, showing distinct ring patterns with d-spacings of c. 2.59 Å and 4.40 Å, consistent with the (131) and (111) planes of nontronite, a smectitic clay. (**h**) Diffraction pattern from the iddingsite 2 phase. In addition to ring patterns, it possesses elongated spots with d-spacings of c. 1.43Å, 2.26Å and 2.43Å, consistent with the (121), (211) and (111) planes of goethite. Scale bars are 5μm.

Fig. 4. Chemistry of iddingsite alteration in fractured olivine (grain 4, area 1) of martian meteorite Y000593 characterized by NanoSIMS ion mapping of the boxed area (yellow) in the left hand BSE (back scatter electron) image. The brecciated morphology of the olivine crystal margins is clearly seen in the S^- map for example. Organic material (measured as CN^-/C^- to exclude any possible contamination from resin) occurs as bands along the margins of the iddingsite filled fracture and extends into the brecciated margins of the altered olivine. Intensity calibration bars are expressed as total counts for FeO^-, O^- and S^-, and as a simple ratio for CN^-/C^-.

Fig. 5. Chemistry of iddingsite alteration in fractured olivine (grain 5, area 2) of martian meteorite Y000593 characterized by NanoSIMS ion mapping of the boxed area (yellow) in the left hand BSE (back scatter electron) image. The brecciated morphology of the olivine crystal margins is especially clear in the S^- map. Organic material (measured as CN^-/C^- to exclude any possible contamination from resin) occurs as a band along the margin of the iddingsite filled fracture and extends someway into the brecciated margins of the altered olivine. Intensity calibration bars are expressed as total counts for FeO^-, O^- and S^-, and as a simple ratio for CN^-/C^-.

Fig. 6. Distribution and elemental mapping of olivine (Ol), iddingsite alteration and organic carbon in Y000593. **(a)** BF (bright field) STEM image of FIB lamella-3 (for location in sample see Fig. 3b) the black boxes correspond to areas that were selected for element mapping. **(b)** High angle annular dark field (HAADF) STEM image of Area a, contains fractured olivine (lower right) adjacent to iddingsite (upper left), element maps shown beneath. **(c)** HAADF STEM image of Area b on the margin of a brecciated and altered olivine crystal (lower right), elemental maps shown in Fig. 7. **Area a** shows a pronounced band of carbon along the margins of the olivine crystal near the boundary with the iddingsite, also in the fractures that brecciate the olivine crystal margin. Crucially the C (red) and Cl (green) maps do not correlate, excluding epoxy as a source for the organic carbon. Element maps were measured using the EDS detector except for the carbon map which is a K-edge EELS map. Red boxes in b and c correspond to locations where Carbon EELS spectra were measured, see Fig. 9. Scale bars is 2μm in (a) and 1 μm in (b and c and the elemental maps).

Fig. 7 Distribution and elemental mapping of olivine, iddingsite alteration and organic carbon in Y000593 corresponding to Area b in FIB lamellae 3 from previous Fig. 6. Area b contains a band of carbon in the upper part of the image at the boundary of iddingsite phases 1 and 2, also ovoid bodies of carbon <300 nm across in the lower right close to the olivine crystal margin. Note that the C and Cl maps do not correlate, excluding epoxy as a source for the organic carbon. Element maps were measured using the EDS detector except for the carbon map which is a K-edge EELS map. Scale bar 1 μm, the brightness/intensity of the colour scale of the elemental maps reflects relative concentrations.

Fig. 8 Distribution and elemental mapping of olivine, iddingsite alteration and organic carbon in Y000593 corresponding to FIB lamellae 1 mapped region 3 (for location in sample see Fig. 3a). **(a)** overview showing brecciated and highly fractured olivine in the top centre, with iddingsite alteration phases 1 and 2, and olivine grain in the lower part of the image, boxed area is enlarged in (b), a small over-thinned region forming a hole in the FIB lamellae is arrowed**. (b)** HAADF image showing the fractured olivine grain with region selected for element mapping shown by the white dashed box. The Carbon EELS map shows the concentration of organic material near the margin of the olivine, and note again that the C and Cl maps do not correlate, excluding epoxy as a source for the organic carbon. Element maps were measured using the EDS detector except for the carbon map which is a K-edge EELS map. Scale bar is 2μm in (a) and 0.5 μm in (b), the brightness/intensity of the colour scale of the elemental maps reflects relative concentrations.

Fig. 9 Structure of the organic carbon found in Y000593 revealed by Energy Electron Loss Spectroscopy (EELS). **(a)** Carbon K-edge EELS reference spectra for calcite, graphite, amorphous carbon and diamond, with the dashed lines showing the 1s → π* electronic transition at ~285 eV and the 1s → σ* exciton at ~292 eV for graphite. **(b)** Carbon K-edge spectra measured from the red boxes in areas a and b of FIB lamellae- 3 closely match the amorphous carbon reference spectrum shown in **(a)**. EELS Carbon K-edge reference spectra were taken from (Garvie and Busek 2006).

Fig. 10 Schematic showing the sequence of events affecting Yamato 000593 and the co-magmatic Nakhla meteorites in the Martian subsurface with development of the olivine microtextures through time. Starting with the planetary scale events (left hand panel) T_1 shows condensation of exogenous organics onto the Martian surface with permafrost in subsurface clinopyroxenites. T_2 shows formation of an impact crater with fracturing and brecciation of the crust, impact heating causing melting of the permafrost, generation of volatile organics from impact gases and possible siderite decomposition. T_3 shows continued hydrothermal alteration with iddingsite formation and organic redistribution due to fluid circulation and possible organic carbon synthesis via Fischer-Tropsch type processes. At the microtextural scale (right hand panel) T_1 shows fresh unaltered olivines in the mafic subsurface of Mars followed by an impact event at T_2 that causes fracturing and micro-brecciation of the olivines, and then at T_3 the formation of aqueous alteration products (iddingsite, dark yellow) and redistribution of organic carbon (red) via hydrothermal circulation. Age constraints (1) from Borg and Drake (2005). Relative location of the Nakhla meteorites and hydrothermal model from Bridges and Schwenzer (2012). GV = Governador Valadares meteorite.

SUPPLEMENTARY

Fig. S1. Chemistry of iddingsite alteration in fractured olivine (grain 5, area 3) of martian meteorite Y000593 characterized by NanoSIMS ion mapping of the boxed area (yellow) in the left hand

BSE (back scatter electron) image. Again the brecciated morphology of the olivine crystal margins is clearly seen in the S^- map, while organic material (measured as CN^-/C^- to exclude any possible contamination from resin) also occurs within most of the iddingsite alteration textures at the olivine crystal margin. Intensity calibration bars are expressed as total counts for FeO^-, O^- and S^-, and as a simple ratio for CN^-/C^-.

Fig. S2. Data from a FIB lamella cut from a resin impregnated chip of Y000593 to document the occurrence of resin in the sample **(a)** Back scatter electron image of the site where the FIB lamella was cut (red line) parallel to the margins of an iddingsite filled fracture; **(b)** Darkfield STEM overview image of the FIB lamella that mainly consists of olivine with a diagonal fracture containing resin introduced during sample preparation, dashed boxed shows area selected for elemental mapping. The TEM-EDS maps clearly show a correlation between the elements C and chlorine, and furthermore an EDS spectra measured from the yellow boxed area shows a clear Cl peak. Scale bar is 5 µm, the brightness/intensity of the colour scale reflects the relative concentration of the individual elements.