CARBONATES IN LAFAYETTE: PREPARATION FOR MARS 2020. J. D. Piercy, J. C. Bridges and L. J. Hicks. Space Research Centre, Leicester Institute of Space and Earth Observation, University of Leicester, UK, LE1 7RH. Email: jdp32@leicester.ac.uk

Introduction: Carbonates are a common product of fluid-rock interactions; water charged with CO_2 from the martian atmosphere results in a weak carbonic acid which, upon reacting with silicates, has the potential to precipitate out carbonate as the fluid cools. The following two reactions show the production of carbonic acid followed by its reaction with fayalite to yield siderite.

$$2CO_2 + 2H_2O \rightarrow 2H_2CO_3$$
$$Fe_2SiO_4 + 2H_2CO_3 \rightarrow 2FeCO_3 + 2H_2O + SiO_2$$

Energy liberated from this process could be utilized by microbes [1] and thus carbonate-bearing regions are a focus for Mars 2020 landing site selection and characterisation [2]. Interpretation of carbonates in martian meteorites can inform us about martian aqueous fluids (composition, pH, temperature of formation) and thus habitability. Since the source of CO_2 is in part the ancient martian atmosphere [3], carbonate minerals also provide a view of past atmospheric conditions.

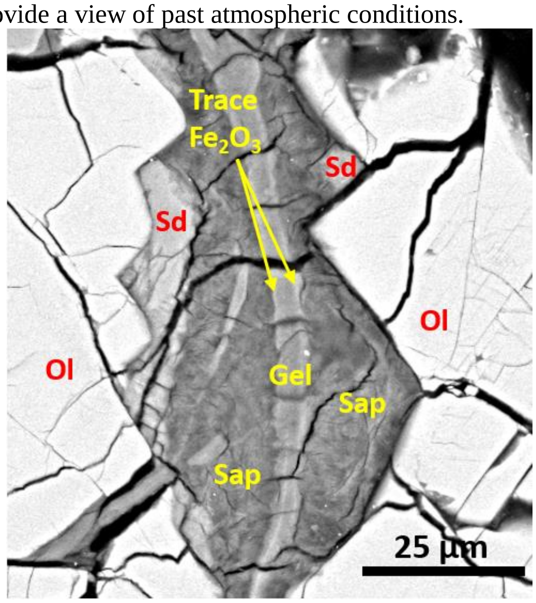

***Figure 1** - BSE image showing Lafayettes olivine(Ol)-hosted hydrothermal assemblage, consisting of siderite(Sd)-saponite(sap)-trace ferric oxide-amorphous smectitic gel.*

Lafayette is one of the nine nakhlites, a group of martian basaltic clinopyroxenitic rocks that formed together 1.3 Ga in a thick lava flow or shallow sill intrusion [4]. The nakhlites display unique alteration assemblages; the most evolved assemblage, which Lafayette hosts, show hydrothermal veins consisting of Ca-rich siderite, ferric phyllosilicates and amorphous smectitic gel, with minor ferric oxide [5, 6, 7].

Methods: The thin section USNM 7849, on loan from the Smithsonian Institution, was characterised through Back Scattered Electron (BSE) imagery and Energy Dispersive x-ray fluorescence Spectroscopy (EDS), using a Phillips Environmental Scanning Electron Microscope (ESEM) XL-30 at the University of Leicester's Advanced Microscopy Centre. Wafers suitable for Transmission Electron Microscopy (TEM) were extracted using Focused Ion Beam (FIB) Milling. TEM was performed using a JEOL 2100+ at the University of Nottingham. Fe-K X-ray Absorption Spectroscopy (XAS) was carried out using the 2.5µm resolution I-18 microfocus spectroscopy beamline at the *Diamond* synchrotron, UK. 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 (XANES) region.

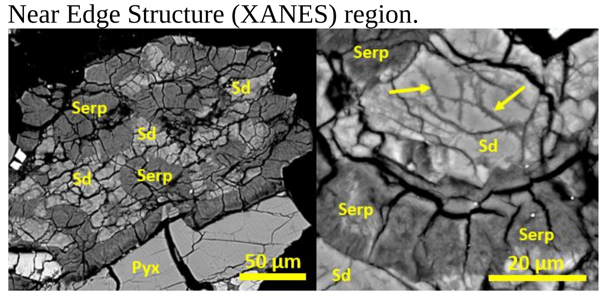

***Figure 2 - Left:** BSE image of Lafayette mesostasis-hosted alteration assemblage, showing a texturally variable assemblage of siderite (Sd) precipitate partially replaced by a radially precipitated serpentine (Serp). **Right:** Close-up of mesostasis siderite being partially dissolved and replaced (arrow) by the adjacent serpentine.*

Mineralogy and Textures: Lafayette carbonates occur in two textural settings; in void space in the meteorite's mesostasis and in fractures cutting olivine grains. The thin section studied here contains the largest abundance of SNC martian carbonate yet reported. Both types of carbonate shows evidence of partial replacement by ferric phyllosilicates (Fig. 1, 2). Textural and compositional differences between the two types of carbonate suggest a difference in formation processes.

Olivine-hosted carbonate comprise 0.8 vol% of the thin section and are situated in the margins of saw tooth fractures (Fig. 1). The compositions of Lafayette olivine carbonate are $Mg_0Cc_{27.3\text{-}28.8}Sd_{46.9\text{-}53.4}Rh_{19.2\text{-}24.2}$ (Fig. 3).

Mesostasis-hosted carbonate comprises 3.2 vol% of the thin section and are found in interstitial areas comparable in size to mesostasis feldspar. These areas display a texturally variable assemblage of Ca-rich siderite and a radially precipitated phyllosilicate, suggestive of void filling rather than replacement. The compositions of mesostasis-hosted carbonate are $Mg_0Cc_{21-42.3}Sd_{57.7-78.9}Rh_{0-4.5}$ (Fig. 3). This range of siderite compositions reflects a varying solution composition during formation where cations could be exchanged more readily than in the olivine fractures.

The Mn component of this carbonate, as well as the lack of Mg in both carbonates, shows that the carbonate formed as a precipitate from an external fluid and not via direct replacement of its host mineral.

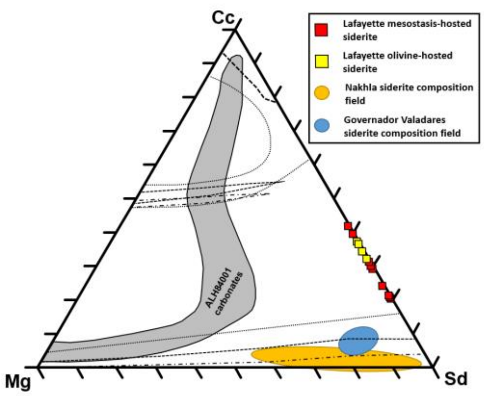

***Figure 3** - Magnesite (Mg), Calcite (Cc), Siderite (Sd) carbonate ternary showing the compositions of both types of carbonate within Lafayette. The graph also shows compositional fields of carbonates within ALH84001 and the nakhlites; Nakhla and Governador Valadares [3]. Calculated stability fields for carbonates formed at 400 °C (dash-dot), 550 °C (dashed) and 700 °C (dotted) are also shown [8].*

TEM: Mesostasis phyllosilicate have 001 basal lattice spacings of 0.8 nm and show di-ochtahedral layering, both consistent with serpentine [5]. Lattice spacings of 1 nm with tri-ochtahedral features were found in the olivine-hosted phyllosilicate, indicating a hydrated saponite [5, 6].

XAS Analysis: Fe-K XANES spectra show that iron in the saponite and serpentine contains significant Fe^{3+} while olivine has an undetectable amount (Fig. 4), suggesting the carbonates formed from fluids which became more ferric as it partially dissolved the carbonate, and not from direct carbonation of silicates.

Discussion: Previous work modelled the nakhlite hydrothermal brine and its precipitates, revealing the Ca-rich siderite crystallised from a fluid that had previously dissolved feldspar and olivine in a 1:4 ratio [7]. The hydrothermal fluid charged with CO_2 infiltrated the nakhlite parent rock via fractures in the mineral grains, and began the preferential dissolution of olivine and feldspar. As the brine cooled the siderite precipitated in the newly created interstitial voids and olivine fractures. The results of analog water-rock reaction experiments are reported in [9]. Our results suggest the carbonates found in Lafayette were precipitated from an evolving ferric fluid in a short amount of time, as shown by XAS analysis and their metastable compositions (Fig. 3). Alternatively, by analogy with terrestrial analog studies, ferrous phyllosilicates could have been oxidized to ferric *in situ* [10].

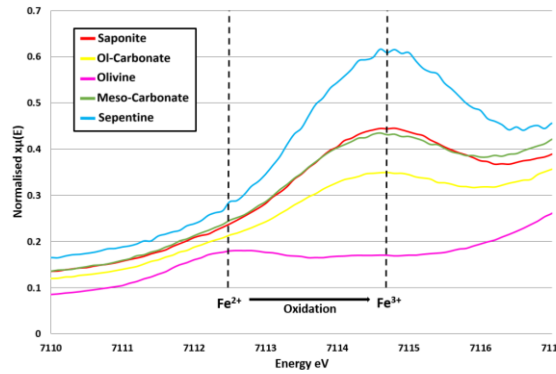

***Figure 4** - Fe-K XANES measurements were taken in order to gather information about the oxidation state of the Fe content. Pre-absorption edge features of Lafayette olivine (pink), ol-carbonate (yellow), ol-saponite (red), meso-carbonate (green) and meso-serpentine (blue) are shown.*

Previous estimates of ~200 mbar pCO_2 equivalent were derived from earlier nakhlite studies [11]. This value represents the residual atmosphere left after atmospheric loss processes which was trapped within the Amazonian martian crust. The large carbonate content of 4 vol% observed within this section, if taken as an average throughout the martian crust, equates to 2200 mbar pCO_2. Considering the thick ancient atmosphere model predicts ~400 mbar pCO_2 trapped as carbonate on current day Mars [12], this new abundance supports the thick model.

Studying these important alteration minerals is vital in preparation for Mars 2020 and other landers. The Nili Fossae graben show the largest remotely detected abundance olivine and carbonate-bearing rocks on Mars [13]. Studying Lafayette carbonates as an analog to sites such as this will allow us to optimise measurements and analyses *in situ*.

References: [1] Neubeck A. et al. (2014) *Planetary and Space Science* **96**, 51-61 [2] Mars 2020 SDT (2013) *NASA*. [3] Bridges J. et al. (2017) *In Press.* [4] Triemann A. et al. (1993) *Geochimica et Cosmochimica Acta* **57**, *4753-4767*. [5] Changela H. and Bridges J. (2011) *Meteoritics* **45**, *1847-1867*. [6] Hicks L. et al. (2014) *Geochimica et Cosmochimica Acta* **136**, 194-210. [7] Bridges J. and Schwenzer S. (2012) *Earth and Planetary Science Letters* **359-360**, 117-123. [8] Anovitz L. and Essene E. (1987) *Journal of Petrology* **28**, 389-414. [9] Bridges J. et al. (2018) *LPSC*. [10] Treiman A. et al. (2014) *American Mineralogist* **99**, 2234-2250. [11] Bridges J. et al. (2001) *Space Science Reviews* **96**, 365-392. [12] Manning C. et al. (2006) *Icarus* **180**, 38-59. [13] Ehlmann B. et al. (2008) *Science* **322**, 1828-1832.