CARBONATES WITHIN LAFAYETTE.

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Introduction: The martian nakhlites contain a unique carbonate-bearing hydrothermal alteration assemblage. Lafayette hosts the most extensive secondary minerals, showing veins containing Ca-rich siderite, ferric saponite, Al-rich ferric serpentine, smectitic amorphous gel and minor ferric oxide [1, 2, 3]. The remaining 10 nakhlites display a variation in their secondary phases, this correlates with the nakhlite depth of formation model [4]. Studying these important alteration minerals is vital in preparation for missions like Mars2020. For instance, Jezero Crater shows carbonate-bearing outcrops [5]. Studying Lafayette carbonates as an analog will help optimise *in situ* measurements and analyses.

The Ca-siderite contained within Lafayette's olivine and mesostasis hosted assemblages display textures indicative of corrosion and replacement by saponite and serpentine respectively. This dissolution contributes to the evolving nature of the fluid just as the dissolution of olivine and mesostasis plagioclase does in the first stages of alteration. Interpretation of these carbonates informs us about the fluid history of the parent rock and thus the habitability of the associated environment. Since the source of CO_2 is ultimately the ancient martian atmosphere, carbonate minerals also allows us to help constrain past pCO_2 models of the martian atmosphere [6]. Here we report on the carbonate dissolution within Lafayette and the effect that has on the nakhlite fluid.

Methods: The thin section USNM 7849 was characterised using an FEI Quanta 650 FEG-SEM. Wafers suitable for Scanning Transmission Electron Microscopy (STEM) imagery were extracted using Focused Ion Beam (FIB) milling on a FEI Quanta 200 3D Dual FIB-SEM. STEM imagery was performed using a JEOL 7200 FEG-SEM. Fe-K X-ray Absorption Spectroscopy (XAS) was carried out using the I-18 microfocus and I-14 nanofocus spectroscopy beamlines at the *Diamond* synchrotron, UK.

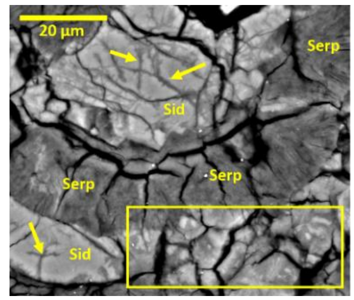


Figure 1 - BSE image of mesostasis assemblage showing siderite and serpentine. Dissolution and replacement textures (arrows and box) are shown.

Mineralogy and Textures: The thin section studied here contains the largest abundance, ~4 %, of martian meteorite carbonate yet reported. Two textural sites for carbonate show evidence of partial replacement by ferric phyllosilicates.

Mesostasis-hosted carbonate comprises ~3.2 vol% of the thin section and is found in interstitial areas. These areas display a texturally variable assemblage of carbonate and radial phyllosilicate (Fig. 1). The compositions of this carbonate $Mg_0Cc_{21-42.3}Sd_{57.7-78.9}Rh_{0-4.5}$ are metastable (Fig. 2). This range of compositions reflects a varying fluid composition where cations could be exchanged more readily than in the olivine fractures. The carbonate grains show veining within them where the evolving fluid has partially replaced it with saponite (Fig. 1; arrows).

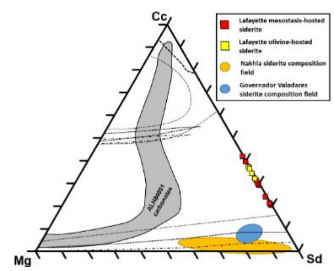


Figure 2 - Magnesite (Mg), Calcite (Cc), Siderite (Sd) ternary showing the compositions of Lafayette carbonates. ALH84001, Nakhla and Governador Valadares carbonate compositions are from [6]. Calculated stability fields for formation at 400 °C (dash-dot), 550 °C (dashed) and 700 °C (dotted) are also shown [7].

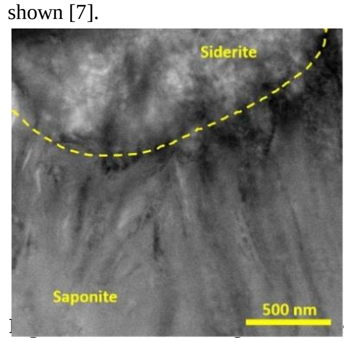
Olivine-hosted carbonates are situated at the margins of sawtooth-shaped fractures. They compromise ~0.8 % of the thin section and up to ~6% of the olivine, the alteration phases can take up ~20 % of the olivine. The compositions of olivine carbonate are $Mg_0Cc_{27.3-28.8}Sd_{46.9-53.4}Rh_{19.2-24.2}$ and again metastable (Fig. 1). Identical replacement textures as seen in the mesostasis carbonate are present.

STEM Imagery*:* Dark Field (DF) imagery of a TEM wafer, taken from an olivine alteration vein, shows the boundary between the carbonate and saponite phases (Fig. 3), highlighting the saponite replacement of carbonate.

X-ray Absorption Analysis: Fe-K XANES analysis showed that the iron in the saponite and serpentine contains significant Fe^{3+} while olivine has an undetectable amount. Measurements of the carbonate also showed some ferric iron, consistent with partial dissolution and replacement by saponite.

Discussion: Our results show that as the nakhlite fluid cooled the carbonate precipitated in the mesostasis and olivine fractures. Once all HCO_3^- had been exhausted the carbonate formation stopped, the ferric fluid dissolved a significant proportion of the existing Ca-siderite, and saponite was precipitated.

The large carbonate content of 4 % observed within this Lafayette section, initially higher prior to the partial replacement by saponite and serpentine, if taken as an upper estimate on the possible 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 [8], this new upper limit is consistent with thick pCO_2 models for ancient Mars.



and saponite boundary (dashed line) from an olivine secondary assemblage.

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