

ODINITE AND SAPONITE REPLACEMENT OF CARBONATE IN THE LAFAYETTE NAKHLITE: PART OF THE CO₂-CH₄ CYCLE ON MARS

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Introduction: The martian nakhlites display unique carbonate-bearing hydrothermal alteration assemblages in two forms; mesostasis-hosted (MH) and olivine-hosted (OH). Lafayette hosts the most abundant and developed assemblages, showing veins containing Ca-rich siderite, ferric saponite, saponitic amorphous ‘gel’ and minor ferric oxide in olivine fractures, and Ca-rich siderite and an unidentified Al-rich ferric serpentine-like mineral in mesostasis areas [1, 2, 3]. This mineralogy points towards key aspects of the ancient carbon cycle on Mars; it is generally assumed that a significant fraction of the ancient CO₂ atmosphere on Mars was trapped as carbonate [4]. However, puzzling aspects of the martian carbon cycle remain, such as the paucity of carbonate detected on Mars’ surface [5] and the source of martian CH₄ [6]. Here we report on the carbonate dissolution and partial replacement by ferric-phyllsilicates in the Lafayette nakhlite in order to provide new insights into the carbonate-CO₂-CH₄ cycle on ancient Mars.

Carbonate Textures and Mineralogy: Two studied thin sections (USNM 7849, CFM) contain carbonate minerals situated in OH and MH assemblages. However, the USNM section contains ~4% compared to the CFM section’s 0.2%, showing a varied formation and dissolution environment. The carbonate dissolution textures seen using SEM-BSE are also varied; incipient corrosion and veining to large-scale replacement can be seen throughout the two sections, although the MH are noticeably more altered than their OH counterparts (Fig. 1).

SEM-EDS and X-ray Absorption Spectroscopy (XAS). EDS compositions reflect the more altered state of MH carbonate as they contain >6 wt% SiO₂, a result of contamination from the intermixed serpentine-like phyllosilicate. This contamination prevents the calculation of reliable endmember values; unlike with the OH carbonates which have values of Mg_{0.0-2.0}Cc_{13.2-40.0}Sd_{17.7-81.9}Rh_{3.1-42.9} and rare Mg₁Cc₄₀Sd₁₇Rh₄₁. Fe-K XAS was carried out using the *Diamond Light Source* synchrotron; similarly, a correlation between increasing dissolution and a shift to higher energies (~2.1 eV) across the carbonates’ XAS spectra was found. OH carbonates show a shift from Fe²⁺ to Fe³⁺ centroid values, whereas the MH carbonates are all Fe³⁺-rich, reflecting their greater abundance of phyllosilicate contamination.

Serpentine-like Mineral: Previous studies [1, 2] have shown that the MH phyllosilicate in the nakhlites has a 0.7 nm d₀₀₁-spacing and 1:1 structure, characteristic of a serpentine-group mineral. However, it is enriched in Fe³⁺ and Si, and depleted in Al when compared to most serpentine-type minerals. Using new EPMA-WDS data and XAS Fe³⁺/ΣFe values, we have refined the MH phyllosilicate identity as the serpentine-like mineral, odinite [7, 8] (Fig. 2).

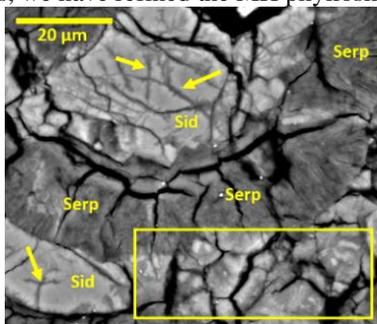


Figure 1 - BSE image of USNM mesostasis assemblage showing siderite and serpentine. Dissolution and replacement textures (arrows and box).

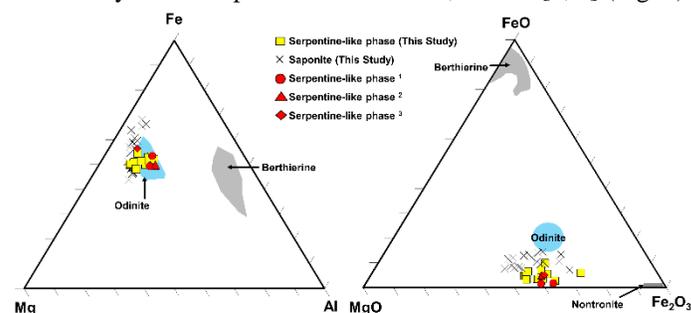


Figure 2 –Ternary plots showing the variations in at. Fe-Al-Mg and wt. FeO-Fe₂O₃-MgO of this study’s Lafayette mesostasis-phyllsilicate compositions, as well as data from [1, 2, 3]; saponite data is also shown for comparison. These are plotted alongside the compositional fields of nontronite, berthierine and odinite taken from [7, 8].

Discussion: The textures and compositional trends observed in this study show that carbonate dissolution and replacement by ferric phyllosilicates is a significant stage of the nakhlite fluid’s evolution. Carbonate dissolution produces bicarbonate anions which can react with water and/or hydroxyl molecules to form carbon dioxide. H₂ produced from oxidation of Fe and the ferric-phyllsilicate formation, analogous to a serpentinisation-like processes, can then act to reduce the carbon in CO₂ and form CH₄ from a Fischer-Tropsch reaction ($4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$). The results of our study illustrate a process of subsurface dissolution to explain the relatively low abundance of detected carbonate on Mars and, if large amounts of carbonate were trapped in the martian crust, a major source of martian methane [10].

References: [1] Hicks L. et al. (2014) *GCA* 136, 194-210. [2] Changela H. and Bridges J. (2010) *MAPS*. 45, 1847-1867. [3] Tomkinson T. et al. (2015) *MAPS* 50, 287-304. [4] Manning C. et al. (2006) *Icar*. 180, 38-59. [5] Ehlmann B. L. and Edwards C. S. (2014) *An. Rev. Earth Planet. Sci.* 42, 291-315. [6] Chassefière E. and Leblanc F. (2011) *PSS* 59, 207-217. [7] Ryan P. and Hillier S. (2002) *Am. Min.* 87, 1607-1615. [8] Ku T. et al. (2003) *Chem. Geo.* 197, 197-213. [9] Xu T. et al. (2000) *Berkeley National Laboratory Report*, LBNL-46992. [10] Piercy J.D. et al. (2021) *GCA* (in rev.).