NAKHLITE CARBONATE AND THE CARBON CYCLE ON AMAZONIAN MARS

J. C. Bridges¹, J. D. Piercy^{1,2} and L. J. Hicks^{1,3}, ¹School of Physics and Astronomy, University of Leicester, UK <u>j.bridges@le.ac.uk</u> ²Now at, Dublin Institute for Advanced Studies, Ireland, ³School of Geology, Geography and the Environment, University of Leicester, UK.

Introduction: The nakhlite secondary alteration assemblage consists mainly of Fe-rich carbonate partially corroded and replaced by ferric saponite and an odinite-like serpentine phase [1,2]. This mineral assemblage and its alteration stages can illustrate key aspects of the Amazonian carbon cycle. For instance, the origin of methane in the Martian atmosphere is one of the key unresolved questions in Mars' atmospheric evolution and current near-surface processes [3,4]. A possible route for methane production was described in [5] which demonstrated that CH₄ is expected to dominate over carbon oxides under the redox conditions associated with martian hydrothermal fluids and the nakhlite secondary minerals. Here we use mineralogical studies of the Amazonian [6] nakhlite secondary assemblage to explore links between the carbonate-bearing crust and routes for organic formation.

Methods and Samples: Mineralogical data on the nakhlite secondary minerals have been gathered with FE-SEM, EDX, WDS, FIB-(S)TEM at University of Leicester's Advanced Microscopy Facility and University of Nottingham, and Fe-K XANES at Diamond Light Source e.g. [1,2]. The 12 nakhlites carry varying abundances and parts of the overall secondary assemblage depending on depth of the parent rock within the nakhlite pile and extent of exposure to the secondary fluid [1,2,7]. We have studied many of the nakhlites as part of this project, but the near pristine nakhlite Lafayette has particular importance due to the abundance of its secondary assemblage and the textural evidence for an evolving fluid. We have anlysed Lafayette sections USNM 7849 and a section originally from the CFM.

Results: Carbonate is up to 4% of one Lafayette thin section, and Mg0.0-2.0Cc13.2-38.6Sd17.7-81.9Rh3.1-42.9 [1]. A key feature of the nakhlite phylloslicate-carbonate assemblage in the nakhlites is that carbonate is variably replaced by ferric saponite in olivine fractures and odinite-like serpentine in mesostasis textural sites (Fig. 1). For instance, another thin section of the same Lafayette meteorite contained only minute traces of unaltered carbonate, most having been replaced. The odinite-like phase has d_{001} -spacings of 0.7 nm and (Fe_{tot}+Mg)/Al at. of 0.8-0.9 [1]. Fe-K XANES show Fe³⁺/ Σ Fe ratios from 0.86-1.0 within the odinite and 0.59-0.96 within the saponite. Small traces of ferrihydrite were identified near the margins of corroded carbonate and saponite.

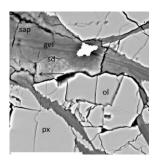


Figure 1. Carbonate Dissolution Features in Lafayette: textural site for Fischer-Tropsch reactions.

Sap saponite, sd siderite, ol olivine, px augite, arrow shows replacement of sd.

Discussion: The nakhlite secondary fluid was initially a HCO₃-charged brine associated with the precipitation of carbonate within olivine and mesostasis sites. Once the fluid's HCO₃ was exhausted, the evolving, neutral-mildly alkaline ≤50 °C brine corroded the carbonate and precipitated the phyllosilicate as a replacement of carbonate and directly within fractures. As the fluid was no longer buffered by Fe²⁺-carbonate, the iron oxidation state increased, as recorded in the Fe³⁺-rich phyllosilicates and precipitation of small traces of ferrihydrite near the margins of corroded carbonate and saponite. Extensive dissolution of such carbonate across the upper martian crust, producing bicarbonate and carbon dioxide, and the coupled formation of ferric phyllosilicates, would lead to the formation of CH₄ in substantial amounts via a Fischer-Tropsch type reaction [8-10]. Such reactions could be substantially inhibited by kinetic factors but the likely relatively high abundance of carbonate and clay-bearing assemblages in much of the Mars upper crust [11] suggest that substantial quantities of CH₄ and PAHs would still have been created. Seasonal release of some trapped CH₄ reservoirs formed from this process are, for instance, of sufficient likely magnitude to explain localised atmospheric CH₄ enrichments detected by Mars Science Laboratory [3]. As more of the crust is being studied via meteorites, MSL [12,13], Mars2020-MSR and orbiters, the role and significance of carbonate-phyllosilicate abundances within the ancient car-

bon cycle and organic reservoirs of Mars will continue to be revealed [14].

References: [1] Piercy J. D., Bridges J. C. and Hicks L. J. (2022) *MAPS* 326:97-118. [2] L.J. Hicks, J.C. Bridges, S.J. Gurman (2014) *GCA* 136: 194-210. [3] Webster C. et al. (2018) *Science*, 360: 1093-1096. [4] Mumma M. J. et al. (2009) *Science*, 323: 1041-1045. [5] Zolotov M. and Shock E. (1999) *J. Geophys. Res. Planets.*, 104:14033-14049. [6] Shih C.-Y. et al. (1999) *MAPS* 34: 647-656. [7] Changela H. G. and Bridges J. C. (2010) *MAPS.*, 45: 1847-1867. [8] Bridges J.C., Hicks L.J and Treiman A. (2019) In 'Volatiles on Mars' pp426. [9] Holm N. G. et al. (2015) *Astrobiology*, 15: 7. [10] Milesi V. et al. (2015) *GCA* 154: 201-211. [11] Ehlmann B. L. and Edwards C. S. (2014) *An. Rev. Earth Planet. Sci.*, 42: 291-315. [12] Thorpe M. et al. (2022) *J. Geophys. Res. Planets.* (in rev.). [13] Rampe E. et al. (2020) *Geochemistry* 80: 125605. [14] Tomkinson T. et al. (2013) *Nat. Comm.*, 4: 2662.