

CONSTRAINING THE NATURE OF FLUID ALTERATION EVENTS IN THE MARTIAN SUBSURFACE USING TRACE ELEMENT SIGNATURES IN NAKHLITES

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Introduction: Nakhrites are pyroxenites that sample a lava flow from the Amazonian period, ~1.3 Ga, on Mars [1, 2]. Of all Martian meteorites, nakhrites are known to have the best evidence for fluid alteration, as they host range of alteration minerals: hydrous Fe,Mg-phyllsilicates (clay minerals), carbonates, sulphates and halides that likely formed during brief aqueous subsurface events [3-5] as recently as ~680 Ma [6]. The most comprehensive alteration model suggests that all the secondary minerals were formed by an episodic event mediated by a low-T hydrothermal brine [3], but alternative models are considered to explain the origin of some alteration minerals. For example the formation of carbonates by dissolution and replacement (carbonation) of olivine [4] or deposition of salts from evaporating surface-derived acidic brine [5]. Varying isotopic D/H signatures across various nakhrites suggest that alteration phases may have been deposited by fluids derived from the martian mantle [7], and/or from crustal/atmospheric reservoirs. In fact, the understanding of alteration history is limited because the majority of interpretations are based primarily on the observation of Fe,Mg-silicates, and limited data exist on textures and chemistry of salt minerals themselves. Moreover, trace element composition of alteration products in nakhrites are rarely reported [5], even though this information is a viable means to constrain alteration events and fluid sources. Building upon recent 2D and 3D studies of secondary minerals in nakhrites [8,9] we have undertaken a non-destructive, synchrotron-based XRF trace element mapping study of a range of alteration phase assemblages in nakhrites.

Samples and Methods: Non-destructive, synchrotron-based XRF mapping was performed on the same Nakhla, Governador Valadares, Lafayette, fragments as [8,9] using beamline I18 at Diamond Light Source, UK [10]. With a beam spot-size of ~2 µm and a step size of 3 µm XRF maps up to ~200 µm × 250 µm were acquired from areas that host either halite, hydrous Fe,Mg-phyllsilicates, Fe,Mg-carbonates, Mn-carbonates, and/or sulphates. Fragments ~5×5×5 mm in size with unpolished and uncoated surfaces were oriented with respect to the incident beam and the detector so as to minimize the effects of topography and shadowing. In order to mitigate the effects of interference and peak overlap at low energies, maps were repeated at energies above and below the absorption edge of the target trace element. XANES point spectra were collected to verify the presence of the trace elements of interest.

Results: Within Nakhla we find that the hydrous Fe,Mg-phyllsilicates contain Cl and K, with some evidence for Br and Rb. Halite contains elevated levels of Br but no K, and occasionally there is an apparent association between Zn and Cl in some halite-bearing assemblages. Ca is present with Mn-carbonates and the Mn-carbonates are usually on top of Fe,Mg-carbonates. There are regions of elevated Zn concentrations close to the Mn-carbonates and Sr is positively correlated with the Ca content of carbonates. There are often concentrations of specific trace elements in grain boundary regions. For example, Cu appears to be concentrated between grains of Mn-carbonate, potentially as a chloride phase as elevated concentrations of Cl are observed in these regions. Y has been observed along the edges of hydrous Fe,Mg-phyllsilicates and As is occasionally observed in small (~5 µm) patches within halite regions. Within Lafayette, the XRF maps clearly resolve the Mn- and Fe,Mg-carbonates, showing the Mn-carbonates to be lying on top of the Fe,Mg-carbonates. Zn appears to be strongly associated with the Mn-carbonates, as does Sr which again is more concentrated in Mn-carbonates that are richer in Ca. No other trace elements are convincingly evident in the XRF maps of Lafayette.

Implications for Fluid Alterations: In both the Nakhla and Lafayette samples, Sr is associated with Ca in the Mn-carbonates and the Zn appears to substitute into the Mn-carbonates. Mn-carbonates appear to have formed after Fe,Mg-carbonates, in agreement with [8], and it is possible that some Ca/Sr-rich carbonates formed later still. There is no clear evidence for intra-granular chemical zoning in any alteration phases. Cu, Y and As appear to be associated with alteration phase grain boundaries in Nakhla but not Lafayette. There is thus tentative evidence that at least one additional fluid-flow event occurred in Nakhla that did not occur in Lafayette. Association of Cl, Cu, Zn and Y with Mn-carbonates in Nakhla may suggest fluid derived from martian surface.

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