Geochemical Perspectives Letters

Tardi-magmatic precipitation of Martian Fe/Mg-rich clay minerals via igneous differentiation

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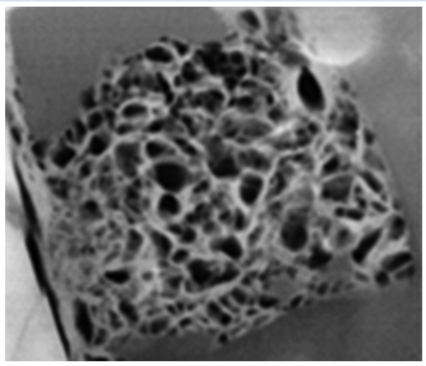
Abstract



Mars is seen as a basalt covered world that has been extensively altered through hydrothermal or near surface water-rock interactions. As a result, all the Fe/Mg-rich clay minerals detected from orbit so far have been interpreted as secondary, *i.e.* as products of aqueous alteration of pre-existing silicates by (sub)surface water. Based on the fine scale petrographic study of the evolved mesostasis of the Nakhla meteorite, we report here the presence of primary Fe/Mg-rich clay minerals that directly precipitated from a water-rich fluid exsolved from the Cl-rich parental melt of nakhlites during igneous differentiation. Such a tardi-magmatic precipitation of clay minerals requires much lower amounts of water compared to production *via* aqueous alteration. Although primary Fe/Mg-rich clay minerals are minor phases in Nakhla, the contribution of such a process to Martian clay formation may have been quite significant during the Noachian given that Noachian magmas were richer in H_2O. In any case, the present discovery justifies a re-evaluation of the exact origin of the clay minerals detected on Mars so far, with potential consequences for our vision of the early magmatic and climatic histories of Mars.

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Letter

Recent discoveries have provided direct evidence that chemically evolved rocks formed over short timescales on planetesimals early in the Solar System (Day *et al.*, 2009; Bischoff *et al.*, 2014; Frossard *et al.*, 2019). However, it is unclear if and how much such evolved rocks contributed to the ancient crust of Mars (Sautter *et al.*, 2015, 2016; Udry *et al.*, 2018; Bouley *et al.*, 2020).

Only rare exposures of evolved rocks containing hydrated silica and/or quartz have been reported from orbit (Christensen *et al.*, 2005; Bandfield, 2006; Carter and Poulet, 2013; Wray *et al.*, 2013). In addition to the small depth analysed, that makes dust and coatings dominate the signal, difficulties pertain to the spectral featureless of the main constituents of evolved rocks (*e.g.*, feldspar and quartz), leading to some much discussed ambiguities (Smith and Bandfield, 2012; Ehlmann and Edwards, 2014; Rogers and Nekvasil, 2015). Because of the presence of Fe/Mg-rich clay minerals interpreted as secondary aqueous alteration products (Gooding *et al.*, 1991; Bridges *et al.*, 2001; Carter and Poulet, 2013; Wray *et al.*, 2013; Hicks *et al.*, 2014), the rare evolved rocks detected from orbit have been interpreted as resulting from the hydrothermal alteration or diagenesis of mafic crustal materials (Smith and Bandfield, 2012; Ehlmann and Edwards, 2014).

Yet, robotic missions evidenced that igneous differentiation induced by fractional crystallisation occurred on Mars (McSween *et al.*, 1999, 2006; Stolper *et al.*, 2013; Sautter *et al.*, 2015, 2016; Udry *et al.*, 2018). The Spirit rover encountered alkaline volcanic rocks, substantially enriched in Na/K-rich plagioclase relative to pyroxene and olivine (McSween *et al.*, 2006), while Curiosity found both fine grained alkali basalts known as mugearites (Stolper *et al.*, 2013) and coarse grained alkali feldspar-bearing lithologies (Sautter *et al.*, 2015, 2016; Udry *et al.*, 2018). Consistently monzonitic clasts have been found in Black Beauty (Humayun *et al.*, 2013; Hewins *et al.*, 2017), while K-feldspar, SiO_2 polymorphs (cristobalite, trydimite and quartz) and even rhyolitic glass have been observed (in addition to apatite and zircon) within nakhlites (Treiman, 2005; Nekvasil *et al.*, 2007; McCubbin *et al.*, 2013; Giesting and Filiberto, 2016).

Here we investigate the paragenesis of the evolved mesostasis of Nakhla, the Martian meteorite eponym for nakhlites. Nakhlites are augite cumulates that differ from each other in the proportion and crystallinity of the mesostasis (Treiman, 2005). They were emplaced ~1.3 Gyr ago as multiple flows, dikes or sills close to the surface (Udry and Day, 2018). The consensus

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is that nakhlites and chassignites sampled different levels of what may have been a single, large igneous complex (McCubbin *et al.*, 2013), with nakhlites having crystallised from the residual melt having first produced chassignites (Udry and Day, 2018).

Like the other nakhlites, Nakhla exhibits few olivine grains and numerous large crystals of augite that are set in a crystalline mesostasis (Fig. 1). All augite crystals in contact with the mesostasis are zoned, from Mg-rich cores to Fe-rich rims. The mesostasis is mainly composed of Na/Ca-plagioclase laths and euhedral titanomagnetite (Fig. 1). In between the Na/Ca-plagioclase laths, the mesostasis exhibits a vermicular texture consisting of nanoscale Cl-apatite and Fe-sulfides together with quartz, K-feldspar and Fe/Mg-rich clay minerals (Figs. 1, 2). In contrast to iddingsite veins crosscutting olivine in nakhlites (Gooding *et al.*, 1991), these Fe/Mg-rich clay minerals display a high porosity and can be found as masses in contact with or within Na/Ca-plagioclase, Cl-apatite, K-feldspar or quartz (Figs. 1, 2). The clay minerals are made of ~40 to 100 nm wide lamellar materials, with stacking height ranging from ~10 to 20 nm and a d-spacing of ~10 Å (Fig. 2). Their mean structural formula, $(K_{0.22}Na_{0.30}Ca_{0.07}(Mg_{0.93}Fe_{0.58}Mn_{0.05}Ti_{0.02}\square_{0.42})(Fe_{0.93}Al_{0.21}Si_{2.86})(O_{10})[(OH,O)_{1.86},Cl_{0.14}])$ according to STEM-EDS analyses, falls within the domain of interstratified or mixtures of Cl-rich saponite and celadonite (Meunier *et al.*, 2008; Meunier, 2010).

The inclusions of Fe/Mg-rich clay minerals within K-feldspar grains (Fig. 2) and the absence of chlorite and/or Al-rich layers are inconsistent with aqueous alteration processes of K-feldspars (Meunier, 2010; Beaufort *et al.*, 2015). None of the Cl-apatite, K-feldspar and quartz grains composing the mesostasis of Nakhla display any alteration texture such as retreating

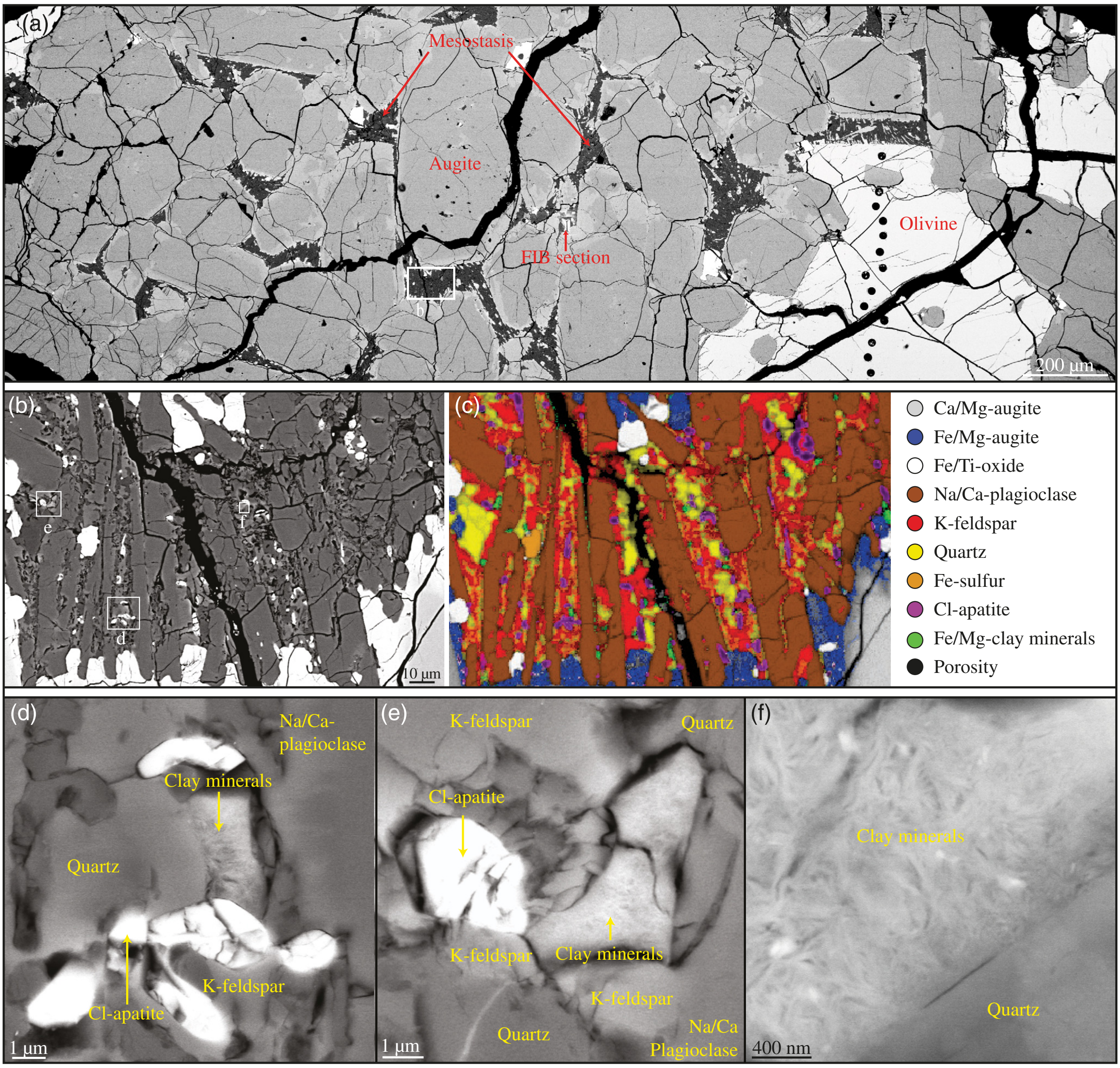

Figure 1 SEM images of the investigated thin section of Nakhla in BSE mode. **(a)** BSE image of the augite cumulate texture of Nakhla. **(b,c)** BSE image of the Nakhla mesostasis **(b)** and corresponding EDXS-based mineralogical map **(c)**. **(d–f)** BSE images of the tardi-magmatic Fe/Mg-rich clay minerals observed in the mesostasis of Nakhla in contact with Na/Ca-plagioclase, K-feldspar, quartz and Cl-apatite.

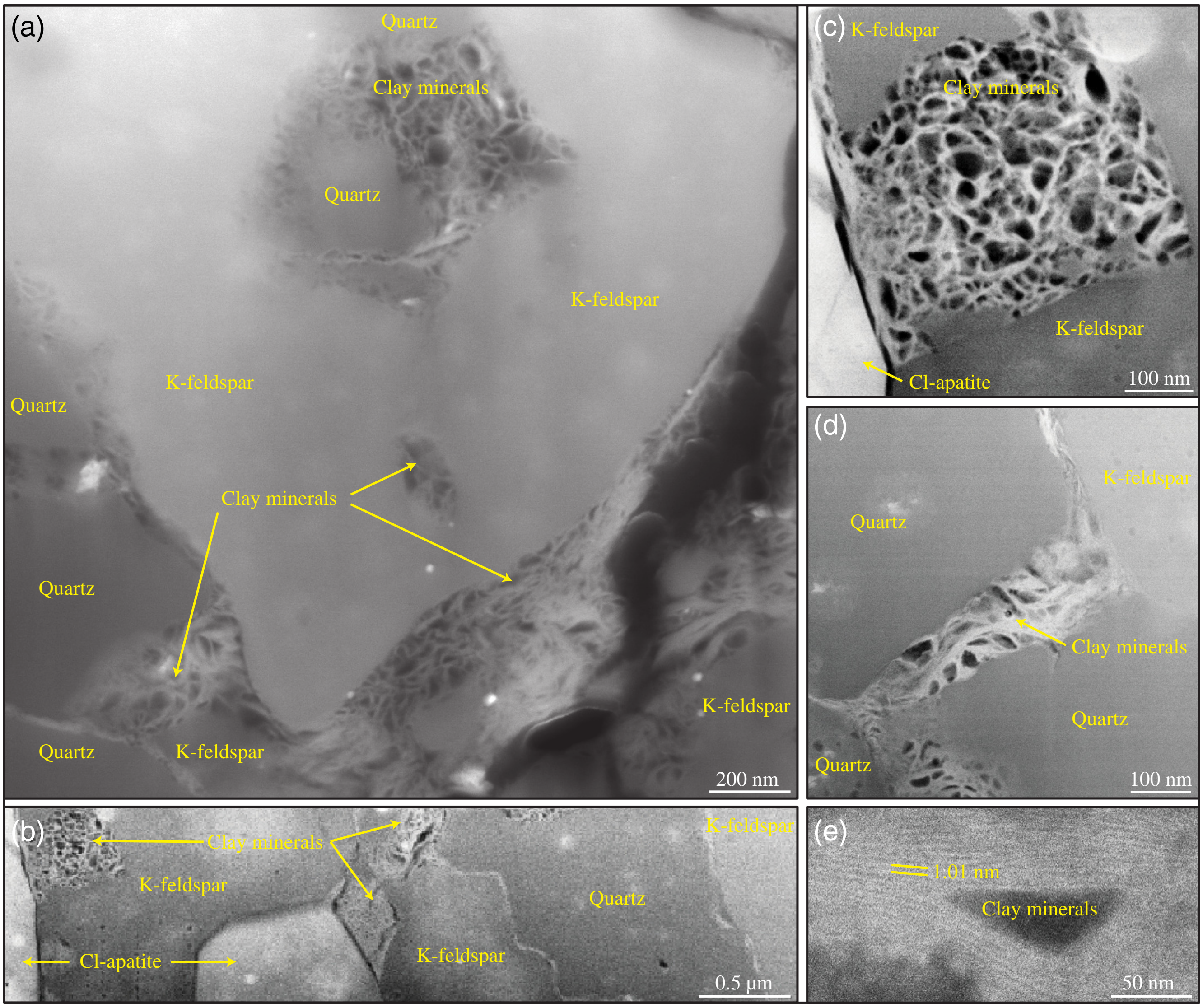

Figure 2 TEM images of the FIB sections extracted from the mesostasis of Nakhla in STEM mode. **(a–e)**. Images of the magmatic Fe/Mg-rich clay minerals minerals observed in the mesostasis of Nakhla in contact with K-feldspar, quartz, Cl-apatite and in inclusions within K-feldspar.

surfaces or pitch-like material resulting from dissolution. In contrast, all these phases exhibit sharp boundaries, even when in contact with the Fe/Mg-rich clay minerals. A halogen content as high as that of these Fe/Mg-rich clay minerals has never been reported for secondary clay minerals (Bailey, 1984). The high chlorine content of the Fe/Mg-rich clay minerals observed in Nakhla is more consistent with a precipitation from a Cl-rich, magma derived fluid (Bailey, 1984), as is the case for the other Cl-rich minerals previously reported in nakhlites, such as apatite, scapolite and amphibole (Filiberto and Treiman, 2009a; McCubbin *et al.*, 2013; Filiberto *et al.*, 2014; Giesting and Filiberto, 2016). In other words, the Fe/Mg-rich clay minerals observed in Nakhla were not produced by aqueous alteration, but rather have a tardi-magmatic origin. Tardi-magmatic precipitation of smectite and celadonite similar to that observed here in Nakhla has been previously reported in terrestrial rocks (Meunier *et al.*, 2008, 2012; Meunier, 2010; Berger *et al.*, 2014, 2018).

Petrographic investigations reveal that the tardi-magmatic Fe/Mg-rich clay minerals observed in Nakhla precipitated at the end of the cooling sequence from a residual water-rich, magma derived, Cl-rich fluid (Fig. 3). According to previous studies, the parental melt of Nakhla results from a mixture of different magmas with a Cl-rich fluid of some kind (McCubbin *et al.*, 2013; Giesting and Filiberto, 2016). The crystallisation of Mg-rich augite cores followed by the overgrowth of Fe-rich rims increased the relative concentrations of Na, Ca and Al in the trapped, residual, evolved melt. Laths of Na/Ca-plagioclase then nucleated together with euhedral titanomagnetite at the surface of the augite grains, before the crystallisation of K-feldspar, quartz and Cl-apatite in between the laths of Na/Ca-plagioclase (Fig. 3). Finally, the observed Fe/Mg-rich clay minerals directly precipitated from the leaving residual water-rich, magma derived, Cl-rich fluid (Fig. 3). The differences in porosity between different pockets of clay minerals might result from the cooling history of the lava flow and/or the variable gas content of the residual water-rich, magma derived, Cl-rich fluids from which the clay minerals precipitated.

The precipitation of Fe/Mg-rich clay minerals after that of quartz might be due the low H_2O content of the parental melt of nakhlites (Weis *et al.*, 2017; Filiberto *et al.*, 2019). In fact, early experimental studies demonstrated that H_2O-poor melts produce feldspar and quartz before phyllosilicates (Naney, 1983). Of note, despite the low H_2O content of the parental melt of

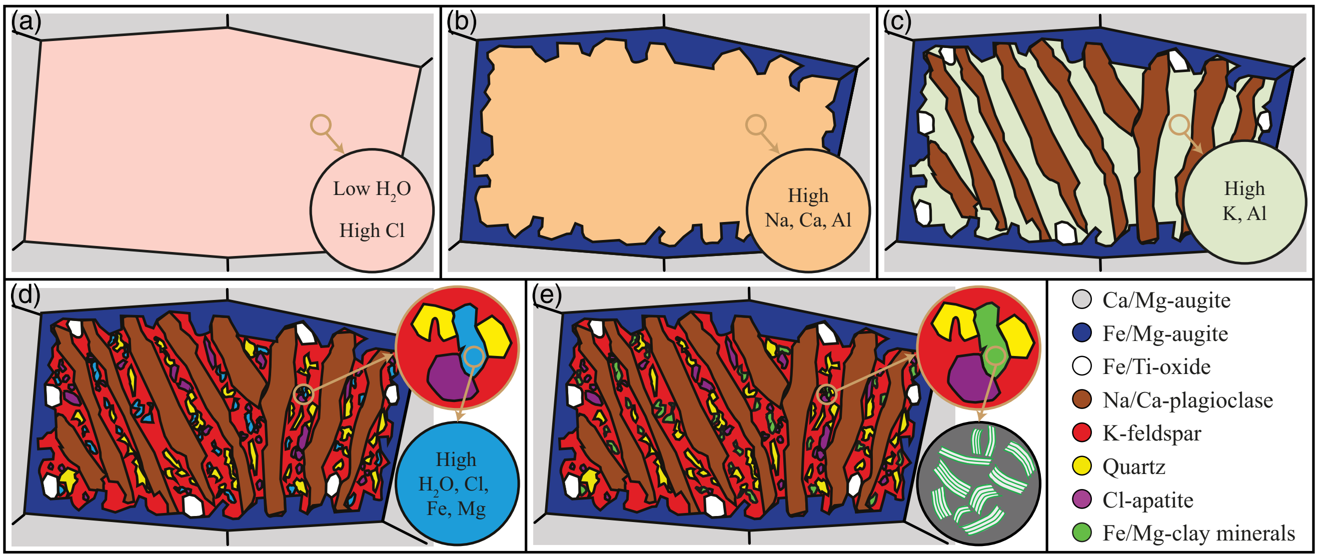

Figure 3 Sketch summarising the crystallisation sequence of the mesostasis of Nakhla. **(a)** Crystallisation of augite and entrapment of a fraction of the residual melt. **(b)** Crystallisation of Fe-rich rims of augite. **(c)** Crystallisation of Na/Ca-plagioclase and Fe/Ti-oxides. **(d)** Crystallisation of K-feldspars, Cl-apatite and quartz. **(e)** Precipitation of Cl-rich Fe/Mg-clay minerals.

nakhlites (*e.g.*, <100 ppm; Weis *et al.*, 2017 and Filiberto *et al.*, 2019), the final mineral assemblage observed here (*i.e.* Cl apatite, K feldspar, quartz and Fe/Mg-rich clay minerals) is typical of evolved/granitic rocks, even though it has long been argued that a significant H_2O content is required to produce such rocks (Campbell and Taylor, 1983). This apparent paradox can be explained by the high Cl content of the parental melt of nakhlites. In fact, the presence of Cl in a magma affects its liquidus temperature and increases pyroxene stability to lower pressures as does H_2O, permitting the residual melt to evolve to lower temperatures before solidification (Filiberto and Treiman, 2009a,b), eventually leading to alkali-rich/felsic compositions like those obtained from H_2O-rich melts (Nekvasil *et al.*, 2004; Whitaker *et al.*, 2008).

Altogether, the results of the present study portend that some the Fe/Mg-rich clay minerals detected on Mars so far may not be the products of the aqueous alteration of pre-existing silicates by (sub)surface water but rather tardi-magmatic clays minerals, as anticipated earlier (Meunier *et al.*, 2012; Berger *et al.*, 2014, 2018). Similarly, some of the evolved units detected from orbit and containing Fe/Mg-rich clay minerals (Christensen *et al.*, 2005; Bandfield, 2006; Carter and Poulet, 2013; Wray *et al.*, 2013) may not be mafic rocks having undergone aqueous alteration processes but rather evolved/granitic materials containing primary Fe/Mg clay minerals that formed *via* igneous differentiation. Given that Noachian magmas were richer in H_2O (Médard and Grove, 2006; Filiberto *et al.*, 2019), both igneous differentiation and tardi-magmatic production of clay minerals may have been quite significant during the Noachian. Determining the exact contribution of these processes during the Noachian could potentially resolve the origin of the Martian dichotomy (Watters *et al.*, 2007) and explain both the missing salt paradox (Milliken *et al.*, 2009) and the amorphous conundrum (Tosca and Knoll, 2009).

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Author Contributions

JCV and SB designed the present study, with critical inputs from CLG and VS. JCV and SB performed the SEM analyses. JCV, SB and CLG performed the TEM analyses. JCV and CLG processed the EXDS data. All authors contributed to the interpretation of the data and discussed their implications. JVC and SB wrote the manuscript, with critical inputs from all authors.

Additional Information

Supplementary Information accompanies this letter at http://www.geochemicalperspectivesletters.org/article2023.

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Supplementary Information

The Supplementary Information includes:

- Materials and Methods
- Supplementary Information References

Materials and Methods

SEM & TEM

Scanning electron microscopy (SEM) and EDXS mapping was performed on a thin section of Nakhla using a SEM-FEG Ultra 55 Zeiss (IMPMC - Paris, France) microscope operating at a 15-kV accelerating voltage and a working distance of 7.5 mm for imaging with backscattered electrons and EDXS mapping. Transmission electron microscopy in scanning mode (STEM) was performed on FIB foils using a Thermofisher Titan Themis 300 microscope operated at 300 keV (CCM – Lille, France). TEM-based hyperspectral EDXS data were obtained using the super-X detector system equipped with four windowless silicon drift detectors with a high sensitivity for light elements. The probe current was set at maximum 200 pA with a dwell time at 10 µs per pixel.

FIB

Focused ion beam (FIB) ultrathin sections were extracted from the mesostasis of Nakhla using an FEI Strata DB 235 (IEMN, Lille, France). Milling at low Ga-ion currents minimises common artefacts including: local gallium implantation, mixing of components, creation of vacancies or interstitials, creation of amorphous layers, local compositional changes or redeposition of the sputtered material on the sample surface (Wirth, 2009).

EDXS data processing

A key aspect of this work is the post-processing of the collected EDXS hyperspectral data, performed using the Hyperspy python-based package (De La Pena *et al.*, 2017). The signal was first denoised using PCA and then fitted by a series of Gaussian functions and a physical model for background/bremsstrahlung. The integrated intensities of the Gaussian functions were used to quantify the compositions of the clay minerals thanks to the Cliff-Lorimer method, using experimentally determined k-factors. Absorption correction was taken into account, which is mandatory to correct for the re-absorption within the sample of oxygen X-rays. These steps correct for the thickness of the sample. Finally, end-member phases were identified and their spectra used as inputs for linear combination fitting (multiple linear least square fits). Pixels of similar composition were given the same colors scaled as a function of the proportion of each phase.

Supplementary Information References

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Wirth, R. (2009) Focused Ion Beam (FIB) combined with SEM and TEM: Advanced analytical tools for studies of chemical composition, microstructure and crystal structure in geomaterials on a nanometre scale. *Chemical Geology* 261, 217–229.