

# Martian Magmatic Clay Minerals Forming Vesicles: Perfect Niches for Emerging Life?

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## Abstract

Mars was habitable in its early history, but the consensus is that it is quite inhospitable today, in particular because its modern climate cannot support stable liquid water at the surface. Here, we report the presence of magmatic Fe/Mg clay minerals within the mesostasis of the martian meteorite NWA 5790, an unaltered 1.3 Ga nakhlite archetypal of the martian crust. These magmatic clay minerals exhibit a vesicular texture that forms a network of microcavities or pockets, which could serve as microreactors and allow molecular crowding, a necessary step for the emergence of life. Because their formation does not depend on climate, such niches for emerging life may have been generated on Mars at many periods throughout its history, regardless of the stability or availability of liquid water at the surface. **Key Words:** Mars—Clay minerals—Magmatism—Habitability—Meteorite. *Astrobiology* 21, xxx–xxx.

## 1. Introduction

**T**HE CONCEPT OF HABITABILITY is essentially tied to the presence of liquid water at (or near) the surface of a planetary body. The surface of Mars was habitable during the Noachian (4.1–3.7 Ga) because liquid water was then both stable and available, at least episodically. Environments likely existed on Noachian Mars with liquid water and metabolic energy sources available for the development of life (Westall *et al.*, 2013; Grotzinger *et al.*, 2014; Kral *et al.*, 2014; Hurowitz *et al.*, 2017; McMahon *et al.*, 2018). This view relies on the widespread occurrence of Noachian Fe/Mg clay minerals interpreted as products of the alteration of preexisting silicates by (sub)surface liquid water (Bibring *et al.*, 2006; Ehlmann *et al.*, 2011; Carter *et al.*, 2013; Sun and Milliken, 2015; Viennet *et al.*, 2019). However, this may not be the entire story. In fact, some clay minerals can directly precipitate from magmatic fluids (Meunier *et al.*, 2008, 2012; Berger *et al.*, 2014, 2018; Viennet *et al.*, 2020). Because these minerals cannot be used as a proxy for the past presence of liquid water, it seems *a priori* difficult to consider such magmatic clay minerals as indicators of habitability. Still, as discussed here, magmatic clay minerals may offer fantastic opportunities for prebiotic reactions.

To date, the only occurrence of martian magmatic Fe/Mg clay minerals has been found in the evolved (alkali/felsic) mesostasis of Nakhla (Viennet *et al.*, 2020), the martian meteorite eponym for nakhlites. Whether these minerals are more than anecdotal on Mars is difficult to determine, especially given the fierce debate over the exact fraction of the martian crust made up of evolved (alkali/felsic) rocks (Sautter *et al.*, 2016; Udry *et al.*, 2018; Bouley *et al.*, 2020). Here, we report the presence of magmatic Fe/Mg clay minerals within the mesostasis of NWA 5790, an unaltered Amazonian nakhlite (~1.3–1.4 Ga; Nyquist *et al.*, 2001). In contrast to that of Nakhla, the mesostasis of NWA 5790 does not exhibit a high level of igneous differentiation, which makes this meteorite more archetypal of the martian crust (Udry *et al.*, 2018).

## 2. Materials and Methods

### 2.1. Section of NWA 5790 investigated

The section of NWA 5790 investigated here is the section B described in the work of Jambon *et al.* (2016). This section was selected because it does not exhibit any trace of terrestrial alteration (Jambon *et al.*, 2016) or “desert varnish” or “caliche,” that is, clay mineral sheets or calcite

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veins produced by alteration (Tomkinson *et al.*, 2015; Balta *et al.*, 2017). The augite and olivine grains of the section investigated do not display any iddingsite, amphibole, or smectite vein (see Supplementary Fig. S1).

SFI ►

## 2.2. Scanning and transmission electron microscopy

AU1 ►

Scanning electron microscopy and energy-dispersive X-ray spectroscopy (EDXS) mapping were performed on a thin section of Nakhla with 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 focused ion beam foils with a Thermo Fisher Titan Themis 300 microscope operated at 300 keV (CCM, Lille, France). Transmission electron microscopy-based hyperspectral EDXS data (see below) were obtained by using the super-X detector system that comprises four windowless silicon drift detectors of high sensitivity. The probe current was set at maximum 200 pA with a dwell time at 10  $\mu$ s per pixel.

## 2.3. Focused ion beam preparations

Focused ion beam (FIB) ultrathin sections were extracted with an FEI Strata DB 235 (IEMN, Lille, France). Milling at low Ga-ion currents minimizes common artifacts, 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).

## 2.4. EDXS data processing

A key aspect of this work is the postprocessing of the collected EDXS hyperspectral data, performed by using the Hyperspy Python-based package (de La Pena *et al.*, 2017). The signal was first denoised by using PCA and then fitted by a series of Gaussian functions. The integrated intensities of the Gaussian functions were used to quantify the spectra with the Cliff-Lorimer method, using experimentally determined k-factors. Special care was taken to correct for absorption effect within the sample, in particular for oxygen X-rays. Absorption correction depends on thickness density,

which can be determined by comparing quantification made by Iron L-lines and Iron K-lines (Morris, 1980). Each pixel was quantified independently, and end-member phases were identified based on mixing diagrams.

## 2.5. Raman spectroscopy

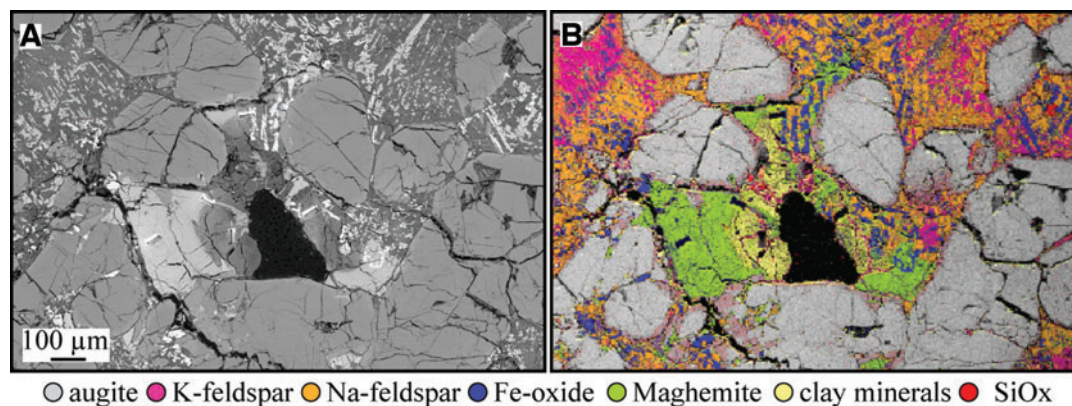
Raman was performed by using a homemade time-resolved Raman spectrometer (Beyssac *et al.*, 2017). The laser is a nanosecond-pulsed DPSS laser operating at 532 nm with a 1.2 ns duration (FWHM) for the pulse, 10 to 2000 Hz repetition rate, and up to 1 mJ output energy per pulse. The laser was focused at the sample surface through a microscope objective ( $\times 20$ , numerical aperture 0.42), and the Raman signal was collected in the backscattering geometry. A Notch filter was used to cut the Rayleigh scattering. The signal was collected in an optical fiber and sent into a modified Czerny-Turner spectrometer manufactured by Princeton Instruments to be measured with a PIMAX4 ICCD camera manufactured by Princeton Instruments.

## 3. Results

Like the other naxhlites, NWA 5790 is an unaltered cumulate rock that exhibits large euhedral or subhedral crystals of augite set in a crystalline mesostasis (Figs. 1 and S1). Consistent with previous reports (Tomkinson *et al.*, 2015; Jambon *et al.*, 2016; Balta *et al.*, 2017), petrographic observations show that the mesostasis of NWA 5790 is made of Na/Ca-plagioclases and K-feldspars embedding skeletal Fe-rich Ti-oxides and Ti-rich magnetites that host ilmenite exsolutions (Fig. 1). In addition to augite grains, the investigated section contains an unaltered euhedral olivine (Fig. S1) and a zone of about the same size composed of fibrous minerals (Fig. 1). This zone exhibits a radial structure, with a central pore of about 200  $\mu$ m in diameter, surrounded by Fe/Mg clay minerals intimately mixed with Fe-Si-Al-Ca nanograins, themselves surrounded by dendrites of maghemite and rather amorphous Fe-Si-Al-Ca materials in contact with augite grains and the mesostasis (Fig. 1 and Supplementary Materials). In contrast to the contact with augite grains, the transition with the mesostasis is not sharp; some Na/Ca plagioclases and skeletal equiaxed Fe-rich Ti oxides are distributed within the observed

◀ F1

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AU3 ►

**FIG. 1.** Scanning electron microscope (SEM) image of the zone of NWA 5790 investigated in backscattered electron (BSE) mode (A) and the corresponding EDXS-based mineralogical map (B). Note the euhedral augite grains with no dissolution features surrounding the dendritic maghemite and Fe/Mg clay minerals. Color images are available online.

dendrites. These dendrites display a nearly paraboloidal fin-  
gerlike shape with side branches, that is, a columnar dendritic  
texture with trunks of a few to hundreds of microns in length  
(Fig. 2), typical of sudden cooling or quenching conditions.

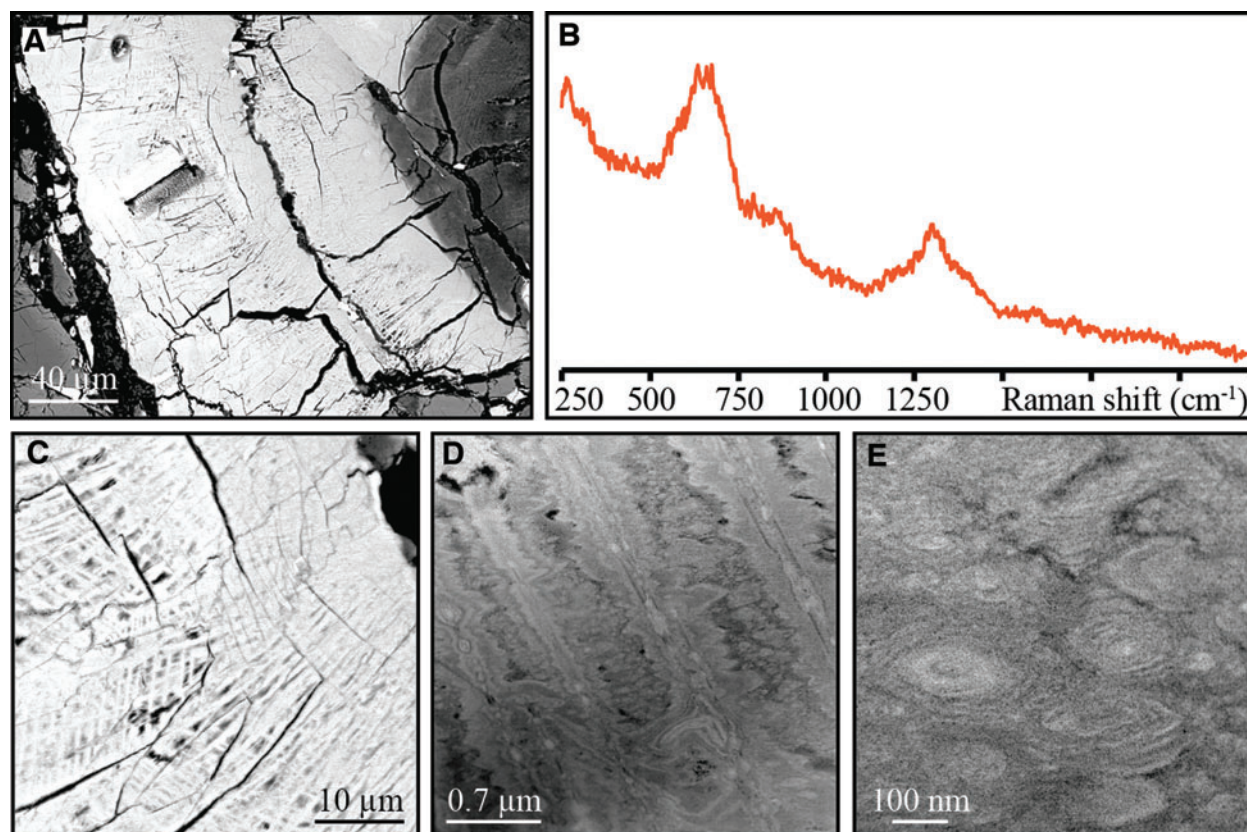
- F2 ▶** The Fe/Mg clay minerals consist of layers of a few hun-  
dreds of nanometers in length stacked over a few tens of  
nanometers, with layer to layer distances of  $\sim 11.8 \text{ \AA}$ , a typ-  
**F3 ▶** ical structure of smectites (Fig. 3). These Fe/Mg clay min-  
erals are chemically heterogeneous, with a mean chemical  
composition falling between nontronite, celadonite, and sap-  
onite (Fig. 3). Most importantly, the observed anticorrela-  
tion between Mg and Cl (Fig. 3) attests to the presence of  
Cl within the structure of these Fe/Mg clay minerals accord-  
ing to the Mg-Cl crystallographic avoidance principle  
(Bailey, 1984). This assemblage of Cl-rich Fe/Mg clay min-  
erals is highly porous and exhibits a network of micro-  
cavities or pockets, from tens of nanometers to several  
**F4 ▶** hundreds of nanometers in diameter (Fig. 4).

#### 4. Discussion

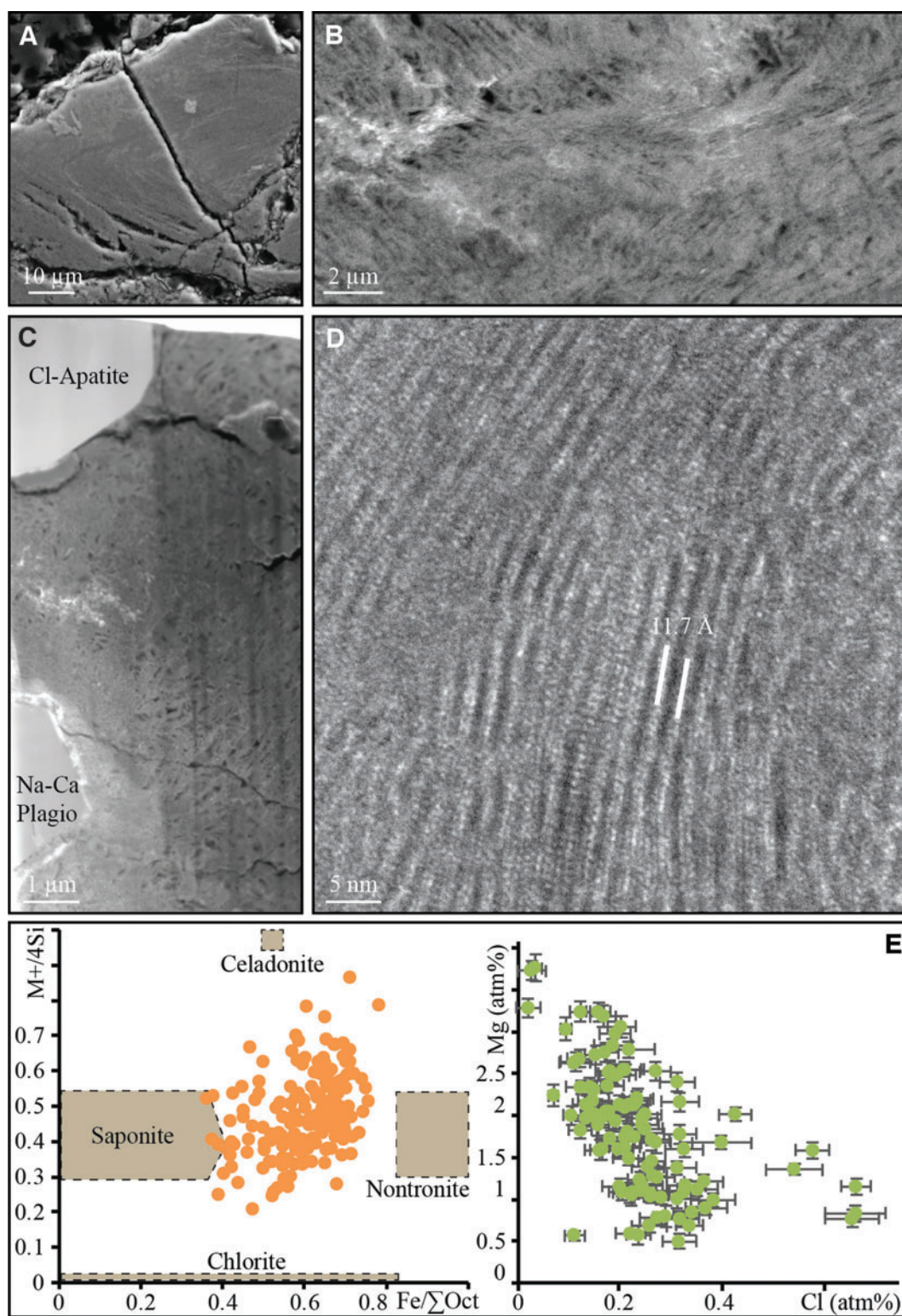
These Fe/Mg clay minerals were clearly not produced via  
the aqueous alteration of preexisting silicates. In fact, the  
section of NWA 5790 investigated here has been recognized  
to be unaltered (Tomkinson *et al.*, 2015; Jambon *et al.*, 2016),  
and the alteration of the Ti-rich and Al-rich mesostasis  
(mainly made of feldspars) would have produced Ti-rich

and Al-rich secondary minerals (Meunier and Velde, 2004).  
In contrast, the clay minerals described here display a low  
Al content (4 wt %) and do not contain any Ti. The Fe and  
Mg contents of these clay minerals could be consistent with  
the alteration of augite, but none of the augite grains of  
NWA 5790 display alteration textures such as retreating  
surfaces or pitchlike features resulting from dissolution. No  
contact with the Fe/Mg clay minerals could be observed as  
well. Also, the high Cl content of these Fe/Mg clay minerals  
is similar to that of Cl-rich magmatic apatites, scapolites,  
and amphiboles found in other nakhlites (Sautter *et al.*,  
2006; McCubbin *et al.*, 2013; Giesting and Filiberto, 2016)  
and that of the magmatic Fe/Mg clay minerals found in  
Nakhla (Viennet *et al.*, 2020).

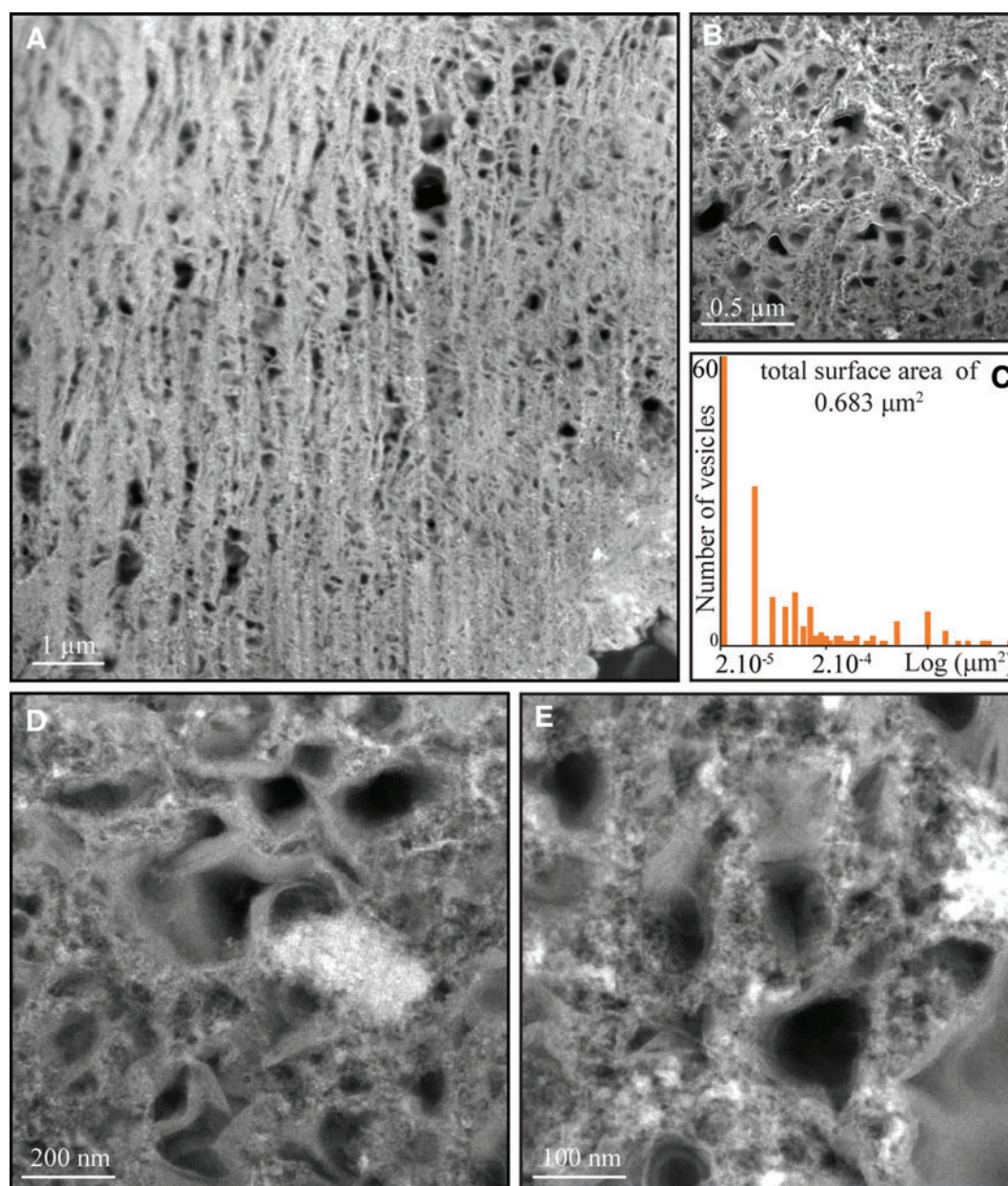
The subhedral/euhedral nature of augite crystals is con-  
sistent with slow growth within a magmatic chamber  
(Treiman, 2005; Jambon *et al.*, 2016; Udry and Day, 2018)  
or within a chilled margin of a lava flow or sill (Tomkinson  
*et al.*, 2015). The crystallization and the accumulation of  
augite grains led to the entrapment of a residual liquid  
enriched in Cl, potentially as a result of contamination by  
an exogenous Cl-rich fluid (McCubbin *et al.*, 2013; Udry  
and Day, 2018). With decreasing temperature, the Na/Ca  
plagioclases and the K-feldspars crystallized together with  
the skeletal equiaxed Fe-Ti oxides and the skeletal Ti-  
magnetites, eventually leading to the exsolution of a Cl/  
Fe-rich brine (Fig. 1). Here, the screw dislocations at the



**FIG. 2.** Dendritic structures. (A) BSE image of the maghemite showing the location of the FIB foil shown in (D, E). (B) Time-resolved Raman spectra of the maghemite. (C) SEM image highlighting the dendritic texture of the maghemite. (D, E) Transmission electron microscope (TEM) images in STEM mode of the FIB section showing the screw shape of the dendritic texture along the main direction and the texture in spiral perpendicularly to the main direction. Color images are available online.



**FIG. 3.** Magmatic Fe/Mg clay minerals. (A) SEM image in BSE mode showing the huge mass of clay minerals. (B) SEM image in BSE mode showing the fibrous texture of the clay minerals. (C) TEM image in STEM mode of the FIB section (location shown in Fig. S2) showing the contact between Fe/Mg clay minerals and non-altered silicates. (D) TEM image in bright field showing the classical structure in sheets of the Fe/Mg clay minerals with a d-spacing of 11.7 Å. (E) Diagram showing the chemical composition of the Fe/Mg clay minerals and indicating a mixture of nontronite, celadonite and saponite (left) and plot showing the Mg content as a function of Cl content (right). Color images are available online.



**FIG. 4.** Magmatic Fe/Mg clay minerals. (A) TEM image in STEM mode showing the vesicles formed by the Fe/Mg clay minerals. (B) Size distribution of the vesicles corresponding to the TEM images in STEM mode (E). (C–E). TEM images in STEM mode showing the vesicles formed by the Fe/Mg clay minerals. Color images are available online.

surface of the augite grains (together with the decrease of solubility of Fe III with decreasing temperature) potentially controlled the very fast precipitation of the observed dendrites, which explains their screw shapes and unidirectional solidification structures (Vernon, 2004). Masses of highly porous Cl-bearing Fe/Mg clay minerals then precipitated from the residual brine (together with, or right before, the Fe-Si-Al-Ca nanograins), that is, before reaching a high level of igneous differentiation in contrast to what occurred in Nakhla (Viennet *et al.*, 2020).

The magmatic production of Fe/Mg clay minerals evidenced here in a martian meteorite archetypal of the martian crust portends that a possibly significant fraction of the Fe/Mg clay minerals detected on Mars so far may not be the

products of the aqueous alteration of preexisting silicates by (sub)surface water, questioning *a priori* the past habitability of Mars. Yet the magmatic Fe/Mg clay minerals described here have chemical and physical properties that offer fantastic opportunities for (prebiotic) organic reactions (Russell and Martin, 2004; Duval *et al.*, 2020). In fact, in addition to enabling electron transfer, their high Fe content may promote the synthesis and breakdown of universal metabolic precursors (Stucki, 2006), while their high Mg content may prompt both ribozyme-catalyzed and non-enzymatic RNA copying reactions (Adamala and Szostak, 2013).

Clay minerals have long been suggested as the perfect means of concentrating organic molecules onto their external surfaces and within their interlayer space so as to

be available for prebiotic reactions (Bernal, 1951; Ferris and Ertem, 1992; Brack, 2013; Lagaly *et al.*, 2013; Theng, 2018). The surface areas of the magmatic Fe/Mg clay minerals described here are very high; external and internal surface areas reach  $30\ \mu\text{m}^2$  and  $670\ \mu\text{m}^2$  per  $\mu\text{m}^3$ , respectively (*cf.* Supplementary Materials). For smectites, this corresponds to  $2.4 \times 10^{14}$  external sites and  $5.8 \times 10^{14}$  internal sites of possible interactions with organic functional groups (*cf.* Supplementary Materials).

Most importantly, the vesicular texture of these magmatic Fe/Mg clay minerals forms a network of chemically heterogeneous microcavities or pockets that offer even more optimal conditions for (prebiotic) organic reactions. In fact, most scenarios of the origin of life require boundaries or membranes (either organic or inorganic) to isolate, concentrate, and protect organic compounds that could eventually interact or react with each other (Szostak *et al.*, 2001; Hanczyc, 2003; Chen and Walde, 2010; Sun *et al.*, 2016). Plus, a boundary is a privileged interface for the formation of gradients that can promote organic reactions and be exploited as an energetic source (Monnard and Walde, 2015; Branscomb *et al.*, 2017; Branscomb and Russell, 2019). Here, more than 600 microcavities or pockets can be counted per  $\mu\text{m}^2$  of clay minerals, with surfaces ranging from  $1 \times 10^{-5}$  to  $1.4 \times 10^{-2}\ \mu\text{m}^2$  (Fig. 4C), each of them potentially a distinct microreactor for organic chemistry. The multiple connections between these microcavities or pockets may allow organic molecules to diffuse freely into, or out of, these microsystems, possibly leading to molecular crowding and, thereby, increasing the probability of achieving prebiotic chemical reactions.

AU2 ►

## 5. Conclusion

The section of the martian nakhlite NWA 5790 investigated here contains a zone composed of magmatic Fe/Mg clay minerals mixed with Fe-Si-Al-Ca nanograins surrounded by dendritic maghemite. These magmatic Fe/Mg clay minerals exhibit a vesicular texture that forms a network of microcavities or pockets that could serve as microreactors for the emergence of life. The fact that the formation of such niches for emerging life can be achieved via the magmatic precipitation of Fe/Mg clay minerals should make these aggregates a focus for research into the origin of life, especially as such magmatic Fe/Mg clay minerals form within liquid-water-poor environments (prebiotic reactions are thermodynamically out of equilibrium in aqueous solution; Lambert, 2008). *In fine*, by evidencing the formation of niches for emerging life on Mars even during the Amazonian, the present study provides a strong rationale for the possible emergence of life on other planetary bodies, including rocky and/or icy ones (such as Ceres, Enceladus, or Europa) on which the production of clay minerals has recently been reported (Waite *et al.*, 2017; Marchi *et al.*, 2019).

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## Author Contributions

J.C.V. and S.B. designed the present study. J.C.V. and S.B. conducted the SEM experiments. J.C.V. and O.B. conducted the Raman experiments. J.C.V., S.B., and C.L.G. conducted the TEM experiments. J.C.V. and C.L.G. performed SEM and TEM data reduction. All authors contributed to the interpretation of the results. J.C.V. and S.B. wrote the manuscript, with critical input from all authors.

## Author Disclosure Statement

No competing financial interests exist.

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#### Abbreviations Used

BSE = backscattered electron  
EDXS = energy-dispersive X-ray spectroscopy  
FIB = focused ion beam  
SEM = scanning electron microscope  
STEM = scanning transmission electron  
microscopy  
TEM = transmission electron microscope



**AUTHOR QUERY FOR AST-2020-2345-VER9-VIENNET\_1P**

AU1: I defined EDXS here and in the abbreviations list. OK?

AU2: I replaced the dots with multiplication  $\times$ 's. OK?

AU3: I defined BSE here and in the abbreviations list. OK?

AU4: Please confirm the descriptions of panels B and C, compared to the figure.