

SEARCHING FOR BIOSIGNATURES ON MARS: EXPERIMENTAL PERSPECTIVES. S. Bernard¹, J.C. Viennet^{1,2}, P. Jacquemot^{1,2}, C. Le Guillou³, E. Balan¹, L. Delbes¹, B. Rigaud⁴, T. Georgelin⁵, M. Jaber², ¹IMPMC, Muséum National d'Histoire Naturelle, Sorbonne Université, CNRS, Paris, France (sbernard@mnhn.fr), ²LAMS, Sorbonne Université, CNRS, Paris, France, ³UMET, Université de Lille, CNRS, Villeneuve-d'Ascq, France, SIMPC, Sorbonne Université, Paris, France, ⁵CBM, CNRS, Orléans, France.

Introduction: Life may have existed on Mars. Pursuing previous successful missions having visited the red planet, upcoming exploration of Mars aims at identifying potential biosignatures [1], with organic carbon obviously constituting the grail to be sought after [2-3]. Paradoxically, and despite the continuous UV irradiation of the surface [4], organic remains of ancient life should be better preserved in ancient rocks on Mars than on Earth: because Mars has no evidence of active plate tectonics [5], its subsurface has acted as a giant freezer since the Noachian (3.7 Ga) [6].

Yet, even sporadic, volcanic events or crater-forming impacts have likely generated transitory hydrothermal systems, altering the subsurface [7-8]. As a corollary, a better mechanistic understanding of the impact of hydrothermal alteration processes on organic biogeochemical signals is of uttermost importance for conducting the future search for organic biosignatures on Mars with any reasonable degree of confidence.

The ExoMars and Mars2020 missions will explore the subsurface of Martian ancient terrains (>3.7 Ga) covered by clay minerals [1]. Because of their high 'organic preservation potential' [9], the presence of clay minerals at landing sites is believed to maximize the chances of detecting diagnostic organic molecules. Nevertheless, little is known regarding the interactions between clay minerals and (biogenic or abiotic) organic compounds under hydrothermal conditions.

Methodology: We experimentally submitted RNA (i.e. the emblematic bioactive organic molecule) to hydrothermal conditions (at 200°C in pure bi-distilled water for 7 days) in equilibrium with a CO₂ atmosphere (to simulate Noachian Martian atmosphere [10]) in the presence of Mg-smectites (i.e. one of the most widespread clay mineral present on Mars and on the future landing sites [1,9]) We conducted additional experiments under the same conditions with RNA in the absence of Mg-smectites and with Mg-smectites in the absence of RNA to serve as controls. The water-insoluble experimental residues were characterized at a multiple length scale using X-ray diffraction and advanced microscopy and spectroscopy tools.

Results: The crystal structure of the Mg-smectites did not suffer significant transformation during the experiments, but XRD data are consistent with the presence of organic compounds within their interlayer spaces. XANES data reveal that the organic compounds associated to smectites mainly contain saturated aliphatic (288 eV) and amide groups (288.2 eV), as well as aromatic and/or olefinic carbons (285 eV) and ketone and/or phenol groups (287.2 eV) (Fig. 1).

In addition, experimental residues also contain some rare organic masses displaying peaks of carboxylic groups (288.5 eV) and conjugated cycles and/or O- or N-heterocycles (285.5 eV), as well as some even rarer aromatic particles displaying peaks of conjugated aromatic cycles (285.3 eV) and conjugated cycles and/or O- or N-heterocycles (285.5 eV) (Fig. 1).

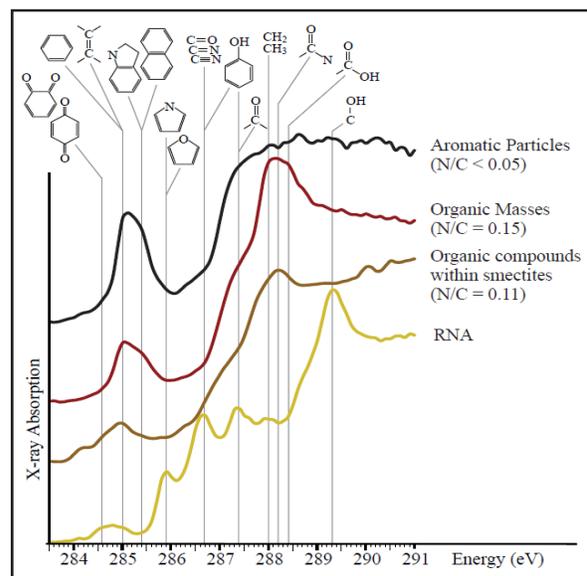


Figure 1: STXM-based XANES spectra of organic compounds encountered in the experimental residues. The spectrum of RNA is shown for comparison.

STEM investigations show that the organo-mineral experimental residues are highly heterogeneous. In addition to organic-rich Mg-smectites, the residues contain (Mg,Ca,Al)-phosphates, Ca-carbonates, as well particles of amorphous SiO₂ (Fig. 2).

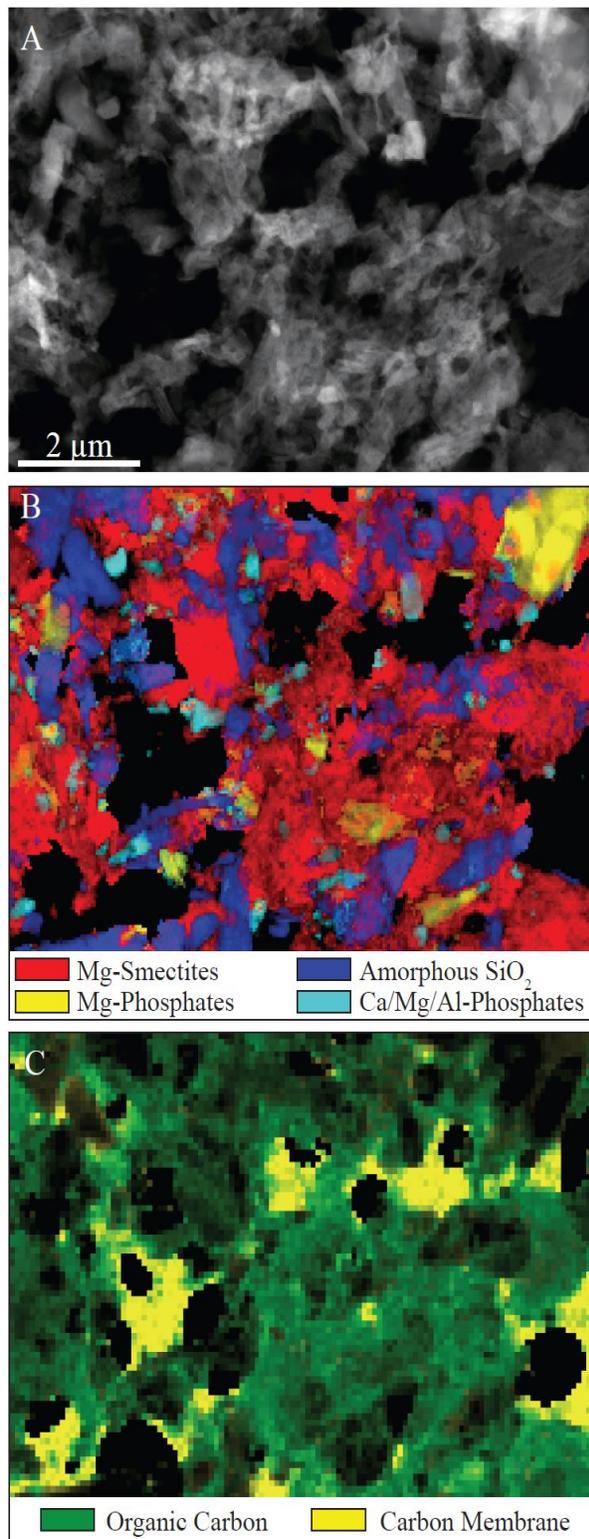


Figure 2: A. STEM image of the residues of experiments. B-C. Maps of minerals and organic compounds.

Discussion: The formation of the observed mineral assemblage can be easily explained. Under hydrothermal conditions, the dissolution of the Mg-smectites together with the interlayer cationic exchange releases Al, Mg and Ca in the system. Ca-carbonates then precipitate, the carbon source being either RNA degradation products or the CO₂ rich atmosphere.

Meanwhile, the phosphate mono-ester groups of RNA undergo hydrolysis, leading to the precipitation of Al-, Ca- and Mg-phosphates. In parallel, N-rich aliphatic organic compounds produced by the degradation of RNA are trapped mainly in the interlayer spaces of the remaining Mg-smectites as a result of cationic exchange (the NH₃⁺ groups of these organic compounds replacing the initial Ca²⁺ cations in the interlayer spaces of the Mg-smectites).

Implications: The present experimental results are of major importance for the upcoming exploration of Mars. Although the trapped organic molecules do not carry any information on the chemical structure of RNA anymore, these experimental results demonstrate that clay minerals can efficiently trap organic carbon under hydrothermal conditions which likely prevailed in the Martian subsurface, confirming the pertinence of digging for organic carbon in the Martian subsurface.

As shown here, the hydrothermal degradation of (N,P)-rich organic molecules leads to the precipitation of a quite uncommon mineral assemblage comprising submicrometric (Al,Mg,Ca)-phosphates and Ca-carbonates together with amorphous silica and clay-organic complexes. Such assemblage may be stable under Martian subsurface conditions and may thus stand for long periods on Mars. Martian targets exhibiting this mineral assemblage will thus constitute highly relevant candidates for sample return as they may result from the hydrothermal degradation of (N,P)-rich organic molecules potentially of biogenic origin.

References: [1] Vago J.L. et al. (2017) *Astrobiology*, 17, 471-510. [2] Westall F. et al. (2015) *Astrobiology*, 15, 998-1029. [3] MacMahon S. et al. (2018), *JGR Planets*, 123, 1012-1040. [4] Fornaro T. et al. (2018), *Life*, 8, 56. [5] Breuer D. & Spohn T. (2003), *JGR Planets*, 108, 5072. [6] Bibring J.P. et al. (2005), *Science*, 307, 1576-1581. [7] Schwenzer S.P. & Kring D.A. (2009), *Geology*, 37, 1091-1094. [8] Osinski G.R. et al. (2013), *Icarus*, 224, 347-363. [9] Ehlmann B.L. et al. (2008), *Nat. Geo.*, 1, 355. [10] Wordsworth R.D. (2016), *Ann. Rev. Earth Planet. Sci.*, 44, 381-408.