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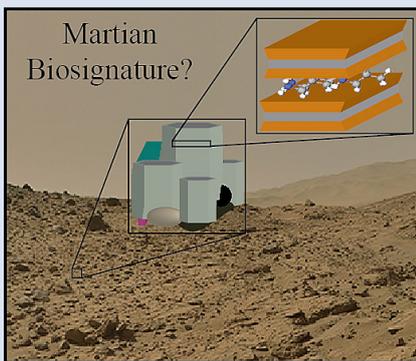
Experimental clues for detecting biosignatures on Mars

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Abstract



Forthcoming exploration of Mars aims at identifying fossil biosignatures within ancient clay-rich formations. The subsurface of Mars has mostly acted as a giant freezer for the last 4 Gyr, thereby preserving potential remains of martian life. Yet, volcanism and impactors have periodically triggered the circulation of hydrothermal fluids, inevitably causing alteration of potentially fossilised biogenic organic materials. It thus appears crucial to quantify the impact of hydrothermal processes on organic biogeochemical signals in the presence of clay minerals. Here, we submitted RNA to hydrothermal conditions in the presence of Mg-smectites. Results show heterogeneous organo-mineral residues, with sub-micrometric phosphates, carbonates and amorphous silica particles together with Mg-smectites with interlayer spaces saturated by N-rich organic compounds. Although the chemical structure of RNA did not withstand hydrothermal conditions, clay minerals efficiently trapped organic carbon, confirming the relevance of drilling for organic carbon in ancient martian sediments. In addition, the

degradation of RNA in the presence of Mg-smectites led to the precipitation of a quite uncommon mineral assemblage that could be seen as a biosignature *per se*. Martian targets exhibiting this mineral assemblage will thus constitute high priority and highly relevant candidates for sample return.

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Letter

Life may have existed on Mars. In fact, some evidence suggest that conditions were favourable for life to exist on Mars during the Noachian (~4.1 to 3.7 Ga), from both the standpoints of liquid water availability and metabolic energy sources (Grotzinger *et al.*, 2014; Kral *et al.*, 2014). Following previous successful missions that visited the red planet, upcoming exploration of Mars aims at identifying potential fossilised biosignatures (Mustard *et al.*, 2013; Westall *et al.*, 2015; Vago *et al.*, 2017), with organic carbon obviously constituting the grail to be sought after (Summons *et al.*, 2008; McMahon *et al.*, 2018). To date, although macromolecular carbon has been detected within most of the martian meteorites (Steele *et al.*, 2016, 2018), only small organic molecules including aromatic, aliphatic, chlorine- and sulfur-rich organic compounds have been measured on Mars (Biemann *et al.*, 1977; Freissinet *et al.*, 2015; Eigenbrode *et al.*, 2018).

Because of the lack of global plate tectonic processes, traces of this life could be preserved in martian sedimentary rocks despite the continuous UV irradiation of the surface

(Cockell, 2002). In fact, the subsurface of Mars has acted as a giant freezer since the Noachian (3.7 Ga) (Clifford *et al.*, 2010). However, even if the surface of Mars has been relatively inactive compared to Earth, volcanism and impactors have periodically triggered the circulation of hydrothermal fluids, inevitably causing alteration of potentially fossilised biogenic organic materials (Abramov and Kring, 2005; Schwenzer and Kring, 2009; Osinski *et al.*, 2013).

In the context of the massive international push for the astrobiological exploration of Mars, the forthcoming ExoMars and Mars2020 missions will explore the subsurface of ancient (>3.7 Ga) clay-rich martian terrains that likely formed in the presence of water (Ehlmann *et al.*, 2008; Mustard *et al.*, 2013; Westall *et al.*, 2015; Vago *et al.*, 2017). Clay minerals, and smectites in particular, are the prime target of these missions because of their strong absorption capacity, low reactivity, and low permeability when compacted (Kennedy *et al.*, 2002; Naimark *et al.*, 2016; McMahon *et al.*, 2018), giving them a high 'potential of biopreservation'. The presence of these minerals at landing sites is thus believed to maximise the chances of detecting diagnostic organic molecules.

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Nevertheless, little is known regarding the interactions between clay minerals and (biogenic or abiotic) organic compounds under hydrothermal conditions that may have existed in the subsurface of Mars. Better constraining the impact of hydrothermal processes on fossilised organic biosignatures thus appears fundamental in conducting the future search for traces of life on Mars with any reasonable degree of confidence. Only laboratory experiments can provide the necessary insights.

RNA is the most emblematic biogenic organic molecule used by all known living organisms, and potentially the most ancient replicating molecule on Earth according to the 'RNA world' hypothesis (Higgs and Lehman, 2014). Mg-smectites are one of the most widespread clay minerals present on Mars and on the future landing sites (Ehlmann *et al.*, 2008; Vago *et al.*, 2017). Here, we heated RNA at hydrothermal conditions in pure bi-distilled water in equilibrium with a CO₂ atmosphere at 200 °C for 7 days in the presence of Mg-smectites. 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. A CO₂ atmosphere was used to simulate Noachian martian atmosphere (Wordsworth, 2016). The water insoluble experimental residues were characterised at different scales using X-ray diffraction and advanced microscopy and spectroscopy tools.

Results show that the presence of Mg-smectites considerably impacts the amount of carbon and nitrogen retrieved in the residues after the experiments. While only 7.8 wt. % of the initial carbon and 1.7 wt. % of the initial nitrogen are found in the organic residues of experiments conducted in the absence of smectite, 36.5 wt. % of the initial carbon and 10.8 wt. % of the initial nitrogen remain in the organo-mineral residues of the experiments conducted with Mg-smectites. These amounts correspond to a mean N/C of 0.11 for the organic component and to TOC values as high as 6.5 wt. % (Table 1), *i.e.* twice the values of most of the hydrocarbon source rocks on Earth (Bernard and Horsfield, 2014). As expected, the presence of clay minerals thus drastically maximises the chances of concentrating, preserving, and ultimately detecting organic molecules.

Table 1 Proportions of carbon and nitrogen (in mass).

Sample	RNA	Mg-smectites-RNA-CO ₂ -200 °C	RNA-CO ₂ -200 °C
Initial mass of organic matter (mg)	-	150	150
Final mass of sample (mg)	-	270	7.0
%wt C	31.6 (±0.07)	6.4 (±0.07)	52.9 (±0.07)
Initial mass of C (mg)		47.4	47.4
Final mass of C (mg)	-	17.3	3.7
% of C preserved		36.5	7.8
%wt N	14.9 (±0.02)	0.9 (±0.02)	5.7 (±0.02)
Initial mass of N (mg)		22.3	22.3
Final mass of N (mg)	-	2.4	0.4
% of N preserved		10.8	1.7

Surprisingly, even though the present experiments were conducted using pure Mg-smectites and pure RNA, the organo-mineral residues are highly heterogeneous. In addition to Mg-smectites, transmission electron microscopy investigations in STEM mode (scanning transmission electron

microscopy) highlight the presence of Ca-carbonates and Mg, Ca and Al-phosphates, together with particles of amorphous silica (Fig. 1). This occurrence of phosphates is attested by diagnostic peaks observed in the XRD pattern (Fig. 2) and the presence of carbonates is confirmed by diagnostic features in the XANES and MIR spectra (Figs. 1 and 2).

The organic carbon of the residues appears essentially coupled with Mg-smectites and exhibits a XANES spectrum very different from that of RNA (Fig. 1). The XANES spectrum of RNA presents a series of peaks attributed to nucleobases (aromatic and olefinic carbons (285 eV), heterocycles (285.9 eV), ketone and phenol groups (286.7 - 287.4 eV)) and ribose (saturated carbons (288.0 eV) and hydroxyl groups (289.3 eV)). In contrast, the organic compounds coupled with smectites in the experimental residues mainly contain amide (288.2 eV) and saturated aliphatic (288.0 eV) groups, as well as aromatic and/or olefinic carbons (285 eV) and ketone and/or phenol groups (287.4 eV). Occurrence of saturated aliphatic groups is also attested by diagnostic C-H stretching bands observed in the ATR-FTIR spectrum (Fig. 2).

In addition to the compounds found with smectites (N/C = 0.11), the experimental residues also contain some rare organic masses (N/C = 0.15) whose spectra display peaks of aromatic and olefinic carbons (285 eV), conjugated (hetero) cycles (285.4 eV) and carboxylic groups (288.4 eV), as well as some even rarer aromatic particles (N/C < 0.05) whose spectra only display peaks of aromatic and olefinic carbons (285 eV) and conjugated (hetero)cycles (285.4 eV) (Fig. 1) (Le Guillou *et al.*, 2018). These compounds are not present in high concentrations, the organic component of the residues essentially consisting of the compounds associated with Mg-smectites, explaining bulk N/C values.

The crystal structure of the Mg-smectites does not suffer significant transformation during the experiments (same hkl reflections on the XRD pattern and similar IR bands related to Mg-OH or Si-O vibrations; Fig. 2). However, the 001 reflection is shifted from 15.51 to 13.31 Å (Fig. 2), indicating a modification of the interlayer spaces. The observed shift is consistent with the presence of organic molecules and/or a mixture of bi- and mono-hydrated cations in the interlayer space (Ferrage *et al.*, 2005; Gautier *et al.*, 2017). Bands at ~1440 and ~1580 cm⁻¹ in the FTIR spectrum of experimental residues are consistent with the presence of NH₄⁺ and R-NH₃⁺ groups, respectively.

The presence of ammonium in the interlayer spaces of smectites is excluded, however. In fact, for those exposed to high vacuum, the 001 reflections of the experimental residues and of the pristine Mg-smectites saturated with NH₄⁺ exhibit a markedly different behaviour (Fig. 2), showing that the interlayer spaces of these smectites are locked by N-rich organic compounds rather than by ammonium. Consistently with XANES data indicating N/C values of 0.11 for these compounds, XRD data show a 001 reflection at 13.55 Å for the Mg-smectites of the residues (Fig. 2) indicating the presence, within the interlayer spaces, of organic compounds containing up to 10 carbon atoms for 1 R-NH₃⁺ group (*i.e.* N/C values of about 0.1) according to the alkylammonium method (Laird *et al.*, 1989). Assuming that R-NH₃⁺ groups totally compensate the loss of Ca²⁺, the Mg-smectites contain 1.3 wt. % of nitrogen, and thus 10.9 wt. % of carbon (N/C = 0.1). Given that the residues exhibit a TOC of 6.5 wt. %, assuming that most of the organic compounds of the experimental residues are within the interlayer spaces of the Mg-smectites leads to a proportion of approximately 60 wt. % of Mg-smectites in the residues, which is quite consistent with TEM data.

The formation of the observed mineral assemblage can be explained as follows (Fig. 3). Under hydrothermal conditions, the dissolution of the Mg-smectites, together with the



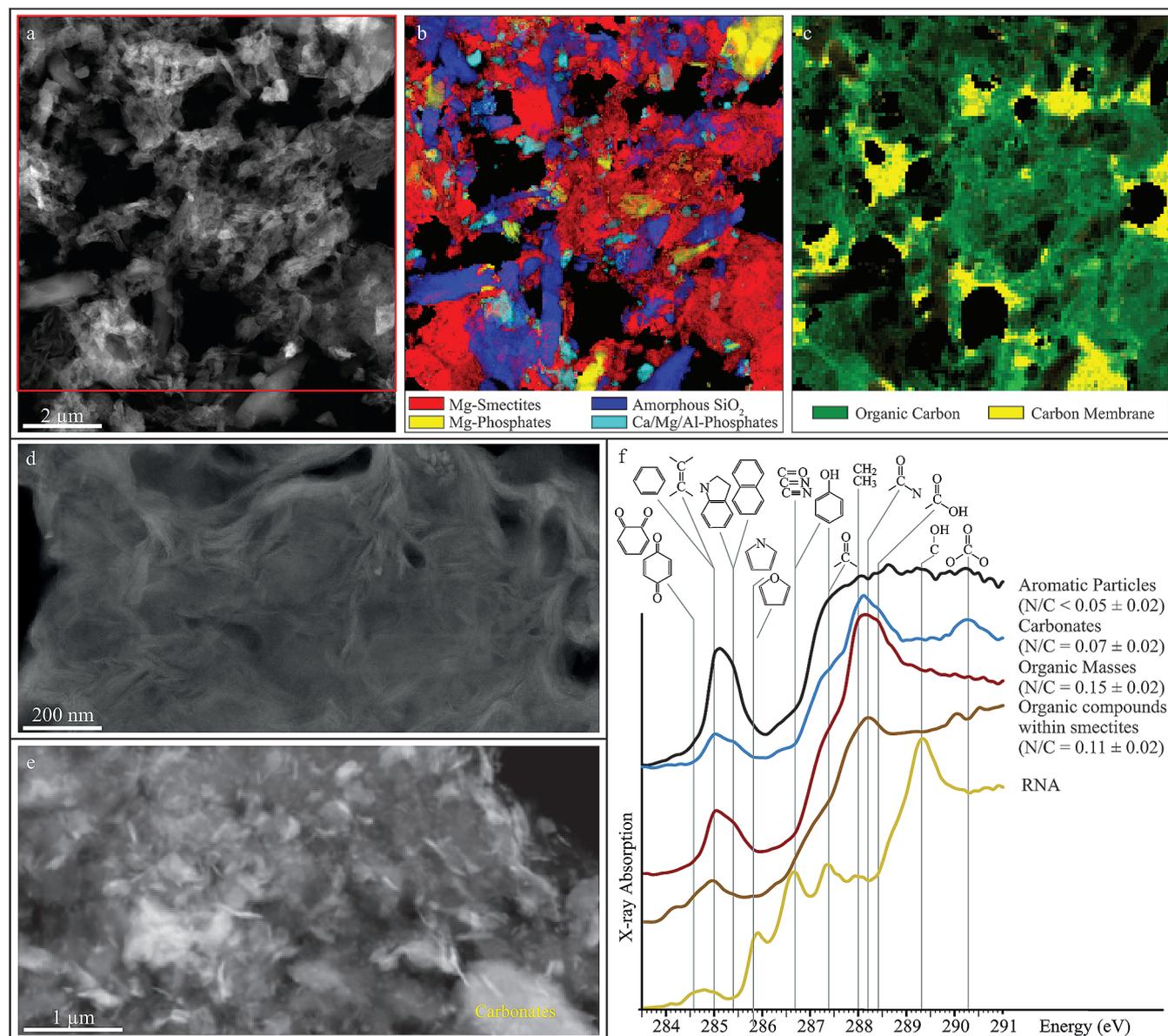


Figure 1 STEM and STXM characterisation of the experimental residues. **(a)** STEM image of the residues of experiments conducted under CO_2 at 200°C in the presence of Mg-smectites and RNA. **(b,c)** Maps of minerals and organic compounds (same area as **a**). **(d)** STEM images of Mg-smectites. **(e)** STEM image of sub-micrometric minerals embedded in organic masses. **(f)** XANES spectra of organic compounds encountered in the residues. The spectrum of RNA is shown for comparison.

interlayer cationic exchange, releases Al, Mg and Ca in the system. Ca-carbonates then precipitate, the carbon source being either RNA degradation products (Sagemann *et al.*, 1999) or the CO_2 rich atmosphere (Viennet *et al.*, 2017, 2019). Meanwhile, the phosphate mono-ester groups of RNA underwent hydrolysis, leading to the precipitation of Al, Ca and Mg-phosphates (Fig. 3; Saxby, 2012). Amorphous SiO_2 particles were formed, as in dissolution experiments (Robin *et al.*, 2016). In parallel, the 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 (Fig. 3). The NH_3^+ groups of these organic compounds replace the initial Ca^{2+} cations in the interlayer spaces of the Mg-smectites (Laird *et al.*, 1989).

Taken altogether, the results of the present experiments are of major importance for the upcoming astrobiological exploration of Mars. Although the organic compounds present in the residues do not carry any information on the chemical structure of the organic starting material, these experimental results demonstrate that clay minerals can efficiently

trap organic carbon under hydrothermal conditions, providing strong support for the strategy of drilling for organic carbon in martian subsurface (Eigenbrode *et al.*, 2018; McMahon *et al.*, 2018).

As shown here, the hydrothermal degradation of (N, P)-rich organic molecules in the presence of Mg-smectites leads to the precipitation of a quite uncommon mineral assemblage comprising sub-micrometric Ca-carbonates and (Al, Mg, Ca)-phosphates, together with amorphous silica and clay-organic complexes. Such an assemblage will be stable under martian subsurface conditions for eons. Martian targets exhibiting this mineral assemblage will thus constitute high priority and highly relevant candidates for sample return because of the likelihood that they result from the hydrothermal degradation of (N, P)-rich biogenic organic molecules. As a corollary, the presence and the nature of organic materials within martian rocks should not be the only 'biosignatures' to consider when searching for traces of life: the nature of the mineral assemblage may be even richer in information.

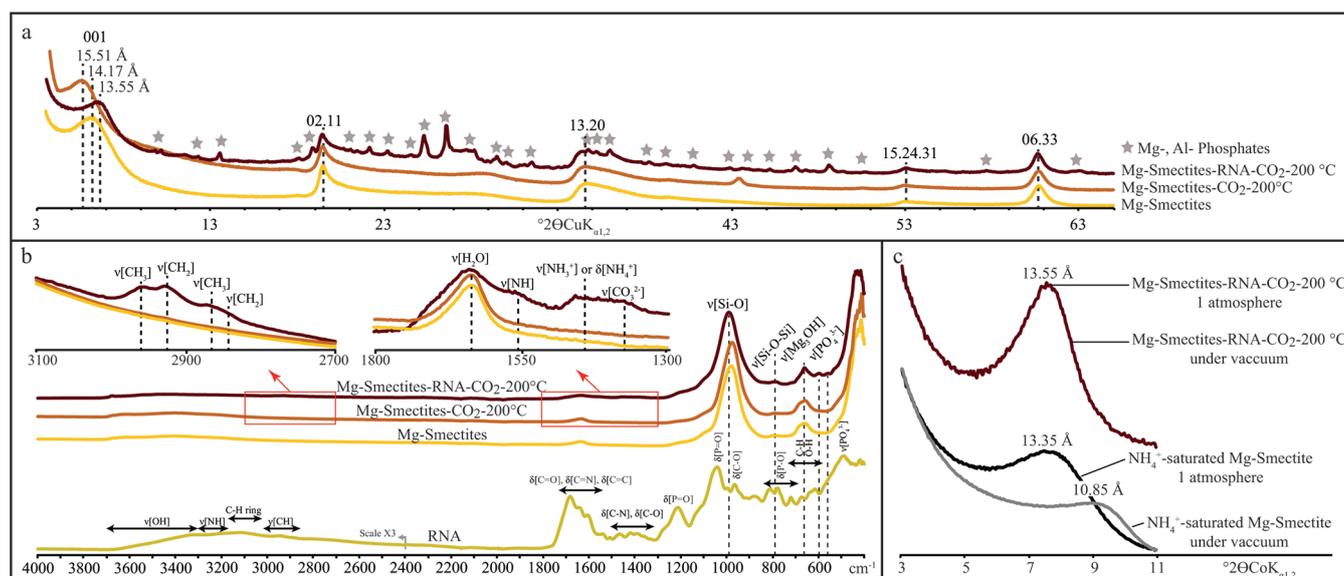


Figure 2 XRD and Mid-IR characterisation of the residues of experiments conducted under CO₂ at 200 °C in the presence or absence of RNA. **(a)** Powder XRD patterns of the synthetic Mg-smectites and of the experimental residues. Values correspond to hkl reflections of the Mg-smectites. **(b)** Mid-infrared ATR spectra of the starting materials (RNA and Mg-smectites) and of the residues. **(c)** XRD patterns at 1 atmosphere and under vacuum of the pristine Mg-smectites saturated with NH₄⁺ and of the residues. Values correspond to the 001 reflection.

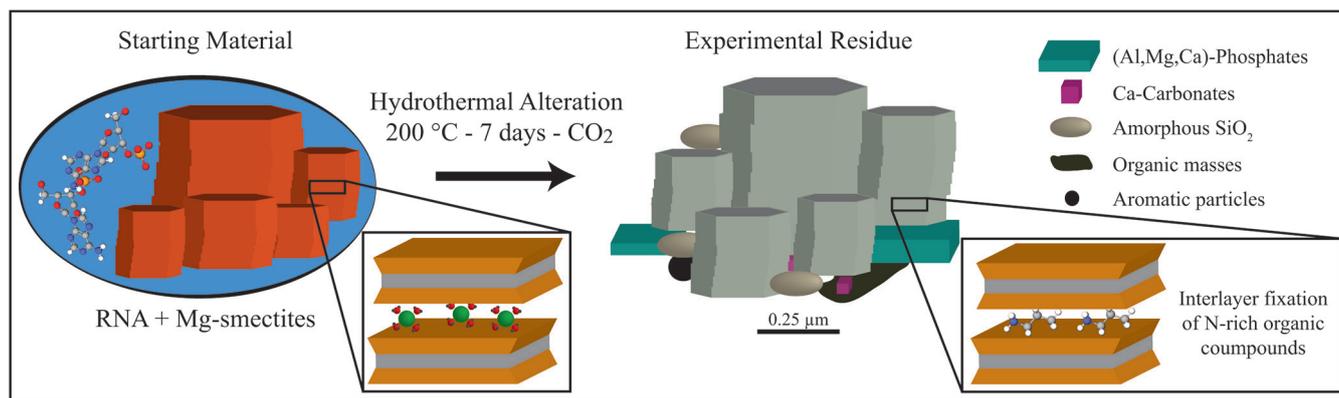


Figure 3 Schematic representation of the results of the present experiments.

In summary, the pilot experiments reported here provide new leads for the (indirect) detection of (biogenic) organic carbon in the martian subsurface. Extrapolating laboratory results to geological timescales is not straightforward (Alleon *et al.*, 2017). Achieving a mechanistic understanding of biosignature taphonomy processes on Mars will require many additional experimental studies.

In addition to offering new perspectives for the search for traces of life on Mars, the present study also provides a strong rationale for the search for potential biosignatures on other planetary bodies, including rocky and/or icy ones (such as Ceres, Enceladus or Europa) on which hydrothermal systems and/or N-rich clay minerals have recently been detected (Carozzo *et al.*, 2018; Nordheim *et al.*, 2018; Marchi *et al.*, 2019). As illustrated here, laboratory experiments are key steps to support astrobiological exploration seeking to provide evidence of the existence of extraterrestrial life.

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Author Contributions

JCV, SB and MJ designed the present study. JCV conducted the hydrothermal experiments. JCV performed CHNS



measurements. JCV, CLG and PJ performed STEM analyses. JCV, SB and CLG performed STXM-XANES analyses. JCV and EB performed IR analyses. JCV and LD performed XRD analyses. All authors contributed to the interpretation of the results. JCV and SB wrote the manuscript, with critical inputs from CLG, EB and MJ.

Additional Information

Supplementary Information accompanies this letter at <http://www.geochemicalperspectivesletters.org/article1931>.



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