

ORGANIC MATTER ASSOCIATED WITH APATITE IN MARTIAN METEORITE CHASSIGNY

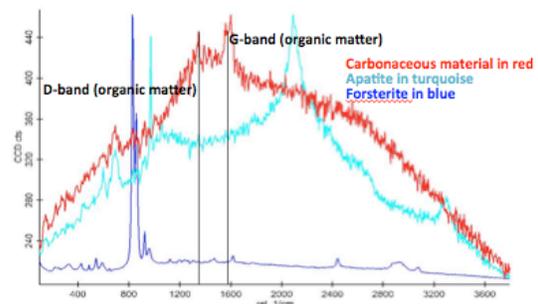
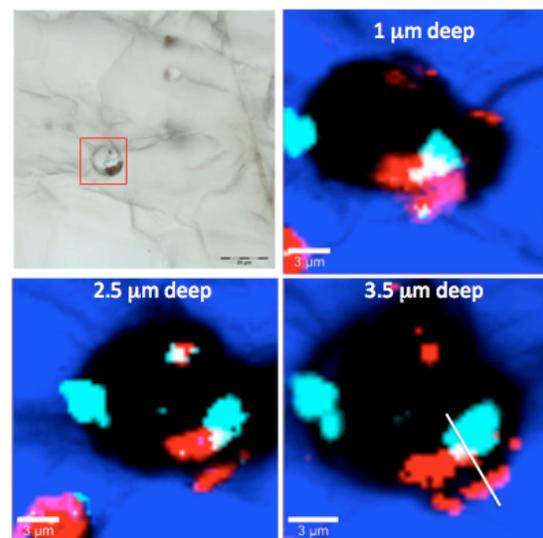
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Introduction: Searching for biologically important elements is key for the search for life beyond Earth. Carbon and Phosphorous are two fundamental biological elements for all life on Earth, as they are basic components of nucleic acids, proteins, lipids and saccharides. Carbon and P are found in Earth's rock record in minerals like graphite and apatite. Graphite associated with apatite has been proposed to be a biosignature on the early Earth were it has been used to propose the existence of an early biosphere more than 3.85 Ga [1] and could also be an important biosignature to look for a record of life on early Mars [2]. However, recent correlated micro-analyses of such mineral associations in the oldest metasedimentary rocks on Earth have highlighted the difficulties in interpreting these mineral and geochemical signatures as unambiguously biological [3-5]. While such mineral associations **can** be unambiguously biological, as in the case of stromatolitic phosphorites and apatitic microfossils [6], correlated micro-analyses have revealed that poorly crystalline graphite associated with apatite, but also with alteration minerals, can also form later in the history of a rock, and possibly have little to do with biological carbon [5]. Alternative non-biological processes that can form organic matter from inorganic carbon in nature include the decarbonation of siderite, Fisher-Tropsch Type (FTT) synthesis, and photochemical organic synthesis.

Associations between disordered organic matter and hydroxylated apatite are reported here for the first time in an extraterrestrial sample. These were found in the Chassigny meteorite which is a volcanic dunite that consists in an olivine cumulate rock from the Martian mantle [7]. Previous studies have provided detailed documentation of hydrated phases: 1) kaersutite amphiboles with up to 0.6%wt -OH) and 2) apatite inclusions within sub-spherical maskelynite grain assemblage with pyroxene and within interstitial maskelynite between olivine cumulates [8]. Other minerals reported from these associations and with several other minerals including pyroxene, maskelynite Cr-rich spinel, ilmenite, and sulfides. We found that Chassigny sulfides are anhedral to subhedral pyrites and Ni-rich pyrrhotites (with up to 3%wt Ni) typically between 10 and 50 microns and that they occur as shattered grains commonly associated with Cr-spinel. Other related and notable mineral associations with these pyrites include maskelynite, orthopyroxene, pyrrhotite spheres, and ferruginous sulfate.

In light of the published results and the new observations reported here, the previous interpretation that apatite and maskelynite represent hydrothermal phases [9] is used here to suggest a transitional stage between the earlier precipitation of Ni-rich pyrrhotite and pyrite in maskelynite, and the later precipitation of disordered organic matter. Our Raman observations shown in the figure (blue = olivine-forsterite, turquoise = apatite, red = organic matter, and black = maskelynite) also confirm that hydroxylated apatites in the Chassigny dunite often occur in association with disordered organic matter in maskelynite (colored in black in the Raman scans), in pyroxene, or in the immediately surrounding olivine.

TEM-EDS analysis of micro-fabricated FIB foils also confirm the previous observations [8] that the maskelynite is also alkali-rich with variable amounts of Ca, Na, and K. Therefore there is a petrogenetic connection between organic matter, hydroxylated apatite, maskelynite, Ni-rich pyrrhotite, and Cr-rich spinel, and orthopyroxene. Such a petrographic context is important because when simple abiotic or biotic organic



molecules condense in clumps and subsequently crystallize, the aromatization of organic molecules will presumably take place on the similar crystal template. The proposed apatite template has a hexagonal dipyramidal structure with space group $P6_3/m$ (point group 6/m), similar to that of graphite which also has a hexagonal dipyramidal structure with a space group of $P6_3/mmc$ (point group 6/m 2/m 2/m). Notably, there is a near-integer factor of 3.85 difference between the unit cell size of apatite and graphite, which is here proposed to grow four unit cells over the template offered by one apatite unit cell. This may constitute a fundamental reason why organic matter is often associated with apatite in various Earth materials, in most life-forms, and also possibly in the origin of life Earth.

Considering the petrological context of organic matter occurrences in the Chassigny dunite, it is proposed here that Fisher-Tropsch Type (FTT) synthesis produced short-chain alkanes during hydrothermal circulation within this rock, when it was a mafic volcanic crustal rock near the surface of Mars (prior to the impact). Optical microscopy revealed rounded olivine grains with linear fields of dozens of 2-30 micron-sized maskelynite melt droplets associated with apatite and opaque organic matter (see figure). Organic matter is often seen to be associated with apatite in these fields, which is interpreted here to represent precipitation from relatively low temperature during hydrothermal circulation. This is suggested to have occurred either in the uppermost crust on Mars or in the magma chamber of the olivine cumulate during the latest stages of the cooling magma chamber. The martian origin of the organic matter is supported by its degree of crystallinity and the inferred crystallization temperature as evaluated from its Raman spectrum that indicate a poorly crystalline and highly disordered structure (see red spectrum in figure above).

This rock is thus interpreted to have been hydrothermally-altered by late fluids that contained sulfide, ferrous iron, phosphate, alkali elements, and inorganic carbon. In this proposed model, the organic matter is hypothesized to have been synthesized under low-temperature hydrothermal conditions, according to estimates from its Raman D- and G-band. This scenario would have unravelled with carbon monoxide and dihydrogen that catalytically reacted either on the Cr-rich spinels distributed throughout the olivine cumulates or on the Ni-rich pyrrhotites.

This interpretation would imply deposition from a warm siliceous, ferruginous, and sulfidic fluid in which carbon monoxide and dihydrogen reacted with Cr-spinels and Ni-rich pyrrhotite to form short-chain alkanes. After emplacement and mineral precipitation/formation, the short-chain alkanes would have been altered and heated by an unknown combination of

factors that might have included further hydrothermal or volcanic-associated heating, shock metamorphism by the planetesimal impactor. Contamination of this meteorite by organic matter during entry into Earth's atmosphere in 1815 cannot be completely excluded, but is unlikely given the petrographic observations of the occurrences.

The combination of the mineral assemblages highlighted here and the occurrence of hydroxylated apatite and hydroxylated amphiboles, is interpreted to reflect hydrothermal circulation near the surface or in the parent magma chamber on Mars prior to the impact event that ejected this crustal fragment into space. Hydrothermal activity on Mars has been previously reported in the form of silica-rich deposits near fumaroles [10] and of jarosite in a martian meteorite [11], and has been hypothesized to potentially provide sources of energy to a potential martian biosphere [12]. This is important, because hydrothermal systems on the modern Earth are known to host active chemosynthetic primary producers with numerous biochemical affinities shared with ancestral primordial microorganisms. Furthermore, hydrothermal systems producing organic carbon precursors to complex macromolecules have been considered to have contributed significantly to the budget of organic molecules that were involved in the origin of life on the earliest Earth. The discovery reported here is thus of great importance for the possibility of life on Mars, for a production mechanism of organic molecules on Mars, and also for possibly offering a natural example of a transition from a prebiotic world to a biological world with microbial life existing almost everywhere liquid water exists today on Earth.

References: [1] Mojzsis, S. J. et al. (1996) *Nature*, [2] Mojzsis et al. (1998) *JGR*, [3] Papineau, D. et al., (2010a) *GCA*, [4] Papineau et al., (2010b) *GCA*, [5] Papineau et al. (2011) *Nature Geosci*, [6] Papineau et al. (submitted), [7] McSween and Treiman (1998) *Rev. Min.*, [8] McCubbin and Nekvasil (2008) *Am. Min.*, [9] McCubbin et al. (2010), [10] Squyres et al. (2008) *Science*, [11] McCubbin et al. (2009) *GCA*, [12] Varnes et al. (2003).