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Hydrothermal alteration experiments: tracking the path from interstellar to chondrites organics

V. Vinogradoff [1], S. Bernard [1], C. Le Guillou [1], M. Jaber [2], L. Remusat [1]

[1]IMPMC, UMR CNRS 7590, Sorbonne Universités, MNHN, UPMC, IRD UMR 206, Paris (vvinogradoff@mnhn.fr / +33 1 40 79 35 43)
[2]LAMS, UMR CNRS 8220, Université paris 06, Paris, France.

Abstract

Organic molecules are detected in primitive carbonaceous chondrites. The origin of these organics, whether formed prior the accretion phase, or in-situ on the parent body, is still a matter of debate. We have investigated experimentally the chemical evolution of interstellar organic molecules submitted to hydrothermal conditions, mimicking asteroidal alteration (T<200°C). In particular, we want to assess the potential catalytic role of clays minerals in the polymerization/degradation of organics. Hexamethylenetetramine (HMT, compound of C-N bonds) is used as a plausible interstellar precursors from icy grains. Experimental products reveal a large diversity of molecules, including nitrogen organic molecules similar to those found in chondrites.

1. Introduction

Organics are widely observed in astrophysical environments, including in molecular clouds, circumstellar envelopes and protoplanetary disks [1].

Astronomical observations of the gas phase show a rich diversity of mainly small molecules (up to 10 atoms), while the composition of the solid phase remains cryptic due to limitations of infrared spectroscopy. Still, the solid phase, composed of dust and icy grains, is supposed richer in complex organic molecules. Laboratory experiments have been performed in an attempt to reproduce processes occurring during stellar formation (UV photolysis, heating effect) affecting these icy grains initially composed of H_2O, CO_2, CO, NH_3, CH_3OH. These experiments yield an organic-rich residue at room temperature, where the hexamethylenetetramine (HMT, $C_6H_{12}N_4$) may constitute more than 50wt% of the total organic residue [2-3]. Experimentally formed in ice from ammonia and formaldehyde [4], HMT has not yet been detected. However, asteroids may have accreted this molecule, and many other formed in icy grains, as primitive constituents.

Asteroids, thought to be meteorites' parent body, are initially formed from icy grains, dust, minerals, and organic molecules sampled in the protosolar nebula [5]. After accretion, parent bodies have all experienced hydrothermal (aqueous) alteration and/or thermal metamorphism at varying degrees. Regarding hydrothermal alteration, the mineral assemblages of meteorites (such as phyllosilicates and carbonates) have recorded these alteration episodes and reveal crucial information regarding the meteorite history. Among meteorites, carbonaceous chondrites are the richest in organic matter, and thus constitute the best targets available to investigate the origins of organics in our solar system [6].

Yet, discriminating the alteration molecular signal from the original molecular signal, i.e. rigorously constraining the impact of hydrothermal alteration on organics, remains highly challenging.

2. Experimental hydrothermalism of interstellar molecules

Two synthetic (organic free) clays minerals comparable to chondritic clays have been selected for our experiments: Na^+ montmorillonite and Fe^{3+} nontronite. Experiments have been conducted at low temperatures (< 150°C), under relatively low pressure (only induced by water liquid/vapor equilibrium), and in an alkaline pH solution to properly mimic processes occurring on asteroids. The impact of the presence of additional molecules such as short carboxylic acids (detected in astrophysical environments) have also been investigated.

On figure 1 are reported the gas-chromatographs of an HMT solution and a mixture containing HMT and carboxylic acids after having been submitted to hydrothermal conditions without mineral during 18 days at pH 10. Thanks to GC-MS, we can identify several new compounds after hydrothermal alteration of HMT, such as methyl pyrazole/imidazole derivatives, methyl pyridine/pyrazine derivatives and many other cyclic nitrogen, up to m/z 254. In the presence of short carboxylic acids, amides are produced (red pics between 4 and 10 min.), including formamide derivatives, while less cyclic nitrogen species are produced.

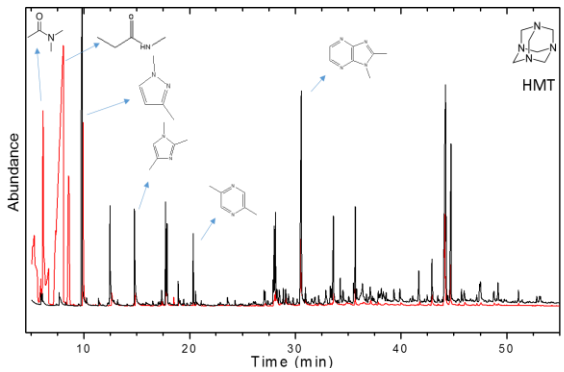

Figure 1. GC Chromatograph obtained from the mixtures after hydrothermal alteration (18 days of at 150 °C, pH 10), in black from HMT solution and in red from HMT+carboxylic acid mixture. (HMT structure is in the right corner.)

On figure 2 are shown the FTIR spectra of solid phases from mixtures of HMT and nontronite recorded before and after having been submitted to hydrothermal conditions during 18 days at pH 10. While no organic signature can be observed with the nontronite before the experiment, absorption features indicating the presence of organics (1400, 1700 and 3300 cm^{-1}) can be noticed after the experiment. The increase of the interlayer spacing of the clay mineral after these experiments, revealed by XRD data, suggests that these likely newly formed organics are trapped within the nontronite interlayers. The same observations have been done with montmorillonite clay and from other solutions of HMT with carboxylic acids.

3. Conclusions

Our study reveals that organic molecules may undergo complex chemical transformations during hydrothermal alteration. In the absence of minerals, HMT leads to many nitrogen cyclic compounds and to amides, which could further evolve into nucleobases or amino acids species. Things appear a bit different in the presence of clays that may trap newly formed organics and thus protect them from subsequent alteration.

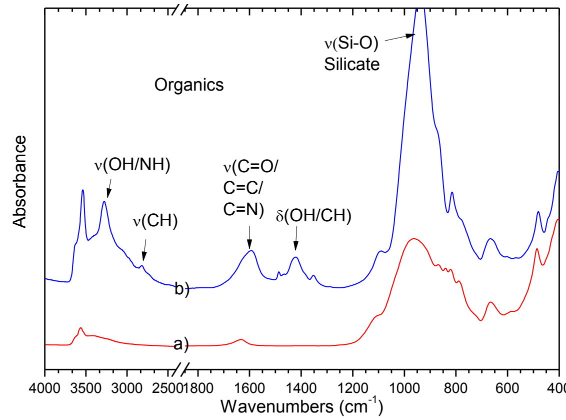

Figure 2 Infrared spectra of a) nontronite before experiment, b) after aqueous reaction with HMT solution, at 150 °C, alkaline pH, during 18 days.

These studies are relevant for understanding the evolution of the organic matter within asteroid and to access its origins.

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