

# Impact of asteroidal hydrothermal alteration on organics

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## Abstract

Unravelling the evolution of simple organic molecules trapped in ices after they were accreted into asteroids requires better constraining how they would be modified by hydrothermal alteration, which happened in carbonaceous chondrites (CC) [1]. We have experimentally investigated the chemical evolution of interstellar organic molecule submitted to hydrothermal conditions mimicking asteroidal alteration. In particular, we investigated the role of phyllosilicates in the preservation/degradation of organic matter. We observed that a simple organic molecule (HMT) undergo complex chemical transformation during hydrothermal alteration, with the formation of an insoluble organic matter. Phyllosilicates have influenced the chemical reactions by concentrating a significant fraction of the newly formed organics.

## 1. Introduction

The origin and evolution of the suite of organic compounds found in chondrites remain complex to disentangle. Whereas they are somehow inherited from the interstellar medium (ISM), further evolutions in the protosolar disk [2] as well as in the parent body [1] have contributed to their present molecular composition. The dust in the ISM is composed of a mixture of organic compounds and/or silicates trapped within ices (<20 K). Irradiation experiments (UV and cosmic rays) performed on ices analogues (from 10 K to 300 K) reproduce many of the molecules observed in the ISM. Annealed above 300 K, these experiments yield an organic-rich residue dominated by hexamethylenetetramine (HMT,  $C_6H_{12}N_4$ ) [3-4]. The parent asteroids of carbonaceous chondrites (CC) have all experienced hydrothermal alteration of variable intensities which has affected the organic matter (OM) [5]. However, the extent of the modification induced by alteration remains unknown and prevents elucidating the question of their pre-accretion history.

## 2. Hydrothermal experiments

Hydrothermal experiments were conducted at 150 °C in Teflon bombs closed in a  $N_2$  atmosphere, for durations up to 31 days. The water pH was set to 10 using KOH. In a first set of experiments, HMT (0.7 M) was submitted to alteration. In a second set, 100 mg of synthetic (organic-free) clays was added (either a Na-montmorillonite or a  $Fe^{3+}$ -nontronite) to investigate the role of the clay mineral structure and composition. Reaction products were characterized by gas-chromatography coupled to mass spectrometry (GC-MS), Infrared spectroscopy (IR), synchrotron-based X-ray absorption near edge structure (XANES) spectroscopy, X-ray diffraction (XRD) and thermogravimetry (TGA).

In the absence of clays, HMT is rapidly decomposed and both soluble and insoluble OM are formed. Most of the reaction occurs in the first 20 days (Fig. 1). After 7 days, a suite of soluble, aromatic nitrogen-bearing molecules and amides, compounds is formed (around 150 species with  $m/z$  of 59 to 254 - 31 days experiment).

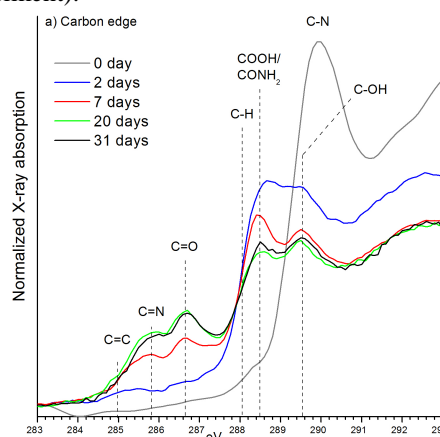


Figure 1: Carbon K-edge XANES spectra of the liquid reaction products of HMT 0.7 M after 0, 2, 7, 20, 31 days. Increase of aromatic, amine and carbonyl functions is observed.

A complex, insoluble N-rich organic compound (< 1 wt.%) is formed after 7 days. Its chemical signature, measured by XANES and IR (Fig. 2), reveals aromatic, carbonyl, amide and carboxylic functions. Its elemental composition is H/C=1.2, N/C=0.26 and O/C=0.31.

In the presence of clays, after 31 days, the number of soluble organic products is reduced; only 36 and 66 species (mainly between  $m/z$  73 to 124, with some higher molecular weight moieties: up to 254  $m/z$ ) are observed from HMT + nontronite and HMT + montmorillonite mixtures, respectively. XRD analysis of the solid residues show an increase of the interlayer spacing, which suggests that organic matter has been inserted within the phyllosilicate interlayers. The solid residue displays infrared features of organic compounds (31 days; Fig. 2). The absorption bands due to OM depend on the nature of the clay. TGA reveals that the sample with nontronite contains up to 6.5 wt.% of organic matter and the sample with montmorillonite up to 8 wt.%, both after 31 days.

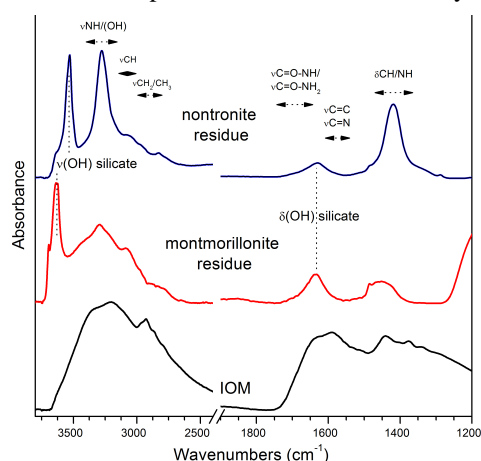


Figure 2: Infrared spectra of the clay products after 31 day long of hydrothermal alteration experiments with HMT, compared to the IOM spectrum at 31 days from HMT alone.

### 3. Discussion and conclusions

Our study reveals that, under hydrothermal conditions, a simple interstellar organic molecule such as HMT is, in a few days, decomposed into a suite of diverse molecular weight soluble compounds and an insoluble N-rich OM. The reaction mechanism starts by the decomposition of HMT into formaldehyde and ammonia. Then, the general evolution of the OM resembles the Maillard reaction, a complex set of reaction which involve amines and sugars through polymerization/condensation and

ultimately the formation of an IOM. If HMT, formaldehyde or ammonia are among the molecules accreted in parent bodies, the above described reaction pathways would have occurred and would constitute an alternative route to form IOM in CC.

The addition of clays in the system drastically modifies the reaction products. The reduced diversity of soluble species could be due to the absorption of their precursors on the clay surfaces or their insertion within the interlayer spaces, which would have prevented them of further reactions.

This may have important implications for the study of chondrites. First, if soluble molecules were absorbed/enclosed, they would not be release by solvent extraction and would constitute a “hidden” OM reservoir, not yet fully investigated. Second, phyllosilicates have heterogeneous compositions and structures both within one given chondrite and in different chondrite groups. Therefore, if different reaction pathways are involved when different clays are present, it could, at least in part, explain the heterogeneity and diversity of OM in chondrites. Finally, the evolution of the OM enclosed in phyllosilicates could be different from the “free” one, which would also lead to different reactivity and transformation behaviour.

Altogether, this study constitutes a step forward to link the molecules observed in the ISM with the molecules observed in CC. The formation of insoluble OM from HMT at low temperature is demonstrated, and we suggest that the importance of the interactions with phyllosilicates may have been so far overlooked and should now be studied in more details in order to fully understand the evolution of organic matter during hydrothermal alteration.

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### References

- [1] Remusat L. (2015), *EMU notes in Mineralogy*, 15, chapter 8. [2] Herbst et van Dishoeck, (2009) *Annu. Rev. Astro. Astrophys* [3] Munoz-Caro G.M., Schutte W.A. (2003) *A&A*, 412, 121. [4] Vinogradoff V., Rimola A., Duvernay F., Danger G., Theulé P., Chiavassa T. (2012), *PCCP*, 14:12309. [5] Alexander et al. (2007), *GCA*, 71, 4380-4403, [6] Le Guillou et al. (2014) *GCA*, 131, 368-392.