SIMULATING THE ASTEROIDAL HYDROTHERMAL ALTERATION OF ORGANIC COMPOUNDS.
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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 [1] as well as in the parent body [2] 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(CH₂)₆N₄) [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-accretionary history.

Here, we experimentally study the chemical evolution of typical interstellar organic molecules (HMT and carboxylic acids) under hydrothermal conditions mimicking asteroidal alteration. In particular, we want to investigate: i) The fate of HMT during alteration, ii) if insoluble organic matter can form, and iii) if phyllosilicates, which are closely associated with OM at the nanometer scale in chondrites [6], have an influence on the nature of the reacted material.

Experimental: Hydrothermal experiments were conducted at 150 °C in Teflon bombs closed in a N₂ atmosphere, for durations up to 31 days. The water pH was set to 10 using KOH. In a first set of experiments, HMT and small chains carboxylic acids were submitted to alteration (solution of 0.7 M HMT and 0.7 M carboxylic acids). In a second set, 100 mg of synthetic (organic-free) clays was added (either a Na-montmorillonite or a Fe³⁺-nontronite) to investigate the role of the clay mineral structure and composition.

Interaction products were characterized by gas-chromatography coupled to mass spectrometry (GC-MS) in order to identify the soluble molecules. Infrared spectroscopy (IR) and synchrotron-based X-ray absorption near edge structure (XANES) spectroscopy were performed to characterize the functional groups at the micro and nano-scale. X-ray diffraction (XRD) was used to study the evolution of the interlayer spacing of the clays and thermogravimetry (TGA) to quantify the abundance of organic matter associated with clays.

Results: 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 has formed (Fig. 2, around 150 species with m/z of 59 to 254 - 31 days experiment - HMT alone).

Figure 1: Carbon K-edge XANES spectra of the liquid reaction products of HMT 0.7 M after 2, 7, 20, 31 days, compared to HMT reference (0 day). 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 (Fig. 1) and IR, reveals aromatic, carbonyl, amide and carboxylic functions. It forms both in the presence and the absence of carboxylic acids in the starting solution. Its elemental composition is H/C=1.2, N/C=0.26 and a 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. 3). 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. Similar results are obtained for experiments including carboxylic acids as well.

Figure 2: Gas Chromatograph (31 days, at 150 °C, pH 10) of the solutions without clay from HMT (in black) and from HMT+carboxylic acid (in red).

**Discussion:** 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 addition of carboxylic acids leads to the additional formation of amide compounds but does not influence the composition of the insoluble OM. We infer that the reaction starts by the decomposition of HMT into formaldehyde and ammonia and that both quickly react to form amine and aromatic, nitrogen-bearing compounds. The general evolution of the OM resembles the maillard reaction, a complex set of interactions which involve polymerization and condensation and ultimately the formation of an insoluble OM. Similar experiments using formaldehyde (in excess) with ammonia also led to an insoluble OM showing similarities with chondritic OM [7]. If HMT, formaldehyde or ammonia are among the molecules accreted in parent bodies, the above described reaction pathways would have occurred and it would constitute an alternative route to form insoluble organic matter in CC.

The addition of clays in the system drastically modifies the reaction products. The reduced diversity of soluble species could be due to their absorption on the clay surfaces or their insertion within the interlayer spaces, which would have prevented them to be detected in the solution. Alternatively, clays could have favored some reaction pathways over others (due to local pH or redox variations, for instance), therefore limiting the diversity.

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 behavior.

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.

Figure 3: Infrared spectra of the HMT+ phyllosilicates experiments at t=0 and t=31 days. Organic matter signatures are observed into the two clay signatures after hydrothermal alteration and are different from the HMT signature into clays at 0 day.