EVOLUTION OF CHONDRITIC INSOLUBLE ORGANIC MATTER UNDER AQUEOUS ALTERATION.

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Introduction: Carbonaceous chondrites contain a significant amount of organic matter, and potentially a source of building blocks for life. CMs, along with CI chondrites have the highest carbon concentrations, ranging between 1.5 and 3.4% [1], most of this carbon being in the form of insoluble organic matter [2]. Most CMs have experienced aqueous alteration since the accretion of ice grains onto/by their parent body [3,4]. Previous studies on CMs and their IOM, including the Paris, often considered as the most prominent example of a weakly altered object [5], have highlighted the effect of these secondary processes [6]. Yet, the mechanisms at work and driving the alteration are not understood.

Degradation experiments offered new insights of the effects of asteroidal alteration processes on the structure and isotopic composition of chondritic IOM [7,8]. Heating at 300 and 500°C in the absence of water is responsible for an increase of the aromatic carbon fraction of the Murchison and Orgueil IOM while it leads to a significant decrease of their D content [7,8]. In presence of water, isotopic evolution has been linked to the fluid composition, and predominantly observed for temperatures above 300°C [9]. While these temperatures certainly overcome laboratory limitations, they are above the peak fluid temperatures in CM parent-body [10]. Here, we subjected the Paris IOM to aqueous conditions at temperatures similar to those experienced by the CM parent-body (i.e. 150°C), and compared the residual IOM to the IOM isolated from newly recovered CMs, Aguas Zarcas (CM2.2 [11], Costa Rica, 2019), and Mukundpura (CM2.0 [12], India, 2017).

Samples and Methods: The IOM of Paris and of the investigated chondrites were isolated by solvent washing and HF/HCl leaching. A starting mixture of 10μL ultrapure water and 10μg of Paris IOM was loaded in pure gold capsule, and into a 23 mL PTFE reactor. The reactor was filled with 12 ml of the same ultrapure water, in order to work at conditions of water vapor saturation pressure. The reactor was then put in an oven with temperature accurately regulated at 150°C for 49 days. Raman spectra were acquired using a Renishaw InVia spectrometer, associated with an argon laser (514.5 nm). To prevent any laser-induced damage, the laser was used at 0.1% of its power, yielding a planar resolution of ~ 2 μm for a power of less than 10 μW delivered at the sample surface. IR spectra were collected on IOM samples deposited on IR transparent

CaF2 windows at the SMIS beamline of the SOLEIL synchrotron (France) using an Agilent Cary 670/620 micro-spectrometer equipped with a 128x128 pixel Focal Plane Array detector (3900-800 cm-1) and with a single point MCT detector (6000-650 cm^{-1}), for a 4cm-1 spectral resolution. Bulk H-isotope measurements were performed on an Elementar VisION interfaced with an Elementar Pyrocube. About 0.9 mg of IOM were loaded into silver capsules. Capsules were stored in an autosampler set at 80°C, then dropped into a 1450°C furnace made in glassy carbon, and flushed by pure He. H- and N-isotope distribution were investigated by NanoSIMS imaging.

Results: Chemical information was obtained through IR spectroscopy (fig. 1A). The CH_2/CH_3 ratio of the Paris IOM also decreases upon alteration, but down to values remaining higher than those of the Aguas Zarcas and Mukundpura IOMs (fig. 1B). Also, the relative aromatic content of the Paris IOM slightly increases upon alteration but remains lower than that of the Aguas Zarcas and Mukundpura IOMs, while loss of carbonyl groups of experimentally altered Paris leads to concentrations comparable to Aguas Zarcas and Mukundpura IOMs (not shown here). Raman investigations reveal a slight evolution of the structure of Paris IOM during the experiments, with a residue being more different from the Aguas Zarcas and Mukundpura IOMs than was the original Paris IOM.
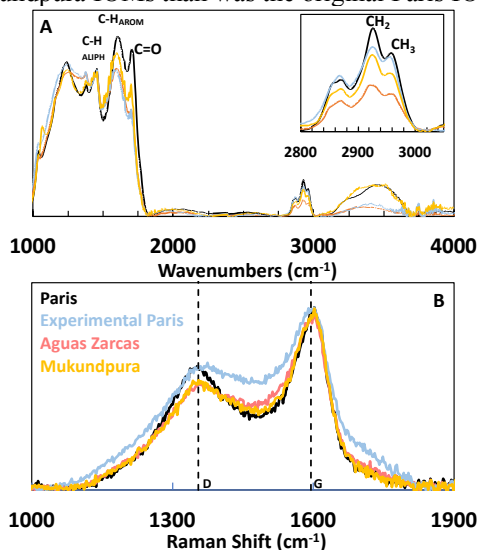
Figure 1. Infrared absorbance (a) and Raman (b) spectra of Paris (black), experimentally altered Paris (blue), and altered CM2 Aguas Zarcas (pink) and Mukundpura (yellow).

The IOM of the CM chondrites shows similar deuterium concentration (fig.2A): $\delta D = 773\pm56$‰, for Paris, 780 ± 91‰ and 836 ± 116‰ for Mukundpura and Aguas Zarcas IOMs, respectively. Upon alteration, hydrogen isotope signature of altered Paris decreases to $\delta D = 640\pm105$‰. While the bulk hydrogen isotopic signature is affected by alteration, the signature of organic hotspot is mostly unchanged (fig.2B,C). Overall, the similarity in bulk hydrogen signature in altered CMs suggest they never experienced temperature as high as 150°C.
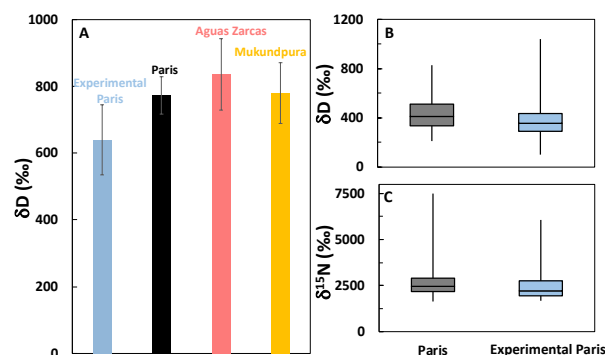
Figure 2. a, Bulk hydrogen isotopes signatures of Paris (black), experimentally altered Paris (blue), and altered CM2 Aguas Zarcas (pink) and Mukundpura (yellow). **c and d,** Evolution of the hot spot distributions for H (analysed on $3600\mu m^2$ surface) and N-isotopes (on $2400\mu m^2$ surface).

Discussion: After experimental alteration, the residue appears to be chemically closer to altered chondrites than to the starting IOM. The decrease of the CH_2/CH_3 ratio (fig.1B) results from to carbon chains shortening, which, for coals, is used as an indication of aromatisation [13]. Aromatisation is also evidenced by a high proportion of aromatic moieties and the low proportion of carbonyl groups in the residual IOM compared to those of the starting material. The low D content of the residual IOM indicates a D-H exchange between the D-rich IOM and the D-poor water, or a preferential loss of D-rich moieties. A link between aromatization and D depletion was experimentally observed during wet pyrolysis of CMs [8]. Here, only a few D-rich hotspots are lost during the experiment, in clear contrast with results of heating experiments conducted on the Orgueil IOM [14], highlighting the influence of water (assuming that the D is carried by similar moieties in the Orgueil IOM).

Yet, although the Paris IOM has evolved during the experiment towards the IOMs of the more altered CM chemically speaking, it has not been the case structurally speaking as highlighted by Raman investigations. This might be due to the experimental conditions (absence of mineral phases, high quantity of water, closed system). Still, it is remarkable that the IOM of almost all CMs exhibit similar Raman spectra.

The working hypothesis is that CMs derive from the same parent-body and the IOMs of the CMs are similar structurally and isotopically speaking. Yet these IOMs are quite different chemically speaking. A cause could be the heterogeneity of the parent body regarding the distribution of ice and the porosity. The high porosity of Paris could explain the preservation of unaltered amorphous silicates [16], a high porosity resulting in a low thermal conductivity preventing the transfer of heat producing by the decomposition of ^{26}Al [17]. CMs exhibiting lower porosity may have been more sensitive to alteration [17]. Although a higher proportion of ice may hamper the rise of temperature since a higher latent heat would be requested to melt more ice [18], it may lead to longer periods of fluid circulation at a lower temperature. Not to mention, a high proportion of ice and/or a high porosity would proportionally decrease the initial ^{26}Al concentration, i.e. the source of heat. In any case, the bulk hydrogen signature does not appear to be correlated to the degree of alteration (fig.2) and may thus inform about the early stages of accretion.

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