



Thermal recalcitrance of the organic D-rich component of ordinary chondrites



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ABSTRACT

Carbonaceous and ordinary chondrites (CCs and OCs) contain insoluble organic matter (IOM) with large D-excess compared to other objects in the solar system. The higher the temperature experienced by CCs, the lower the D/H ratio of their IOM. It seems to be the opposite for OCs. Here, we report NanoSIMS H- (and N-) isotopic imaging of IOM of three OCs that experienced thermal metamorphism in the sequence Semarkona, Bishunpur and GRO 95502. In addition, we performed flash heating experiments on the IOM of GRO 95502 at 600 °C and characterized the residues using NanoSIMS, Raman and XANES spectroscopy. The present study shows that, in contrast to IOM of CI, CM and CR, IOM of OCs exhibits very few D-rich (or ¹⁵N-rich) hotspots. Furthermore, although the evolution of the molecular structure of OC and CC IOM is similar upon heating, their D/H ratios do not follow the same trend: the D/H of OC IOM drastically increases while the D/H of CC IOM decreases. In contrast to CC IOM, the D-rich component of which does not survive at high temperatures, the present results highlight the thermal recalcitrance of the D-rich component of OC IOM. This suggests that CCs and OCs did not accrete the same organic material, thereby challenging the hypothesis of a common precursor on chondritic parent bodies. The present results support the hypothesis that OC IOM contains an organic component that could originate from the interstellar medium.

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1. Introduction

Chondrites are often considered to be the witnesses of solar system formation (Weisberg et al., 2006). Their components are believed to have formed during the collapse of the parent molecular cloud and solar nebula evolution. They are consequently the targets for many studies aiming to understand the processes of formation of the constituents of planetesimals and planets. The origin of volatile reservoirs in the early solar system is the subject of intense debate, with implications for the origin of water and life on Earth. In this respect, carbonaceous chondrites (CCs) have received most of the attention because they are the most organic- and water-rich chondrites (CCs may contain up to a few weight percent of carbon). Two types of organic matter are usually distinguished (Remusat, 2015): the organic matter that is soluble in water and organic solvents, and the insoluble organic matter (IOM). The IOM constitutes the major part of the total organic material and is generally studied after isolation from the minerals by acid treatments

using HF-HCl (Robert and Epstein, 1982) or CsF-HCl (Alexander et al., 2007).

The molecular, structural and chemical composition of CC IOM has been extensively documented (Remusat, 2015 and references herein). It corresponds to a macromolecule made of small aromatic units linked by short aliphatic chains that contains hetero-elements (N, S, O) (Hayatsu et al., 1980; Remusat et al., 2005; Cody and Alexander, 2005; Orthous-Daunay et al., 2010) and organic radicals (Binet et al., 2002, 2004). Type 1 and 2 CC IOM is enriched in heavy isotopes of H and N relative to terrestrial organic matter, with the exception of some CMs having near-atmospheric IOM N isotopic compositions (Robert and Epstein, 1982; Yang and Epstein, 1983; Alexander et al., 2007, 2010), and exhibits micron-sized hotspots enriched in D and ¹⁵N (Busemann et al., 2006; Nakamura-Messenger et al., 2006; Remusat et al., 2009). These hotspots have been interpreted as remnants of interstellar organic compounds (Busemann et al., 2006; Nakamura-Messenger et al., 2006) or evidence of an early irradiation of the solar system (Remusat et al., 2009). Of note, at least for Murchison (CM chondrite), these hotspots disappear when the IOM is submitted to thermal treatment at 600 °C under He atmosphere (Remusat et al., 2009).

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Despite the abundance of available samples, much less is known about organic matter in ordinary chondrites (OCs). In contrast to most CCs, which experienced aqueous alteration on parent bodies, most OCs experienced thermal metamorphism that may have led to the complete degradation of organics (Yang and Epstein, 1983; Alexander et al., 2010). Although the two falls Semarkona (LL3.0) and Bishunpur (LL3.15) exhibit some signs of secondary hydrous alteration (i.e. processes on the parent body; Alexander et al., 1989; Sears et al., 1995). Raman spectroscopy investigations on IOM have shown that Semarkona is, by far, the most pristine unequilibrated ordinary chondrite (UOC). IOM experienced a metamorphic temperature peak well below 250 °C (Quirico et al., 2003; Busemann et al., 2007); this temperature is consistent with estimates from mineral assemblage ($T < 260$ °C – Alexander et al., 1989) and sulfide thermometry (230 °C – Zanda et al., 1995). The IOM of OCs is generally richer in D than that of CCs and exhibits anticorrelated D/H and H/C ratios, in contrast to CC IOM (Alexander et al., 2007, 2010). No D- or ^{15}N -rich hotspot has ever been reported in OC IOM, as recently illustrated by NanoSIMS images of the IOM of the Krymka meteorite (LL3.2) showing no heterogeneities in D/H (Alexander et al., 2010).

The present study reports NanoSIMS H- and N- isotopic imaging of IOM of three UOCs that experienced different thermal metamorphism: Semarkona (LL3.0), Bishunpur (LL3.15) and Grosvenor Mountains (GRO) 95502 (L3.2). In addition, we document the molecular signature and structural properties of the IOM of GRO 95502 before and after flash heating experiments. The results highlight the thermal recalcitrance of the D-rich component of OC IOM and suggest that the original precursors of CC and OC organic matter were different.

2. Experimental

2.1. Samples

IOM has been isolated from three UOCs of increasing metamorphic grades: Semarkona (LL3.0), Bishunpur (LL3.15), and GRO 95502 (L3.2). Semarkona and Bishunpur IOM was prepared by Yang and Epstein (1983) by classical HF/HCl dissolution. This IOM has been stored since then at room temperature, in a glass vial sealed by a Teflon cap and protected from the sunlight. Fifty milligrams of GRO 95502 IOM (hereafter called GRO IOM) were recently isolated from 20 g of meteorite using a similar protocol (Piani et al., 2012a). An aliquot of GRO IOM was subjected to flash pyrolysis at 600 °C under a He atmosphere. The (organic) residue was recovered and is hereafter called GROpyr. Orgueil IOM, prepared by Remusat et al. (2005), was used as a reference material.

Aliquots of these IOM samples were pressed into cleaned indium foil and gold coated (20 nm thick) to improve charge compensation during NanoSIMS imaging. Portions of GRO IOM and GROpyr samples were also finely powdered in an agate mortar and deposited on Si_3N_4 windows for Raman and XANES (X-ray absorption near edge structure) investigations.

2.2. NanoSIMS settings

Isotopic images were acquired using the Cameca NanoSIMS 50 installed at the National Museum of Natural History in Paris, France. A 16 keV primary Cs^+ beam was used to collect the secondary ions H^- and D^- during a first run (to obtain δD images), and $^{16}\text{O}^-$, $^{12}\text{C}_2^-$, $^{12}\text{C}^{14}\text{N}^-$, $^{12}\text{C}^{15}\text{N}^-$ and $^{32}\text{S}^-$ during a second run (for N/C and $\delta^{15}\text{N}$ images). The use of the ion ratio $^{12}\text{C}^{14}\text{N}^-/^{12}\text{C}_2^-$ reduces topographic effects on the N/C measurements (Thomen et al., 2014; Alleon et al., 2015). The primary beam was set to 8 pA for H isotope and to 3 pA for N isotope measurements, leading to spatial resolutions of about 300 and 150 nm, respectively.

We collected 256×256 pixel images covering $20 \times 20 \mu\text{m}^2$ with a raster speed of 2 ms/pix. Prior to each analysis, a $25 \times 25 \mu\text{m}^2$ pre-sputtering was applied using a 600 pA primary current for 6 min (corresponding to a Cs^+ fluence of 2.2×10^{17} at cm^{-2}) in order to remove the gold coat, clean the surface, and reach the sputtering steady state (Thomen et al., 2014). We used Hamamatsu discrete dynode electron multipliers with a dead time of 44 ns in multi-collection mode. For H isotopes, the mass spectrometer was set to a mass resolving power of 4000, and to 8000 for N isotopes to resolve isobaric interferences, such as $^{12}\text{C}^{14}\text{N}^-$ from $^{12}\text{C}_2\text{H}_2^-$ and $^{32}\text{S}^-$ from $^{16}\text{O}_2^-$. The vacuum in the analysis chamber never exceeded $5 \cdot 10^{10}$ Torr.

The collected NanoSIMS data were then processed with the L'Image software developed by Larry Nittler, Carnegie Institution in Washington DC, USA. Each image being a stack of several frames, the first step consists of aligning each frame using a correlation algorithm and applying the same shift in X and Y to all the pixels of a single frame. Then, ratio images can be generated. Each ratio is corrected using a calibration line (see supplementary material), determined by measuring four known reference samples (which in the meantime allow checking the instrument stability): a terrestrial Type 3 kerogen, a charcoal and the IOM of Orgueil and GRO 95502 (previously measured by gas source mass spectrometry by Alexander et al., 2007). Each calibration line is calculated using a linear regression and the R program was used to determine uncertainties associated with the calibration (Table S1). All the uncertainties reported in this study are one standard deviation; we propagated (using quadratic sum) counting statistics uncertainties on each regions of interest (ROI) and uncertainties arising from the calibration lines, reflecting the external precision of our measurements (e.g., the standard deviation for independent measurements repeated several times on the same sample).

Isotopic ratios are expressed in delta units, following the relation: $\delta(\text{‰}) = (\text{R}_{\text{sple}}/\text{R}_{\text{std}} - 1) \times 1000$, with R_{sple} being the sample isotopic ratio and R_{std} a reference ratio, such as Standard Mean Ocean Water (SMOW: $\text{D}/\text{H} = 155.76 \times 10^{-6}$) for H isotopes and air for N isotopes ($^{15}\text{N}/^{14}\text{N} = 3.67 \times 10^{-3}$). Isotopic anomalies in D (or in ^{15}N) are defined as ROIs consisting of at least 50 pixels ($0.3 \mu\text{m}^2$) meeting individually the requirement $|(D/H)_{\text{pixel}} - (D/H)_{\text{average}}|/\sigma > 2$ (or $|(^{15}\text{N}/^{14}\text{N})_{\text{pixel}} - (^{15}\text{N}/^{14}\text{N})_{\text{average}}|/\sigma > 2$), where $(D/H)_{\text{pixel}}$ (or $(^{15}\text{N}/^{14}\text{N})_{\text{pixel}}$) is the isotopic ratio of the pixel, $(D/H)_{\text{average}}$ (or $(^{15}\text{N}/^{14}\text{N})_{\text{average}}$) the average ratio of the image and σ the statistical error for each pixel (Table S2). Anomalies can be significantly positive or negative, reflecting enrichment or depletion in D (or ^{15}N) compared to the average of the image, respectively. The heterogeneity in the D/H ratio can be investigated using pixel histograms showing the distributions of δD (or $\delta^{15}\text{N}$) values of individual pixels within each image. The occurrence of positive micron-scale anomalies can be noticed on these histograms. They result in tails on the right side of histograms but do not affect the full width at half maximum (FWHM). Of note, some of these anomalies may correspond to presolar grains (e.g. Floss and Stadermann, 2009). Data are reported in the supplementary material (Tables S2 and S3).

2.3. Raman and STXM/XANES characterization

Raman data were collected on powdered samples using the Renishaw INVIA microspectrometer operating at IMPMC following the procedure described in Bernard et al. (2008). Twenty spectra were collected on each IOM to capture their homogeneous or heterogeneous nature. Spectra were measured from 500 to 3500 cm^{-1} at constant room temperature using the 514.5 nm wavelength of a 50 mW Modulaser Argon laser (green laser) focused on the sample through a Leica DMLM microscope with a long working distance

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