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1 **Molecular and isotopic behavior of Insoluble Organic Matter of the Orgueil**
2 **meteorite upon heating.**

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15
16 **ABSTRACT**

17
18 Organic matter contained in carbonaceous chondrites may have evolved due to aqueous
19 and/or thermal evolution on the parent body. The thermal behavior of the insoluble organic
20 matter (IOM) of the Orgueil meteorite was investigated. The evolutions of structural and
21 molecular properties were assessed by Raman, infrared and XANES spectroscopies, the H-
22 and N-isotopic compositions by NanoSIMS. The starting IOM is a disordered organic
23 macromolecule presenting a high degree of cross-linking. Hydrogen and Nitrogen isotope
24 distributions are heterogeneous with the occurrence of numerous micron-sized hot spots
25 enriched in heavy isotopes of H or N. After 1 hour at 300°C, there is subtle modification of
26 the structural ordering and the isotopic compositions. After 1 hour at 500°C, the structure
27 evolves toward condensation. Indeed, FTIR and XANES data are consistent with a continuous
28 evolution of the molecular structure toward an increase of aromatization, starting at 300°C
29 and becoming more intense at 500°C. The bulk D-enrichment is significantly reduced and D-
30 rich hot spots are lost at 500°C. The experimental evolution of the δD is consistent with
31 observations of IOM isolated from lightly altered carbonaceous chondrites. In contrast, the
32 ¹⁵N-rich hot spots seem insensitive to high temperature up to 500°C and bulk $\delta^{15}N$ remains
33 constant. The thermal evolution of H- and N- isotopes is decoupled, indicating that the D-rich
34 and ¹⁵N-rich moieties exhibit different thermal recalcitrance.

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1-INTRODUCTION

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Carbonaceous chondrites may have constituted the principal provider of water and prebiotic organic matter to the Early Earth. Understanding the origin of organic compounds in carbonaceous chondrites is crucial to assess how organic matter synthesis happened in the solar system, in protoplanetary disk and on the asteroids. It may also improve our knowledge of the emergence of life on Earth or in other places of the solar system. Insoluble organic matter (IOM) is the largest organic component recovered in carbonaceous chondrites. It represents more than 75 wt. % of the total organic matter recovered from these meteorites (Remusat, 2015; Alexander et al., 2017). Its elemental composition varies from one chondrite group to another. The average elemental formula for the IOM of the Orgueil (CI), Murchison (CM2) and Al Rais (CR2) meteorites is $C_{100}H_{60-80}O_{16-18}N_3S_{2-7}$ (Alexander et al., 2010; Derenne and Robert, 2010). This complex macromolecule is made of small aromatic units connected by short and branched aliphatic chains resulting in a high degree of cross-linking (Gardinier et al., 2000; Sephton et al., 2004; Cody and Alexander, 2005; Derenne et al., 2005; Wang et al., 2005; Vinogradoff et al., 2017). Oxygen occurs as ether or ester groups in aliphatic bridges, pyrroles may constitute the main N-rich reservoir (Hayatsu et al., 1980; Sephton et al., 1999; Remusat et al., 2005a; Remusat et al., 2005b). Sulfur is involved in several S-rich organic moieties, with variations, including the degree of S-oxidation, depending on the chondrite group and the petrologic type, e.g. depending on the degree of thermal metamorphism or aqueous alteration (Orthous-Daunay et al., 2010).

Unraveling the isotopic record in chondritic IOM may lead to a better understanding of the origin of organic compounds in chondrites (Remusat, 2015). In type 1 and 2 chondrites, IOM is characterized by a large D-enrichment compared to other H-rich components including phyllosilicates (Robert and Epstein, 1982; Alexander et al., 2010; Piani et al., 2015). In comparison, the IOM of CV, CO and other type 3 (and higher) carbonaceous chondrites show modest D-enrichments, with the exception of a few reduced CV (Alexander et al., 2007). Furthermore, IOM in CI, CM and CR chondrites shows numerous micron-sized D-rich domains, called D-rich hot spots (Busemann et al., 2006; Nakamura-Messenger et al., 2006; Remusat et al., 2009), with δD values reaching 20,000 ‰ for the IOM of some CR chondrites. These hot spots have been interpreted as the consequence of ionization in the early solar system and/or a cold chemistry in interstellar like conditions. D-rich hot spots seem to withstand hydrothermal alteration (Remusat et al., 2010) but are sensitive to thermal stress hence type 3 CO chondrites are devoid of D-rich hot spots (Remusat et al., 2009; Remusat et

70 al., 2016). The differences in the distribution of H isotopes between and within each class of
71 carbonaceous chondrites remain a subject of debates. It may be the consequence of pre-
72 accretionary processes or parent body processes, or both (Remusat, 2015).

73 Nitrogen isotopes also show specific signatures between carbonaceous chondrites.
74 With the exception of CR chondrites and a few CM chondrites, $\delta^{15}\text{N}$ in chondritic IOM does
75 not diverge much from the composition of terrestrial organic compounds (Alexander et al.,
76 2007), all of them being enriched compared to solar system N_2 (Marty et al., 2011).
77 Nevertheless, CI, CM and CR chondrites exhibit ^{15}N -rich hot spots (Busemann et al., 2006;
78 Nakamura-Messenger et al., 2006), with $\delta^{15}\text{N}$ up to 3,000 ‰ in the IOM of the Bells CM
79 chondrite. Although D-rich hot spots have been shown to result from local concentrations in
80 organic radicals (Remusat et al., 2009), very little is known about the carrier of the ^{15}N
81 enrichments and the places where these enrichments occurred.

82 Thermal degradation experiments can reveal properties of some constituents of the
83 chondritic IOM depending on their thermal sensitivity. Such experiments can also be useful to
84 investigate the behavior of the IOM when carbonaceous chondrites are subjected to thermal
85 processes like the thermal metamorphism on chondrite parent bodies. In a previous study
86 using pyrolysis experiments (e.g. increasing temperature in inert gas), Okumura and Mimura
87 (2011) showed that IOM in chondrites expresses a different behavior than terrestrial kerogen
88 upon heating. Of note, evolution of chondritic IOM is different under thermal experiments in
89 presence of water (Yabuta et al., 2007; Oba and Naraoka, 2009) ; such experiments may be
90 relevant to understand the evolution of organic matter under hydrothermal conditions. It must
91 be noted that the presence of minerals also influence the evolution of IOM, by playing
92 catalytic role hence affecting the kinetics of the reactions (Kebukawa et al., 2010).

93 The present paper intends to investigate the evolution of the structural, molecular,
94 elemental and isotopic properties of the Orgueil IOM upon pyrolysis (e.g. under inert gas)
95 using Raman and infrared spectroscopy, STXM/XANES and NanoSIMS imaging. Our results
96 are compared with the results of a similar experiment performed on the IOM of ordinary
97 chondrites (Remusat et al., 2016). We chose the Orgueil IOM as its molecular and isotope
98 properties are similar to many IOMs of type 1 and 2 (*i.e.* hydrated) carbonaceous chondrites,
99 including CM chondrites, that were intensively studied for the past four decades (Remusat,
100 2015; Alexander et al., 2017). Moreover, Orgueil is the most abundant chondrite of the CI
101 class, which has the closest composition to the protoplanetary disk (Lodders et al., 2009).
102 Hence, we assume that the Orgueil IOM, despites intense aqueous alteration on the parent

103 body (Bunch and Chang, 1980), contains primitive organic components present during the
104 early stages of the solar system.

105

106 **2- METHODS**

107

108 The IOM of the Orgueil meteorite was isolated following the protocol described in (Remusat
109 et al., 2005b). Elemental analysis reveals that the acid residue is constituted by 91% of
110 organic material, the reminder being inorganic minerals resisting the HF/HCl digestion
111 procedure.

112

113 2.1 Heating experiment

114

115 Orgueil IOM was heated at 300 °C and 500 °C. These two temperatures are common
116 temperatures of RockEval experiments. It is generally considered that free organic moieties
117 are volatilized at 300 °C, while kerogen undergoes cracking reactions at 500 °C (van Krevelen,
118 1981). Heating experiments were conducted with an ETR tubular furnace at Laboratoire des
119 Génie des Procédés et Matériaux (Ecole Centrale Paris, France). This furnace operated in an
120 Ar inert atmosphere (99.9999%) with a maximum operational temperature of 1200 °C.
121 Ceramic crucibles were filled with powdered samples (5–15 mg) and carefully located in the
122 middle of the tube to ensure a homogeneous temperature across the sample. The argon flow
123 rate was 30 L/min and the pressure within the tube was 2 bars. A 10 °C/min heating rate was
124 applied until the desired temperature (300 or 500°C) was attained. The temperature was then
125 maintained for 1 hour. At the end of the experiment, the furnace was allowed to cool down
126 freely. The maximum cooling duration was 6 h for the 500°C experiment.

127

128 2.2 Raman spectroscopy

129

130 Raman spectra were acquired using a LabRam HR800 (Horiba Jobin-Yvon)
131 spectrometer coupled with a 514.5 nm excitation wavelength generated by a Spectra Physics
132 argon ion laser. The laser beam was focused using a 100x objective, generating a 0.9 µm
133 diameter laser spot. The laser power at the sample surface was set at 300 µW and the
134 acquisition time was 60 s. The spectrometer was equipped with a 600 gr.mm⁻¹ grating and
135 spectra were acquired in the 700-2000 cm⁻¹ spectral range.

136 Raman spectra are dominated by two broad first-order peaks in disordered organic
137 material; the so-called D and G bands (Wopenka, 1993; Beyssac et al., 2003). The spectra
138 were processed using a multi-step analytical technique. The first step is to remove the
139 fluorescence background, assuming a linear shaped baseline in the 800-2000 cm^{-1} spectral
140 range. Then, the spectra were normalized by setting the G band peak maximum to 1. The two
141 bands were analyzed with a Lorentzian Breit–Wigner-Fano fit. The D band was fitted with the
142 Lorentzian profile and the G band with the Breit-Wigner-Fano profile (Ferrari and Robertson,
143 2000). Raman spectral parameters finally derived from these processed spectra are the width
144 at half maximum for each band (FWHM-G and FWHM-D), peaks position (ω_G and ω_D) and
145 the peak intensity ration (I_D/I_G).

146

147 2.3 FTIR spectroscopy

148

149 Infrared spectra were acquired using a Bruker Hyperion 3000 microscope coupled
150 with a Bruker Vertex FTIR spectrometer equipped with liquid nitrogen cooled MCT detector.
151 Transmission spectra were acquired between 700 and 4000 cm^{-1} with a 4 cm^{-1} spectral
152 resolution. Measurements were performed in an environmental cell, under secondary vacuum
153 ($\sim 10^{-7}$ mbar) and at 80 °C to remove adsorbed water. IOM powder was crushed between two
154 Ila diamond windows (3 mm diameter, 500 μm thick) in order to obtain a thin and flat sample
155 ($\sim 1 \mu\text{m}$). The typical size of the infrared spot on the sample was $\sim 50 \times 50 \mu\text{m}$.

156 The spectra were baseline corrected using splines functions, and were normalized by
157 setting the absorbance of the aromatic band centered at 1600 cm^{-1} to 1. Three semi-
158 quantitative tracers were determined: (1) A_{ali} , as the integrated absorbance of the
159 CH/CH₂/CH₃ massif (2800-300 cm^{-1}), estimates the relative aliphatic abundance; (2)
160 $R_{\text{CH}_2/\text{CH}_3}$, as the ratio of the peak intensities of the anti-symmetric modes of CH₂ and CH₃,
161 estimates the relative variation of the CH₂ versus CH₃ functional groups; (3) A_{CO} , as the peak
162 intensity of the band at $\sim 1700 \text{ cm}^{-1}$, estimates the relative abundance of the carbonyl C=O
163 group. The uncertainties on A_{ali} and A_{CO} are estimated to be $\sim 15\%$, and) $R_{\text{CH}_2/\text{CH}_3}$ to be
164 $\sim 10\%$.) $R_{\text{CH}_2/\text{CH}_3}$ is poorly sensitive to baseline correction.

165

166 2.4 STXM/XANES

167

168 XANES (X-ray Absorption Near Edge Structure) data were collected using the STXM
169 (scanning transmission X-ray microscope) located on the 10ID-1 SM beamline (Kaznatcheev

170 et al., 2007) at the Canadian Light Source (CLS). This beamline uses soft X-rays (130–2500
171 eV) generated with an elliptically polarized undulator (EPU) inserted in the 2.9 GeV
172 synchrotron storage ring (250–150 mA). The microscope chamber is evacuated to 100 mTorr
173 after sample insertion and back-filled with He. Energy calibration is accomplished using the
174 well-resolved 3p Rydberg peak at 294.96 eV of gaseous CO₂ for the C K-edge. Alignment of
175 images of stacks and extraction of XANES spectra were done using the aXis2000 software
176 (ver2.1n). Although normalization of XANES data is generally performed by dividing the
177 spectrum (after subtraction of a power law background) by the value of the linear function
178 used to fit a given portion the post-edge region (typically from 320 to 340 eV) extrapolated at
179 the ionization threshold of carbon (typically 291.5 eV - Bernard et al., 2010), the appropriate
180 physical way to estimate to the total carbon content is to fit the carbon pre-edge (270-280eV)
181 and post-edge (370-390 eV) regions with the f₂ component of the carbon atom scattering
182 factor up to an energy at which the EXAFS oscillations are no longer present, i.e. up to 380-
183 390 eV for carbon (Alleon et al., 2015; Le Guillou et al., 2018). Here, following the
184 alternative method proposed and validated by Le Guillou et al. (2018), we normalized the
185 spectra (after subtraction of a power law background) by dividing them by their integrated
186 area from the pre-edge region up to the mean ionization energy of carbon (e.g. 282-291.5 eV),
187 this area being a direct proxy of the total carbon quantity. The C-XANES spectra shown in
188 the present study are for homogeneous organic-rich areas of several hundreds of nanometers.
189 Although radiation damage per unit of analytical information was shown to be typically 100-
190 1000 times lower in STXM-XANES spectroscopy than in TEM-EELS (Hitchcock et al.,
191 2008), the C-XANES data shown here were collected following the procedures for X-ray
192 microscopy studies of radiation sensitive samples recommended by Wang et al. (2009).

193

194 2.5 NanoSIMS imaging:

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196 Samples were pressed on clean indium foil and gold coated (20 nm thick) for
197 NanoSIMS imaging. All the isotopic images were acquired on the Cameca NanoSIMS 50
198 installed at MNHN Paris. δD and $\delta^{15}N$ images were recorded at the same location, but during
199 two separate runs, one after the other in the course of the same session. We used a 16 keV
200 primary Cs⁺ beam to collect secondary ions of H⁻ and D⁻ in a first step (to obtain δD images)
201 and ¹⁶O⁻, ¹²C₂⁻, ²⁶CN⁻, ²⁷CN⁻ and ³²S⁻ in a second step (for N/C and $\delta^{15}N$ images). We chose to
202 use the ion ratio ²⁶CN⁻/¹²C₂⁻ in order to lower the topographic effects on the N/C

203 measurements (Thomen et al., 2014). The primary beam was set to 8 pA for H isotopes and to
204 3 pA for N isotope measurements, leading to a spatial resolution of about 300 and 150 nm,
205 respectively. We collected 256×256 pixel images covering 20×20 μm² with a raster speed of
206 2ms/pix. Prior to each analysis, we applied a 25×25 μm² presputtering using a 600 pA
207 primary current during 6 minutes (corresponding to a Cs⁺ fluency of 2.2×10¹⁷ at.cm⁻²) to
208 insure coating removing, cleaning surface, and reaching the sputtering steady state (Thomen
209 et al., 2014). We used Hamamatsu discrete dynode electron multipliers with a dead time of 44
210 ns in multicollecion mode. For H isotopes, we set the mass spectrometer to a mass resolving
211 power of 4000; for N isotopes it was increased to 8000 to be able to resolve interferences like
212 ¹²C¹⁵N⁻ from ¹³C¹⁴N⁻ and ³²S⁻ from ¹⁶O₂⁻. Each location was also imaged, during a separate
213 session, using a 3 pA Cs⁺ beam and the combined analysis mode to acquire images of H⁻ with
214 one B-field and ¹²C⁻, ¹⁶O⁻, ²⁸Si⁻ with a second one (raster speed set at 3 ms/pix for each B-
215 field). This allows determining H/C ratio. During the session, the vacuum did not exceed
216 5×10¹⁰ torr.

217 All NanoSIMS data were processed with L'image software developed by Larry
218 Nittler, Carnegie Institution in Washington DC, USA. Each image being a stack of several
219 frames, the first step consists in aligning each frame using a correlation algorithm and
220 applying the same shift in X and Y to all the pixels of a single frame. Then, ratio images
221 could be generated. Each isotopic ratio and the N/C ratio are corrected using calibration lines,
222 determined by measuring 4 known reference samples: terrestrial type 3 kerogen from Virginia
223 and charcoal as well as the IOM of Orgueil and GRO 95502 meteorites (Remusat et al.,
224 2016). For the chondritic IOMs, we used the ratios measured by gas source mass spectrometry
225 by Alexander et al. (2007). Each calibration curve was calculated by linear regression using
226 the R program. H/C ratios were corrected using the H/C ratio of Orgueil IOM reported by
227 Alexander et al. (2007). All the uncertainties reported in this study are 1 sigma errors; we
228 propagated (using quadratic sum) counting statistics uncertainties on each measurement
229 (depending on the total counts in each object) and uncertainties arising from the calibration
230 lines, reflecting the external precision of our measurements (e.g. the variability we can report
231 for independent measurements repeated several times in the course of this session).

232

233 Isotopic ratios may be expressed in delta units, following the relation:

234

$$\delta(\text{‰}) = (\text{R}_{\text{sple}} / \text{R}_{\text{std}} - 1) \times 1000$$

235 with R_{sple} being the sample isotopic ratio and R_{std} the ratio of a terrestrial standard.
236 Commonly used standards are: Standard Mean Ocean Water (SMOW: $D/H= 155.76 \times 10^{-6}$) for
237 H isotopes and Air for N ($^{15}\text{N}/^{14}\text{N}= 3.67 \times 10^{-3}$).

238

239

240

3- RESULTS

241

3.1 Molecular and structural evolution

242

243
244 The evolution of the elemental ratios of the Orgueil IOM upon heating was assessed
245 by NanoSIMS (figure 1 and table 1). The N/C remains constant within error bars at 300°C,
246 and decreases at 500°C. As a consequence, the organic residue after heating still contains a
247 comparable amount of nitrogen as the starting material. This may indicate that nitrogen is
248 contained in thermally stable moieties. On the other hand, the H/C decreases as temperature
249 increases: compared to the starting IOM, there is a 5.6 times decrease at 300°C, followed by a
250 further hydrogen depletion that results in H/C being 8.5 times lower at 500°C.

251 The FTIR spectrum of the Orgueil IOM (figure 2) shows typical IR absorption
252 features of IOM recovered from carbonaceous chondrites (Kebukawa et al., 2011; Orthous-
253 Daunay et al., 2013). We observe three developed peaks in the range 2800-3000 cm^{-1}
254 attributed to aliphatic C-H stretching modes of CH, CH₂ and CH₃ groups: CH₃ asymmetric
255 stretching mode at 2955 cm^{-1} , CH₂ asymmetric stretching mode at 2925 cm^{-1} , symmetric CH₃
256 and CH₂ stretching modes at 2873 cm^{-1} and ~ 2850 cm^{-1} (as a shoulder and hardly visible),
257 respectively. The band at 1050 cm^{-1} may correspond to the C-O stretch of primary alcohol
258 (Coates, 2000). The intense band at 1700 cm^{-1} is due to the carbonyl C=O stretching mode,
259 and the 1590 cm^{-1} band corresponds to the aromatic C=C stretching mode. Several bands in
260 the range 1000-1500 cm^{-1} are related to other stretching, bending and deformation modes of
261 the organic network, in addition to the aromatic skeletal mode at 1210 cm^{-1} . We also observe
262 three small features due to out of plane bending modes of aromatic C-H at 759, 823 and 893
263 cm^{-1} , while the aromatic C-H stretching mode at 3050 cm^{-1} is hardly seen in the starting IOM,
264 and unobserved in other samples. The FTIR spectrum of the starting Orgueil IOM is in
265 agreement with the spectra previously reported by Gardinier et al. (2000) and Orthous-
266 Daunay et al. (2013) and with the spectrum of the IOM of another CI chondrite, Ivuna
267 (Kebukawa et al., 2011).

268 After heating, we observe a significant modification of the FTIR spectrum of the
269 Orgueil IOM (figure 2). At 300°C, the C=O stretching absorption is significantly reduced and
270 the C-O stretching mode gradually disappear. In the meantime, the relative absorption of the
271 CH₂ and CH₃ asymmetric stretching modes indicates an increase of the CH₂/CH₃ ratio while
272 the overall aliphatic carbon content decreases. At 500°C, we notice further progress following
273 these trends, with an extreme reduction of the C=O stretching feature, and a much higher
274 CH₂/CH₃ ratio, whereas the aliphatic carbon content is only slightly decreasing. Overall, the
275 evolution in the FTIR signature upon heating points to a significant loss of O and a decrease
276 of the alkyl group abundance, *i.e.* the release of short aliphatic side chains (methyl, ethyl and
277 propyl groups) as a consequence of thermal stress. The persistence of the three aliphatic C-H
278 stretching modes at 500°C shows that aliphatic carbon remains hence the small polyaromatic
279 units did not merge significantly into a big aromatic structure, in agreement with the Raman
280 analysis (see below). Overall, the semi-quantitative ratios vary as following: $A_{CO} = 1.1 - 0.78$
281 $- 0.48$; $R_{CH_2/CH_3} = 1.09 - 1.36 - 1.99$ and $A_{ali} = 53-26-32$, for the initial IOM and heated at 300
282 and 500°C, respectively. The drop of A_{ali} between the unheated and heated IOMs is consistent
283 with the drop of the H/C ratio. The higher aliphatic abundance in the sample heated at 500°C
284 with respect to that heated at 300°C is unexpected. In fact, the error bars on these two values
285 (15%) slightly overlap, and we cannot exclude a nugget effect due to IOM heterogeneity (H/C
286 is a bulk measurement over a ~mg sample, while micro-IR measurements were collected on a
287 ~ng sample).

288 The C-edge XANES spectrum (figure 3) of the Orgueil IOM exhibits a strong
289 absorption at 285.2 eV corresponding to C=C bonds in aromatic rings and another intense
290 band at 288.6 eV corresponding to COOH groups consistent with other chondrite IOMs
291 (Cody et al., 2008; De Gregorio et al., 2013; Le Guillou et al., 2014; Remusat et al., 2016).
292 Other weaker feature can be observed at 290.6 eV, corresponding to aliphatic C-C bonds.
293 Aliphatic C-H bonds produce only a faint absorption at 287.7 eV, which appears as a soft
294 shoulder in the spectrum. Other small features at 289.2 and 289.5 eV correspond to C-OH
295 groups. These bands evolve gradually when the temperature increases: three main
296 observations can be highlighted. (1) The contribution of the C=C bonds significantly
297 increases and shifts a little towards higher energies, due to the growth of aromatic units
298 (Bernard et al., 2010). (2) The COOH and C-OH contributions decrease, showing a loss of O-
299 rich groups. (3) The small contributions of aliphatic C-H and C-C bonds fade away at 500°C.

300 The structural evolution as probed by Raman spectroscopy indicates an increase in
301 ordering consistent with the condensation process (figure 4). Orgueil IOM shows a Raman

302 spectrum consistent with a disordered organic macromolecule, with broad G and D bands
303 having comparable intensities (Bonal et al., 2006; Quirico et al., 2009). At 300°C, the IOM
304 remains poorly organized as indicated by similar D-band width and I_d/I_g ratio as the starting
305 IOM. At 500°C, structural order increases: FWHM-D and I_d/I_g follow a typical trend of
306 thermal metamorphism of IOM in chondrites (Bonal et al., 2006), i.e. the increasing and
307 sharpening of the D band.

308 In conclusion, molecular and structural analysis shows that Orgueil IOM undergoes a
309 slight increase of the degree of organization as a consequence of O and H loss in addition to
310 an increasing contribution of aromatic over aliphatic carbon. The N/C, though, seems to be
311 only slightly affected by heating. That may be related to the occurrence of N-heterocycles,
312 *e.g.* pyrrole moieties, as the main reservoir of N in the Orgueil IOM (Remusat et al., 2005b).
313 This evolution is coupled with the modifications of the H and N isotope distributions as
314 described hereafter.

315

316 3.2 Isotopic evolution upon heating

317

318 NanoSIMS imaging reveals the heterogeneous distribution of N-isotopes in Orgueil
319 IOM (Figure 5), as observed in type 1 and 2 carbonaceous chondrites (Busemann et al., 2006;
320 Nakamura-Messenger et al., 2006; Floss and Stadermann, 2009). Bulk $\delta^{15}\text{N}$ (defined as the
321 average image value) is around 30‰: a consistent value with gas source measurements for the
322 Orgueil IOM: $\delta^{15}\text{N} = 30.7 \pm 0.2\text{‰}$ (Alexander et al., 2007). Several hot spots with significantly
323 heavier isotopic composition, *e.g.* $130\text{‰} < \delta^{15}\text{N} < 230\text{‰}$, occur (Figure 6 and table S1). These
324 values are significantly lower than the hot spot values determined for the IOM of CR
325 chondrites (Busemann et al., 2006; Floss and Stadermann, 2009) and Tagish Lake
326 (Nakamura-Messenger et al., 2006). As already observed in some CR chondrites (Floss and
327 Stadermann, 2009), Orgueil IOM exhibits some ^{15}N -depleted organic grains, hereafter called
328 cold spots, with $\delta^{15}\text{N}$ down to $-192 \pm 34\text{‰}$ (Figure 6).

329 Such heterogeneous distribution of N-isotopes with localized positive (and a few
330 negative) anomalies is also observed after heating at 300°C and 500°C. Nevertheless, the
331 abundance of hot spots (and cold spots) is lower. We estimate the relative abundance of
332 isotopic anomalies, or areal extent, by the ratio of the surface area covered by isotopic
333 anomalies normalized to the total analyzed surface area. We notice that the areal extent is
334 decreasing from 3.6% in Orgueil IOM down to 1% for Orgueil 500 (see table 1). Now looking

335 at the isotope composition of these hot spots, they cover a comparable range in Orgueil 300
336 and the starting IOM. $\delta^{15}\text{N}$ remains $< 400\text{‰}$ in Orgueil 500. The average image values are
337 also comparable for the three samples, indicating that heating has an influence on the
338 abundance of N-isotopic anomalies, but not on their magnitude (both positive and negative).

339 The picture is significantly different for H-isotopes (Figure 7). The Orgueil IOM has
340 already been shown to present several D-rich hot spots (Remusat et al., 2009). Here, these hot
341 spots span a range $2000\text{‰} < \delta\text{D} < 4000\text{‰}$ (see Figure 8 and table S2) consistent with D-rich
342 hot spots so far reported in the IOM of several carbonaceous chondrites (Busemann et al.,
343 2006; Nakamura-Messenger et al., 2006) but absent in primitive ordinary (Remusat et al.,
344 2016) and enstatite (Piani et al., 2012) chondrites. After heating at 300°C , the average value
345 reaches $\delta\text{D} = 1200 \pm 130\text{‰}$, while the starting material has $\delta\text{D} = 750 \pm 130\text{‰}$ (close to the gas
346 source mass spectrometry measurement, (Alexander et al., 2007)). The maximum hot spot
347 value rises up to $5400 \pm 250\text{‰}$ but their abundance decreases (see tables 1 and S2). At 500°C ,
348 the average δD drops to 425‰ and all the isotopic anomalies are gone.

349 It then appears that, whereas the organic material responsible for the occurrence of D-
350 rich hot spots is thermally labile, it can resist up to 300°C . Moreover, there is a D-poor
351 component that has been lost during this heating step, which occurs concomitantly with a
352 decrease in COOH and C-OH groups. This observation is consistent with stepped pyrolysis –
353 isotope ratio measurements reported back in the 80's: a large amount of H having $\delta\text{D} \approx 0\text{‰}$
354 was indeed released at temperature $< 300^\circ\text{C}$ from the Orgueil IOM (Robert and Epstein,
355 1982). This component could correspond to exchangeable H, associated with COOH and C-
356 OH groups, inherited from the chemistry employed for IOM isolation. It could also be
357 terrestrial hydrogen (*e.g.* water) sticking to the IOM. It could alternatively be an
358 extraterrestrial component, having an isotopic composition closer to the average δD of total
359 hydrogen contained in the CI chondrites (Alexander et al., 2012).

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4- DISCUSSION

365

366 4.1 Evolution of Orgueil IOM upon heating: comparison with previous experimental studies.

367

368 Our experiment shows that upon heating, the molecular structure of the Orgueil IOM
369 evolves as a consequence of a net loss of H and O, while the N content slightly decreases. The
370 modest evolution of the N/C ratio under thermal stress is in agreement with nitrogen in
371 Orgueil IOM mostly occurring as thermally stable pyrrole groups (Remusat et al., 2005b).
372 The small decrease of the N content is likely related to the loss of nitrile groups, a minor
373 component of CI IOMs (Remusat et al., 2005b; Dobrica et al., 2011). The aliphatic carbon
374 content decreases rapidly at 300°C, and slightly afterwards at 500°C. In the meantime, there is
375 a significant loss in methyl groups (-CH₃) over methylene groups (-CH₂) indicating that
376 reticulation increases as the whole molecular structure is modified. XANES data reveal that
377 smaller aromatic units get larger with temperature increase. The combined evolutions of
378 aromatic and aliphatic carbons promote the decrease of the H/C ratio. The ordering of the
379 IOM, as revealed by Raman spectroscopy, shows little evolution at 300°C, but a clear
380 modification at 500°C shown by I_d/I_g and FWHM-D. The observed evolution of the Raman
381 spectra is typical of the reorganization of the IOM structure induced by temperature increase
382 (Beysac and Lazzeri, 2012). Nevertheless, the organic residue obtained after the pyrolysis at
383 500°C remains poorly ordered and contains less large aromatic structures compared to most
384 of the thermally processed CC, as revealed by Raman (Bonal et al., 2006), likely due to short
385 heating duration in the oven (only 1h).

386 Looking at isotope compositions, heating induces a loss of D-rich organic moieties
387 whereas N-isotope composition appears slightly affected (see next section for discussion
388 about these isotopic trends). The loss of D from Orgueil IOM as a consequence of
389 temperature increase is expected because D-rich moieties are likely aliphatic or related to
390 organic radicals, both known to be thermally labile (Keller et al., 2004; Remusat et al., 2006;
391 Delpoux et al., 2011). A similar observation was reported for Murchison IOM (Remusat et al.,
392 2009): flash pyrolysis at 650°C of this IOM resulted in the total destruction of D-rich hot
393 spots, and a decrease of the bulk δD. It must be noted that this behavior is opposite to the
394 evolution of the δD of IOM in ordinary chondrites (Remusat et al., 2016) likely reflecting a
395 different D-rich organic reservoir in each IOM.

396 Okumura and Mimura (2011) performed gradual pyrolysis experiments (under He
397 flux) on the Murchison IOM. They observed that, with increasing temperature, H/C and O/C
398 decreased significantly whereas N/C remained stable, in agreement with our observations. As
399 a consequence of heating, labile fragments, mostly constituted by aliphatic chains and 1 or 2
400 aromatic ring units, were lost and the residue was getting more aromatic. They did follow the

401 evolution of the δD of IOM upon heating and concluded that the labile organic groups are
402 relatively more D-rich than the average IOM, and the thermally stable part is D-depleted. This
403 confirms the heterogeneous nature of IOM in CC.

404 Other heating experiments have been reported in the literature. However, most of them
405 were performed under hydrothermal conditions, *e.g.* in presence of water. For instance, Oba
406 and Naraoka (2009) subjected Murchison IOM at temperatures up to 330°C in the presence of
407 water. They observed a significant decrease of δD in the IOM, from 986‰ down to 25‰, a
408 decrease of H/C (from 0.62 down to 0.31) and O/C (0.22 to 0.1) and an almost constant N/C.
409 Yabuta et al. (2007) exposed the Murray IOM to similar hydrothermal conditions (300°C) but
410 for longer durations (6 days instead of 3) than Oba and Naraoka (2009). Their results are
411 remarkably consistent: N/C ratio almost constant, H/C reduced by a factor of 0.8 and δD
412 dropped from 792 ‰ down to -41‰. Yabuta et al. (2007) also observed a significant
413 reduction of $\delta^{15}N$, from 17.3‰ to -6.8‰. The comparison of the NMR spectra of Murray
414 IOM before and after the hydrothermal experiment revealed a loss of aliphatic C, an increase
415 in aromatic C and a loss of O-bearing groups (Yabuta et al., 2007). Although the evolution
416 trends expressed by the molecular properties and the elemental ratios may look similar in
417 comparison to our experiment, the magnitudes of the H/C decrease and the D-depletion are
418 different. At 300°C, in our experiment, H/C is divided by a factor of 5 whereas δD slightly
419 increases. In the hydrothermal experiments, at 300°C, H/C was reduced by a factor of 0.7 and
420 0.8, and δD dropped from 986‰ down to 65‰ and from 792 ‰ down to -41‰, in the
421 experiments of Oba and Naraoka (2009) and the experiments of Yabuta et al. (2007),
422 respectively. This clearly shows that the presence of water in hydrothermal conditions may
423 promote chemical reactions that result in the formation of organic groups with a D/H
424 signature close to the signature of the water used in the hydrothermal experiments. In other
425 words, the presence of water exerts a strong influence on the evolution of IOM structure and
426 composition when temperature increases. Furthermore, the hydrothermal experiments are
427 performed in closed system conditions, in contrast to our experiments under Ar flow which
428 are in open system conditions. Hence, in our experiments, as well as for the experiment
429 performed by Okumura and Mimura (2011), the released organic moieties are pushed away
430 by the inert gas and isolated from the residual IOM. In hydrothermal experiments, the
431 products of decomposition can react with the residual IOM and lead to the formation of
432 byproducts that may condense with the residual IOM.

433

434 4.2 Different evolution of H and N isotope signatures upon heating: decoupling of D and ¹⁵N-
435 rich organic components having different origins.

436

437 The most striking result of our study is the decoupling of the H and N-isotope
438 signatures: the behavior of D and ¹⁵N-rich components under thermal stress are drastically
439 different. Whereas ¹⁵N-rich moieties seem poorly affected by heating, D-rich ones are
440 destroyed within 1h at 500°C. This shows that hydrogen and nitrogen heavy isotope
441 enrichments are not born by the same organic reservoirs; hence these enrichments may have
442 distinct origins. Keller et al. (2004) reported that the ¹⁵N-rich organic matter in interplanetary
443 dust particles (IDPs) is more refractory than the D-rich hydrocarbon. They indeed characterize
444 several IDPs having undergone various degrees of heating during atmospheric entry and
445 notice a correlation with δD and δ¹⁵N of their organic matter. They concluded that D and ¹⁵N-
446 rich organic reservoirs were distinct, they had different molecular properties and were likely
447 formed in different environments. This echoes with our experiment on Orgueil IOM
448 indicating that its D and ¹⁵N-rich components may be similar as those in IDPs.

449 D-enrichment may be mostly related to organic radicals, known to be sensitive to
450 temperature increase (Remusat et al., 2009) and these radicals may sign the occurrence of
451 irradiation events during the birth of the solar system (Laurent et al., 2014; Gavilan et al.,
452 2017) or photolysis of interstellar icy grains (Agarwal et al., 1985). These enrichments may
453 also be related to cold temperature chemistry, via ion/molecule reactions or gas-grain
454 interactions (Geiss and Reeves, 1981; Sandford, 2002). Much less is known for ¹⁵N-
455 enrichments. Whereas hot spots were ascribed to presolar grains (Floss and Stadermann,
456 2009), the ¹⁵N-enrichments observed in different kinds of organic molecules, including amino
457 acids (Elsila et al., 2012), have been interpreted as the fingerprint of enriched NH₃ formed by
458 ion/molecule reactions in the ISM that later constituted the source of N in organic matter
459 recovered in CC (Pizzarello and Bose, 2015). The preservation of both bulk δ¹⁵N and ¹⁵N-rich
460 hot spots in our heating experiment shows that the carrier of the ¹⁵N-rich organic material is
461 thermally stable. In the meantime, this component is sensitive to aqueous alteration, *e.g.* to
462 interaction with water, as shown by hydrothermal experiments (Yabuta et al., 2007; Pizzarello
463 and Bose, 2015). Hence, the ¹⁵N-rich organic material in CC is sensitive to fluid circulation,
464 but much less to temperature elevation in anhydrous conditions.

465 The occurrence of organic components exhibiting different thermal recalcitrance and
466 different H and N isotope compositions clearly points to IOM heterogeneity (within and
467 between samples). Furthermore, the different behavior of organic moieties in IOM towards

468 temperature and water, hence to secondary processes on the parent body, may explain the
469 distinct trend of isotope ratios observed between the different classes of chondrites whereas
470 their molecular structures both show evidence of aromatization process (Alexander et al.,
471 2010; Remusat et al., 2016). As suggested earlier, IOM is a mixture of several organic
472 components that were likely accreted as discrete organic particles having experienced
473 different temperature or irradiation conditions in the disk before the accretion of the parent
474 bodies (Remusat et al., 2010). For instance, the OC parent body accreted a thermally
475 recalcitrant D-rich organic component, absent on the CC parent body (Remusat et al., 2016).
476 Having different behavior toward thermal or hydrothermal stress, these organic components
477 will evolve differently on the parent bodies resulting in the variability observed at the bulk,
478 micron and molecular scales. It must be noted that the occurrence of different organic
479 precursors accreted on the CC and OC parent bodies confirms that they formed from distinct
480 isolated reservoirs (Kruijer et al., 2017). Hence, the location and the time of parent body
481 formation have profound consequences on the molecular and isotopic properties of the
482 organic matter now detected in primitive chondrites.

483

484 4.3 Comparison with observations in carbonaceous chondrites: understanding the effects of
485 secondary processes on the parent body.

486

487 The observed evolution of Orgueil IOM upon heating can be compared to natural CC
488 to assess the influence of temperature on the chemical and isotopic properties of IOM in these
489 meteorites. The δD , $\delta^{15}N$, H/C and N/C of the IOM of various CC show several interesting
490 features considering the heated CC: namely CO, CV and heated CM chondrites (Alexander et
491 al., 2007; Alexander et al., 2010). For all of them, H/C decreases with temperature; δD tends
492 to follow the same trend. Moreover, it was observed that the IOM in heated CC is devoid of
493 D-rich hot spots (Remusat et al., 2009). Assuming that heated CM chondrites accreted the
494 same organic precursors as regular CM chondrites, heating resulted in a significant decrease
495 in H/C and a net loss of D. Overall, these observations for natural objects are consistent with
496 our experimental results, which indicates that heating is responsible for the low H/C and δD
497 observed in the IOM of CC that experienced thermal metamorphism. Noticeable exceptions
498 are a few reduced CV chondrites (Leoville and Vigarano): they show a significant D-
499 enrichment despite low H/C; they have indeed experienced relatively high temperature (Bonal
500 et al., 2006). This may relate to the influence of minerals on the parent body of these CV

501 chondrites, or the influence of close/open system conditions. More experiments, in close
502 systems and in the presence of minerals representative of CV matrices are required in order to
503 better constrain the observed difference in the evolution of oxidized and reduced CV
504 chondrites (Bonal et al., 2016), and assess the influence of the fluid during the evolution of
505 IOM on the CV parent body.

506 Now looking at N, the picture is more obscure. CV chondrites show much lower N/C
507 than CO or heated CM chondrites (Alexander et al., 2007; Alexander et al., 2010). Moreover,
508 the IOMs of CV chondrites (and especially oxidized CV) are the most ^{15}N -depleted. For CV
509 and CO chondrites, a decrease in N/C is associated with ^{15}N -depletion, and seems correlated
510 with the increase of the temperature experienced by the IOM on the parent body (Bonal et al.,
511 2006; Bonal et al., 2007). Such an evolution is not consistent with the trend observed in our
512 experiment, indicating that: (1) the N-rich moieties in the CO and CV organic precursors are
513 different compared to CI or (2) additional chemical reaction occurred during the thermal
514 metamorphism on the CO and CV parent bodies, likely due to the presence of the matrix
515 minerals, and they induced more damages than pure heating on the N-rich moieties. In the
516 case of CM chondrites, the comparison of the IOM of heated and non-heated chondrites tends
517 to indicate that heating has a small influence on N/C, but $\delta^{15}\text{N}$ drastically increases with
518 temperature. If the evolution of the N content is overall the same as in our experiments, the
519 trend for N-isotopes is different. Again, this suggests that: (1) the CM parent body accreted
520 ^{15}N -rich organic moieties that are thermally recalcitrant (and are absent in the IOM recovered
521 from CI), (2) the presence of minerals during the heating on the CM parent body impacted the
522 N-rich moieties, or (3) the presence of water during the heating process induces drastic
523 changes in the behavior of ^{15}N -rich organic moieties. Nevertheless, upon the thermal
524 evolution from non-heated to heated CM chondrites, the H and N isotope compositions are
525 decoupled; this is consistent with the thermal evolution of the Orgueil IOM.

526 One may argue that, with the noticeable exception of CM chondrites (gathering heated
527 and non-heated objects), the above discussion is strongly dependent on the assumption that all
528 CC have accreted the same IOM precursors, which remains a commonly accepted hypothesis
529 (Vinogradoff et al., 2017). There are very few meteorites that show different degrees of
530 secondary processes within the same stone or fall. Herd et al. (2011) and Alexander et al.
531 (2014) have investigated the IOM from several fragments of the Tagish Lake meteorite
532 showing different degrees of secondary processes. Although the main difference between the
533 different fragments is related to aqueous alteration, the effect of temperature is significant
534 (Alexander et al., 2014). From the most pristine to the most altered fragments, they observed:

535 a significant decrease of H/C associated with an increase of the aromatic/aliphatic ratio and a
536 decrease of the δD . Both N/C and $\delta^{15}N$ remain comparable between fragments, as in the
537 present experiments. These observations are consistent with our data and seems to confirm the
538 statement of Alexander et al. (2014) that temperature constitutes a major factor controlling the
539 evolution of the IOM in the Tagish Lake parent body, as well as in other carbonaceous
540 chondrites.

541

542

5- CONCLUDING REMARKS

543

544 We have conducted heating experiments on the IOM of the Orgueil meteorite. This
545 experiment was conducted in an inert gas. This allows investigating the effects of pure
546 heating. The molecular structure of the IOM underwent condensation: H and O are lost;
547 methyl groups are lost and aromatic units get larger, hence ordering increases. This evolution
548 is consistent with observations in the IOM of CO, CV and heated CM chondrites.

549 The H-isotope composition of CC IOM is strongly affected by heating; the D-rich
550 organic component appears thermally labile. This was expected considering that significant
551 D-enrichment was shown to be connected to labile H reservoirs: aliphatic groups and organic
552 radicals (Remusat et al., 2006; Remusat et al., 2009). In the meantime, N/C and $\delta^{15}N$ show
553 little variation. This may confirm that N mainly occurs as heteroaromatic structures, more
554 thermally stable.

555 Our experiment, performed in an open system conditions, may also relate to
556 protoplanetary disks, hence it may bring constrains on the heating experienced by organic
557 matter in the gas phase prior accretion on parent bodies. Assuming that IOM in CC derives
558 from precursors formed in cold environments that could be thermally reprocessed on their
559 route to the location of the parent body accretion closer to the sun, we can estimate that they
560 were not exposed to higher temperature than 300°C for more than 1 hour (e.g. ≈ 600 K), in
561 order to preserve D-enrichments. ^{15}N -rich precursors may have experienced up to 500°C (e.g.
562 ≈ 800 K), as they are more thermally recalcitrant.

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764 Figure Captions:

765

766 Figure 1: Elemental ratios of Orgueil IOM before and after heating at 300°C and 500 °C,
767 determined by NanoSIMS. The black solid squares represent N/C atomic ratios, showing
768 small variation when considering error bars. Open diamonds represent H/C atomic ratios that
769 clearly indicate hydrogen depletion upon heating.

770

771 Figure 2: FTIR spectra of Orgueil IOM before and after heating at 300°C and 500°C. Spectra
772 were normalized to the C=C stretching band at 1590 cm⁻¹. The massif in the range 2800-3000
773 cm⁻¹ corresponds to aliphatic C-H modes, peaks at 759, 823 and 893 cm⁻¹ to aromatic C-H
774 modes. C=O and C=C bonds are probed by peaks at 1700 and 1590 cm⁻¹, respectively. The
775 Peak at 1050 cm⁻¹ corresponds to amines or alcohol (Coates, 2000). The comparison of the
776 different spectra indicates that upon heating, alkyl and carbonyl group abundance is
777 decreasing, and the CH₂/CH₃ ratio is increasing. These evolutions are more drastic at 500°C.

778

779 Figure 3: XANES spectra of Orgueil IOM before (solid line) and after heating at 300°C
780 (dashed line) and at 500°C (dotted line). Peak assignment: 285.2-285.6 eV, C=C bonds; 288.6
781 eV, COOH groups; 287.7 and 290.6 eV, aliphatic groups; 289.2 and 289.5 eV, C-OH groups.
782 The increasing contribution of aromatic C at the expense of aliphatic C shows aromatization.
783 In addition, the aromatic C peak is shifting toward higher values and is broadening.

784

785 Figure 4: A- Raman spectra of Orgueil IOM before and after heating at 300°C and 500°C. B:
786 Deconvolution parameters reveal a limited structural evolution at 300°C followed by an
787 increase of the sp² ordering related to the thermal stress at 500°C, as shown by the increasing
788 Id/Ig and the decreasing D-band width.

789

790 Figure 5: NanoSIMS images of N-isotope distribution in Orgueil IOM before and after
791 heating at 300 and 500°C. The N-isotope signature appears only slightly disturbed by heating
792 up to 500°C.

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794 Figure 6: Nitrogen isotopic composition of heated and unheated IOM of Orgueil. In all the
795 samples we observe both ¹⁵N-rich and poor micron sized area, called hot and cold spots,
796 respectively. The bulk δ¹⁵N remains constant upon heating. The range of the isotopic

797 anomalies (both positive and negative) is similar in all the samples. However, the abundance
798 of micron-sized isotopic anomalies is decreasing with increasing temperature.

799

800 Figure 7: NanoSIMS images of H-isotope distribution in Orgueil IOM before and after
801 heating at 300°C and 500°C. The starting IOM is reported as a reference. D-rich hot spots are
802 lost at 500°C, but remain at 300°C. The average D/H is increasing at 300°C, and then
803 decreasing significantly at 500°C.

804

805 Figure 8: Hydrogen isotopic composition of Orgueil IOM before and after heating at 300°C
806 and 500°C. Bulk values are indicated by the points on the left-hand side of the plot. At 500°C,
807 the D-rich hot spots are destroyed. They however resist to heating at 300°C.

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812 Table 1: average values obtained from NanoSIMS imaging. Uncertainties correspond to 1 σ
813 sigma error (68% interval of confidence) and are calculated taking in account counting
814 statistics and error on the calibration curve.

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Sample	$\delta^{15}\text{N}$ (‰)	N-hot spots areal extent	δD (‰)	H-hot spots areal extent	N/C ($\times 10^{-2}$)	H/C ($\times 10^{-2}$)
Orgueil	30 \pm 5	3.6 %	750 \pm 130	4.4 %	3.5 \pm 0.25	67 \pm 8
Orgueil 300	22 \pm 4	1.9 %	1200 \pm 130	2.2 %	3.8 \pm 0.25	12 \pm 2
Orgueil 500	22 \pm 5	1%	427 \pm 130	0%	3.0 \pm 0.25	8 \pm 1

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