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# 1 Assessing the effect of aqueous alteration on soluble organic matter in 2 primitive carbonaceous chondrites: the case of Asuka 12236.

3  
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6 Kopplin<sup>5,6,7</sup>.

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15 **Keywords:** meteorites; aqueous alteration; soluble organic matter; amino acids; FTICR; liquid  
16 chromatography; extraterrestrial carbon.

## 17 Abstract

18  
19 Carbonaceous chondrites (CC) are considered the closest solid material to the composition of the early  
20 Solar System and can provide information on the origin of organic matter (OM) in the system and on  
21 Earth. Despite being primitive, their parent bodies have undergone secondary processes shortly after  
22 their formation (hydrothermal or metamorphism alterations) that blur their initial organic or mineral  
23 composition. The most primitive CC members are hence very precious to study the original composition.  
24 Here, we report the characterisation of the soluble organic matter (SOM) of Asuka 12236 classified  
25 among the most primitive members of the CM group in comparison with the SOM from other CM  
26 chondrites: Paris, Murchison and Aguas Zarcas. Analysis of these SOM were performed using several  
27 analytical techniques including elemental analysis, high resolution mass spectrometry and liquid  
28 chromatography coupled to different mass spectrometers. Our results show that Asuka 12236 has the  
29 lowest H content among the CMs studied here, and presents heterogeneity in its C content, likely  
30 indicating variable degrees of aqueous alteration. High resolution mass spectrometry analysis reveals  
31 that Asuka 12236 has a molecular diversity similar to the SOM of Murchison and Aguas Zarcas but with  
32 higher abundance of sulfur compounds more similar to Paris SOM. The content of organomagnesium-  
33 compounds indicates no high pressure or temperature stress but rather mid-temperature aqueous

34 alteration for Asuka 12236, like Murchison SOM, but unlike Paris or Aguas Zarcas SOM. From liquid  
35 chromatography coupled with mass spectrometry analysis, we observed the highest concentration of  
36 amino acids in Asuka 12236 compared to the other CM chondrites considered here. Amino acids are  
37 mainly of alpha forms, witnessing of a Strecker formation or a formose-type reaction under low amounts  
38 of water, in agreement with the low H content recorded in this peculiar chondrite. This study of the SOM  
39 of chondrites with different alteration degrees highlights that organic compounds may be transformed  
40 much more rapidly than the minerals during hydrothermal alteration. This OM evolution depends on the  
41 amount of water and/or the temperature and/or pressure, leading towards significant transformation from  
42 one chondrite to another while the mineralogy can indicate a low degree of alteration. In addition to  
43 better assess the initial OM in chondrites, the impact of aqueous alteration on organic matter calls for  
44 additional laboratory experimentation.

45

## 46 1. Introduction

47 Carbonaceous chondrites (CC), considered the most primitive meteorites, can contain up to 5 % of  
48 organic matter (OM)<sup>1</sup>. They can thus provide insight into the initial composition of OM in the  
49 protoplanetary disk (see reviews by Remusat et al. <sup>2</sup> and Alexander et al. <sup>3</sup>). Their parent bodies, the  
50 asteroids, were formed among the first bodies of the solar system 4.56 billion years ago, and have  
51 remained virtually unchanged over time from the planets. However, mineralogical studies have revealed  
52 that secondary alteration processes have occurred in the CC parent bodies during the first tens of  
53 thousands of years after their formations <sup>4</sup>. These traces of alteration processes range from aqueous  
54 alteration (liquid fluid) to metamorphism (high temperature/pressure) which could have blurred the  
55 initial organic signatures in the same way as the minerals have been transformed. In this line, the less  
56 altered CCs are particularly interesting to study this secondary alteration and obtain clues about the  
57 initial composition of the accreted OM. The Mighei-subtype CC group (CM) contains some meteorites  
58 having low alteration degrees with a ~2wt% abundance of carbon, making them the most interesting  
59 samples for such studies compared to other sub-type groups <sup>5</sup>.

60 To date, classification of the CC regarding the alteration degree (numbers from 1 to 3.0, the latter being  
61 the less altered) is only based on petrographic criteria such as volume of iron metal, phyllosilicates  
62 composition and quantity, and the chondrule composition <sup>6</sup>. Other criteria such as the hydrogen content  
63 (equivalent to water) has been proposed to be related with the alteration degree <sup>7</sup>. The organic matter in  
64 CC could also be an indicator of the alteration degree, but the impact of hydrothermal alteration on this  
65 OM is poorly constrained. This OM generally comprises a fraction of soluble organic matter (SOM) and  
66 a large content of insoluble organic matter (IOM) with a wide diversity of chemical families, which can  
67 provide clues on the hydrothermal history of the CC<sup>2,8,9</sup>. Among the organic molecules found in CCs,  
68 amino acids and nucleobases are particularly targeted to obtain information on the impact of the

69 hydrothermal process. Indeed, amino acids have different mechanisms of formation leading to different  
70 ratios between  $\alpha$ ,  $\beta$ ,  $\gamma$ , *etc* amino acids depending on the amount of water<sup>10,11</sup>. Compared to amino acids,  
71 nucleobases have been much less studied in chondrites because of analytical issues<sup>12</sup>. Nucleobases do  
72 present many isomers (as amino acids), which raise difficulties to conclude about their strict assignation  
73 and do not have chiral properties to discriminate about their extraterrestrial or terrestrial origin. A  
74 thorough and holistic characterization of the organic matter in CC is hence of prime importance for  
75 correlation with the alteration degree.

76 This study focuses on a very primitive CM, found in Antarctica in 2012 and recently classified as CM2.9:  
77 Asuka 12236<sup>13,14</sup>. Asuka 12236 has been jointly reported to have experienced very low degree of  
78 alteration with two other CMs, Asuka 12169 (3.0) and Asuka 12085 (2.8)<sup>13,15</sup>. We chose to study this  
79 CM chondrite due to its higher abundance of matrix (linked to the carbon abundance) and its availability  
80 for organic matter analysis, which require large mass. Its mineralogy reveals only few secondary  
81 alteration minerals such as phyllosilicates, and a high abundance of presolar grains indicating that its  
82 parent body would have undergone a low degree of secondary processes<sup>13,14</sup>. We questioned the low  
83 aqueous alteration degree of Asuka 12236, established by its mineralogy, by characterizing its soluble  
84 organic matter (SOM), and comparing it with SOM extracted from chondrites of the same subtype group  
85 but with different aqueous alteration degrees.

86 We have here studied and compared the SOM composition of Asuka 12236 with Paris (CM2.7-2.8)<sup>16</sup>,  
87 Murchison (CM2.5)<sup>6</sup> and Aguas Zarcas (CM2)<sup>17</sup> by analyzing their elemental content (C, H, N, S) in  
88 bulk grains, and their SOM using Fourier-transform ion cyclotron resonance ultra-high resolution mass  
89 spectrometry (FTICR-MS). In addition, a new analysis searching for amino acids and nucleobases in  
90 our fragment of Asuka 12236 was performed using a new analytical workflow (liquid chromatography  
91 coupled with mass spectrometry). Results were compared to the previous analysis of Asuka 12236<sup>18</sup>  
92 and with other chondrites from literature data<sup>19,20,21</sup>. This SOM comparison between CM chondrites  
93 highlights the effect of the low alteration degree of Asuka 12236. In particular, amino acids are key  
94 molecules as they can be tracers of the degree of hydrothermal alteration.

## 95 2. Materials and methods

### 96 2.1. Meteorite samples

97 Fragments of Asuka 12236 were retrieved during an expedition on the Nansen Ice field in East  
98 Antarctica in 2012 by VUB-ULB (Vrije Universiteit Brussel-Université Libre de Bruxelles) and  
99 allocated by the Royal institute of the Natural Sciences in Bruxelles. All the glassware material was  
100 washed and sonicated with methanol (Sigma Aldrich, UPLC grade), and sterilized at 120°C for 24  
101 hours before use. All procedure of the meteorite extraction took place under a sterilised laminar flow  
102 hood (Thermo Fisher Scientific). To remove any surface contamination from the fragment (e.g.,

103 terrestrial dust), the whole meteorite fragment of 365 mg was sonicated with 1mL of milliQ water  
104 (Merck, conductivity < 18.2 MΩ.cm<sup>-1</sup>). After centrifugation and removal of the supernatant, the rock  
105 was dried in a laminar flow hood (Thermo Fisher Scientific) for 10 hours. The fragment was  
106 subsequently crushed into smaller pieces for analysis. Other meteorites (Murchison, Paris and Aguas  
107 Zarcas) analyzed and discussed here were provided from personal collections and have followed the  
108 same procedure.

## 109 2.2. Extraction and Analysis

### 110 2.2.1. Elemental analysis

111 Elementary analyses to determine the proportion of elements C, H, N and S in the bulk were carried out  
112 on each chondrite (Asuka 12236, Paris, Aguas Zarcas and Murchison), taking two grains for each of  
113 about 2 mg. The analysis was performed using a Thermo Finnigan EA 1112 analyzer at the Spectropole  
114 of the *Fédération des Sciences Chimiques* in Marseille, France. Samples were combusted at 970 °C  
115 under helium gas with a flow at 140 mL/min. Gas released by combustion were separated by  
116 chromatography column and analysed using a thermal conductivity detector. The analytical error of the  
117 measure is about 0.1 wt.%.

### 118 2.2.2. FTICR analysis 150-1000 m/z

119 A total of <20 mg of each meteoritic material (for Asuka 12236, Paris, Aguas Zarcas) were used to  
120 extract the SOM with solvents allowing the preservation of meteoritic organics as described in Schmitt-  
121 Kopplin et al.<sup>9</sup>. The fragments were crushed and extracted with methanol (Sigma Aldrich, UPLC grade)  
122 at room temperature. The data of Murchison FTICR analyses are taken from the study published by  
123 Schmitt-Kopplin et al.<sup>9</sup>.

124 The analyses were performed using a high-field FT-ICR mass spectrometer from Bruker Daltonics with  
125 a 12-T magnet from Magnex in a timedomain transient with 4 megawords, Fourier-transformed into a  
126 frequency domain spectrum. The frequency domain was afterward converted to a mass spectrum using  
127 the SolarIX Control program of Bruker Daltonics. In total, 3,000 scans were accumulated for each mass  
128 spectrum in a mass range of 92–1,000 amu. Ions were accumulated for 300 ms before ICR ion detection.  
129 The ESI source (Apollo II; Bruker Daltonics) was used in negative ionization mode. The methanolic  
130 solutions were injected directly into the ionization source by means of a microliter pump at a flow rate  
131 of 120 μL·h<sup>-1</sup> in ESI with a source heating temperature of 200 °C. After internal calibration, the mass  
132 spectra were exported to peak lists at a signal-to-noise ratio ≥3. Elemental formulas were calculated  
133 combinatorically within a mass accuracy window of ±0.2 ppm for each peak in batch mode by an in-  
134 house software tool and validated via the senior-rule approach/cyclomatic number, assuming valence 2  
135 for S.

136 FT-ICR-MS analysis enables highly resolved ( $R > 10^6$  at  $m/z$  200) and accurate chemical mass analysis  
137 of electrospray generated ions within a 200-ppb error window over a wide mass range from  $m/z$  100 to

138 1000. These exact masses of the ions can routinely be converted into unique compositional formula  
139 bearing the light elements C-, H-, N-, O-, S-, Mg (or any other element in the target), also taking account  
140 of their possible Cl and Na adducts and of their natural isotopic abundance.

141 The solvent extracts generated thousands of individual signals that were converted into elementary  
142 compositions (formulae); these are all represented in a van Krevelen type of diagrams (H/C vs. O/C) or  
143 related (H/C vs m/z) in which each formula is represented by a dot (the size of the dot is proportional to  
144 its relative intensity) as a projection of the relative oxygenation degree (O/C) and saturation degree  
145 (H/C) for various classes of compound types (CHO, CHNO, CHOS, CHNOS).

### 146 2.2.3. Chromatographic analysis

147 Chromatographic analyses were done only on the Asuka 12236 extracts. Data for other meteorites were  
148 found in the literature (Paris: <sup>19</sup>; Muchison: <sup>20</sup>; Aguas Zarcas: <sup>21</sup>). Although amino acid analyses have  
149 already been done on Asuka 12236 <sup>18</sup>, in view of the heterogeneity of a meteorite we also performed  
150 amino acids analyses on our fragment, along with nucleobases analysis and compared it with previous  
151 work on Asuka 12236 and other chondrites.

152 Two different extractions of the SOM of Asuka 12236 were performed for these chromatographic  
153 analyses, one at 100 °C and another one at room temperature, both for 24h. For the 100 °C extraction,  
154 226 mg of Asuka 12236 were powdered in an agate mortar and extracted with 1.2 mL of milliQ water  
155 (conductivity < 18.2 MΩ.cm<sup>-1</sup>) in a closed vial for 24h. For the room temperature extraction (25 °C) 108  
156 mg were crushed in 1.0mL of milliQ water in a closed vial for 24h. After centrifugation, aqueous  
157 supernatants were aliquoted. For each extraction, one aliquot of 400μL was taken for the  
158 chromatography analysis. These two different aliquots were dried under N<sub>2</sub> flow (>99.999%, Air Liquid  
159 ALPHAGAZ 1) and remixed in 100μL of milliQ water. Procedural blanks were produced following the  
160 same procedure as the meteorite extraction (with 1.2 mL or 1mL of milliQ water at 100 °C or 25 °C  
161 respectively). This extraction technique without desalting, acid hydrolysis or derivatization steps allows  
162 access to the most pristine material of the meteorite. Indeed, the pre-treatment usually carry out on  
163 meteorite extracts often increase the loss and transformation of compounds in addition to introduce  
164 analytical biais <sup>21,22</sup>.

165 Two types of chromatographic analyses were carried out on these extracted SOM fractions of Asuka  
166 12236, a non targeted analysis and then a targeted one to search, detect and quantify nucleobases and  
167 amino acids.

#### 168 2.2.3.1. *Non targeted analysis of SOM between 50-750 m/z with UPLC-HRMS*

169 Non-targeted analysis of Asuka 12236 SOM fraction was performed following the procedure described  
170 in Serra et al. <sup>21</sup>. Briefly, the meteorite extract was analysed by liquid chromatography coupled with  
171 High-Resolution Mass Spectrometer (Q-Exactive, Hybrid Quadrupole-Orbitrap Mass Spectrometer,

172 Thermo Fisher Scientific) in the range of 50 to 750 m/z. This technique of high resolution allows to  
173 obtain the exact molecular ion mass of the compounds. See method detail in supplementary text.

#### 174 *2.2.3.2. Targeted analysis of SOM with UPLC-MRM-MS analysis*

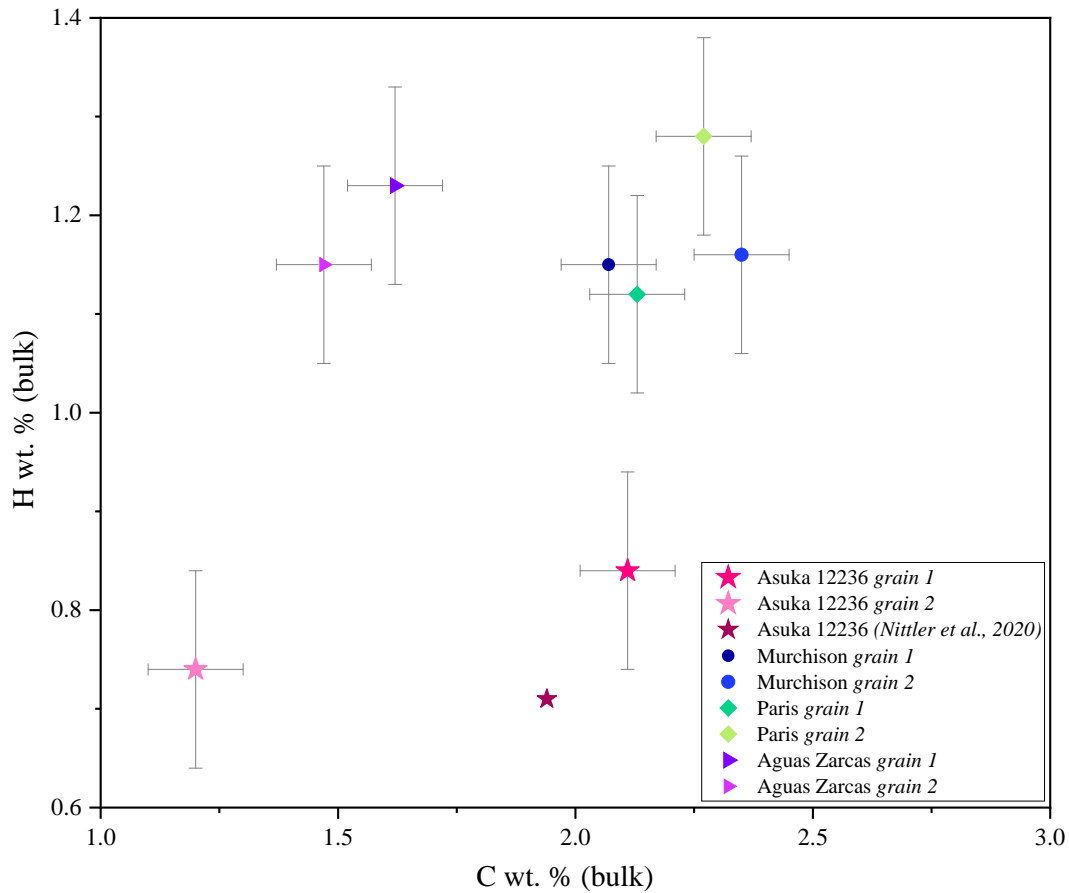
175 From the 100 $\mu$ L aliquot of the Asuka 12236 water extracts, 10 $\mu$ L were diluted by a factor 5 in water.  
176 For compound quantification, a standard addition procedure was performed. The standard addition  
177 procedure is used to facilitate amino acid identification due to the important matrix effects observed in  
178 meteoric samples impacting both retention times and intensities, which is different according to the  
179 amino acids <sup>21</sup>. Three standard solutions (SA) (SA-1, SA-2 and SA-3) were prepared (see table S2 in  
180 supplementary informations for the different concentrations). Five microliters of each of the standard  
181 solutions were added in 10  $\mu$ L meteoritic extract. Finally, 5  $\mu$ L of this latest solution were injected.

182 A Shimadzu Nexera X2 UPLC system coupled to a 8060 triple quadrupole mass spectrometer (TQ MS)  
183 (Shimadzu) was used. This technique used multiple reaction monitoring mass spectrometry (MRM-MS)  
184 and enabled to obtain the identification of molecules from their transition (see Serra et al. <sup>21</sup> for MRM  
185 transitions and MS parameters). 53 amino acids and the 5 natural nucleobases (adenine, cytosine,  
186 thymine, guanine, uracil) were targeted with this method. Ionization was carried out by an ESI source  
187 working in the positive mode (see details in Serra et al. <sup>21</sup>). Amino acid enantiomers and nucleobases  
188 were separated on a chiral column (Crownpak CR (+), Chiral Technologies,). Elution was carried out at  
189 600  $\mu$ L.min<sup>-1</sup> with water:methanol (95:5) with 0.5 % trifluoroacetic acid (Sigma-Aldrich).

190 The error bars on the concentrations were calculated from the directing coefficient and the y-intercept  
191 determined by the method of least squares for the corresponding line of 4 points (SA-0; SA-1, SA-2 and  
192 SA-3). Co-elution were observed for some amino acids (most of the time enantiomers) so their  
193 concentration are given as one single amino acid in Table 2. In the case of isomer co-elution, we  
194 also treated the signal as if it was a single amino acid and assumed that the co-eluted amino acids  
195 in the meteorite were in the same ratio as those in the standard. The concentration reported in Table  
196 2 for the co-eluted amino acids is then the total.

197 3. Results

198 3.1. Elemental analysis



199

200 **Figure 1.** Elemental analysis of C and H atoms in the different bulk fragments of Asuka 12236, Aguas  
201 Zarcas, Paris and Murchison measured in this study (see Table 1 for the data). Elemental analysis of  
202 one sample of Asuka 12236 from Nittler et al.<sup>23</sup> is reported for comparison. Error bars are 0.1wt%.

203 Elemental analysis of Asuka 12236 (two grains analyzed in this study and one by Nittler et al.<sup>23</sup>)  
204 revealed high heterogeneity in C content and more limited variability in H content (Figure 1, Table 1).  
205 Compared to Murchison (CM 2.5), Aguas Zarcas (CM2/CM1), and Paris (CM2.7-2.8), Asuka 12236  
206 presents a low H content (<0.9 wt.%). To note, the grains of Paris analyzed here are likely from the most  
207 aqueously altered lithology because of the relatively high H content<sup>16,24</sup>.

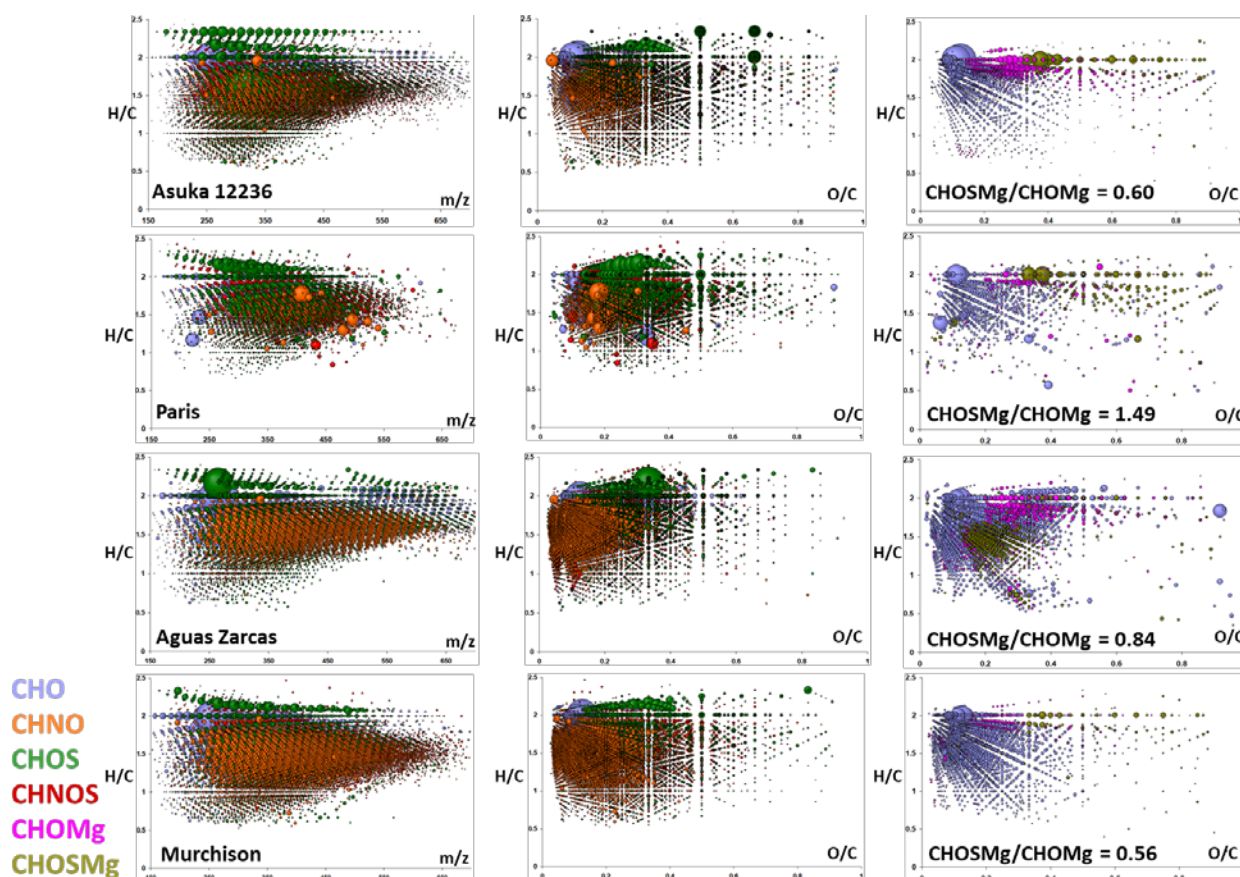
208 Asuka 12236 also contained sulfur (2.2-2.7 wt.%; Table 1), in a similar abundance to the other CM  
209 chondrites studied here, ranging between 2.5 and 4.3 wt.% (Murchison has the highest S content).  
210 Remarkably, the nitrogen content in the grains appears correlated with the carbon content of Asuka  
211 12236, indicating its likely involvement in organic molecules. In addition, the N/C ratio of Asuka 12236  
212 is the highest (~0.06) among the measured CM chondrites (0.04-0.05; Table 1).

213 **Table 1.** The bulk Hydrogen, Carbon, Nitrogen and Sulfur elemental composition of chondrites analyzed  
 214 in this study. For each meteorite, two grains were analyzed.

	C %wt.	N %wt.	H %wt.	S% wt.	N/C	H/C
Asuka 12223 (grain 1)	2.11	0.13	0.84	2.67	0.06	0.40
Asuka 12236 (grain 2)	1.20	0.07	0.74	2.15	0.06	0.62
Asuka 12236 <sup>23</sup>	1.94	0.12	0.71	/	0.06	0.37
Murchison (grain 1)	2.07	0.09	1.15	4.29	0.04	0.56
Murchison (grain 2)	2.35	0.10	1.16	3.02	0.04	0.49
Paris (grain 1)	2.13	0.10	1.12	3.11	0.05	0.53
Paris (grain 2)	2.27	0.11	1.28	2.19	0.05	0.56
Aguas Zarcas (grain 1)	1.62	0.06	1.23	2.98	0.04	0.76
Aguas Zarcas (grain 2)	1.47	0.06	1.13	2.54	0.04	0.77

215

216 **3.2. High resolution and non-targeted analysis of SOM: FTICR**



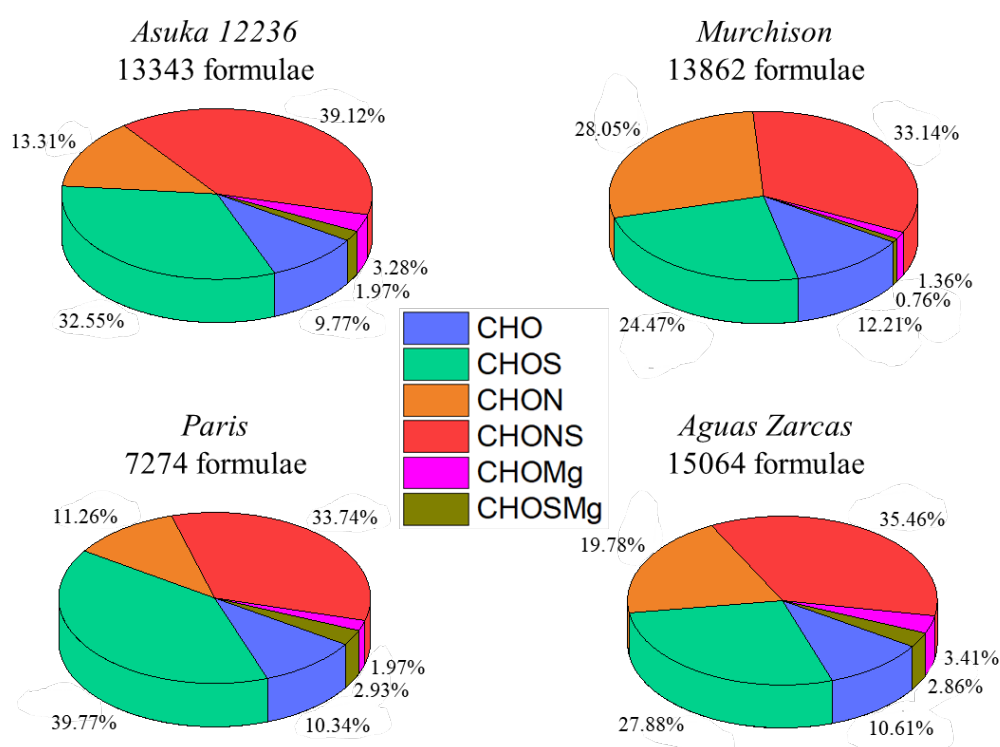
217

218 **Figure 2.** Mass spectrometry data represented in van Krevelen diagrams of Asuka 12236 compared to  
 219 Paris, Aguas Zarcas and Murchison meteorite. The colour code is expressed in the figure and the bubble  
 220 sizes are related to the original signal intensity in the mass spectra.

221 The FTICR-MS ESI(-) profiles of the methanol extracts of Asuka 12236 showed a complex and dense  
 222 mass spectrometric signature with molecular signal distribution roughly in between Murchison/Aguas  
 223 Zarcas and Paris. Asuka 12236 shows a diversity in low H/C molecules versus m/z ( $0.5 < H/C < 1$ ) similar  
 224 to Murchison and Aguas Zarcas, but resembles more of the Paris signature because of the poor  
 225 distribution seen in high molecular masses (550-650 m/z). We note a unique linear molecular  
 226 distribution of the CHOS formulae with high H/C ratio for Asuka 12236.

227 The Van Krevelen H/C versus O/C highlighted the differences in term of carbon oxidation state/oxygen  
 228 content in the formulae (Figure 2, Figure S1), and Asuka 12236 had a high abundance of highly  
 229 oxygenated compounds very similar to Aguas Zarcas also for its number of N and S per formulae (Figure  
 230 S1).

231 The chemical families of organomagnesium compounds (CHOMg) were demonstrated to reflect high  
 232 pressure stress<sup>25</sup> while the sulfurized organomagnesium compounds (CHOSMg) reflect high  
 233 temperature stress<sup>26</sup>. Asuka 12236 shows similarity to Murchison in the temperature pressure history  
 234 with a CHOSMg/CHOMg ratio of 0.60 and 0.56, respectively. However, Paris shows the highest value  
 235 of the ratio reflecting possible thermal processing of the sample. Aguas Zarcas shows a high abundance  
 236 in CHOSMg (rather aromatic) leading to the increase in the ratio and reflecting its previously described  
 237 thermal history<sup>27</sup>.



238

239 **Figure 3.** Relative distribution of the chemical families containing C, H, N, O, S and Mg atoms observed  
 240 by FTICR in the SOM of Asuka 12236, Aguas Zarcas and Paris compared to the Murchison meteorite.

241 Asuka 12236 contains around 13343 different formulae composed of C, H, N, O, S and Mg, essentially  
242 CHONS followed by the CHOS families. Compared with Murchison and Aguas Zarcas, measured under  
243 the same conditions (extraction, method and instrument), Asuka 12236 has a similar SOM diversity with  
244 a slightly higher sulfurization such as already observed with Aguas Zarcas. The Paris meteorite,  
245 considered to be very primitive, presented the same relative abundance for the molecular family as  
246 Asuka 12236 but twice less diverse in composition (Figure 3).

247

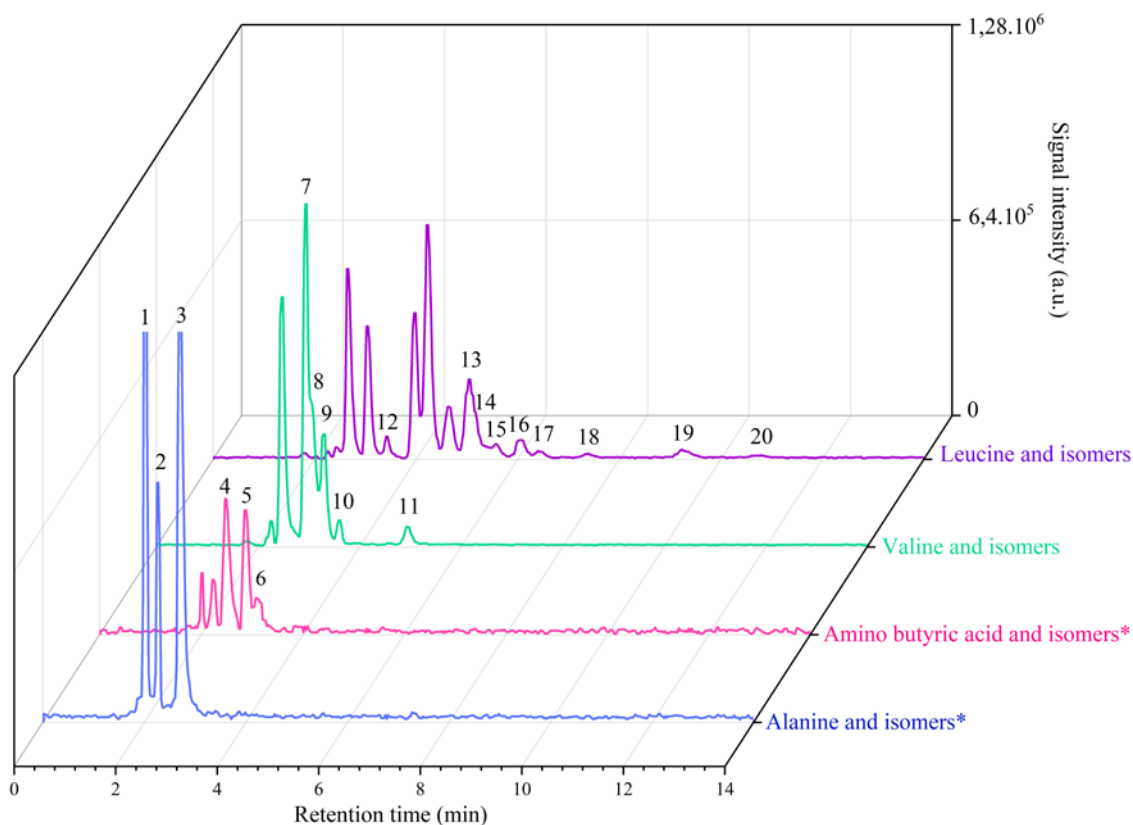
### 248 3.3. Targeted analysis of Asuka 12226 SOM using liquid chromatography coupled with 249 mass spectrometry

250 Analyses searching for amino acids and nucleobases were done on our fragment of Asuka 12236 without  
251 acid hydrolysis of the extract, to reveal only the free amino acid content and investigate the effect of the  
252 low aqueous alteration degree on such polar molecules.

253 Two complementary analyses were done using Ultra Performance Liquid Chromatography coupled with  
254 High Resolution Mass Spectrometry (UPLC-HRMS) for the profiling of compounds with identification  
255 using their exact molecular ions masses and Ultra Performance Liquid Chromatography coupled with  
256 Multiple Reaction Monitoring Mass Spectrometry (UPLC-MRM-MS) to confirm amino acid and  
257 nucleobase identifications based on their MS characteristic transitions, and to provide their  
258 quantification. The analytical protocol is based on the work of Serra et al. <sup>21</sup> allowing analysis without  
259 any derivatisation nor desalting steps. Because of important matrix effect in meteorite samples (both in  
260 the intensity peak and shift of the retention time) as already observed in previous study <sup>21</sup> the  
261 quantification of amino acids is obtained by standard addition procedure.

262 Here, we were also especially attentive to extraction procedure and bias during analysis of the targeted  
263 molecules. To test the effect of temperature extraction, we have extracted the SOM from Asuka 12236  
264 at 100°C and at room temperature (25°C).

265 After a first analysis in UPLC-HRMS (see UPLC-HRMS analysis in supplementary text), the final  
266 identification and quantification for amino acids and natural nucleobases were carried out coupling  
267 chiral column and mass tandem spectrometry apparatus to obtain fragmentation pattern (UPLC-MRM-  
268 MS) (see methods). The method allowed for a precise separation in a very short time analysis of a wide  
269 range of amino acid enantiomers (example in Figure 4).



271

272 **Figure 4.** Chiral separation using UPLC-MRM-MS on the aqueous extract at 100 °C of Asuka 12236.  
 273 **1-20 :** 1. sarcosine ; 2. D-alanine ; 3.  $\beta$ -alanine + L-alanine ; 4. N-ethylglycine ; 5. 2AIBA + D-2-ABA  
 274 + L-3-ABA ; 5. L-2-ABA ; 6. D-3AIBA + L-3-AIBA +  $\gamma$ -ABA ; 7. D/L-isovaline + D-valine ; 8. L-valine ;  
 275 9. D-norvaline ; 10. 5-aminovaleric acid ; 11. L-norvaline ; 12. D/L- $\beta$ -leucine ; 13. D-alloisoleucine ; 14.  
 276 D-isoleucine ; 15. L-alloisoleucine ; 16. L-isoleucine ; 17. D-leucine ; 18. D-norleucine ; 19. L-leucine ;  
 277 20. L-norleucine. \* Signals were increased by ten to be shown on the same intensity scale.

278 Over the 53 amino acids present in the standard solution (D and L forms), 43 were detected by UPLC-  
 279 MRM-MS in the 100°C extract and 41 in the room temperature extract (D/L -serine were not detected at  
 280 room temperature) (Table 2). Arginine and tyrosine detected by UPLC-HRMS were not confirmed by  
 281 UPLC-MRM-MS analysis and were therefore isomers in the first analysis (Table S3). Proline was a  
 282 contaminant of the MRM-MS apparatus and therefore cannot be included in the list of quantified  
 283 compounds. While histidine was not detected in UPLC-HRMS (Table S3) it has been detected by UPLC-  
 284 MRM-MS analysis, which has better selectivity in a sample of this complexity (Figure S4).

285 Of note, no known amino acid or natural nucleobase contamination was found in the procedural blanks,  
 286 only an unknown isomer of alanine was observed in the blank extracted at 100 °C indicating no  
 287 terrestrial amino acid contamination during extraction or analytical procedures.

288 Cytosine, adenine and guanine previously detected by UPLC-HRMS were not validated in both extracts  
 289 by UPLC-MRM-MS. For example, in figure S3 the different signals obtained on the two apparatuses  
 290 for guanine in the 100°C extract were in reality indicative of a guanine isomer, confirmed with the  
 291 procedure of standard addition.

292 Quantification by UPLC-MRM-MS was performed using standard addition method (Table 2). The  
 293 standard addition procedure is illustrated for alanine, leucine, valine and aminobutyric acids families in  
 294 figure S5. A significant matrix effect in retention time is observed for various amino acids such as L -  
 295 isoleucine, D -leucine, D -norleucine, L -leucine, L -norleucine and histidine, and the standard addition  
 296 procedure allow to confirm their identification. The concentrations of 39 and 37 amino acid enantiomers  
 297 were respectively quantified in the 100°C and room temperature water extracts of Asuka 12236. For  
 298 glycine, we were not able to firmly quantified it because of its bad ionization in ESI mode and matrix  
 299 effect <sup>21,28</sup>. Regarding histidine, which has never been detected in a meteorite, a possible quantification  
 300 is reported in table 2, however, due to co-elution of the enantiomers and the non identification by UPLC-  
 301 HRMS we can not firmly confirm its indigeneous nature.

302 **Table 2.** Concentrations of identified free amino acids (ppb) in Asuka 12236 water extracts at 100°C  
 303 and room temperature determined by standard addition with UPLC-MRM-MS (see Materials and  
 304 Method). Data are compared to previous identification and quantification of free amino acids by LC-  
 305 FD-TOF/MS of Asuka 12236 <sup>18</sup>, extracted by water for 24h at 100°C but analysed after desalting and  
 306 derivatization with OPA/NAC (no hydrolysis).

307 Signs are: -: Not investigated; #: detected but not quantified due to interfering peaks or other  
 308 analytical issue; \*:possible quantification for histidine; <sup>A</sup>: co-elution observed for D-2-aminobutyric  
 309 acid and L-2-aminobutyric acid in the work from Glavin et al. <sup>18</sup>.

310

Form of amino acids	Amino acids	Asuka 12236 (free content)		
		Tamb	100°C	Glavin et al, 2020
α	glycine	#	#	11635 ± 225
α	sarcosine	55573 ± 9847	33996 ± 3895	-
α	D-alanine	93106 ± 39053	19158 ± 2172	2227 ± 89
β	β-alanine	43485 ± 9360	19263 ± 3012	1167 ± 54
α	L-alanine			2316 ± 89
α	2-aminoisobutyric acid	960 ± 52	4009 ± 298	1753 ± 20
α	D-2-aminobutyric acid			1547 ± 103 <sup>A</sup>
β	L-3-aminobutyric acid			329 ± 11
α	L-2-aminobutyric acid	1024 ± 52	2160 ± 553	1547 ± 103 <sup>A</sup>
β	D-3-aminoisobutyric acid	288 ± 115	1050 ± 239	#
β	L-3-aminoisobutyric acid			#
γ	γ-aminobutyric acid			206 ± 10

$\alpha$	<i>D</i> -serine	0	225 ± 98	129 ± 6
$\alpha$	<i>L</i> -serine			292 ± 8
$\alpha$	<i>D</i> -isovaline	1570 ± 195	4228 ± 858	457 ± 36
$\alpha$	<i>L</i> -isovaline			480 ± 24
$\alpha$	<i>D</i> -valine			597 ± 12
$\alpha$	<i>L</i> -valine	577 ± 70	1412 ± 140	668 ± 24
$\alpha$	<i>D</i> -norvaline	686 ± 101	1279 ± 157	284 ± 6
$\delta$	5-Aminovaleric acid	132 ± 75	330 ± 112	-
$\alpha$	<i>L</i> -norvaline	#	#	291 ± 6
$\beta$	<i>D</i> - $\beta$ -leucine	123 ± 89	179 ± 71	-
$\beta$	<i>L</i> - $\beta$ -leucine			-
$\alpha$	<i>D</i> -alloisoleucine	526 ± 37	707 ± 197	-
$\alpha$	<i>D</i> -isoleucine	145 ± 54	281 ± 25	#
$\alpha$	<i>L</i> -alloisoleucine	135 ± 71	247 ± 33	-
$\alpha$	<i>L</i> -isoleucine	349 ± 103	400 ± 75	#
$\alpha$	<i>D</i> -leucine	179 ± 33	268 ± 52	#
$\alpha$	<i>D</i> -norleucine	156 ± 67	194 ± 44	-
$\alpha$	<i>L</i> -leucine	470 ± 81	339 ± 34	#
$\alpha$	<i>L</i> -norleucine	206 ± 60	194 ± 60	-
$\alpha$	<i>D</i> -aspartic acid	613 ± 35	1148 ± 149	226 ± 27
$\alpha$	<i>L</i> -aspartic acid	394 ± 88	984 ± 102	240 ± 13
$\alpha$	<i>D</i> -glutamic acid	#	#	93 ± 10
$\alpha$	<i>L</i> -glutamic acid	#	#	132 ± 15
$\alpha$	<i>D</i> -phenylalanine	264 ± 74	468 ± 109	-
$\alpha$	<i>L</i> -phenylalanine	304 ± 102	430 ± 84	-
$\alpha$	<i>D</i> -histidine*	74 ± 33*	369 ± 39*	-
$\alpha$	<i>L</i> -histidine*			-
$\alpha$	<i>D</i> -threonine	175 ± 47	1101 ± 118	#
$\alpha$	<i>D</i> -homoserine	242 ± 61	407 ± 180	#
$\alpha$	<i>L</i> -threonine			#
$\alpha$	<i>L</i> -homoserine			115 ± 33

311

312 Based on the chiral analysis, we quantified two enantiomers of phenylalanine, aspartic acid, norleucine,  
313 leucine, isoleucine and alloisoleucine. We observed racemic proportions in the case of the *L/D*-  
314 phenylalanine, *L/D*-aspartic acid, and *L/D*-norleucine, which indicate that they are probably not terrestrial  
315 contamination. Isotopic analyses of these detected amino acids should be performed to definitely  
316 validate their origin. Excesses in *L* form were observable for leucine and isoleucine, which are classical  
317 Earth contaminations (Table 2). However, alloisoleucine has an enantiomeric excess in *D*-form. This  
318 can be explained by the epimerization at the C2-level to its diastereoisomers *L*-isoleucine<sup>29,30</sup> as it is  
319 observed in other chondrites like CM Murchison and the CM Murray<sup>31</sup>.

320 For the extraction of small amino acids, like alanine isomers, the concentration obtained is higher in the  
321 room temperature extract (Figure S6-A). In contrast, the larger amino acids are present at a higher  
322 concentration with the extraction at 100°C (Figure S6-B). We thus observed an anti correlation between  
323 C2-C3 amino acids and C4 and more amino acids, which might suggest an effect of the extraction  
324 temperature.

325 Moreover, standard addition procedures highlighted the presence of many more isomers than those  
326 reported in Asuka 12236 extract (Figure S4; Figure S5; Table 2). We estimated that there are probably  
327 significantly more amino acids in the Asuka 12236 SOM than those firmly identified.

## 328 4. Discussion

### 329 4.1. A global look to the diversity of the SOM

330

331 Elemental analysis has revealed differences in the C and H content in the bulk of the chondrite  
332 suggesting some degree of heterogeneity in Asuka 12236 and in its OM distribution. As many CMs,  
333 Asuka 12236 can also present several lithologies since it has not been characterized as a breccia<sup>13</sup>,  
334 enlightening this heterogeneity. According to Alexander et al.<sup>7</sup>, it is possible to correlate the proportion  
335 of H to the amount of water seen by the parent body of the meteorite and thus to its alteration degree  
336 <sup>7,32</sup>. Asuka 12236 with  $0.71 < \text{H \% wt.} < 0.84$  measured in this study, is therefore classified among the  
337 least altered chondrites (Figure 1), in agreement with its mineralogy<sup>13,14</sup>.

338 The diversity of polar organic molecules in Asuka 12236 has been revealed by FTICR-MS analysis,  
339 showing the occurrence of around 13211 molecular formulae containing C, H, O, N and S, almost as  
340 much as in Murchison<sup>9</sup>. Most of the families present are sulphur-rich organic molecules (CHONS and  
341 CHOS) with a total of 72% for the Asuka 12236 SOM. A similar proportion is observed in the Paris  
342 SOM (74%), while Murchison and Aguas Zarcas contain around 58 and 63% respectively (Figure 3).  
343 Such distributions in the chondrites thus appear not to be correlated with the bulk abundance of sulfur  
344 seen by elemental analysis (Table 1), which also displayed inorganic sulfur. Interestingly, Paris and  
345 Asuka 12236, both classified as very primitive<sup>13,14,16</sup>, have the same proportion of sulfur organic  
346 compounds. However, this organic sulfur does not present the same molecular distribution (Figure 2).  
347 The formation and evolution of sulfur-bearing phases in meteorites are uncertain, and to which extend  
348 secondary processes such as aqueous and mid-temperature heating could have allowed for the  
349 incorporation of sulfur with the organic molecules, remains unknown and needs further investigation.  
350 For example, Aguas Zarcas was shown to have a large heterogeneity in its matrix, and the extensive  
351 sulfurization of the OM (mainly under the form of polysulfurized compounds) was proposed to result  
352 from intensive aqueous alteration and heating<sup>27</sup>. Complementary investigations on the speciation of

353 sulfur (aromatic vs aliphatic) in the SOM of Asuka 12236 and Paris in addition to the one in their IOM,  
354 could aid in deciphering the effect of aqueous alteration on the sulfur matter<sup>33,34</sup>.

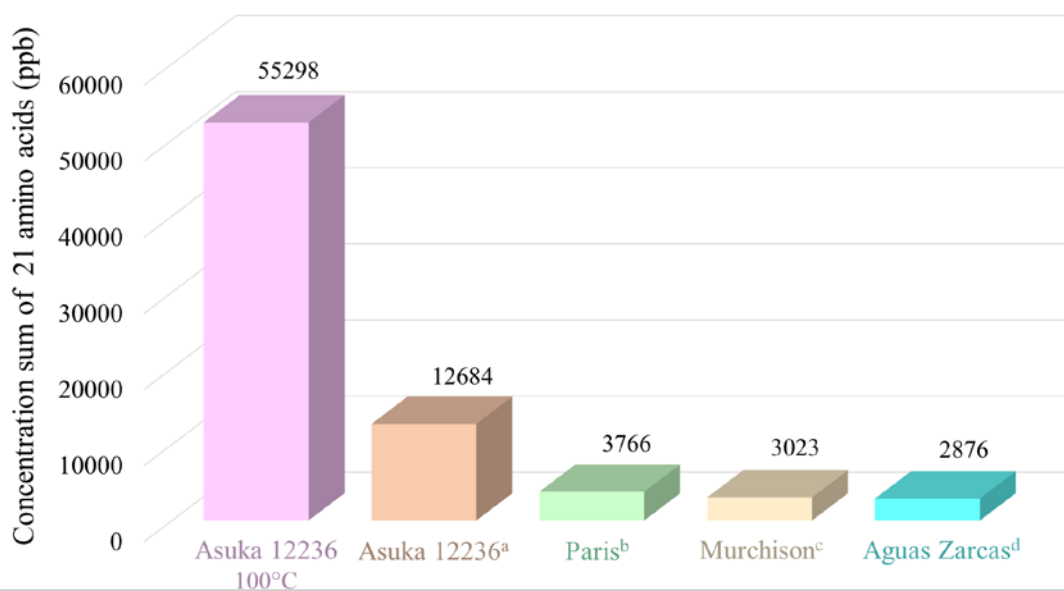
355 In addition, chemical families of CHOMg and CHOSMg have been proposed to provide information on  
356 high pressure and high temperature stress respectively undergone by the parent body<sup>25,26</sup>. The  
357 distribution of these compounds in Asuka 12236 is similar to Murchison composition, suggesting that  
358 the parent body of Asuka 12236 did not experience high pressure and high temperature conditions. On  
359 the contrary, Paris SOM seems to have undergone temperature stress seen by the high  
360 CHOSMg/CHOMg ratio (Figure 2), while petrologically classified as primitive as Asuka 12236. These  
361 results show that Asuka 122236 is hence only reflecting a low degree of aqueous alteration and  
362 temperature, in agreement with its mineralogy<sup>13,14</sup>.

363

#### 364 4.2. A closer look to amino acids and nucleobases

365

366 Asuka 12236 SOM not only has a very high diversity of amino acids but also the highest concentration  
367 of free amino acids to date, as previously shown by Glavin et al.<sup>18</sup> and observed here in our fragment.  
368 Comparing the sum of the concentration of 22 free amino acids present in the SOM of Asuka 12236  
369 with those in the SOM of Paris, Murchison and Aguas Zarcas, we notice a concentration between 15 to  
370 20 times higher in Asuka 12236 than for the other CM chondrites (Figure 5).



371

372 **Figure 5.** Sum of the concentration of 21 free amino acids for different meteorite extracts at 100 °C.  
373 (L/D alanine,  $\beta$ -alanine, L/D-2-aminobutyric acid, 2-aminoisobutyric acid, L/D-3-aminobutyric acid, L/D-  
3-aminoisobutyric acid,  $\gamma$ -aminobutyric acid, L/D-aspartic acid, L/D-glutamic acid, L/D-leucine, L/D-  
374 valine and L/D-isovaline). From left to right: Asuka 12236 extracted at 100°C (this work), Asuka 12236  
375

376 *studied by Glavin et al.,*<sup>18</sup> (a); *Paris studied by Martins et al.,*<sup>19</sup> (b); *Murchison studied by Glavin et al.*  
377 *<sup>20</sup> (c); Aguas Zarcas studied by Serra et al.,*<sup>21</sup> (d). *Data presented here for comparison were from*  
378 *chondrites extracted at 100°C then analyzed without acid hydrolysis ( free content in amino acids) but*  
379 *with different analytical techniques than here, involving desalting and derivatization steps (for Paris*  
380 *and Murchison analyses).*

381

382 The numerous and abundant amino acids found in Asuka 12236 are in agreement with previous analysis  
383 done by Glavin et al.<sup>18</sup> and their relative abundance is comparable in both studies (the smallest being  
384 the most important like alanine and isomers) (Table 2). The difference in the abundance in amino acids  
385 in our study compared to Glavin et al.<sup>18</sup> (5 times higher here) could be due to heterogeneity between  
386 the meteorite samples analysed (in agreement with elemental analysis, Figure 1). Indeed, this  
387 heterogeneity of organic matter within a single chondrite has already been observed on Murchison, for  
388 example, with numerous amino acid analyses on different fragments using the same protocol yielding  
389 significantly different amounts<sup>22</sup>. Furthermore, the difference observed can also be the result of the  
390 applied analytical protocol<sup>21,35,36</sup>. The analytical strategy used here was done without desalting nor  
391 derivatization steps on the extract, avoiding as much as possible the loss of small polar molecules. New  
392 extraction techniques for the detection of amino acids in extremely small samples for return mission  
393 also avoid desalting and HCl hydrolysis steps<sup>35,36</sup>.

394 Among the CM chondrites, only one other meteorite has revealed such a high concentration of amino  
395 acids: Yamato 791198<sup>37,38</sup>, a CM2 with a similar degree of alteration as Murchison<sup>7,39</sup>. When taking  
396 the same 22 amino acids into account in figure 5, Yamato 791198 has about 33175 ppb of free amino  
397 acids, which is closer to the 55298 ppb reported for Asuka 12236 compared to others. Nonetheless,  
398 Yamato 791198 is more altered than Asuka 12236 and information on its bulk SOM composition (for  
399 example by FTICR) are missing.

400 The distribution of amino acids detected in Asuka 12236 SOM is consistent with an abiotic formation  
401 process, the smallest being the most abundant (sarcosine, *L/D*-alanine) (Table 2). One of the favored  
402 ways in aqueous conditions of forming amino acids is by Strecker reaction leading to the formation of  
403  $\alpha$ -amino acids (such as glycine, sarcosine, *L/D*-alanine; Table 1). Michael's addition allows the formation  
404 of  $\beta$ -amino acids and requires a larger amount of water than Strecker's synthesis<sup>10</sup>. Asuka 12236 with a  
405 large amount of  $\alpha$ -amino acids is consistent with a preferential formation by Strecker reaction and a low  
406 amount of water. These results are in agreement with the previous studies correlating the relative  
407 abundance of amino acid forms to the aqueous alteration degree<sup>11,22</sup>. In addition, another mechanism of  
408 amino acid formation can occur during aqueous alteration: the formose ammoniated reaction, which can  
409 compete with the Strecker synthesis depending on the availability and abundance of precursors (HCN  
410 versus H<sub>2</sub>CO and NH<sub>3</sub>). In this case, not only  $\alpha$ -amino acid but also  $\beta$  and  $\gamma$  can be produced<sup>40-42</sup>. In

411 addition, amino acids as well as their precursors may have been formed during the evolution of ices from  
412 the dense molecular cloud to the protoplanetary disk, and therefore be initially incorporated into  
413 primitive bodies<sup>43,44</sup>. The high abundance of amino acids found in Asuka 12236 relative to the Paris  
414 chondrite is nonetheless surprising since both are primitive meteorites with a rather low degree of  
415 aqueous alteration. Altogether, it seems possible that the Paris and Asuka 12236 parent bodies, while  
416 being both CMs, did not receive the same initial pool of organic matter, the parent body of Asuka 12236  
417 being initially richer in amino acids or in their precursors than that of Paris. Furthermore, as Paris SOM  
418 undergone temperature stress unlike Asuka 12236 (Figure 2), its amino acid or precursor contents could  
419 have been degraded during the alteration.

420 Even if Asuka 12236 is classified with a low degree of alteration, it has nevertheless undergone some water  
421 hydration with the likely transformation of the OM. For example, studies on organic molecules such as  
422 hexamethylenetetramine and other polar molecules (i.e. aldehydes) show a rapid degradation under low  
423 heating aqueous condition (150°C)<sup>40-42,45,46,47</sup>. Here, our extraction at 100°C of the SOM can mimic the  
424 conditions of a higher aqueous alteration and may thus have transformed some of the organic compounds  
425 hindering the real organics distribution. For example, we have observed that the extraction temperature  
426 (100°C versus room temperature) has an impact on the amino acids distribution (Figure S6). We may  
427 suggest that chemical reactions can occur during the extraction, especially for amino acids.

428 In addition, natural nucleobases were expected in Asuka 12236, because it belongs to the CM group<sup>48</sup>.  
429 However, none of the five natural nucleobases were identified in the SOM of Asuka 12236 thanks to the  
430 two complementary mass spectrometric analyses (UHPLC- HRMS and MRM-MS). Instead, many isomers  
431 are likely present (Figure S3) but the lack of standards did not allow their identifications and request further  
432 investigations. Interestingly, Murchison and Aguas Zarcas do contain guanine in their SOM<sup>21,48,49</sup> which  
433 could suggest that nucleobases are related to the aqueous alteration degree.

434

### 435 4.3. A wider look to the primitivity of the chondrite

436

437 According to its mineralogy, Asuka 12236 was classified as part of the CM group with a low water  
438 alteration degree: CM2.9<sup>13</sup>. This classification is based on petrographic information such as iron  
439 volume, volume of phyllosilicates and mafic silicates in the chondrules or measurement of the chemical  
440 composition of the phyllosilicates<sup>13,14</sup>.

441 We questioned here the low aqueous alteration degree of Asuka 12236, seen by its mineralogy, by  
442 characterizing its soluble organic matter (SOM), and comparing it with SOM extracted from chondrites  
443 having higher degree of aqueous alteration. At first glance, such task can be seen as particularly difficult  
444 due to the large uncertainties regarding the initial organic abundance and composition in the parent body,

445 and the conditions of aqueous alteration (including minerals). Several hints from its organic content  
446 indicate that Asuka 12236 has nonetheless undergone a low degree of mid-temperature aqueous  
447 alteration: 1) the low content in H equivalent to the water content in hydrated minerals (Figure 1); 2) the  
448 high N/C ratio, while nitrogen bearing molecules are sensitive to aqueous alteration (Figure 1; Table 1)  
449 <sup>45,50</sup>; 3) the low ratio CHOMg/CHOSMg indicating no high pressure or temperature stress (Figure 2)  
450 <sup>25,26</sup>; 4) the large abundance of amino acids whereas these molecules are sensitive to alteration (Table  
451 2; Figure 5) <sup>18,51</sup>; 5) the proportion of  $\alpha$ -amino acids over the  $\beta$ ,  $\delta$  and  $\gamma$  amino acids testifying of a  
452 formation mechanism with a low water content (Table 2) <sup>11,18,22</sup>.

453 Compared to the Paris chondrite, considered as a very primitive chondrite, Asuka 12236 has both greater  
454 diversity and abundance of SOM and amino acids <sup>19</sup>, while being mineralogically classified as less  
455 altered than Paris <sup>13</sup>. Similar to Paris, Asuka 12236 has nonetheless clearly some signs of aqueous  
456 alteration but highly scattered and scarce <sup>16,24,13,14</sup>.

457 Several scenarios can account for the evolution of organic matter in primitive chondrites, including  
458 Asuka 12236: 1) the composition of the accreted organic material, which can differ somehow from one  
459 source to the other (gas phase, ice-solid,...); 2) the conditions of aqueous alteration (quantity of fluid,  
460 temperature, pH); 3) the nature of the minerals around that will also be affected by aqueous alteration,  
461 changing the fluid conditions and type of interactions <sup>52</sup>. Even if the degree of alteration is low, the  
462 transformation of the organic matter may not be negligible leading to difficult correlations between the  
463 organic composition and alteration degree. We hypothesized that even if Asuka 12236 has undergone a  
464 low degree of aqueous alteration, its organic matter has rapidly reacted to this alteration with water,  
465 likely increasing the diversity of molecules to as high as more altered chondrites (like Murchison). This  
466 increase in organic diversity has been observed on asteroid analogs under aqueous alteration conditions  
467 <sup>40,42,45,46</sup>.

468 However, probably due to a limited quantity of water in Asuka 12236, the chemical alteration stopped  
469 and signs of low alteration degree on the OM remain (such as the high abundance of  $\alpha$ -amino acids).  
470 More studies are requested to assess if the composition of organic matter in meteorites may enable a  
471 more precise sensing of water alteration effects, which are the least predictable compared to pressure or  
472 temperature effects.

## 473 5. Conclusions

474

475 Here, from its content in soluble organic matter and in comparison with others chondrites, we try to  
476 understand the effect of aqueous alteration in Asuka 12236 OM, in agreement with its alteration degree  
477 as defined by the petrology (classified as CM2.9<sup>13</sup>). Elemental bulk analysis presents heterogeneity in  
478 the sample likely reflecting different lithologies in the chondrite. The overview of the molecular

479 compounds presented in Asuka 12236 shows a high diversity of molecules, close to the Murchison one  
480 but with a richer composition in sulfur molecules (CHOS and CHONS families) more similar to Paris.  
481 However, the molecular distribution of the SOM shows that Asuka 12236 is less altered than Paris,  
482 which suffered from temperature stress.

483 Targeted analysis searching for amino acids and nucleobases was performed on Asuka 12236 SOM.  
484 None of the five natural nucleobases are detected in the SOM of Asuka 12236 but isomers are present.  
485 Yet, a high diversity of amino acids is quantified (~ 40 amino acids with standard addition procedure),  
486 dominated by  $\alpha$ -amino acids showing a preferential formation by Strecker or a formose type reactions.  
487 The abundance in amino acids found in Asuka 12236 is the highest to date among the CM chondrites.  
488 The SOM composition in Asuka 12236 can reflect a low degree of mid-temperature aqueous alteration  
489 since hints of primitivity remain ( $\alpha$ -amino acids, low H content).

490 This study reinforces the difficulty of linking a low degree of alteration with the composition of OM  
491 since the organic compounds might be transformed much more rapidly than minerals during an episode  
492 of hydrothermal alteration. Additional studies on organic matter from the most primitive chondrites  
493 (such as Asuka 12269, the next in line after Asuka 12236) could bring new pieces for the alteration  
494 puzzle in carbonaceous asteroids<sup>15</sup>. Overall, we need also to better assess the transformation of the  
495 initial OM that was present in the protoplanetary disk during the first stage of aqueous alteration in the  
496 parent body to better understand the current organic composition of chondrites.

497

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499

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510

## 511 7. Supporting information

512

513 Supplementary information is provided to detail the chromatographic methods and present more graphic  
514 results for the high-resolution analysis and the targeted analysis of amino acids.

515

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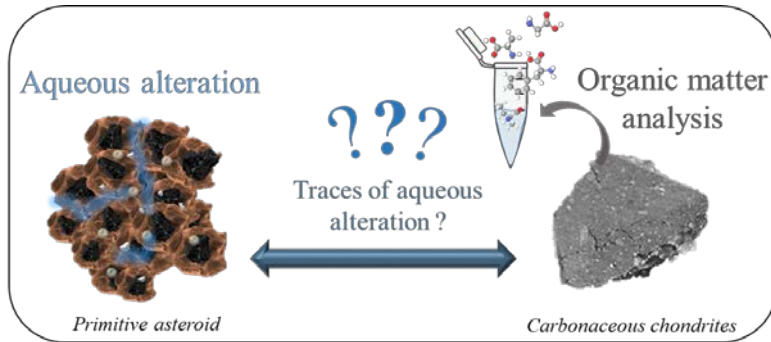
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