AQUEOUS ALTERATION ON ASTEROIDS SIMPLIFIES SOLUBLE ORGANIC MATTER MIXTURES

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1 AQUEOUS ALTERATION ON ASTEROIDS SIMPLIFIES SOLUBLE ORGANIC MATTER MIXTURES

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6 ABSTRACT

8 Biologically relevant abiotic extraterrestrial soluble organic matter (SOM)
9 has been widely investigated to study the origin of life and the chemical
10 evolution of protoplanetary disks. Synthesis of biologically relevant
11 organics, in particular, seems to require aqueous environments in the early
12 solar system. However, SOM in primitive meteorites includes numerous chemical
13 species besides the biologically relevant ones and the reaction mechanisms
14 that comprehensively explain the complex nature of SOM are unknown. Besides,
15 the initial reactants, which formed before asteroid accretion, were
16 uncharacterized. We examined the mass-distribution of SOM extracted from
17 three distinct Tagish Lake meteorite fragments, which exhibit different
18 degrees of aqueous alteration though they originated from a single asteroid.
19 We report that mass-distributions of SOM in the primordial fragments are well
20 fit by the Schulz-Zimm (SZ) model for the molecular weight distribution
21 patterns found in chain-growth polymerization experiments. Also, the
22 distribution patterns diverge further from SZ with increasing degrees of
23 aqueous alteration. These observations imply that the complex nature of the
24 primordial SOM 1) was established before severe alteration on the asteroid,
25 2) possibly existed before parent body accretion, and 3) later became
26 simplified on the asteroid. Therefore, aqueous reactions on asteroids are not
27 required conditions for cultivating complex SOM. Furthermore, we found that
28 overall H/C ratios of SOM decrease with increasing of aqueous alteration, and
29 the estimate of H loss from the SOM is 10-30%. Organics seem to be a
30 significant H_2 source that may have caused subsequent chemical reactions in
31 the Tagish Lake meteorite parent body.

33 1. INTRODUCTION

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35 Abiotic organic compounds are common and widely distributed in solar system
36 objects (Schmitt-Kopplin et al. 2010). Understanding their formation
37 mechanism requires accurate knowledge of their composition at the time of
38 planetesimal accretion, 4.5 Gy ago, which is complexified by geological
39 processes that occurred on these small bodies over the history of the solar
40 system. In particular, the low-temperature alteration of asteroids, which
41 normally took place a few My after accretion at temperatures ranging from ~0℃
42 to ~150℃ under aqueous conditions (Suttle et al. 2021) is considered to be an
43 important driver of chemical evolution. This process may have played an
44 essential geological role for producing the building blocks of life, for
45 example, through amplification of L-isovaline excesses (Glavin & Dworkin
46 2009). A challenge of meteoritic organics studies is to distinguish the pre-
47 accretionary (hereafter "primordial") features from the secondary components
48 that are produced by geological processes on their original asteroidal parent
49 bodies. Inorganic components are distinct across the different chondrites
50 classes and groups: examples include refractory abundances (e.g., Wasson &
51 Kallemeyn 1988), oxidation states (e.g., Urey & Craig 1953), bulk stable-
52 isotope compositions (e.g., Warren 2011), and the size distribution of
53 chondrules (e.g., Jones 2012). On top of the variation of the initial
54 materials, the degree of aqueous alteration and thermal metamorphism can vary
55 for a given meteorite group.
56 In our study, we examine the Tagish Lake carbonaceous chondrite, an organic
57 rich (~2.5 wt.% organic C), C2 ungrouped meteorite (Grady et al. 2002) that
58 fell on the frozen lake on January 18th in 2000 in northwestern British
59 Columbia, Canada. After the fall, several hundred grams were recovered on the
60 25th and 26th of January and these meteorite fragments that had minimum
61 exposure to terrestrial organics are so called "pristine" samples. Later, in
62 the spring 2000, more meteorite fragments were recovered and these are so
63 called "degraded" samples because of terrestrial water contamination (Brown
64 et al. 2000). That pristine collection has provided us a unique opportunity
65 to study abiotic organics and the effects of aqueous alteration on its parent
66 body (e.g., Herd et al. 2011; Gilmour et al. 2019; Simkus et al. 2019). The
67 Tagish Lake meteorite is comprised of several lithologies that experienced
68 different degrees of secondary processing on the same parent body (Zolensky
69 et al. 2002). We selected three different previously well-studied
70 lithologies: TL5b, TL11h, and TL11i. As a part of the rock, the organics
71 experienced the same geological processes as adjoining inorganic minerals
72 whose textures recorded the degrees of aqueous alteration. Observed trends
73 within the organic matter in Tagish Lake have previously been tied to the

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76 degree of aqueous alteration, in the order TL5b (the least altered) < TL11h <
77 TL11i (Herd et al. 2011; Blinova et al. 2014a; Gilmour et al. 2019). The TL5b
78 has the most abundant anhydrous minerals fraction among the three samples.
79 The petrologic type is similar to CM2. Using the bulk rock mineral abundance
80 of TL5b (Blinova et al. 2014), the degree of hydration is 2.7 in the
81 previously developed scale (Howard et al. 2013). The TL11h and TL11i are
82 relatively altered rocks. The fraction of anhydrous silicates is TL11h >
83 TL11i, and the most similar well-known lithology for the two samples is type
84 1 alteration of CM chondrites (Gilmour et al., 2019).
85 A previous study of insoluble organic matter (IOM) present in Tagish Lake
86 revealed that modification due to the aqueous alteration on the parent body
87 positively and linearly correlates with δD values and H/C ratios, which have
88 been interpreted to reflect the effects of varying degrees of aqueous
89 alteration. For example, the IOM in TL5b (the least altered) have the highest
90 H/C ratios and heavy δD values among the samples from the pristine Tagish Lake
91 collection (Figure 1(b) in Alexander et al. 2014). Thus, one could imagine
92 that the vast majority of soluble organic matter was also subject to
93 reactions that lead to synthesis or degradation due to their nature to be
94 reactive; indeed, the SOM in Tagish Lake shows similar relationships (Herd et
95 al. 2011; Hilts et al. 2014). Even if the alteration effect does not seem to
96 modify the structure of the macromolecules in the IOM greatly, it may have a
97 dramatic impact on smaller molecules comprising the SOM, either producing
98 them or significantly changing their structure. In particular, the SOM in
99 carbonaceous chondrites is of significant interest, especially the presence
100 of potential biologically relevant compounds such amino acids, sugars, and
101 fatty acids. In Tagish Lake, the most prominent bulk SOM includes
102 monocarboxylic acids (MCAs) and amino acids that are heterogeneously
103 distributed (Hilts et al. 2014). However, it is still unclear concerning what
104 pre-accretionary precursors were present and which formation processes
105 occurred. Thus, it is ambiguous how the organics present in chondrites were
106 formed from those pre-accretionary materials. To identify evidence of aqueous
107 alteration of SOM on asteroidal parent bodies, we obtained high-resolution
108 mass spectra of three types of lithologies found in Tagish Lake that
109 experienced different levels of aqueous alteration. We applied a holistic
110 approach to the size distribution of organic molecules. First, we assessed
111 the size diversity of SOM molecular distributions by using the number of
112 heteroatoms, and Double Bond Equivalent values (DBE = C+1−H/2+N/2) to
113 estimate the level of unsaturation. Second, we fit the data by using a known
114 polymer synthesis model. These data allow one to test previously suggested

128 reaction pathways of organic matter formation in carbonaceous chondrites such
129 as a formose-like reaction (e.g., Furukawa et al. 2019).
130
131   2. METHOD
132
133 Approximately 10mg of powdered samples were extracted by using a methanol and
134 toluene (1:2) mixture. The meteorite extract and solvent were separated from
135 the meteorite powder by centrifuging. The direct infusion technique was used
136 with a high-resolution mass spectrometer, Thermo LTQ Orbitrap XL instrument
137 coupled with an electrospray ionization (ESI) source, in the m/z range of
138 150—800. The positive ions were analyzed with a resolving power of m/Δm ~
139 100000 at m/z = 400u.
140
141   3. RESULTS
142
143 We found that the structures in the individual mass-spectrum from the three
144 extracts from 5b, 11h, 11i are distinct in terms of their size distributions
145 and relative DBE values. From one sample to another, the molecular size
146 distribution narrows as the degree of aqueous alteration increases. The mass
147 spectra of TL5b can be split into several sub spectra in which the DBE and
148 the number of O and N atoms are invariant for the sake of clarity. The shape
149 of the envelope of these sub spectra, plotted in Fig 1 appears to be similar
150 regardless of a number of heteroatoms or DBE value. With CHNO only involved
151 in this study, sub spectra turn out to be individual CH_2 families and they
152 indeed are well fit by the Schulz-Zimm (SZ) distribution that models the
153 molecular weight distribution of chain-growth polymerization experiments
154 (Scholz 1939; Zimm 1948), see Fig 2. Overall goodness of fit (R^2) for the
155 individual CH_2 family (number of family members >10) are shown in S3. Notably,
156 the distribution pattern becomes asymmetric and sharp with increasing degree
157 of aqueous alteration and the most intense peak of a CH_2 family decreases in
158 mass with increasing degree of aqueous alteration. These deviations from the
159 SZ distribution seen in the mass spectra are associated with the degree of
160 aqueous alteration. The spiked and tailing from a SZ distribution indicates
161 that the size diversity is reduced in a CH_2 family as shown by entropy values
162 calculated for a given CH_2 family (Fig 2D).
163 The results indicate that the hydrogen content in the compounds decreases in
164 more altered samples. While the SOM mass-range among the samples are
165 unchanged, the maximum DBE increases (Fig 3). The same figure shows that the
166 least altered sample is the only one that has heavy molecules with low DBE

169 (yellow). The altered samples systematically populate the highest DBE domains
170 (blue). This trend indicates that the carbon atoms in these compounds became
171 oxidized. This trend is also observed in the chemical formulae that are
172 common among the three spectra (black in Fig 3). Normalized intensities among
173 the three samples indicate that the larger DBE intensity increases with
174 higher degree of alteration given an equal number of carbons in the formulae.
175 Furthermore, we can see that the relatively small molecule intensities are
176 higher in the most altered sample for the same CH_2 family S5.
177
178   4. DISCUSSION
179
180 It is shown in Fig 1 that a high degree of similarity exists in terms of
181 pattern regardless of the number of N or O atoms in the chemical formulae.
182 The least altered sample is the one where the SZ model explains the
183 observations the best for each individual family and with the best
184 repeatability among the sample family set. These qualities make the SZ model
185 a good candidate to interpret the growth mechanism responsible for the CH_2
186 variability observed in the mass spectrum. The applicability of the SZ model
187 to different families is remarkable because these patterns and their
188 stability are unlikely to result from reactions caused by a particular
189 functional group (i.e., heteroatoms). It is natural to assume that
190 heteroatoms, which can polarize molecules, should have played a significant
191 role if polymerization occurred in an aqueous fluid in the presence of
192 inorganic ions on the parent body. Therefore, if CH_2 chains grew during
193 aqueous alteration, one would expect distinct CH_2 polymerization patterns
194 depending on the type and number of heteroatoms. On the contrary, the
195 ubiquity of the SZ patterns tends to show that the complex organic mixture
196 has been synthesised by homogeneous reactions allowing a high degree of
197 branching carbon chains (Pladis & Kiparissides 1998).
198 The presence of the SZ pattern provides insights into the formation pathways
199 of the organic compounds in the least altered Tagish Lake sample. Many
200 chemical reaction pathways invoked in previous studies to explain chondrite
201 organics cannot explain the SZ pattern found in the primordial CH_2
202 polymerization. In particular, condensation reactions in aqueous environments
203 on the parent body that have been proposed to account for IOM-like residues
204 (Cody et al. 2011) or alkylated homologs of N-bearing cyclic compounds
205 (Naraoka et al. 2017) are not capable of explaining the observed SOM
206 distribution. In general, step-growth polymerization involves reactions
207 between two functional groups provided by the monomers and generate molecular

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209 weight variability well described by so-called Anderson-Flory-Schultz
210 distributions (Förtsch et al. 2015) (see the best fit S6). Such distributions
211 can be found in Fischer-Tropsch type synthesized mixtures and abiotic RNA
212 polymerization (Spaeth & Hargrave 2020), etc. Therefore, the step-growth
213 hypothesis can be rejected in favour of chain-growth polymerization to
214 explain the CH_2 family groups observed in the least altered sample.
215 For the altered samples where a significant deviation from the SZ
216 distribution is found, two hypotheses can be invoked to explain the
217 difference with more primordial samples. One may argue that their occurrence
218 in the most altered part of Tagish Lake is fortuitous and they are simply a
219 mixture of several homologous series from primordial organic compounds. So,
220 one simple polymerization profile cannot describe them. This possibility
221 cannot be strictly ruled out. However, three remarks should be noted. 1) The
222 observed SOM represents the bulk compositions. It is shown that the bulk
223 elemental compositions of the three lithologies are relatively isochemical
224 (Blinova et al. 2014b) (S7). Thus, sample heterogeneity caused by chondrite
225 accretion processes for the inorganic components are likely less pronounced.
226 2) Although the Tagish Lake meteorite contains foreign clasts, the
227 compositions of the individual specimens TL5b, TL11h, and TL11i appear to be
228 consistent and can thus be described as lithologies (Blinova et al. 2014a).
229 3) The distortion from a SZ distribution is gradually enhanced with
230 increasing degree of alteration. Such an inclination is not expected if the
231 trend was caused by a simple mixture of multiple primordial organic
232 components. Indeed, even chromatographic separation would not be able to
233 distinguish molecules resulting from several synthesis processes in the case
234 that they are identical.
235 The alternative, which is favoured here according to Occam's razor principle,
236 is that secondary processes modified an initial synthesis pattern. Although
237 TL5b is the least altered sample, it is an altered rock (petrologically
238 classified as type 2). Therefore, it is not surprising to see evidence of
239 alteration effects on SOM in our result. A previous study located amorphous
240 silicates in the lithology TL5b matrix, which was interpreted to infer a
241 relatively low alteration temperature ≦ 50 °C (Blinova et al. 2014a). We can
242 recognize these mild alteration effects in our measured SOM distribution.
243 Although most CH_2 families in the least altered sample, TL5b, maintained their
244 SZ profile throughout the alteration, as depicted by data points with higher
245 entropy and R^2 values close to 1 (Fig 2D), some distortions from the SZ
246 profile are found in a few CH_2 families. That alteration evidence is depicted
247 as the yellow data points with lower entropy and smaller R^2 values (Fig 2D).

250 Therefore, the SZ pattern extrapolated from the three samples can be taken as
251 representative of the original soluble organic makeup that was perhaps
252 established before accretion of the Tagish Lake parent body. The possible
253 chemical reaction field to establish the SZ profile is not limited to aqueous
254 conditions or low temperature. For example, the polymers can be synthesized
255 from gas by chain-growth reactions (Alves et al. 2021). And, high temperature
256 gas phase experiments can form various organics ranging from IOM-like
257 material to small molecules comparable to SOM, as well as the production of
258 the Xenon mass fraction observed in the matrix known as the Q-phase (Kuga et
259 al. 2015; Kuga et al. 2017; Bekaert et al. 2018). The SOM mass distributions
260 of those materials indeed can be well fit by the SZ model (S8). We show the
261 distributions and the SZ fit in a figure together with the data (S9). These
262 high-temperature reactions provide an interesting pathway to form SOM. High-
263 temperature conditions can be found in irradiated parts of the solar nebula.
264 Extra-terrestrial samples also record massive high-temperature processing of
265 protoplanetary disk materials by the widespread occurrence of chondrules.
266 These formed under high temperature and high ambient gas pressure transient
267 events (by evaporating the gas during their formation) in the solar nebula
268 (Alexander & Ebel 2012) and references therein. We do not rule out the
269 possibility of the formation mechanisms besides in a vapor phase. And yet,
270 forming the SZ profile of the SOM complex before accretion is plausible and
271 consistent with the rest of the chondrite components.
272 Aqueous alteration processes resulted in an oxidized signature (that is, the
273 loss of H) of the SOM, which is consistent with the previously observed
274 linear correlation in H/C ratios and δD of Tagish Lake IOM (Cody & Alexander
275 2005; Alexander et al. 2007; Herd et al. 2011; Alexander et al. 2014) and
276 inferences from previous IOM and SOM studies (Hilts et al. 2014; Quirico et
277 al. 2018). The present measurement shows that the larger molecules were
278 spared from removal throughout the alteration (Fig 3) as depicted in the
279 point clouds. A chemical change is observed in the composition of the
280 individual molecules: the most altered samples shift towards higher DBE. Such
281 hydrogen elimination reactions can take place by adding energy to a system.
282 The H-loss from organics was confirmed after heating meteorite IOM (Yabuta et
283 al. 2007; Oba & Naraoka 2009) and after irradiating meteorite SOM (Orthous-
284 Daunay et al. 2019). In the reactions that occurred during aqueous
285 alteration, the processes were likely facilitated by heating of the parent
286 asteroids. It is likely that such raised temperature conditions caused the
287 same reaction mechanisms that resulted in hydrogen loss in both IOM and SOM.
288 This hypothesis can be tested by comparing the degree of H-loss between the

IOM and the SOM. Averaged H/C ratios of SOM and that of IOM decrease with increasing alteration degree, TL11i (the most altered) < TL11h < TL5b (the least altered). By using TL5b as a reference, we semi-quantitatively estimated the H-loss in TL11h and TL11i SOM. The estimated H-loss from SOM was approximately 10-30%, while that from IOM it was 18% and 30% for TL11h and TL11i, respectively (S10). And, this consistent H-loss caused by alteration in both SOM and IOM indicates that the primordial organics compounds matured during the alteration regardless of their size. As a consequence of oxidation in both SOM and IOM, organics released Hydrogen to the environment, likely affecting subsequent chemical reactions on the asteroids. Hydrogen is also known to be produced by metal oxidation during the aqueous alteration on the chondrite parent bodies. Therefore, at least two distinct mechanisms can be major contributors of H_2 in chondrite parent bodies. The hydrogen degassing has been considered to an essential step to explain H-isotope heterogeneities found in chondrite components. Alexander et al. 2010 suggested that the Rayleigh-type fractionation, caused by H_2 degassing, can create D-rich water by the equilibrium between remaining deuterium-rich H_2 and water. Subsequently, the D-rich water-organic reactions may have produced D-rich organics. Moreover, H_2 in the environment has been considered to react with oxide metals. H_2 produced from organics could have reacted with surrounded minerals including carbonates (Zolotov et al. 2006 and Guo and Eiler 2007). Interestingly, the total abundance of carbonate minerals in the three Tagish Lake lithologies also correlates with the degree of aqueous alterations 8, 5, and 4 vol% for TL5b (the least altered), TL11h, and TL11i (the most altered), respectively. If carbonate minerals were decomposed with H_2 (Guo and Eiler 2007), further C-isotope studies in the individual carbonate grains in the three samples may reveal details concerning the organic and inorganic carbon chemistry and the timing relative to the H_2 producing events.

In addition to the loss of hydrogen, the alteration produced an increase in small molecules (shift to low mass in Fig 2. and supplemental figures). Previously observed MCA in Tagish Lake meteorite are abundant, 100 ppm for bulk rock (Pizzarello et al. 2001). The minimum estimate for individual lithologies are 500 ppm for 5b and 11h, 300 ppm for 11i (Hilts et al. 2014). Previous studies showed that the concentration distribution of MCA CH_2 families in the Tagish Lake meteorite changed with increasing alteration (Hilts et al. 2014, Fig 6b). The abundance of MCA with carbon number ranging from 4 to 10 in TL5b became low relative to formic acid (C1) and acetic acid (C2) in TL11i. The diminished diversity in size by alteration is consistent

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337 with the overall trend seen in Fig 2. The distribution becomes sharper when
338 compared to the less altered broad spectrum due to a decrease for large
339 carbon number molecules and an increase at small carbon numbers. Thus, our
340 study agrees with the Hilts et al. (2014) results and extends the
341 observations to ~4200-5000 chemical formulae.
342 Finally, our results can be utilized for assessing the SOM alteration degree
343 in samples that have experienced aqueous alteration on their various
344 chondritic components. For example, Naraoka and Hashiguchi (2018) found that
345 alkylpiperidines are more abundant in Yamato 002540 (CR) than that found in
346 Murray (CM2), while alkylpyridines concentrations are high in Murray relative
347 to Yamato 002540. By investigating their mass distributions, one can estimate
348 the degree of alterations that had taken place on their parent bodies.
349 Furthermore, studies of samples such as those from the asteroid missions to
350 Ryugu and Bennu that were brought back by the JAXA Hayabusa2 and or will be
351 brought back the NASA OSIRIS-Rex spacecraft, respectively, can be impacted by
352 our findings. These asteroids consist of carbonaceous chondrite material that
353 has undergone parent body alteration. For example, one can assess the bio-
354 related molecular synthesis found due to parent body alteration by
355 calculating the residual from the SZ model for homologous series as used in
356 this study.
357
358   5. CONCLUSION
359
360 We studied the mass-distribution of SOM extracted from three distinct Tagish
361 Lake meteorite fragments. We found that 1) the mass-distributions of the SOM
362 found in the primordial fragments can be explained by using the Schulz-Zimm
363 model; 2) the mass distribution pattern becomes asymmetric and sharper with
364 increasing degrees of aqueous alteration; and 3) the carbon atoms in these
365 compounds became more oxidized with increasing degrees of aqueous alteration.
366 These observations imply that the complex nature of the primordial SOM 1) was
367 established before severe alteration on the asteroid and that mechanisms
368 accounting for the alteration can be explained by chain-growth
369 polymerization; 2) was possibly established in the solar nebula; 3) was
370 simplified on the asteroid; and 4) matured together with IOM. Therefore, it
371 appears that the reaction pathways that have been suggested for explaining
372 complex SOM on asteroids are not necessarily correct since the complexities
373 seem to be preexisting even though aqueous reactions were necessary to
374 synthesize specific biotically relevant compounds such as amino acids (Koga
375 et al. 2021), ribose (Furukawa et al. 2019), or RNA (Cafferty and Hud 2014).

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377 Furthermore, one can identify which organic chemical formulae were
378 preferentially synthesized through metamorphism and alteration on asteroids
379 relative to other solar nebula materials by measuring deviations from the SZ
380 model.
381

387

388   Appendix
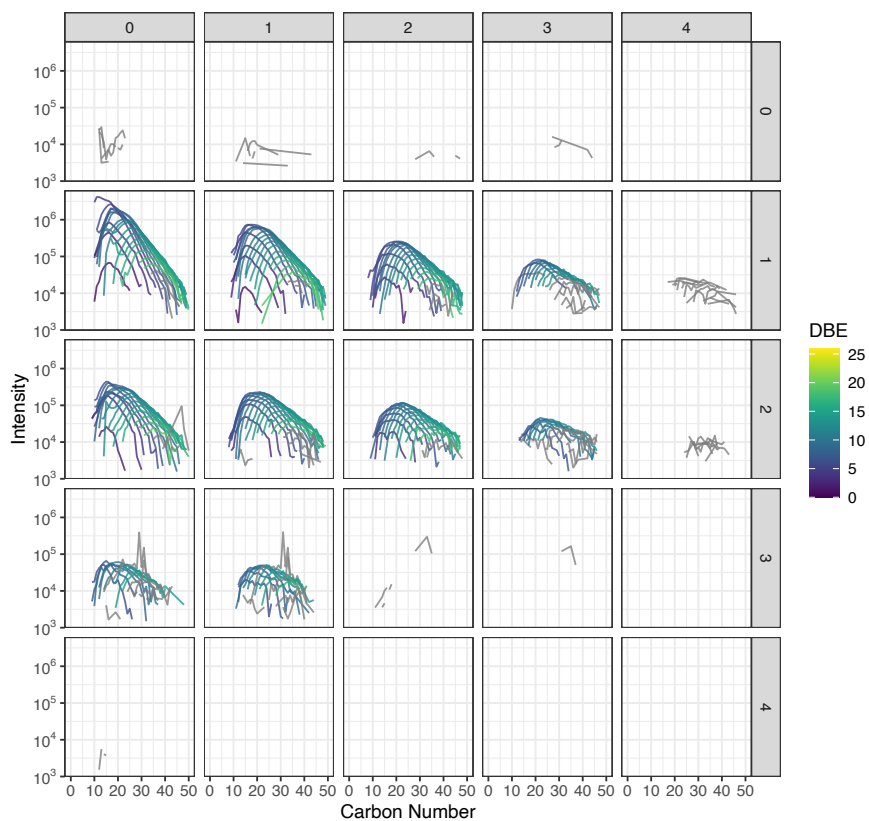389

390

391   1.   Orbitrap Measurement Methods
392 The SOM extracted from the Tagish Lake meteorite powder was measured by the
393 high-resolution mass spectra, Thermo LTQ Orbitrap XL instrument coupled with
394 an Electrospray ionization (ESI) source in the m/z range of 150—800 at the
395 University of Grenoble Alps. The positive ions were analyzed with a resolving
396 power of $m/\Delta m \sim 100000$ at m/z = 400u. For the analyses, the direct infusion
397 technique was used. The SOM, together with the solvent, was injected
398 continuously into the Orbitrap at the flow rate of 3 μl/min. The flow rate was
399 controlled by the syringe pump attached to the instrument, and the PEEK
400 capillary tube was used. One direct infusion analysis took approximately 30
401 min.
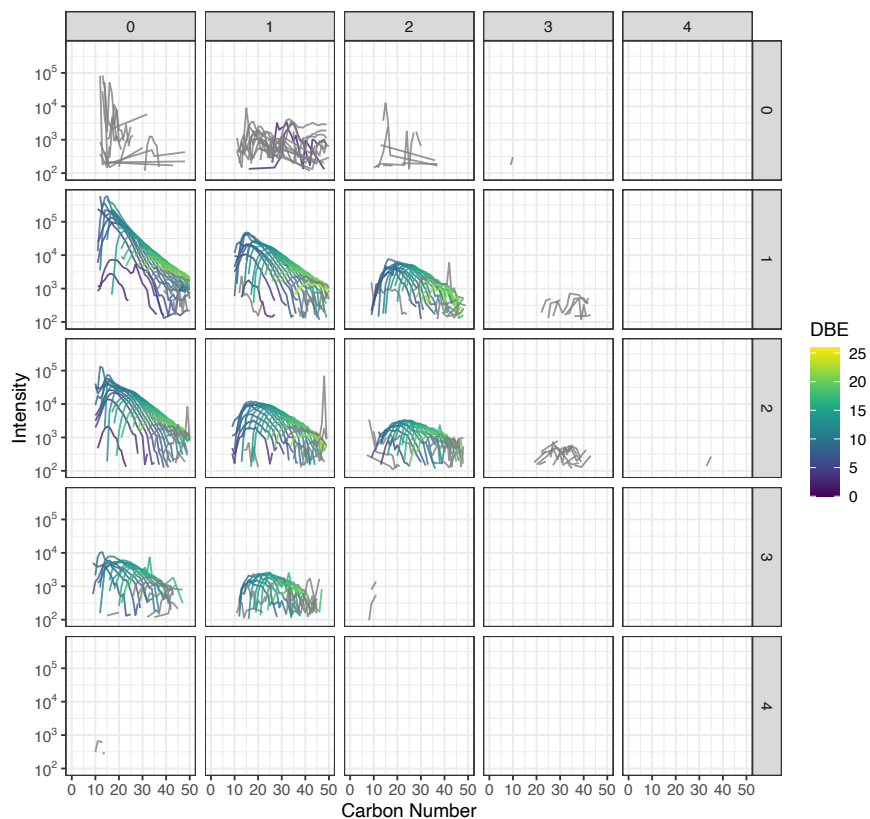402

403   2.   Data Analyses
404 After we acquired the spectra, we utilized post-processing data analysis
405 tools, which have been developed in-house at IPAG. ATTRIBUTOR was used for
406 main data analyses, and the following data treatment was applied using in-
407 house code written in R language. The post-processing includes peak
408 detection, noise rejection, and mass-drift correction. After we refined the
409 mass spectra, we assigned the chemical formula to the detected peaks. The
410 chemical formulae were assigned using 12C, 13C, H, 14N, and 16O. The assigned
411 chemical formulae were filtered based on the offset from the ideal mass
412 calculated based on the assigned chemical formula. The filter was ±1.5 ppm. In
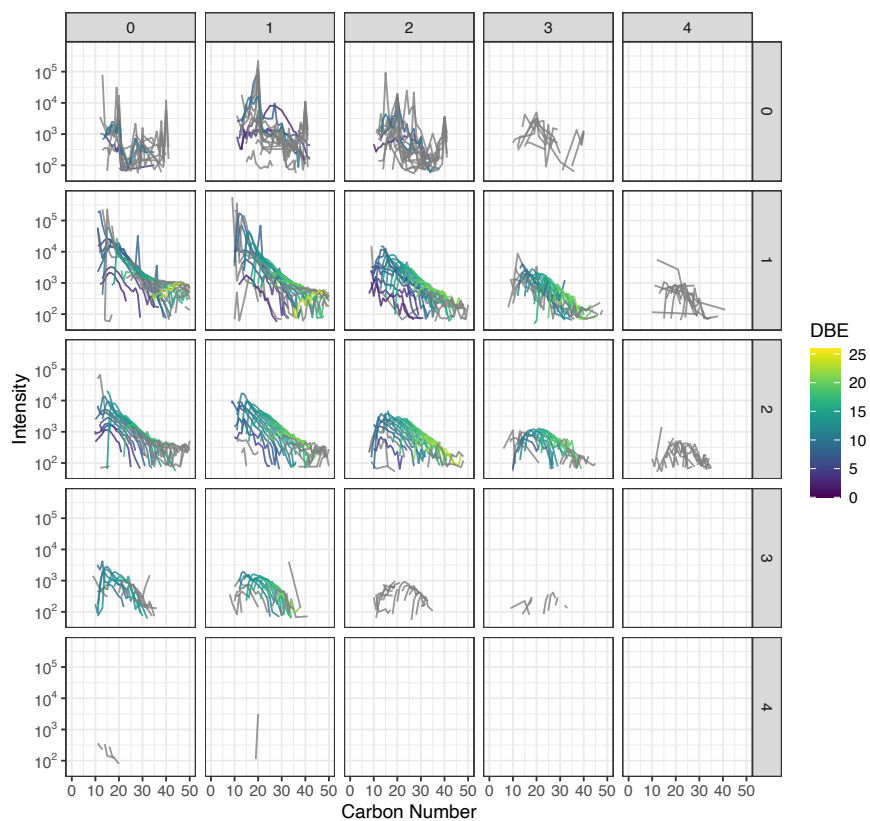413 this paper, we only used the chemical formula assigned with the 12C.

rows = numbers of N atoms and columns = numbers of O atoms

S1: Modified mass spectra as a function of carbon number. The results are from the samples, TL5b. We treated the stoichiometric formulae varying in CH_2 as a repeating unit and call them as CH_2 family respect to DBE values after the chemical assignment. They are treated similar to alkyl homologous compounds that identified in previous study of Murchison meteorite (Naraoka et al. 2017). The data were also organized by the number of heteroatoms, N and O coloured by DBE values. The data in grey are filtered out for the figure 2. The filtering criteria is number of peaks in a CH_2 family is larger than 10 and calculated entropy > 2 and the goodness of the SZ fit > 0.5.

rows = numbers of N atoms and columns = numbers of O atoms

S2: Modified mass spectra as a function of carbon number. The results are from the samples, TL11h. We treated the stoichiometric formulae varying in CH_2 as a repeating unit and call them as CH_2 family respect to DBE values after the chemical assignment. They are treated similar to alkyl homologous compounds that identified in previous study of Murchison meteorite (Naraoka et al. 2017). The data were also organized by the number of heteroatoms, N and O coloured by DBE values. The data in grey are filtered out for the figure 2. The filtering criteria is number of peaks in a CH_2 family is larger than 10 and calculated entropy > 2 and the goodness of the SZ fit > 0.5.

rows = numbers of N atoms and columns = numbers of O atoms

436

437 **S3:** Modified mass spectra as a function of carbon number. The results are from
438 the samples, TL11i. We treated the stoichiometric formulae varying in CH_2 as a
439 repeating unit and call them as CH_2 family respect to DBE values after the
440 chemical assignment. They are treated similar to alkyl homologous compounds
441 that identified in previous study of Murchison meteorite (Naraoka et al. 2017).
442 The data were also organized by the number of heteroatoms, N and O coloured by
443 DBE values. The data in grey are filtered out for the figure 2. The filtering
444 criteria is number of peaks in a CH_2 family is larger than 10 and calculated
445 entropy > 2 and the goodness of the SZ fit > 0.5.

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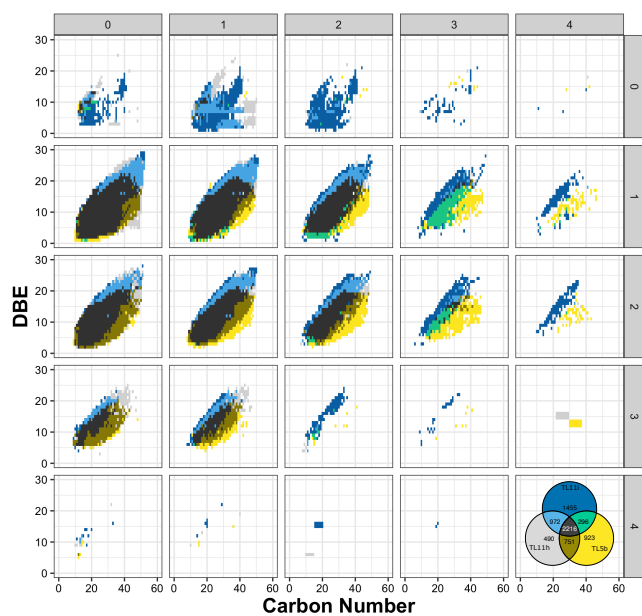
rows: number of N atoms
cols: number of O atoms

S4: The common and divergence of assigned chemical formulae. The individual box is organized the number of heteroatoms in the chemical formulae. One pixel indicates one chemical formula. The data were color-coded by samples (see Venn diagram). The least altered samples tend to be plotted at the bottom of the point clouds in the individual boxes (yellow). The altered samples tend to be plotted at the top of the point clouds in the individual boxes (blue). This trend indicates that the compounds became oxidized, which is either become more cyclic or forming double bonds.

row = number of N atoms and cols = number of O atoms

460

row = number of N atoms and cols = number of O atoms

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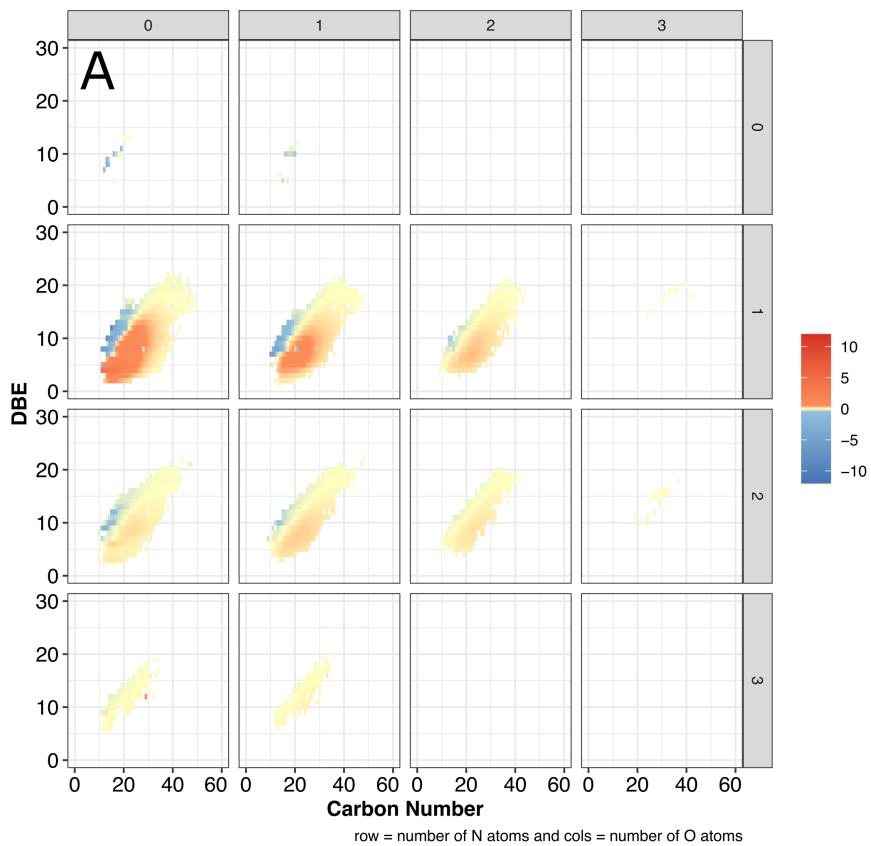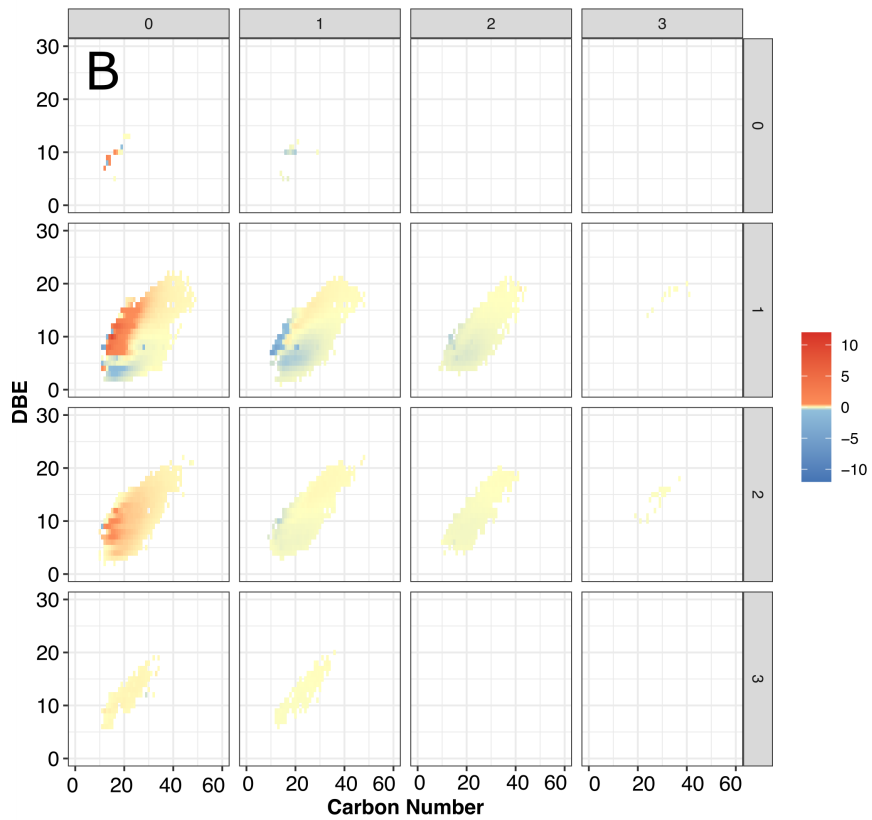
row = number of N atoms and cols = number of O atoms
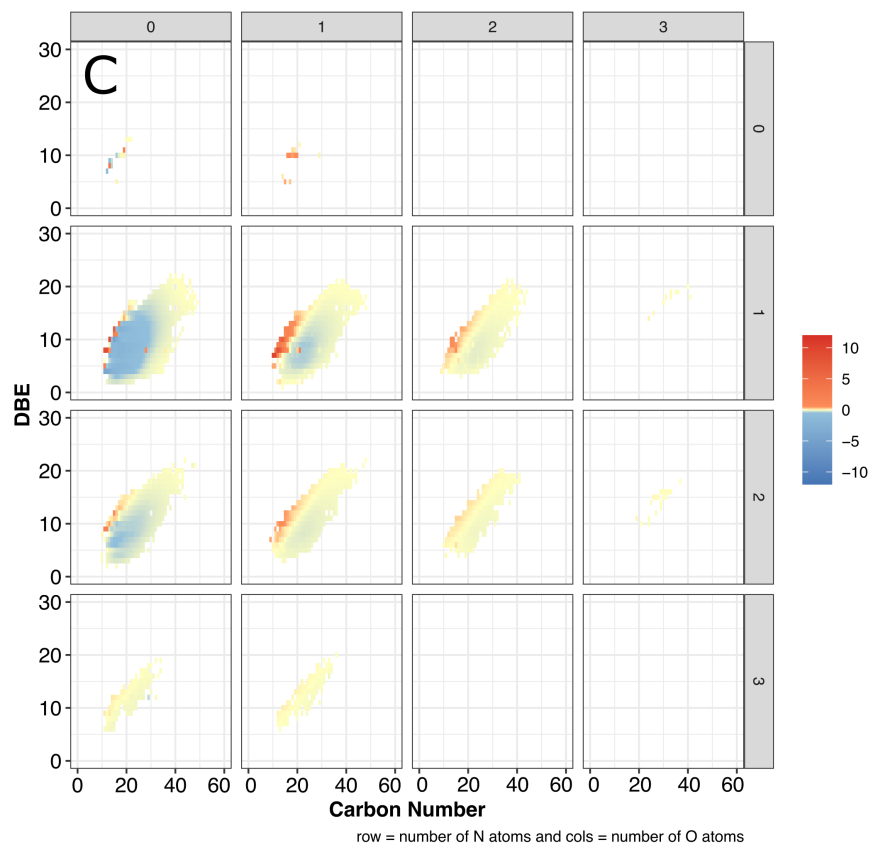
S5: The common chemical formulae, sample 5b, sample 11h, and sample 11i (at the center of the Venn diagram see S4). Normalized intensities among the three samples. The figure A, B, C, represent the sample 5b, 11h, 11i, respectively. The positive (red) or negative (blue) index indicates that the intensities that are higher or lower than the normalized average intensities. With an increasing degree of alteration, the larger DBE chemical formulae intensity increases.
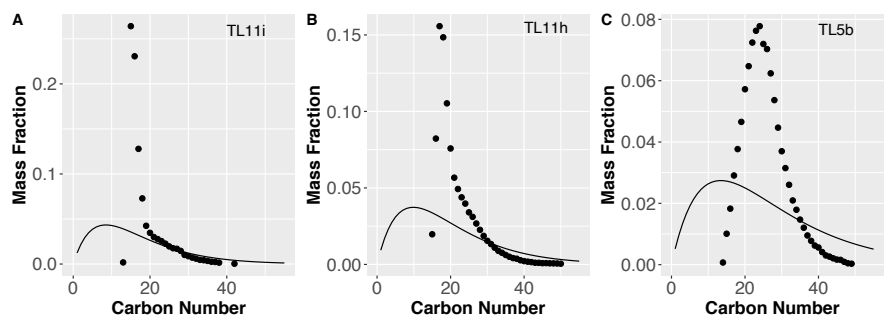
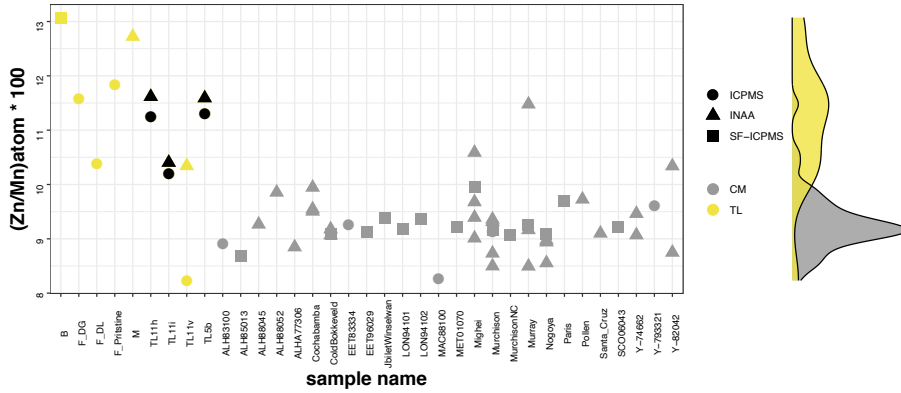**S6:** An example CH$_2$ family, C$_{14}$H$_9$NO + (CH$_2$)$_n$ **(A–C).** Same data are plotted in the Fig2 (A–C). Black solid line is the best fit of Anderson–Flory–Schultz (AFS) distribution to the data set. The data are not well explained by the AFS model.

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486 **S7:** Bulk Zn/Mn ratios of the Tagish Lake meteorite, CM group based on the
487 previouslly reported data. The moderately volatile element, Mn, and volatile
488 element, Zn, the ratio is one of the representations of accretionary material
489 diversity. Assuming that the scatter within the CM is an example of a typical
490 variety of chondrite groups, the samples used in this study TL11h, TL11i, and
491 TL5b (black symbols) are homogeneous, while Tagish Lake lithology TL11v, for
492 example, shows relatively large heterogeneity. That disagreement in the aliquots
493 can indicate the contamination from the foreign clast, which was located in the
494 Tagish Lake meteorite. On the contrary, the lithology, TL11h, TL11i, and TL5b,
495 are closer to the average Tagish Lake meteorite value. Their duplicate analyses
496 by the different aliquots using the distinct analytical techniques well agree
497 with each other.
498 Tagish Lake meteorite data includes followings: B (Braukmüller et al. 2018);
499 F_DG (Disturbed_G) (Friedrich et al. 2002); F_DL (Disturbed_L) (Friedrich et
500 al. 2002); F_Pristine (Pristine) (Friedrich et al. 2002); M (Mittlefehldt
501 2002); TL11h, TL11i, TL11v, and TL11v (Blinova et al. 2014b). CM chondrites
502 data are previously reported INAA and ICP-MS data (Braukmüller et al. 2018;
503 Friedrich et al. 2002; Grady et al. 1987; Kallemeyn & Wasson 1981;
504 Mittlefehldt 2002; Wlotzka et al. 1989).
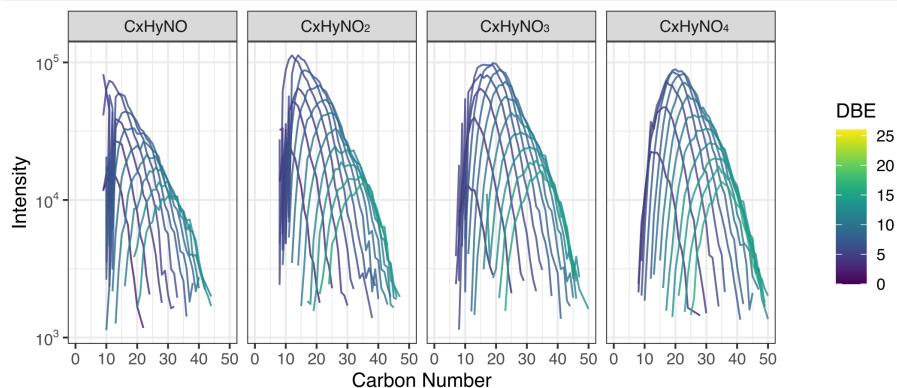
S8: Modified mass spectra as a function of carbon number. The results are from the samples, Nebulotron material (Zandanel 2021). We had conducted SOM extraction and analyses under the same manner with Tagish Lake meteorite (Isa et al. 2019). We treated the stoichiometric formulae varying in CH_2 as a repeating unit and call them as CH_2 family respect to DBE values after the chemical assignment. They are treated similar to alkyl homologous compounds that identified in previous study of Murchison meteorite (Naraoka et al. 2017). Molecules bearing N(1) and O(1-4) were selected and organized by the number of O. They are coloured by DBE values.
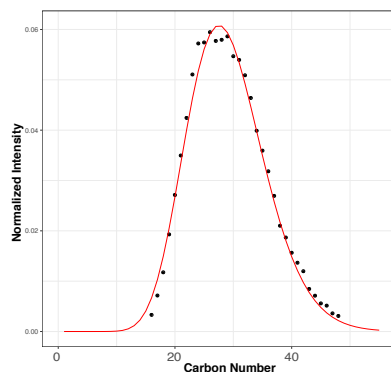
S9: Schulz‑Zimm (SZ) fit for the data of Nebulotoron (the data are same as S9). An example CH_2 family, $C_{14}H_9NO + (CH_2)_n$ is selected.

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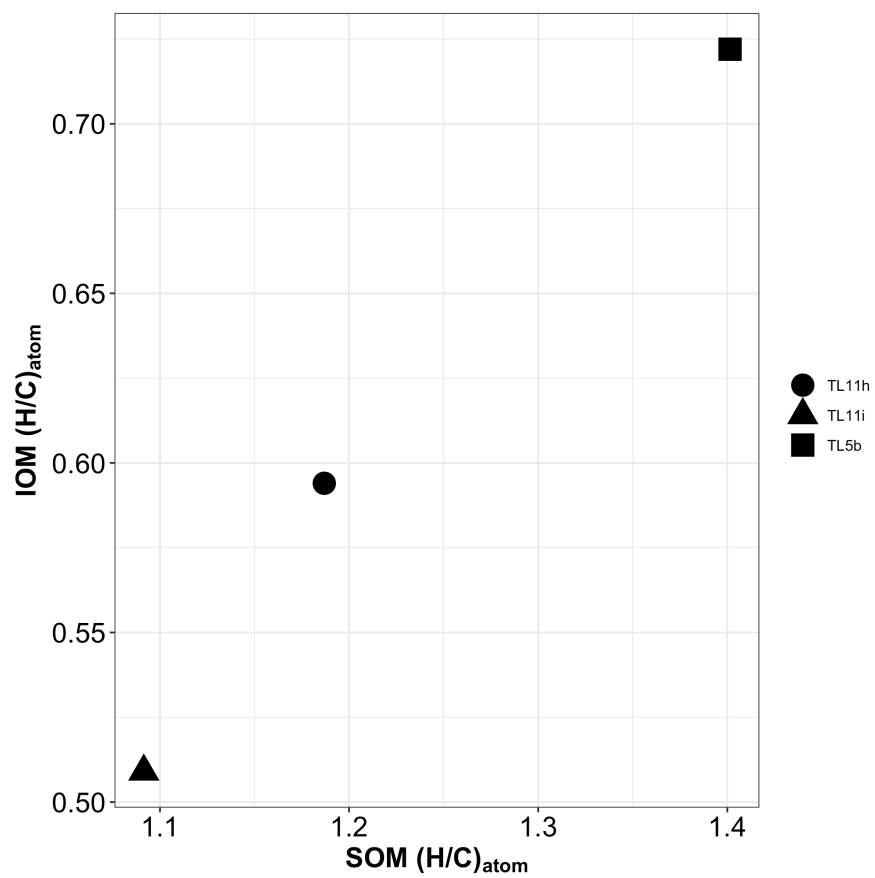
S10: The atom H/C ratio of SOM vs. atom H/C ratio of IOM. The SOM H/C ratios were calculated by averaging over the N-bearing assigned ions' relative intensity. For the bulk SOM H/C ratio, which is filled squared symbol in the figure, we used all the assigned spectra. The IOM data are from previous study (Alexander et al. 2014).

Table S1. Bulk rock mineralogy and componets of Tagish Lake samples

	5b	11h	11i
	wt %	wt %	wt %
Forsterite	39	15	19
Magnetite	30	18	19
Pyrrhotite	8	8	4
Enstatite	3	n/d	n/d
Dolomite	2	n/d	n/d
Siderite	10	10	7
Calcite	2	0	1
Clinochlore	n/d	48	48
Amorphous	7.6	1.7	2.6
	vol%	vol%	vol%
Chondrules	30	25	5
Magnetites	18	15	15
Sulfides	7	4	2
Isolated silicate	10	1	5
Carbonate	8	5	4
Lithic fragments	2	10	13
Matrix	25	42	54

The data from Blinova et al. 2014a

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