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# AQUEOUS ALTERATION ON ASTEROIDS SIMPLIFIES SOLUBLE ORGANIC MATTER MIXTURES

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1 AQUEOUS ALTERATION ON ASTEROIDS SIMPLIFIES SOLUBLE ORGANIC MATTER MIXTURES

2

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4 HERD<sup>4</sup>, VERONIQUE VUITTON<sup>3</sup>, and LAURÈNE FLANDINET<sup>3</sup>

5

6

ABSTRACT

7

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<sub>2</sub> source that may have caused subsequent chemical reactions in  
31 the Tagish Lake meteorite parent body.

32

33

1. INTRODUCTION

34

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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°C  
42 to ~150°C 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 18<sup>th</sup> in 2000 in northwestern British  
59 Columbia, Canada. After the fall, several hundred grams were recovered on the  
60 25<sup>th</sup> and 26<sup>th</sup> 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  $\delta D$  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  $\delta D$  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

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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  $m/\Delta m \sim$   
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

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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<sub>2</sub> family S5.

#### 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<sub>2</sub>  
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<sub>2</sub> chains grew during  
193 aqueous alteration, one would expect distinct CH<sub>2</sub> 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<sub>2</sub>  
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<sub>2</sub> 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  $\leq 50$  °C (Blinova et al. 2014a). We can  
242 recognize these mild alteration effects in our measured SOM distribution.  
243 Although most CH<sub>2</sub> 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<sup>2</sup> values close to 1 (Fig 2D), some distortions from the SZ  
246 profile are found in a few CH<sub>2</sub> families. That alteration evidence is depicted  
247 as the yellow data points with lower entropy and smaller R<sup>2</sup> values (Fig 2D).

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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  $\delta D$  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

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296 IOM and the SOM. Averaged H/C ratios of SOM and that of IOM decrease with  
297 increasing alteration degree, TL1li (the most altered) < TL1lh < TL5b (the  
298 least altered). By using TL5b as a reference, we semi-quantitatively  
299 estimated the H-loss in TL1lh and TL1li SOM. The estimated H-loss from SOM  
300 was approximately 10-30%, while that from IOM it was 18% and 30% for TL1lh  
301 and TL1li, respectively (S10). And, this consistent H-loss caused by  
302 alteration in both SOM and IOM indicates that the primordial organics  
303 compounds matured during the alteration regardless of their size. As a  
304 consequence of oxidation in both SOM and IOM, organics released Hydrogen to  
305 the environment, likely affecting subsequent chemical reactions on the  
306 asteroids. Hydrogen is also known to be produced by metal oxidation during  
307 the aqueous alteration on the chondrite parent bodies. Therefore, at least  
308 two distinct mechanisms can be major contributors of H<sub>2</sub> in chondrite parent  
309 bodies. The hydrogen degassing has been considered to an essential step to  
310 explain H-isotope heterogeneities found in chondrite components. Alexander et  
311 al. 2010 suggested that the Rayleigh-type fractionation, caused by H<sub>2</sub>  
312 degassing, can create D-rich water by the equilibrium between remaining  
313 deuterium-rich H<sub>2</sub> and water. Subsequently, the D-rich water-organic reactions  
314 may have produced D-rich organics. Moreover, H<sub>2</sub> in the environment has been  
315 considered to react with oxide metals. H<sub>2</sub> produced from organics could have  
316 reacted with surrounded minerals including carbonates (Zolotov et al. 2006  
317 and Guo and Eiler 2007). Interestingly, the total abundance of carbonate  
318 minerals in the three Tagish Lake lithologies also correlates with the degree  
319 of aqueous alterations 8, 5, and 4 vol% for TL5b (the least altered), TL1lh,  
320 and TL1li (the most altered), respectively. If carbonate minerals were  
321 decomposed with H<sub>2</sub> (Guo and Eiler 2007), further C-isotope studies in the  
322 individual carbonate grains in the three samples may reveal details  
323 concerning the organic and inorganic carbon chemistry and the timing relative  
324 to the H<sub>2</sub> producing events.

325 In addition to the loss of hydrogen, the alteration produced an increase in  
326 small molecules (shift to low mass in Fig 2. and supplemental figures).  
327 Previously observed MCA in Tagish Lake meteorite are abundant, 100 ppm for  
328 bulk rock (Pizzarello et al. 2001). The minimum estimate for individual  
329 lithologies are 500 ppm for 5b and 1lh, 300 ppm for 1li (Hilts et al. 2014).  
330 Previous studies showed that the concentration distribution of MCA CH<sub>2</sub>  
331 families in the Tagish Lake meteorite changed with increasing alteration  
332 (Hilts et al. 2014, Fig 6b). The abundance of MCA with carbon number ranging  
333 from 4 to 10 in TL5b became low relative to formic acid (C1) and acetic acid  
334 (C2) in TL1li. 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 Hiltz 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.

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## 357 5. CONCLUSION

358  
359 We studied the mass-distribution of SOM extracted from three distinct Tagish  
360 Lake meteorite fragments. We found that 1) the mass-distributions of the SOM  
361 found in the primordial fragments can be explained by using the Schulz-Zimm  
362 model; 2) the mass distribution pattern becomes asymmetric and sharper with  
363 increasing degrees of aqueous alteration; and 3) the carbon atoms in these  
364 compounds became more oxidized with increasing degrees of aqueous alteration.  
365 These observations imply that the complex nature of the primordial SOM 1) was  
366 established before severe alteration on the asteroid and that mechanisms  
367 accounting for the alteration can be explained by chain-growth  
368 polymerization; 2) was possibly established in the solar nebula; 3) was  
369 simplified on the asteroid; and 4) matured together with IOM. Therefore, it  
370 appears that the reaction pathways that have been suggested for explaining  
371 complex SOM on asteroids are not necessarily correct since the complexities  
372 seem to be preexisting even though aqueous reactions were necessary to  
373 synthesize specific biotically relevant compounds such as amino acids (Koga  
374 et al. 2021), ribose (Furukawa et al. 2019), or RNA (Cafferty and Hud 2014).  
375

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.

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384 framework of the Investissements d'Avenir program (ANR-15-IDEX-02), through  
385 the funding of the "Origin of Life" project of the Univ. Grenoble-Alpes.  
386

#### 387 Appendix

##### 388 1. Orbitrap Measurement Methods

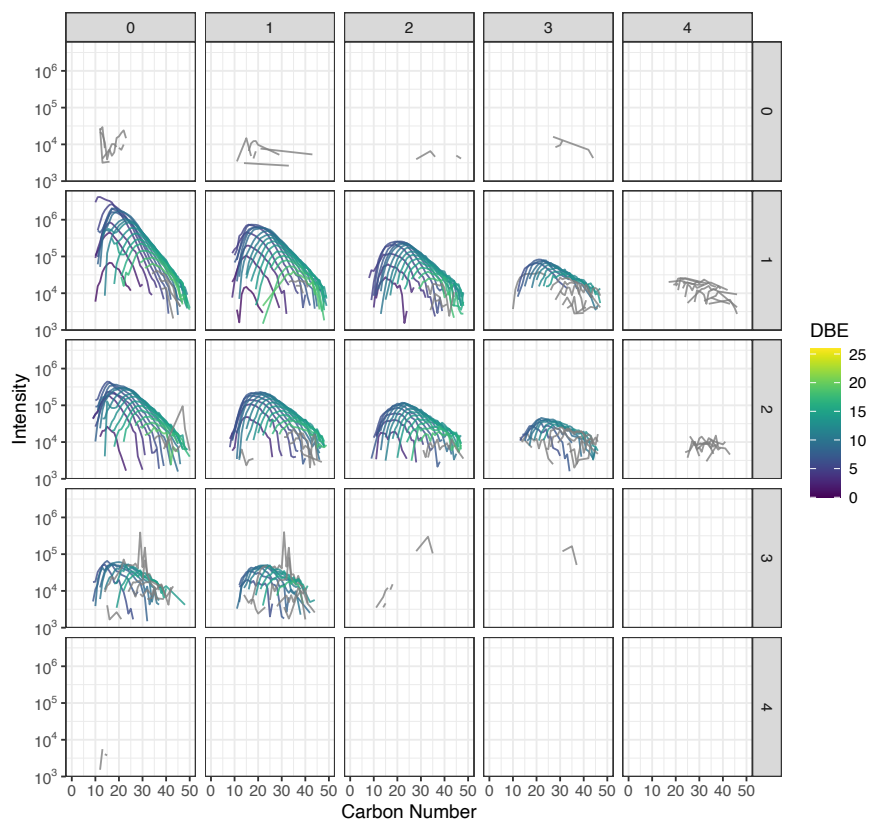
389 The SOM extracted from the Tagish Lake meteorite powder was measured by the  
390 high-resolution mass spectra, Thermo LTQ Orbitrap XL instrument coupled with  
391 an Electrospray ionization (ESI) source in the m/z range of 150–800 at the  
392 University of Grenoble Alps. The positive ions were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

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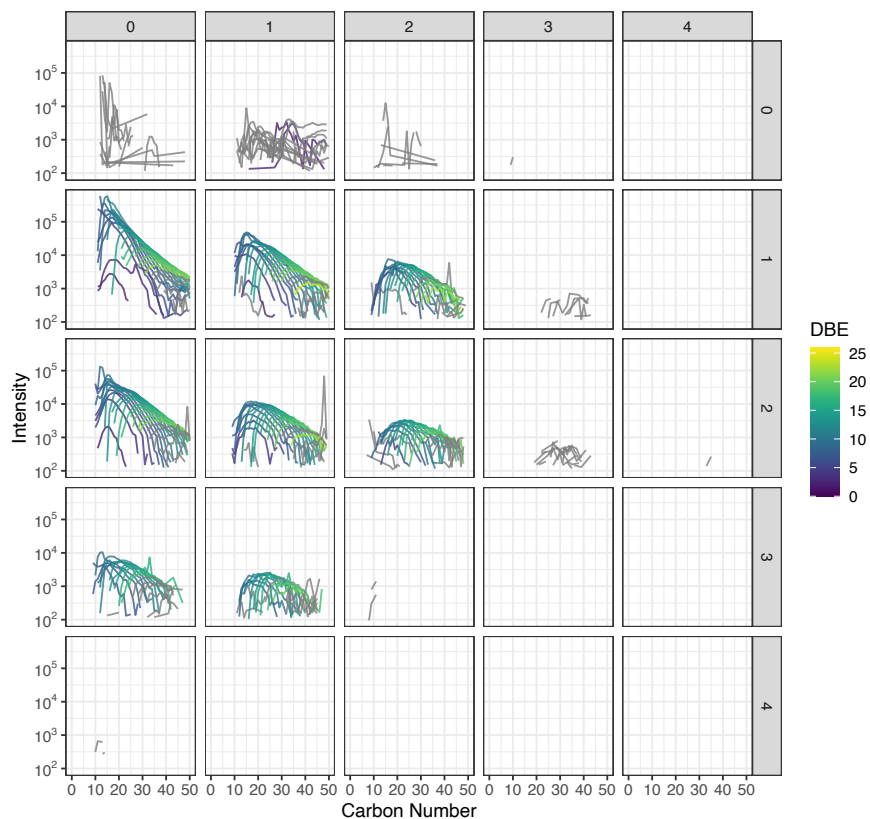
##### 402 2. Data Analyses

403 After we acquired the spectra, we utilized post-processing data analysis  
404 tools, which have been developed in-house at IPAG. ATTRIBUTOR was used for  
405 main data analyses, and the following data treatment was applied using in-  
406 house code written in R language. The post-processing includes peak  
407 detection, noise rejection, and mass-drift correction. After we refined the  
408 mass spectra, we assigned the chemical formula to the detected peaks. The  
409 chemical formulae were assigned using 12C, 13C, H, 14N, and 16O. The assigned  
410 chemical formulae were filtered based on the offset from the ideal mass  
411 calculated based on the assigned chemical formula. The filter was  $\pm 1.5 \text{ ppm}$ . In  
412 this paper, we only used the chemical formula assigned with the 12C.  
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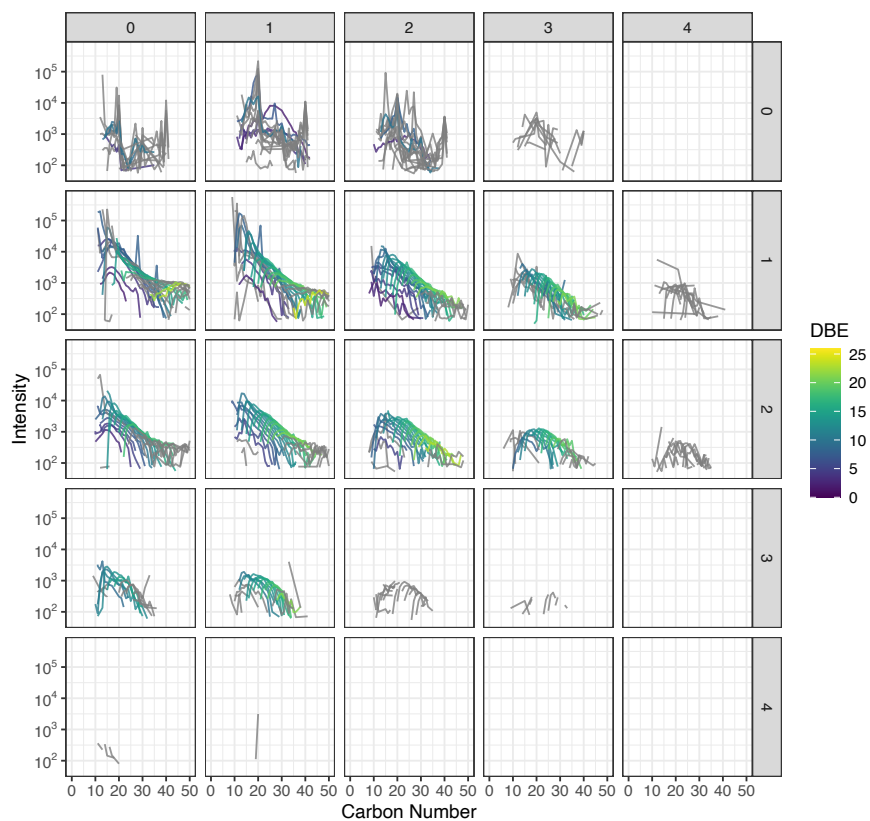
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414 rows = numbers of N atoms and columns = numbers of O atoms  
 415 **s1:** Modified mass spectra as a function of carbon number. The results are from  
 416 the samples, TL5b. We treated the stoichiometric formulae varying in  $\text{CH}_2$  as a  
 417 repeating unit and call them as  $\text{CH}_2$  family respect to DBE values after the  
 418 chemical assignment. They are treated similar to alkyl homologous compounds  
 419 that identified in previous study of Murchison meteorite (Naraoka et al. 2017).  
 420 The data were also organized by the number of heteroatoms, N and O coloured by  
 421 DBE values. The data in grey are filtered out for the figure 2. The filtering  
 422 criteria is number of peaks in a  $\text{CH}_2$  family is larger than 10 and calculated  
 423 entropy  $> 2$  and the goodness of the SZ fit  $> 0.5$ .  
 424



425 rows = numbers of N atoms and columns = numbers of O atoms  
 426 **S2:** Modified mass spectra as a function of carbon number. The results are from  
 427 the samples, TL11h. We treated the stoichiometric formulae varying in  $\text{CH}_2$  as a  
 428 repeating unit and call them as  $\text{CH}_2$  family respect to DBE values after the  
 429 chemical assignment. They are treated similar to alkyl homologous compounds  
 430 that identified in previous study of Murchison meteorite (Naraoka et al. 2017).  
 431 The data were also organized by the number of heteroatoms, N and O coloured by  
 432 DBE values. The data in grey are filtered out for the figure 2. The filtering  
 433 criteria is number of peaks in a  $\text{CH}_2$  family is larger than 10 and calculated  
 434 entropy  $> 2$  and the goodness of the SZ fit  $> 0.5$ .  
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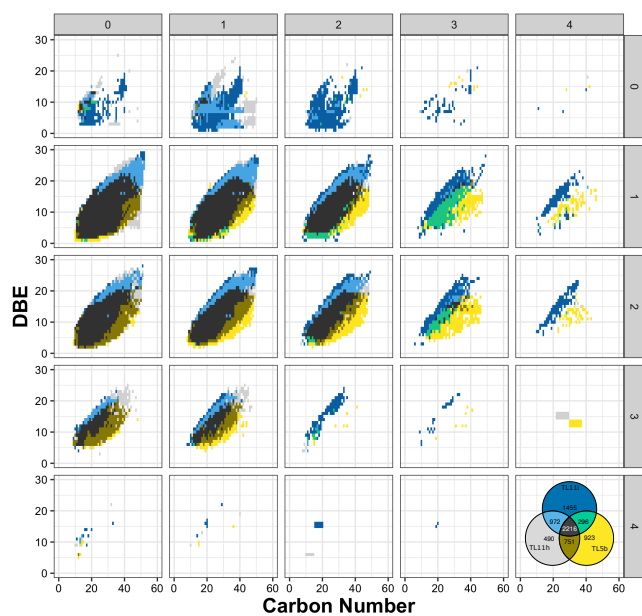


436 rows = numbers of N atoms and columns = numbers of O atoms

437 **S3:** Modified mass spectra as a function of carbon number. The results are from  
 438 the samples, TL111. We treated the stoichiometric formulae varying in CH<sub>2</sub> as a  
 439 repeating unit and call them as CH<sub>2</sub> 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<sub>2</sub> family is larger than 10 and calculated  
 445 entropy > 2 and the goodness of the SZ fit > 0.5.

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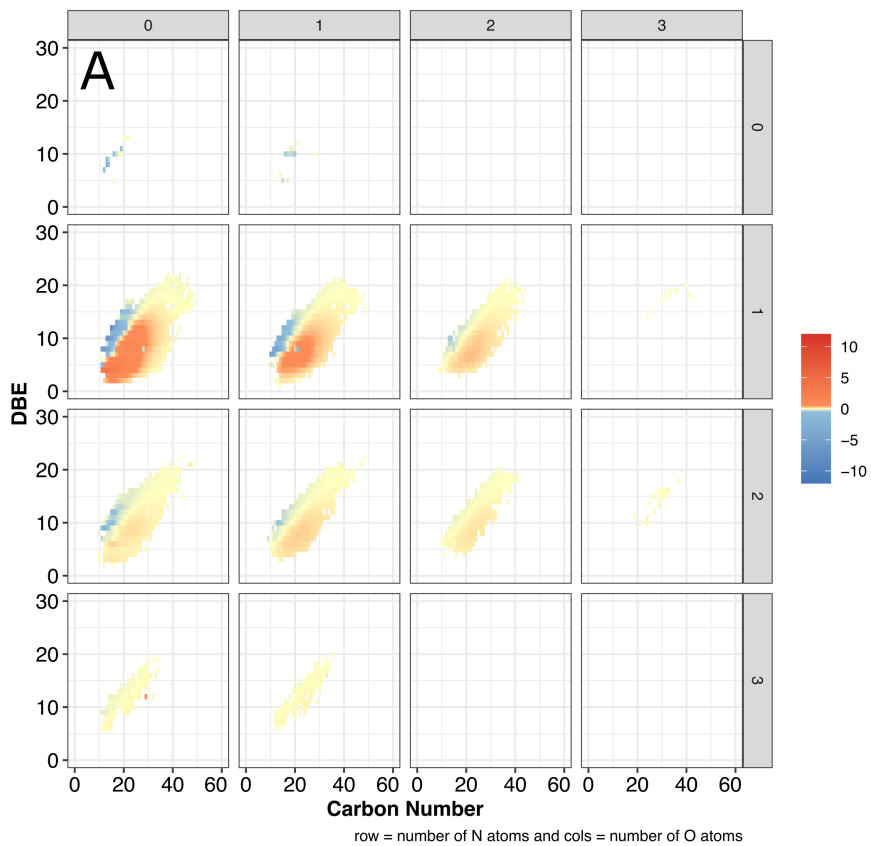
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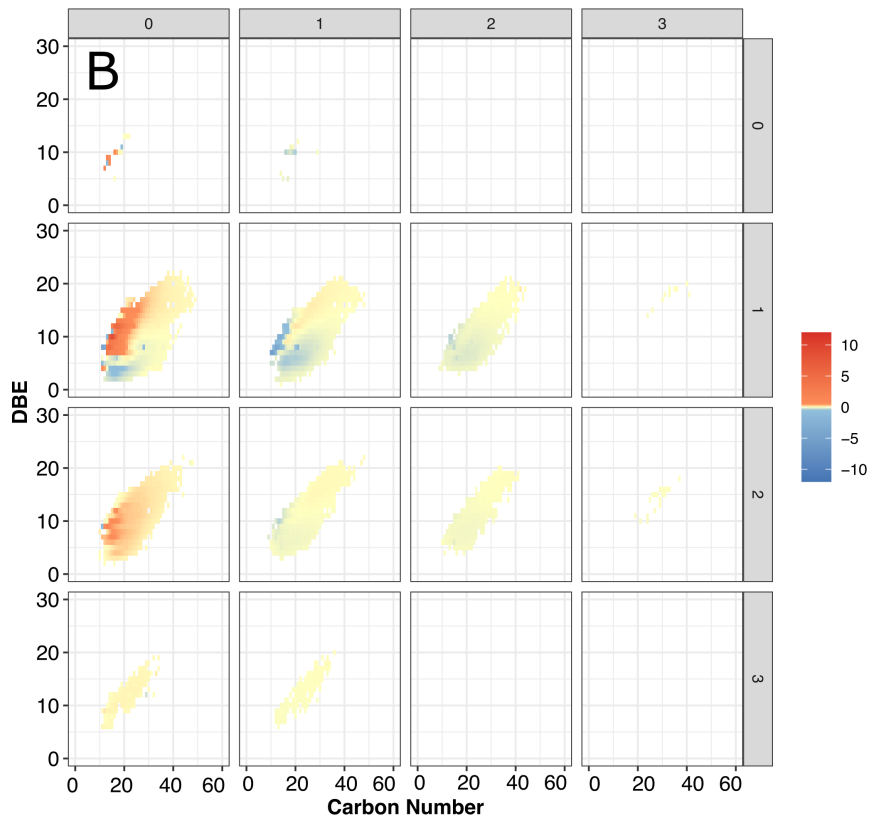
rows: number of N atoms  
cols: number of O atoms

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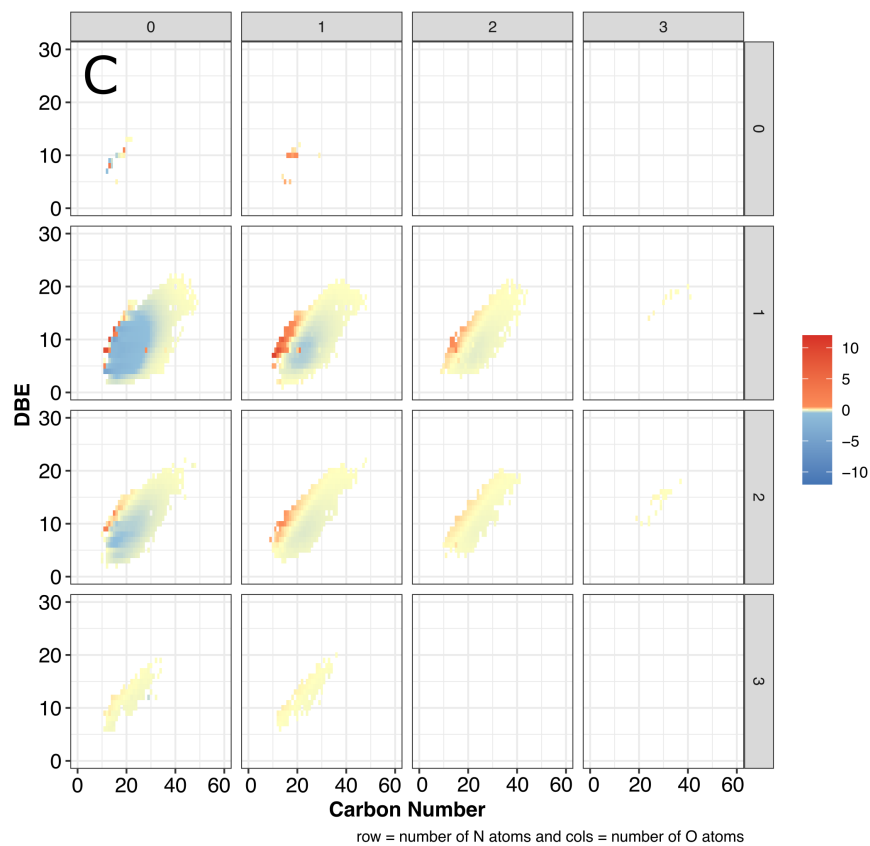
**S4:** The common and divergence of assigned chemical formulae. The individual box is organized the number of heteroatoms in the chemical formulae. One pixel indicates one chemical formula. The data were color-coded by samples (see Venn diagram). The least altered samples tend to be plotted at the bottom 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



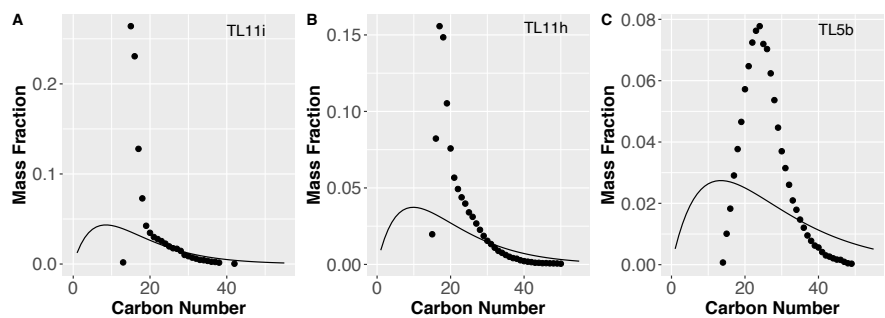
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465 **S5:** The common chemical formulae, sample 5b, sample 11h, and sample 11i (at the  
466 center of the Venn diagram see S4). Normalized intensities among the three  
467 samples. The figure A, B, C, represent the sample 5b, 11h, 11i, respectively.  
468 The positive (red) or negative (blue) index indicates that the intensities that  
469 are higher or lower than the normalized average intensities. With an increasing  
470 degree of alteration, the larger DBE chemical formulae intensity increases.

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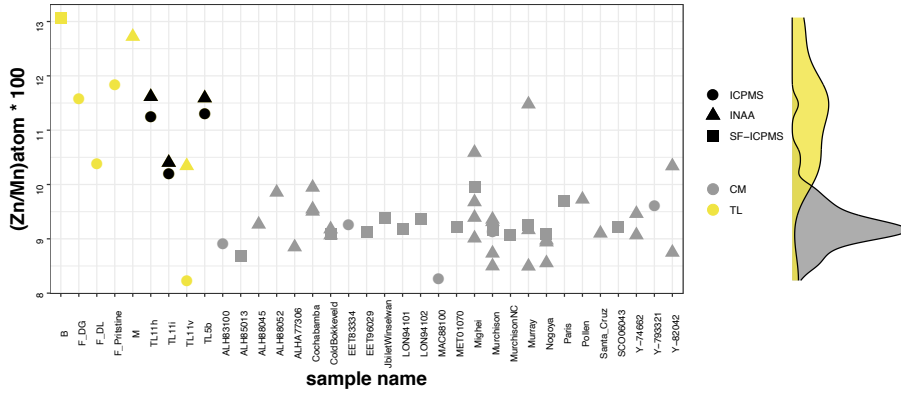
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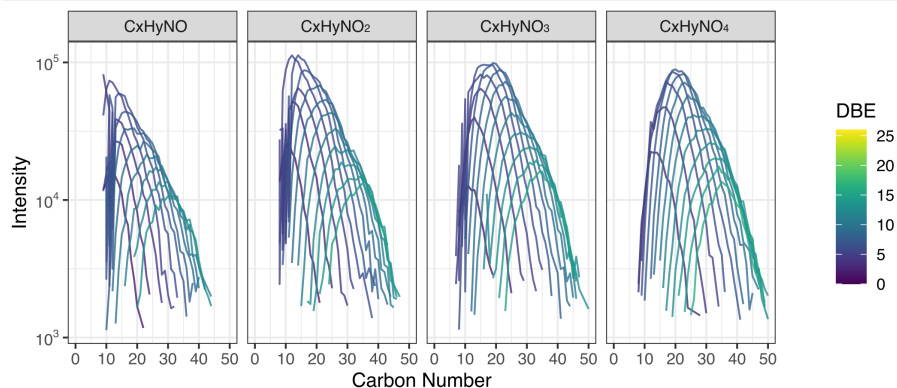
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 475 **S6:** An example  $\text{CH}_2$  family,  $\text{C}_{14}\text{H}_9\text{NO} + (\text{CH}_2)_n$  (A-C). Same data are plotted in the  
 476 Fig2 (A-C). Black solid line is the best fit of Anderson-Flory-Schultz (AFS)  
 477 distribution to the data set. The data are not well explained by the AFS  
 478 model.  
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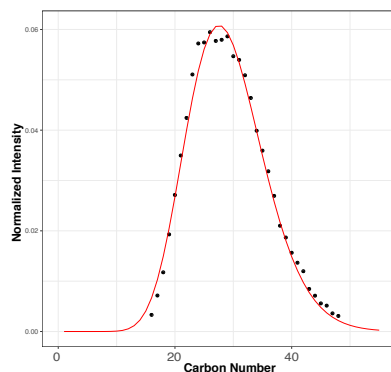


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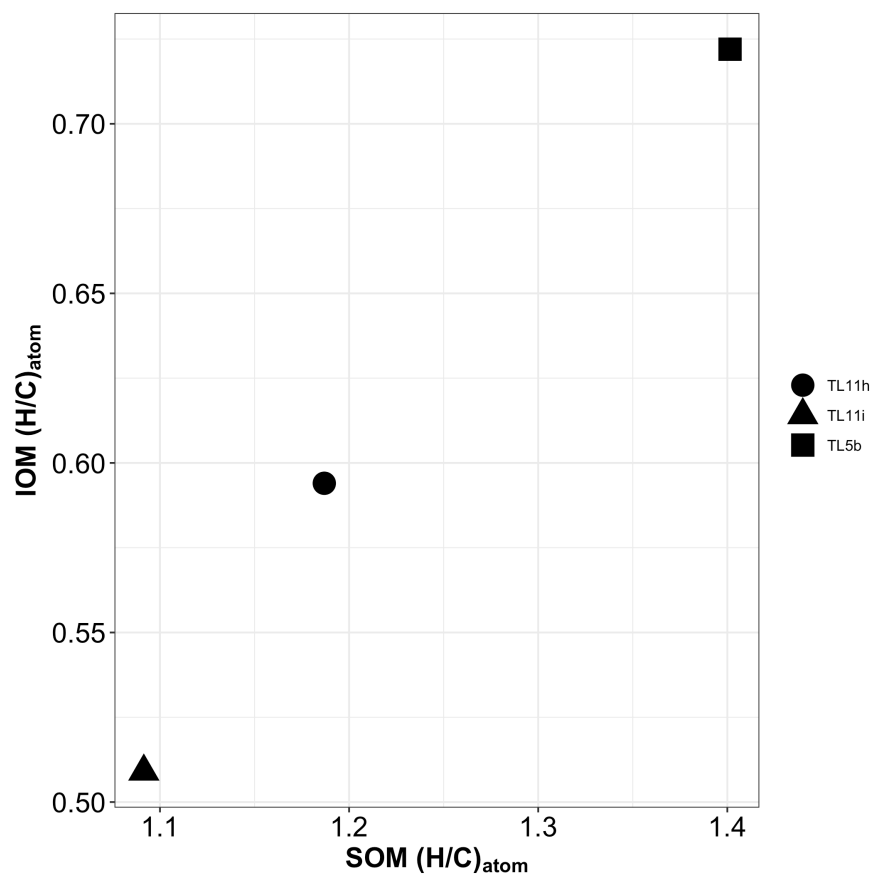
**S7:** Bulk Zn/Mn ratios of the Tagish Lake meteorite, CM group based on the previously reported data. The moderately volatile element, Mn, and volatile element, Zn, the ratio is one of the representations of accretionary material diversity. Assuming that the scatter within the CM is an example of a typical variety of chondrite groups, the samples used in this study TL11h, TL11i, and TL5b (black symbols) are homogeneous, while Tagish Lake lithology TL11v, for example, shows relatively large heterogeneity. That disagreement in the aliquots can indicate the contamination from the foreign clast, which was located in the Tagish Lake meteorite. On the contrary, the lithology, TL11h, TL11i, and TL5b, are closer to the average Tagish Lake meteorite value. Their duplicate analyses by the different aliquots using the distinct analytical techniques well agree with each other. Tagish Lake meteorite data includes followings: B (Braukmüller et al. 2018); F\_DG (Disturbed\_G) (Friedrich et al. 2002); F\_DL (Disturbed\_L) (Friedrich et al. 2002); F\_Pristine (Pristine) (Friedrich et al. 2002); M (Mittlefehldt 2002); TL11h, TL11i, TL11v, and TL11v (Blinova et al. 2014b). CM chondrites data are previously reported INAA and ICP-MS data (Braukmüller et al. 2018; Friedrich et al. 2002; Grady et al. 1987; Kallemeyn & Wasson 1981; Mittlefehldt 2002; Wlotzka et al. 1989).



505 **S8:** Modified mass spectra as a function of carbon number. The results are from  
 506 the samples, Nebulotron material (Zandanel 2021). We had conducted SOM  
 507 extraction and analyses under the same manner with Tagish Lake meteorite (Isa  
 508 et al. 2019). We treated the stoichiometric formulae varying in  $CH_2$  as a  
 509 repeating unit and call them as  $CH_2$  family respect to DBE values after the  
 510 chemical assignment. They are treated similar to alkyl homologous compounds  
 511 that identified in previous study of Murchison meteorite (Naraoka et al. 2017).  
 512 Molecules bearing N(1) and O(1-4) were selected and organized by the number of  
 513 O. They are coloured by DBE values.  
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516 **S9:** Schulz - Zimm (SZ) fit for the data of Nebulotron (the data are same as S9).  
 517 An example  $CH_2$  family,  $C_{14}H_9NO + (CH_2)_n$  is selected.  
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521 **S10:** The atom H/C ratio of SOM vs. atom H/C ratio of IOM. The SOM H/C ratios  
 522 were calculated by averaging over the N-bearing assigned ions' relative  
 523 intensity. For the bulk SOM H/C ratio, which is filled squared symbol in the  
 524 figure, we used all the assigned spectra. The IOM data are from previous study  
 525 (Alexander et al. 2014).  
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Table S1. Bulk rock mineralogy and components 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
Clinocllore	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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#### REFERENCES

- 530 Alexander, C. M. O. D., Fogel, M., Yabuta, H. & Cody, G. D. The origin and  
531 evolution of chondrites recorded in the elemental and isotopic compositions  
532 of their macromolecular organic matter. *Geochim. Cosmochim. Acta* (2007).  
533 Alexander, C. M. O. D., Newsome, S. D., Fogel, M. L., Nittler, L. R.,  
534 Busemann, H., & Cody, G. D. (2010). Deuterium enrichments in chondritic  
535 macromolecular material—Implications for the origin and evolution of  
536 organics, water and asteroids. *Geochimica et Cosmochimica Acta*, 74(15), 4417–  
537 4437.  
538 Alexander, C. M. O. D., Cody, G. D., Kebukawa, Y., Bowden, R., Fogel, M. L.,  
539 Kilcoyne, A. L. D., ... & Herd, C. D. K. (2014). Elemental, isotopic, and  
540 structural changes in Tagish Lake insoluble organic matter produced by parent  
541 body processes. *Meteoritics & Planetary Science*, 49(4), 503–525.  
542 Alexander, C. M. O. D. & Ebel, D. S. Questions, questions: Can the  
543 contradictions between the petrologic, isotopic, thermodynamic, and

544 astrophysical constraints on chondrule formation be resolved? *Meteorit.*  
545 *Planet. Sci.* 47, 1157–1175 (2012).  
546 Alves, R. F., Casalini, T., Storti, G., & McKenna, T. F. (2021). Gas-Phase  
547 Polyethylene Reactors—A Critical Review of Modeling Approaches.  
548 *Macromolecular Reaction Engineering*, 2000059.  
549 Bekaert, D. V. et al. High-temperature Ionization-induced Synthesis of  
550 Biologically Relevant Molecules in the Protosolar Nebula. *Astrophys. J.* 859,  
551 142 (2018).  
552 Blinova, A. I., Zega, T. J., Herd, C. D. K. & Stroud, R. M. Testing  
553 variations within the Tagish Lake meteorite-I: Mineralogy and petrology of  
554 pristine samples. *Meteorit. Planet. Sci.* 49, 473–502 (2014a).  
555 Blinova, A. I., Herd, C. D. K. & Duke, M. J. M. Testing variations within the  
556 Tagish Lake meteorite-II: Whole-rock geochemistry of pristine samples.  
557 *Meteorit. Planet. Sci.* 49, 1100–1118 (2014b).  
558 Braukmüller, N., Wombacher, F., Hezel, D. C., Escoube, R., & Münker, C.  
559 (2018). The chemical composition of carbonaceous chondrites: Implications for  
560 volatile element depletion, complementarity and alteration. *Geochimica et*  
561 *Cosmochimica Acta*, 239, 17–48.  
562 Brown, P. G., Hildebrand, A. R., Zolensky, M. E., Grady, M., Clayton, R. N.,  
563 Mayeda, T. K., ... & Mazur, T. R. (2000). The fall, recovery, orbit, and  
564 composition of the Tagish Lake meteorite: A new type of carbonaceous  
565 chondrite. *Science*, 290(5490), 320–325.  
566 Cafferty, B. J., & Hud, N. V. (2014). Abiotic synthesis of RNA in water: a  
567 common goal of prebiotic chemistry and bottom-up synthetic biology. *Current*  
568 *opinion in chemical biology*, 22, 146–157.  
569 Cody, G. D. & Alexander, C. M. O. D. NMR studies of chemical structural  
570 variation of insoluble organic matter from different carbonaceous chondrite  
571 groups. *Geochim. Cosmochim. Acta* 69, 1085–1097 (2005).  
572 Cody, G. D. et al. Establishing a molecular relationship between chondritic  
573 and cometary organic solids. *Proc. Natl. Acad. Sci.* (2011)  
574 doi:10.1073/pnas.1015913108.  
575 Förtsch, D., Pabst, K. & Groß-Hardt, E. The product distribution in Fischer-  
576 Tropsch synthesis: An extension of the ASF model to describe common  
577 deviations. *Chem. Eng. Sci.* 138, 333–346 (2015).  
578 Friedrich, J. M., Wang, M. S., & Lipschutz, M. E. (2002). Comparison of the  
579 trace element composition of Tagish Lake with other primitive carbonaceous  
580 chondrites. *Meteoritics & Planetary Science*, 37(5), 677–686.  
581 Furukawa, Y., Chikaraishi, Y., Ohkouchi, N., Ogawa, N. O., Glavin, D. P.,  
582 Dworkin, J. P., ... & Nakamura, T. (2019). Extraterrestrial ribose and other

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Deleted: Deamer, D., Dworkin, J. P., Sandford, S. A., Bernstein, M. P. & Allamandola, L. J. The First Cell Membranes. *ASTROBIOLOGY* vol. 2 (2002).†



587 sugars in primitive meteorites. Proceedings of the National Academy of  
588 Sciences, 116(49), 24440-24445.

589 Gilmour, C. M., Herd, C. D. K. & Beck, P. Water abundance in the Tagish Lake  
590 meteorite from TGA and IR spectroscopy: Evaluation of aqueous alteration.  
591 Meteorit. Planet. Sci. 54, 1951-1972 (2019).

592 Glavin, D. P. & Dworkin, J. P. Enrichment of the amino acid L-isovaline by  
593 aqueous alteration on CI and CM meteorite parent bodies. PNAS April vol. 7  
594 (2009).

595 Grady, M. M., Graham, A. L., Barber, D. J., Aylmer, D., Kurat, G., Ntaflou,  
596 T., ... & Spettel, B. (1987). Yamato-82042: An unusual carbonaceous chondrite  
597 with CM affinities.

598 Grady I, M. M., Verchovsky, A. B., Franchi, A., Wright, P. & Pillinger, C. T.  
599 Light element geochemistry of the Tagish Lake CI2 chondrite: Comparison with  
600 CII and CM2 meteorites. Meteoritics & Planetary Science vol. 37  
601 <http://www.uark.edu/meteor> (2002).

602 Guo, W. & Eiler, J. M. Temperatures of aqueous alteration and evidence for  
603 methane generation on the parent bodies of the CM chondrites. Geochim.  
604 Cosmochim. Acta 71, 5565-5575 (2007).

605 Herd, C. D. K. et al. Origin and Evolution of Pre biotic Organic Matter as  
606 Inferred from the Tagish Lake Meteorite. Science (80-. ). 332, 1304-1307  
607 (2011).

608 Hilts, R. W., Herd, C. D. K., Simkus, D. N. & Slater, G. F. Soluble organic  
609 compounds in the Tagish Lake meteorite. Meteorit. Planet. Sci. 49, 526-549  
610 (2014).

611 [Howard, K. T., Alexander, C. O. D., Schrader, D. L., & Dyl, K. A.](#)  
612 [Classification of hydrous meteorites \(CR, CM and C2 ungrouped\) by](#)  
613 [phyllosilicate fraction: PSD-XRD modal mineralogy and planetesimal](#)  
614 [environments. Geochimica et Cosmochimica Acta, 149, 206-222 \(2015\).](#)

615 Jones, R. H. (2012). Petrographic constraints on the diversity of chondrule  
616 reservoirs in the protoplanetary disk. Meteoritics & Planetary Science,  
617 47(7), 1176-1190.

618 Koga, T., Parker, E. T., McLain, H. L., Aponte, J. C., Elsila, J. E.,  
619 Dworkin, J. P., ... & Naraoka, H. (2021). Extraterrestrial hydroxy amino  
620 acids in CM and CR carbonaceous chondrites. Meteoritics & Planetary Science.

621 Kallemeyn, G. W., & Wasson, J. T. (1981). The compositional classification of  
622 chondrites-I. The carbonaceous chondrite groups. *Geochimica et Cosmochimica*  
623 *Acta*, 45(7), 1217-1230.

624 Kuga, M., Marty, B., Marrocchi, Y. & Tissandier, L. Synthesis of refractory  
625 organic matter in the ionized gas phase of the solar nebula. Proc. Natl.

626 Acad. Sci. U. S. A. 112, 7129–7134 (2015).  
627 Kuga, M., Cernogora, G., Marrocchi, Y., Tissandier, L. & Marty, B. Processes  
628 of noble gas elemental and isotopic fractionations in plasma-produced organic  
629 solids: Cosmochemical implications. *Geochim. Cosmochim. Acta* 217, 219–230  
630 (2017).  
631 Mittlefehldt, D. W. (2002). Geochemistry of the ungrouped carbonaceous  
632 chondrite Tagish Lake, the anomalous CM chondrite Bells, and comparison with  
633 CI and CM chondrites. *Meteoritics & Planetary Science*, 37(5), 703–712.  
634 Naraoka, H., Yamashita, Y., Yamaguchi, M. & Orthous-Daunay, F. R. Molecular  
635 Evolution of N-Containing Cyclic Compounds in the Parent Body of the  
636 Murchison Meteorite. *ACS Earth Sp. Chem.* 1, 540–550 (2017).  
637 Oba, Y. & Naraoka, H. Elemental and isotope behavior of macromolecular  
638 organic matter from CM chondrites during hydrous pyrolysis. *Meteorit. Planet.*  
639 *Sci.* 44, 943–953 (2009).  
640 Orthous-Daunay, F. R. et al. Ultraviolet-photon fingerprints on chondritic  
641 large organic molecules. *Geochim. J.* 53, 21–32 (2019).  
642 Pizzarello, S. et al. The organic content of the Tagish Lake meteorite.  
643 *Science* (80-. ). 293, 2236–2239 (2001).  
644 Pladis, P. & Kiparissides, C. A comprehensive model for the calculation of  
645 molecular weight-long-chain branching distribution in free-radical  
646 polymerizations. *Chemical Engineering Science* vol. 53 (1998).  
647 Quirico, E. et al. Prevalence and nature of heating processes in CM and C2-  
648 ungrouped chondrites as revealed by insoluble organic matter. *Geochim.*  
649 *Cosmochim. Acta* 241, 17–37 (2018).  
650 Scholz, G. V. Über die Kinetik der Kettenpolymerisationen. V 1 ). Der  
651 Einflöfi verschiedener Reaktionsarten auf die Polymoleklnarität 2 ).  
652 *Zeitschrift für Phys. Chemie* 43, 25–46 (1939).  
653 Schmitt-Kopplin, P. et al. High molecular diversity of extraterrestrial  
654 organic matter in Murchison meteorite revealed 40 years after its fall. *Proc.*  
655 *Natl. Acad. Sci. U. S. A.* 107, 2763–8 (2010).  
656 Simkus, D. N. et al. New insights into the heterogeneity of the Tagish Lake  
657 meteorite: Soluble organic compositions of variously altered specimens.  
658 *Meteorit. Planet. Sci.* 54, 1283–1302 (2019).  
659 Spaeth, A., & Hargrave, M. (2020). A polyaddition model for the prebiotic  
660 polymerization of RNA and RNA-like polymers. *Life*, 10(2), 12.  
661 Suttle, M. D., King, A. J., Schofield, P. F., Bates, H., & Russell, S. S.  
662 (2021). The aqueous alteration of CM chondrites, a review. *Geochimica et*  
663 *Cosmochimica Acta*.  
664 Urey, H. C. & Craig, M. The composition of the stone meteorites and the

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665 origin of the meteorites. *Geochim. Cosmochim. Acta* 4, 36–82 (1953).  
666 Warren, P. H. Stable-isotopic anomalies and the accretionary assemblage of  
667 the Earth and Mars: A subordinate role for carbonaceous chondrites. *Earth*  
668 *Planet. Sci. Lett.* 311, 93–100 (2011).  
669 Wasson, J. T. & Kallemeyn, G. W. K. Compositions of chondrites. *Philos.*  
670 *Trans. R. Soc. London. Ser. A, Math. Phys. Sci.* 325, 535–544 (1988).  
671 Wlotzka, F., Spettel, B., Palme, H., & Schultz, L. (1989). Two new CM  
672 chondrites from Antarctica: Different mineralogy, but same chemistry.  
673 *Meteoritics*, 24, 341.  
674 Yabuta, H. et al. The insoluble carbonaceous material of CM chondrites: A  
675 possible source of discrete organic compounds under hydrothermal conditions.  
676 *Meteoritics & Planetary Science* vol. 42 <http://meteoritics.org> (2007).  
677 Zimm, B. H. The scattering of light and the radial distribution function of  
678 high polymer solutions. *J. Chem. Phys.* 16, 1093–1099 (1948).  
679 Zandanel, A. E. (2021). Fluid-rock interactions on icy moons (Doctoral  
680 dissertation, Université Grenoble Alpes [2020-....]).  
681 Zolensky, M. E. et al. Mineralogy of Tagish Lake: An ungrouped type 2  
682 carbonaceous chondrite. *Meteorit. Planet. Sci.* 37, 737–761 (2002).  
683 Zolotov, M. Y., Mironenko, M. V., & Shock, E. L. (2006). Thermodynamic  
684 constraints on fayalite formation on parent bodies of chondrites. *Meteoritics*  
685 *& Planetary Science*, 41(11), 1775–1796.