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What is the meaning of hydrogen-to-carbon ratio determined in Archean organic matter?

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25

26 **Abstract**

27 The search for hydrocarbon molecular biomarkers in Archean metasediments is
28 of prime importance for deciphering the early evolution of life. Suitable criteria
29 are required to identify promising targets for further molecular biomarkers.
30 Possible criteria include the Hydrogen-to-Carbon (H/C) atomic ratio used as a
31 proxy of the aliphatic content of the kerogen matrix. However, H/C ratio values
32 exhibit large variation in Archean kerogens and their significance remains poorly
33 understood. In this study, we thus investigate the significance of the H/C ratios of
34 Archean kerogens by combining elemental analyses, Nanoscale Secondary Ion
35 Mass Spectrometry (NanoSIMS), Rock-Eval pyrolysis and Raman spectroscopy.
36 First, NanoSIMS investigations show the H/C ratio of kerogen can be
37 compromised by residual minerals. In addition, Rock-Eval pyrolysis underlines
38 the fact that thermal cracking of Archean kerogens does not just release
39 hydrocarbon covalently linked to the macromolecular network but also a complex
40 mixture of organic pools distinguished by their thermal maturity. Therefore, the
41 H/C ratio alone cannot be used to probe the preservation of aliphatic compounds
42 bound to kerogen since it can be biased by the presence of (i) residual bitumen, as
43 well as (ii) refractory organic matter in secondary hydrothermal veins whose
44 syngeneicity is debatable. Rock-Eval pyrolysis then provides a useful and
45 complementary method to check the significance of H/C atomic ratio as a proxy
46 for hydrocarbon preservation in Archean kerogens.

47

48 **Keywords: Bitumen, Carbonization, Early life, Kerogen, NanoSIMS,**
49 **Precambrian, Raman, Rock-Eval pyrolysis**

50

51 **1. Introduction**

52

53 The origin of the oldest traces of life on Earth has been investigated through
54 chemical and thermal degradation of organic matter (OM) from Archean silicified
55 sediments (Brocks et al., 1999, 2003a; Marshall et al., 2007; Ventura et al., 2007;
56 Derenne et al., 2008). In addition to the numerous debates about the syngeneity
57 of putative molecular biomarkers (Marshall et al., 2007; Rasmussen et al., 2008;
58 French et al., 2015), the preservation of aliphatic moieties in OM from Archean
59 silicified sediments remains an open issue (Bourbin et al., 2012a). Thus, French
60 et al. (2015) highlighted the need to identify promising targets for further
61 hydrocarbon biomarker investigation by combining various approaches such as
62 elemental analyses, Raman spectroscopy and Rock-Eval pyrolysis.

63

64 In contrast to soluble hydrocarbons thought to be highly sensitive to
65 contamination, hydrocarbons released through the thermal cracking of covalent
66 bonds of the insoluble OM, the so-called kerogen macromolecular structure, are
67 considered syngenetic (Brocks et al., 2003b; Marshall et al., 2007; Derenne et al.,
68 2008). Because of thermal alteration extending to greenschist/amphibolite facies
69 metamorphism in Archean metasediment (Westall et al., 2006; Sugitani et al.,
70 2007; 2015; Delarue et al., 2016), the macromolecular network of Archean
71 kerogens is often depleted in aliphatic moieties (Bourbin et al., 2012a) as

72 reflected by Hydrogen-to-Carbon (H/C) atomic ratios mostly below 0.3 (Hayes et
73 al., 1983; Marshall et al., 2007). Nevertheless, several studies indicated that
74 some Archean kerogens can also be characterized by H/C atomic ratios higher
75 than 0.3, reaching values up to 0.6 (Hayes et al., 1983; Marshall et al., 2007;
76 Derenne et al., 2008; French et al., 2015; Ferralis et al., 2016). A H/C atomic ratio
77 up to 0.6 in kerogen from the 3.45 Gyr-old Warrawoona Formation (Derenne et
78 al., 2008) has been considered inconsistent with the prehnite-pumpellyite and
79 lower greenschist facies metamorphism undergone by the host rock (Marshall et
80 al., 2007). This interpretation points toward the presence of aliphatics that do not
81 belong to the Archean kerogen. Thus, additional H source(s) may have
82 compromised the use of H/C atomic ratio as an indicator of aliphatic hydrocarbon
83 covalently linked to the kerogen matrix. Moreover, the syngeneity of additional
84 hydrocarbon sources can be questioned, because only hydrocarbons linked to the
85 kerogen are definitely considered as syngenetic, as stressed above.

86

87 As a screening tool to depict OM quality, Rock-Eval pyrolysis provides
88 quantitative information about the composition of OM through the Total Organic
89 Carbon (TOC) content and the Hydrogen and Oxygen Indices (HI and OI), the
90 latter two being correlated with H/C and O/C ratios, respectively (Espitalié et al.,
91 1977; 1985a; 1985b; Peters, 1986). Beyond these parameters, Rock-Eval pyrolysis
92 also provides information to characterize source/reservoir rocks and kerogens as
93 part of petroleum exploration. Thus, S1 peaks (effluents released during an
94 isothermal heating at 300°C) are widely recognized as being related to free and
95 adsorbed compounds whereas S2 peaks (effluents released during pyrolysis above

96 300°C) are usually attributed to the thermal cracking of insoluble OM (Romero-
97 Sarmiento et al., 2016). However, (i) solid bitumen, i.e. insoluble OM formed
98 during the solidification of generated bitumen (Curiale, 1986; Jacob, 1989; Sanei
99 et al., 2015), and (ii) heavy bitumen can yield significant amounts of
100 hydrocarbons in the S2 peak, especially in the 350-450°C range (Delvaux et al.,
101 1990; Grundman et al., 2012; Jarvie, 2012; Han et al., 2015; Hackley and
102 Cardott, 2016). Thus, an S2 peak may be produced by the thermal cracking of a
103 composite organic mixture consisting of kerogen, solid bitumen and heavy
104 bitumen which can bias HI determination but also the quantitative assessment of
105 the thermal maturity of kerogen through the Rock-Eval-derived TpkS2
106 parameter, the temperature corresponding to the maximum release of
107 hydrocarbons during pyrolysis of kerogen (Espitalié, 1986; Behar et al., 2001).

108 A large part of Archean metasediments underwent hydrothermalism leading to
109 their induration through early silicification, which drastically reduced rock
110 porosity (Ledevin et al., 2014). Silicification may have then limited OM migration
111 during thermal alteration provided that silicification was nearly
112 contemporaneous with sedimentary OM deposition on Archean seafloors. If
113 correct, Archean silicified metasediments should act as a source-reservoir system
114 possibly containing a mixture of kerogen, solid bitumen and heavy bitumen,
115 which may in turn explain why some Archean OM have high H/C atomic ratios
116 that seem at odds with their thermal alteration. However, such an issue remains
117 undocumented although Rock-Eval pyrolysis has been used to characterize
118 Archean OM, focusing on the determination of the TOC content, the HI index and
119 the TpkS2 (Brocks et al., 2003b, Spangenberg and Frimmel, 2004; Marshall et

120 al., 2007; French et al., 2015). Thus, Brocks et al. (2003) reported that pyrolysis
121 of ca. 2.7 Gyr-old kerogen did not yield enough hydrocarbons to provide reliable
122 HI and TpkS2 values, in line with the low H/C ratio usually observed in Archean
123 kerogens. To date, Rock-Eval pyrolysis has not been applied to Archean kerogens
124 exhibiting unusually high H/C ratio (in comparison to most Archean kerogens),
125 although a careful analysis of the pyrograms would help in determining whether
126 the aliphatic hydrocarbons are covalently linked to the kerogen macromolecular
127 network.

128

129 Our purpose was therefore to study the significance of the H/C atomic ratio
130 determined on isolated Archean OM, exploring the occurrence of additional H
131 sources. To this end, isolated Archean OM samples were investigated by Rock-
132 Eval pyrolysis. In addition, Nanoscale Secondary Ion Mass Spectrometry
133 (NanoSIMS) was performed on selected isolated Archean OM characterized by
134 distinct H/C ratios to check whether H/C atomic ratios were biased by H in
135 remaining minerals. Finally, the syngeneity of additional H sources was
136 addressed using Raman spectroscopy.

137

138 **2. Material and Methods**

139 **2.1. Studied sites**

140

141 Organic matter was isolated from 12 Archean cherts (Table 1). Seven Farrel
142 Quartzite samples (GGR2, GRW10, ORW9, GFWEX1-1b, MGTKS1up, MGTKS1
143 and MGTKS3 samples; 3.0 Ga; Table 1) were collected from the Goldsworthy

144 greenstone belt in the Pilbara Craton, Western Australia. Three samples
145 (GFWEX1-1b, MGTKS1 up and MGTKS1) are bedded black chert and contain
146 microfossils (Sugitani et al., 2007; Delarue et al., 2017; Tartèse et al., 2017). They
147 are assumed to have been deposited in a shallow evaporitic basin with input of
148 hydrothermal fluids (Sugahara et al., 2010). GGR2 is a black chert interbedded
149 with sandstone from the lower unit of the Farrel Quartzite. ORW9 and GRW10
150 are laminated black cherts from the cherty succession, which conformably
151 overlies the Farrel Quartzite that is assigned to the Cleaverville Formation.

152 The 99SA07 chert (3.3 Ga; Table 1) was sampled in the Barberton greenstone
153 belt, Onverwacht Group, located in the upper part of the Josefsdal Valley, South
154 Africa. The Josefsdal chert sample consists of silicified volcanoclastic sediments.
155 It is laminated and contains phyllosilicate grains and silica veins (Westall et al.,
156 2006).

157 The 07SA22 chert (3.4 Ga; Table 1) was sampled in the Barberton greenstone
158 belt, South Africa. It consists of silicified detrital sediment comprising volcanic
159 grain, fluid inclusions, and CM floccules (Bourbin et al., 2012b).

160 The 4 of 03/08/85 chert (3.4 Ga; Table 1) was collected in the Warrawoona Group,
161 Pilbara Craton, Marble Bar Greenstone Belt, Western Australia. It mainly
162 consists of revealed large micro-crystalline silica grains, fractures filled with
163 quartz and OM floccules (Bourbin, 2012).

164 The microfossil-bearing Panorama chert (3.4 Ga; Table 1) has been identified in
165 the East Pilbara Terrane of the Pilbara Craton, Western Australia. This
166 formation is typically of 8–11 m thickness and is composed of various rock types,
167 including siliciclastic sedimentary rocks such as sandstone and shale, carbonates

168 (mainly bedded and stromatolitic dolomite), chert, and volcanoclastic rock
169 (Sugitani et al., 2015).

170 In addition to Archean samples, OM from the Silurian “Zalesie Nowe” chert (Holy
171 Cross Mountains, Bardo Syncline, Poland) was studied as a reference for
172 immature kerogen (Table 1). Zalesie Nowe is representative of typical Paleozoic
173 primary cherts composed of cryptocrystalline and mostly homogeneous quartz
174 with a small admixture of phyllosilicate minerals. The Zalesie Nowe chert is
175 distinctly laminated and consists of well-defined, horizontally extended
176 undulating laminae that are 10–40 cm thick and composed of amorphous dark
177 brown to brownish-red organic material. OM has been identified mostly as fossil
178 remnants of algae and benthic cyanobacterial mats. Graptolites indicate a
179 Llandovery (early Silurian) age for these samples (Kremer and Kazmierczak,
180 2005).

181

182 **2.2. Organic Matter Isolation**

183

184 Isolation of OM was performed on about *ca.* 300 g of crushed rock. Carbonates
185 were removed at room temperature using hydrochloric acid (HCl; 37%; reagent
186 grade) to minimize the formation of fluorides during hydrofluoric acid (HF)/HCl
187 maceration. Samples were then centrifuged and washed with distilled water until
188 reaching neutrality. Concentration of OM was achieved through acid maceration
189 at room temperature in a mixture of HF (40%, reagent grade) and HCl (2/1, v/v;
190 reagent grade). Samples were centrifuged and washed with distilled water to
191 reach neutrality. Neoformed fluorides were then degraded using HCl (37%;

192 reagent grade) at 60°C (24 hours). After HCl hot acid maceration, the isolated
193 OM matter was centrifuged/washed with distilled water until reaching
194 neutrality. Finally, samples were air-dried at 60°C after final rinsing in acetone.

195

196 **2.3. Elemental analyses and Rock-Eval pyrolysis**

197

198 Bulk elemental analyses for carbon (± 0.4 wt.%) and hydrogen (± 0.2 wt.%)
199 contents were conducted by the SGS Company using thermal conductivity
200 according to ASTM D 5294.

201

202 Isolated OM was analyzed using Rock-Eval 6 (Vinci Technologies) following the
203 standard pyrolysis protocol described in Behar et al. (2001). Briefly, pyrolysis is
204 performed in a N₂ atmosphere and comprises two steps of pyrolysis, first an
205 isothermal phase held for 3 minutes followed by a rise in pyrolysis temperature
206 from 300 to 650 °C at a rate of 25°C.min⁻¹. After pyrolysis, the residual material
207 was then heated from 300 to 800 °C under purified air in an oxidation oven in
208 order to calculate TOC value (see Behar et al., 2001 for further details about
209 calculation procedure). During pyrolysis, the amounts of released effluents,
210 considered as hydrocarbons (HC) were continuously quantified by a flame
211 ionization detector [S1 and S2, for the first and second pyrolysis steps,
212 respectively, in mg HC/g of sample] while released CO and CO₂ were
213 continuously and simultaneously monitored by infrared detectors during both
214 pyrolysis (S3CO and S3CO₂) and combustion (S4CO and S4CO₂). The
215 quantification of the amounts of effluents led to the determination of the TOC

216 (wt.%) and of the Hydrogen Index (HI, defined as $S_2 \times 100 / \text{TOC}$, in mg HC/g of
217 TOC). The pyrolysis temperature associated with the maximum release of
218 hydrocarbons, called “Tpks₂” was determined. Note that we used Tpks₂ rather
219 than T_{max} (T_{max}= Tpks₂– ΔT_{max}; Behar et al., 2001). For comparison, a
220 ΔT_{max} of ca. 40 was used to turn T_{max} values from the literature into Tpks₂
221 values (Boussafir et al., 2012).

222

223 **2.4. Raman microspectroscopy**

224

225 The Raman study was performed using a Renishaw inVia micro-spectrometer
226 equipped with a 532nm argon laser at 20 mW. The spectrometer was first
227 calibrated using a silicon standard before each session. For each sample analysis,
228 the laser was focused using a DMLM Leica microscope with a ×50 objective and
229 the spectra were recorded in the 1000–1900 cm⁻¹ Raman shift wavenumber
230 range. The laser power at the sample surface was kept below 1 mW to prevent
231 thermal alteration of kerogens (Everall et al., 1991).

232

233 **2.5. NanoSIMS microprobe**

234

235 The elemental composition of isolated OM was analyzed *in situ* using the
236 CAMECA NanoSIMS 50 ion microprobe at the NanoSIMS facility of the Museum
237 National d’Histoire Naturelle (MNHN) in Paris, France. For NanoSIMS
238 measurements, isolated OM were pressed and coated with 20 nm of gold. Before
239 each analysis, the sample surface was pre-sputtered using a 3 nA Cs⁺ primary

240 beam current (ES3 = 30 μm ; AS3 = 150 μm) in order to avoid surficial
241 contamination and to achieve a saturation fluence of Cs^+ , leading to constant
242 secondary ion emissions (Thomen et al., 2014).

243
244 Analyses were then carried out using a *ca.* 300 pA Cs^+ primary current on 40 μm
245 \times 40 μm areas (256 \times 256 pixels), slightly smaller than the pre-sputtered areas in
246 order to avoid pre-sputtering edge artifacts. Secondary $^{12}\text{CH}^-$, $^{12}\text{C}^{13}\text{C}^-$ and $^{12}\text{C}^{14}\text{N}^-$
247 were collected simultaneously in electron multipliers. A 15 % energy filtering was
248 used to avoid overlapping between the $^{12}\text{C}^{13}\text{C}^-$ and $^{12}\text{C}^{12}\text{CH}^-$ secondary species
249 peaks. All the NanoSIMS data were corrected for a 44 ns dead time on each
250 electron multiplier and processed using the Limage software (developed by L.
251 Nittler, Carnegie Institution, Washington DC, USA).

252
253 Areas where $^{12}\text{CH}^-$, $^{12}\text{C}^{13}\text{C}^-$ and $^{12}\text{C}^{14}\text{N}^-$ ionic species are co-emitted were selected
254 in order to minimize any effect of residual hydrogenated minerals (that would
255 only emit H but no C or N in the case of hydrated silicates, for example). In each
256 analyzed area, 4 μm^2 regions of interest (ROIs) were defined.

257
258 Note that only five out of the eleven Archean kerogens were analysed by
259 NanoSIMS due to facility availability. These five were selected either because (i)
260 their bulk H/C atomic ratio values encompass values commonly reported for
261 Archean kerogens or (ii) their anomalously high H/C atomic ratio values were
262 assumed to result from the presence of hydrated minerals (Delarue et al., 2016).

263

264 **2.6. Scanning Electron Microscopy**

265

266 Isolated OM from the Panorama sample was resuspended in ethanol that was
267 then pipetted and filtered on a polycarbonate filter (10 μm pore size). The
268 polycarbonate filter was then directly gold coated (20 nm thick). Observations
269 were performed with a TESCAN VEGA II SEM operating with an accelerating
270 voltage of 15 kV at the Museum National d'Histoire Naturelle (MNHN) facility.

271

272 **3. Results and Discussion**

273 **3.1. Hydrogen-to-Carbon ratios determined on isolated Archean organic** 274 **matter**

275

276 In the present set of studied isolated OM, H/C atomic ratios determined either by
277 bulk analysis or using NanoSIMS range between 0.15 and 1.35 (Table 1). These
278 values encompass H/C values usually reported on Archean kerogens (Hayes et
279 al., 1983; Marshall et al., 2007; French et al., 2015; Ferralis et al., 2016). TOC
280 values determined through Rock-Eval pyrolysis range between 3.7 and 51.0 wt.%
281 (Table 1). Most of these values are close to those determined through elemental
282 analyses (Delarue et al., 2016) except for GRW10 and GFWEX1-1b, for which
283 Rock-Eval-derived TOC values are nearly half those previously determined using
284 elemental analysis. This may be related to the heterogeneity of isolated OM in
285 the test sample. In addition, the lowest TOC values (below 25%; Table 1)
286 exhibited by some samples indicate that the acid treatment was not always
287 efficient in removing the mineral matrix from the corresponding cherts. In these

288 cases, H/C ratio may be biased by some contribution of H originating from
289 residual hydrogenated mineral(s), especially neoformed fluorides (Durand, 1980).
290 By excluding mineral phases using molecular ions strictly related to OM, we
291 obtain a linear relationship between $^{12}\text{CH}/^{12}\text{C}^{13}\text{C}$ ionic ratio and H/C ratio for
292 the MGTKS3, 99SA07 and MGTKS1 samples (Fig. 1). This correlation suggests
293 that the H/C ratio (ca. 1.35) of the 07SA22 isolated OM is largely overestimated
294 (up to 800%) by residual hydrogenated minerals, as previously suspected
295 (Delarue et al., 2016). In addition, the very low H/C ratio (0.15) computed by
296 NanoSIMS is compatible with the very low HI determined by Rock-Eval
297 pyrolysis, suggesting, in turn, that the HI value is not biased by these residual
298 minerals.

299

300 Furthermore, based on this correlation, the measurement of the $^{12}\text{CH}/^{12}\text{C}^{13}\text{C}$ -
301 ionic ratio in the 4 of 03/08/85 isolated OM sample leads to a H/C ratio of ca.
302 0.64(Fig. 1). This value is consistent with the one previously determined by bulk
303 elemental analysis on another sample from the Warrawoona Formation
304 (PPRG006; H/C = 0.62; Derenne et al., 2008). Such a high H/C ratio has been
305 suggested to be related to a significant contribution of aliphatic moieties linked to
306 the kerogen matrix (Derenne et al., 2008). However, Marshall et al. (2007)
307 questioned the origin of these compounds because the metamorphic grade
308 undergone by the Warrawoona Formation (prehnite-pumpellyite to lower
309 greenschist) may be too high to preserve such large amounts of aliphatics linked
310 to the kerogen matrix. In the following, we used Rock-Eval pyrolysis to track the
311 origin of hydrocarbons released upon pyrolysis of isolated Archean OM.

312

313 **3.2. The “apparent” low thermal maturity of Isolated Archean organic**
314 **matter: an influence of residual bitumen**

315

316 For 7 out of the 10 studied Archean OM, HI-values are low, ranging between 2
317 and 22 mg HC/g of TOC (Table 1). Such values are in the same range as those
318 reported by Brocks et al. (2003b) and they are in line with the low H/C ratio
319 commonly observed in Archean kerogens. In contrast, the isolated OM from
320 GRW10, MGTKS1 and 4 of 03/08/85 present rather high HI values of 65, 82 and
321 217 mg HC/g of TOC, respectively (Table 1). Moreover, these isolated Archean
322 organic matter samples are the same as those which exhibit the highest H/C
323 values (determined by elemental analysis and/or NanoSIMS), ranging from
324 between 0.55 to 0.85 (Table 1).

325 The Zalesie Nowe kerogen is characterized by Rock-Eval parameters (HI=240 mg
326 HC/g TOC and $T_{pkS2} = 478$ °C; Table 1) and an S2 Gaussian curve (Fig. 2)
327 commonly observed for the thermal release of hydrocarbonaceous compounds
328 covalently linked to the kerogen matrix of thermally-altered OM (Behar et al.,
329 2001; Grundman et al., 2012). Note that this T_{pkS2} is close to those previously
330 determined on this Silurian chert ($T_{pkS2} = 482-488$ °C, i.e. $T_{max} = 442-448$ °C;
331 Bauersachs et al., 2009). In contrast to this Silurian kerogen, the isolated
332 Archean OM was characterized by pyrograms displaying shoulders and/or
333 multimodal release of hydrocarbons (Fig. 2). Most of the isolated Archean OM
334 exhibits a relatively high S1 peak followed by a less intense and large S2 peak
335 with a maximum release of hydrocarbons ranging between ca. 326 and 448°C

336 (Fig. 2, Table 1). Such low TpkS2 values are at variance with the metamorphism
337 up to greenschist metamorphism facies undergone by the host rocks. Indeed, the
338 latter is associated with TpkS2 values higher than ca 475°C (Tmax = 436-464°C;
339 Spangenberg and Frimmel, 2004). These pyrolytic features should then be
340 regarded as anomalies.

341 Contamination by oil-based drilling mud lubricant is classically invoked to
342 explain large S1 and S2 shoulders (Peters, 1986). However, this cause is unlikely
343 to explain the high S1 peak and the release of hydrocarbons at low S2 pyrolysis
344 temperature in the presently studied rocks as they were sampled from outcrop.

345 High S1 and especially S2 shoulders at low pyrolysis temperature may also be
346 caused by the presence of indigenous thermolabile OM, such as residual heavy oil
347 (Clementz, 1979) or solid bitumen (Sanei et al., 2015). In the following, the term
348 “thermolabile” is used to account for the OM which is cracked at rather low
349 temperature but which does not belong to the macromolecular network of the
350 kerogen. Indeed, we cannot preclude the existence of non-volatile solid bitumen,
351 the existence of which cannot be addressed by studying isolated OM. Indeed,
352 further investigations studying OM in its mineralogical context are required (e.g.
353 in situ approach; Bernard et al., 2012; Sanei et al., 2015). Although the
354 aforementioned coexistence of solid bitumen is not excluded, S2 shoulders can be
355 assigned to the presence of residual bitumen as evidenced by SEM in the
356 Panorama sample. Indeed, the Panorama isolated OM is an ideal target when
357 looking for non-thermally degraded bitumen because it underwent a mild-
358 thermal alteration in comparison to other studied Archean OM, as revealed by
359 comparison between Raman spectra (Delarue et al., 2016).

360 SEM imaging of the Panorama isolated OM reveals the existence of bitumen
361 droplets as revealed by surface degassing features caused by the SEM beam (Fig.
362 3a). Despite the high fluorescence level rendering the Raman spectra less
363 accurate (Fig. 3b), the bitumen droplets share a similar structural order with the
364 surrounding OM (Fig. 3b), consistent with previous Raman spectra acquired on
365 other OM samples from the Strelley Pool Formation (Lepot et al., 2013). In turn,
366 we interpret these elements as showing that the bitumen underwent the same
367 degree of thermal alteration as the host rock. It may thus be syngenetic, even
368 though bitumen recovered in Archean rocks is commonly assigned to
369 contamination. However, it also implies that residual bitumen and related
370 hydrocarbons can bias the determination of the H content of the macromolecular
371 structure of the Archean kerogens.

372 From a molecular point of view, and in contrast to previous studies stating that a
373 first pyrolysis step at low temperature (ca. 300 to ca. 350°C) is enough to release
374 thermolabile compounds (Brocks et al., 2003b; Marshall et al., 2007; Derenne et
375 al., 2008), Rock-Eval pyrograms show that this first pyrolysis step is not
376 systematically sufficient to ensure (i) the thermal desorption of the whole
377 residual bitumen content, which can be trapped or adsorbed within/onto the
378 surface of kerogen (Oehler et al. 1977), or (ii) the cracking of solid bitumen.
379 Indeed, release of thermolabile OM still occurs at pyrolysis temperatures up to
380 400°C, when using the thermal degradation program of the Rock-Eval device.
381 This echoes previous observations indicating that heavy fractions of petroleum
382 release hydrocarbons in the 350 to 450°C range (Clementz, 1979). Considering
383 that the study of the molecular composition of Archean hydrocarbons by

384 analytical pyrolysis was performed using a faster rise in pyrolysis temperature,
385 we suggest that the energy provided by pyrolysis at 300-350°C was not enough to
386 release the entire content of thermolabile hydrocarbons. Hence, the molecular
387 content observed at higher pyrolysis and in a faster rise in pyrolysis temperature
388 can encompass hydrocarbons originating from both (i) the pyrolysis of
389 thermolabile compounds and (ii) the thermal cleavage of the kerogen matrix.

390

391 **3.3. Evidence for multiple phases of OM by Rock-Eval pyrolysis**

392

393 In addition to the presence of S2 shoulders occurring at low pyrolysis
394 temperature, the pyrograms from the isolated Archean OM are characterized by
395 the release of hydrocarbon effluents at higher pyrolysis temperature, as reflected
396 by one or two well-defined S2 peaks ranging from between 471 and 586°C (Fig.
397 2). In total, 7 out of 10 isolated Archean OM samples are characterized by the
398 release of hydrocarbons in a narrow pyrolysis temperature range (576 to 586°C).
399 Such high pyrolysis temperatures are in line with the metamorphic grade
400 undergone by these Archean rocks, ranging between prehnite-pumpellyite to
401 greenschist facies (Marshall et al., 2007; Sugitani et al., 2007). They correspond
402 to the thermal cleavage of kerogen-bound hydrocarbon. Nonetheless, multiple
403 generation of hydrocarbons upon pyrolysis has also been observed in the GRW10,
404 MGTKS1up, MGTKS3 and the 4 of 03/08/85 isolated OM (Fig. 2). The multimodal
405 release of hydrocarbons points towards the existence of two distinct pools of OM
406 generating hydrocarbons at high pyrolysis temperature. This interpretation is
407 supported by the existence of two different types of OM within the GRW10 chert,

408 as revealed by both microscopy and *in situ* Raman spectroscopy (Figs. 3c,d)
409 showing that OM dispersed within the mineral matrix and that from
410 hydrothermal veins do not exhibit similar Raman first-order spectrum.
411 Indeed, in thermally-altered OM, the ratio between the intensities of the D and G
412 bands (I_D/I_G) has been shown to describe the evolution of the structural order of
413 OM during thermal alteration (Oberlin, 1984; Jehlicka and Bény, 1992; Jehlicka
414 et al., 2003; Rouzaud et al., 2015). The Raman spectrum determined on OM
415 contained within a mineral matrix is typically observed in OM that has
416 undergone thermal alteration up to 320-350°C (Fig. 3d; Lahfid et al., 2010) and
417 is, therefore, consistent with the greenschist facies metamorphism undergone by
418 the metasediments from the Farrel Quartzite (Sugitani et al., 2007). In
419 comparison to this OM, which exhibits an I_D/I_G ratio of ca. 1.5, OM from a
420 hydrothermal vein presents a higher I_D/I_G ratio (ca. 2.0; Fig. 3d). Such a Raman
421 spectrum is generally assigned to a metamorphic peak temperature above 400°C
422 (Beyssac et al., 2002), suggesting that the “hydrothermal“ OM has undergone a
423 higher thermal alteration than OM from the mineral matrix. Note that in the
424 following, we distinguish between primary hydrothermalism, i.e.
425 contemporaneous hydrothermal activity (Westall et al., 2015a, 2015b), and
426 secondary hydrothermalism occurring after rock formation. In addition to higher
427 thermal alteration possibly related to secondary hydrothermalism, other factors
428 may also imply changes in the structural order of OM. Studying OM from the 2.0
429 Gyr-old Zaonega Formation, Van Zuilen et al. (2012) showed that graphite films
430 along mineral surfaces can even be formed under greenschist metamorphism
431 facies usually associated with OM characterized by a lower structural order. For

432 these authors, peculiar geological conditions, such as hydrothermal circulation,
433 can imply local changes in the structural order of OM. Although not fully
434 understood, such local processes also likely explain the observed difference in the
435 structural order between OM from the sedimentary matrix and from secondary
436 hydrothermal veins.

437 Since OM from hydrothermal veins does not have the same structural order as
438 OM from the sedimentary matrix, it is not possible to draw conclusions as to
439 syngeneity of the two types. In turn, and in the absence of unequivocal criteria
440 to determine its syngeneity, the occurrence of OM originating from
441 hydrothermal veins must be taken into account to avoid any bias in the
442 determination of the H/C atomic ratio of the kerogens related to OM from the
443 main mineral matrix, especially in hydrothermally-altered metasediments such
444 as Archean geological records. Therefore, characterization of the molecular
445 content of Archean kerogens through thermal degradation should be performed
446 on selected areas of the sample that are devoid of hydrothermal veins.

447

448 **4. Conclusion**

449 Rock-Eval pyrolysis of isolated OM from several Archean samples reveals the co-
450 occurrence of various OM pools characterized by different thermal stabilities. In
451 contrast to non-metamorphosed kerogen, as exemplified by the Zalesie Nowe
452 kerogen, pyrolysis of the Archean OMs shows that they do not consist solely of
453 hydrocarbons linked to the macromolecular structure of insoluble OM.
454 Accordingly, the H/C atomic ratios determined on isolated Archean OM do not
455 solely correspond to syngenetic hydrogenated organic compounds linked to the

456 kerogen matrix. Instead, they can also reflect the H composition of minerals as
457 revealed by NanoSIMS, of thermally labile residual bitumen and/or solid
458 bitumen, and of OM from secondary hydrothermal veins generating hydrocarbons
459 at high pyrolysis temperature, for which syngeneity is still an open issue.
460 Because of the low amount of hydrocarbons linked to the syngenetic Archean
461 kerogen matrix, any residual trace of bitumen or OM from secondary
462 hydrothermal veins can bias the use of the H/C ratio associated with the
463 macromolecular network. This study shows that Rock-Eval pyrolysis provides a
464 useful tool (i) to evaluate the significance of H/C atomic ratio as a proxy for
465 hydrocarbon preservation in Archean kerogens, and also (ii) to better constrain
466 the source of hydrocarbons released during thermal analytical degradation
467 providing in turn, a frame for future molecular investigations.

468

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477 anonymous reviewer for their insightful comments.

478

479 **Figure captions**

480 **Figure 1:** Linear relationship between the $^{12}\text{CH}/^{12}\text{C}^{13}\text{C}$ ionic ratio determined
481 with NanoSIMS and bulk H/C atomic ratio determined with bulk analyses. Using
482 the linear relationship between the $^{12}\text{CH}/^{12}\text{C}^{13}\text{C}$ molecular ionic ratio and bulk
483 H/C atomic ratio, the H/C atomic ratio values of sample 07SA22 (ca 0.15) and of
484 sample 4 of 03/08/85 (ca 0.64) kerogen samples were computed. Error bars
485 represent the standard errors related to the mean $^{12}\text{CH}/^{12}\text{C}^{13}\text{C}$ ionic ratio
486 determined on selected regions of interest (ROI).

487

488 **Figure 2:** Rock Eval pyrograms of Silurian (0.42 Gyr-old) and Archean (3.0 to 3.5
489 Gyr-old) silicified cherts. Left column shows the whole pyrograms and the
490 corresponding TpkS2 values (bold character). Right column focuses on the
491 hydrocarbon released/generated during the second step of pyrolysis involving a
492 rise in pyrolysis temperatures from 300 to 650 °C at a rate of 25°C.min⁻¹. TpkS2
493 values are indicated in bold character whereas other pyrolysis temperatures
494 associated with a release of hydrocarbons are indicated in regular character.

495

496 **Figure 3:** (a) SEM image of a bitumen droplet recovered within the Panorama
497 kerogen. (b) Raman spectra measured on the bitumen droplet presented in Fig 3a
498 and on surrounding OM. (c) GRW10 thin section photography illustrating the
499 existence of hydrothermal veins cutting siliclastic successive deposits (mineral
500 matrix). (d) Raman spectra determined on OM from the mineral matrix (red
501 Raman spectra) and from the hydrothermal vein (blue Raman spectra) observed
502 within the GRW10 thin section presented in (c)

503

504

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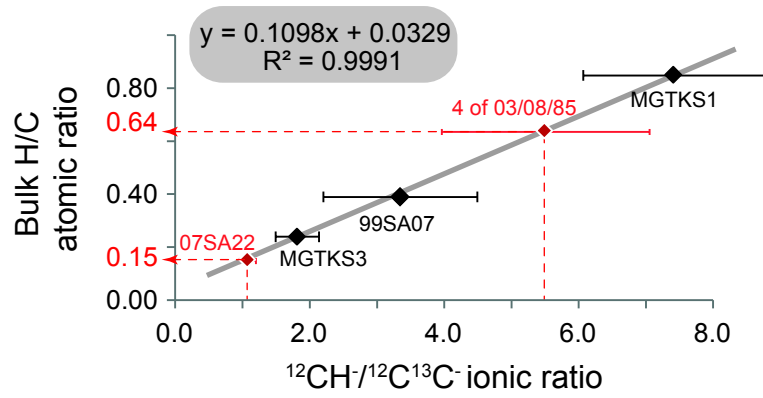
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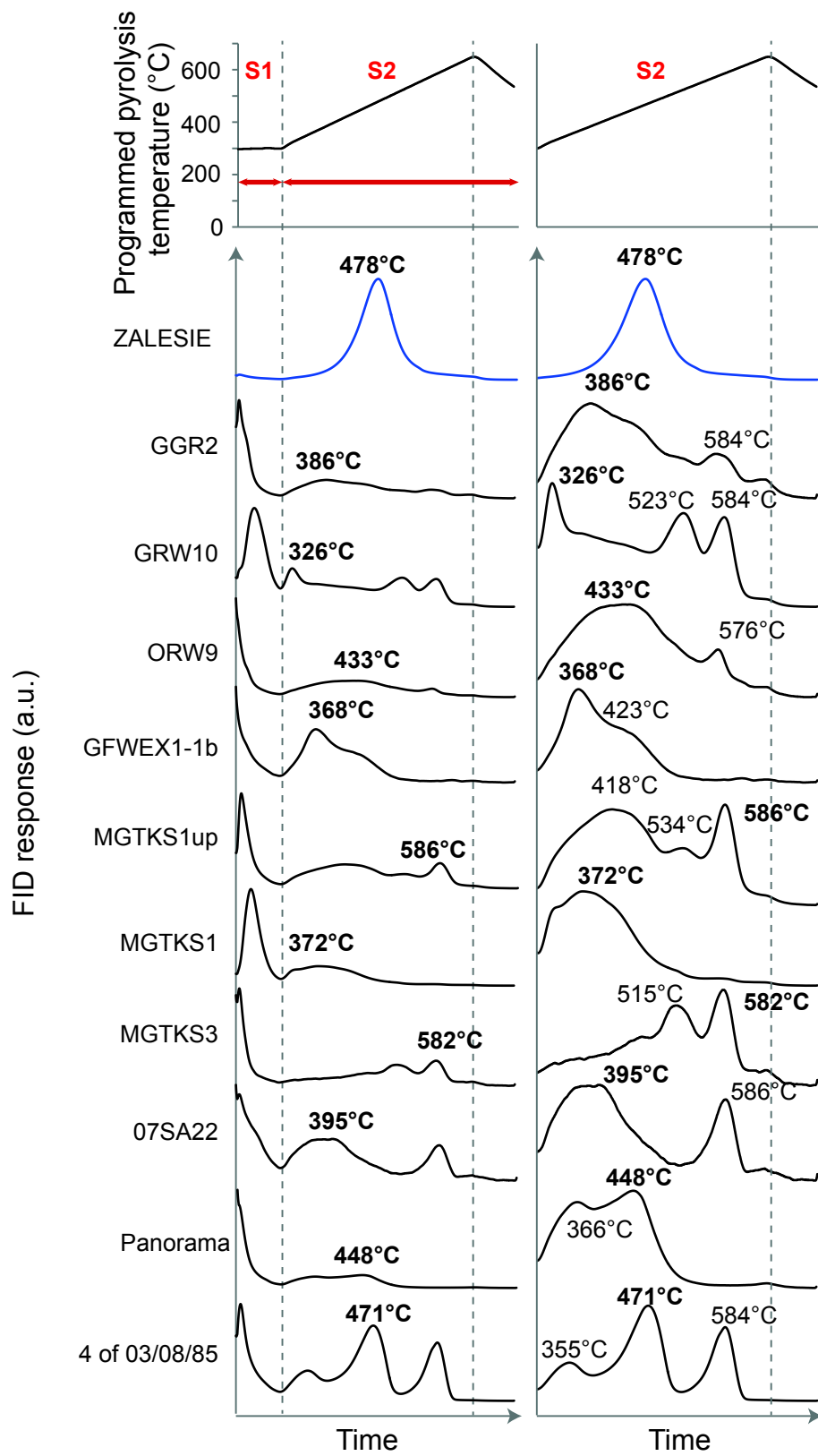
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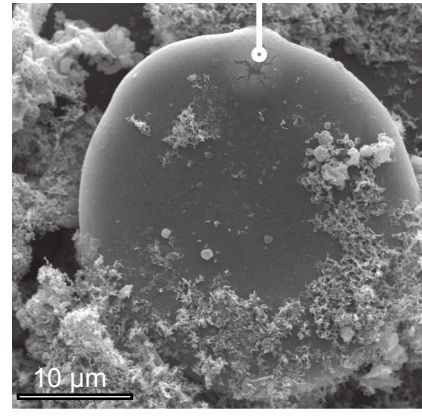
Table 1: Rock-Eval-derived parameters (S1, S2, TpkS2, TOC and HI) and H/C atomic ratios determined on Silurian (0.42 Gyr-old) and Archean (3.0 to 3.5 Gyr-old) silicified cherts. H/C ratios were determined with bulk elemental analysis and with NanoSIMS using the ratio between the $^{12}\text{C}^{13}\text{C}^-$ and $^{12}\text{C}_2^-$ molecular ionic species. “n.d.” indicates that parameter was not determined.

Sample name	Geological Formation, country	Age (Gyr)	S1 (mg/g)	S2 (mg/g)	TpkS2 (°C)	TOC (w.%)	HI (mg/g TOC)	H/C (Bulk analysis)	$^{12}\text{C}^{13}\text{C}^- / ^{12}\text{C}_2^-$	H/C (NanoSIMS)
ZALESIE	Zalesie Nowe, Poland	0.42	2.6	122.5	478	51.1	240	0.95	n.d.	n.d.
GGR2	Farrel Quartzite, Australia	3.0	0.5	0.9	386	18.5	5	0.42	n.d.	n.d.
GRW10	Farrel Quartzite, Australia	3.0	12.0	19.1	326	29.5	65	0.55	n.d.	n.d.
ORW9	Farrel Quartzite, Australia	3.0	0.5	1.1	433	20.7	5	0.38	n.d.	n.d.
GFWEX1-1b	Farrel Quartzite, Australia	3.0	1.0	3.0	368	17.1	18	0.31	n.d.	n.d.
MGTKS1up	Farrel Quartzite, Australia	3.0	2.4	5.5	586	40.8	14	0.30	n.d.	n.d.
MGTKS1	Farrel Quartzite, Australia	3.0	36.1	30.8	372	37.7	82	0.85	7.4	0.85
MGTKS3	Farrel Quartzite, Australia	3.0	0.4	0.9	582	46.9	2	0.24	1.8	0.23
99SA07	Kromberg, South Africa	3.3	n.d.	n.d.	n.d.	n.d.	n.d.	0.39	3.4	0.40
07SA22	Hoeggonoeg, South Africa	3.4	0.3	0.7	395	17.6	4	1.35	1.1	0.15
Panorama	Strelley Pool, Australia	3.4	4.6	5.4	448	24.2	22	n.d.	n.d.	n.d.
4 of 03/08/85	Warrawoona, Australia	3.5	2.3	8.0	471	3.7	217	n.d.	5.5	0.64

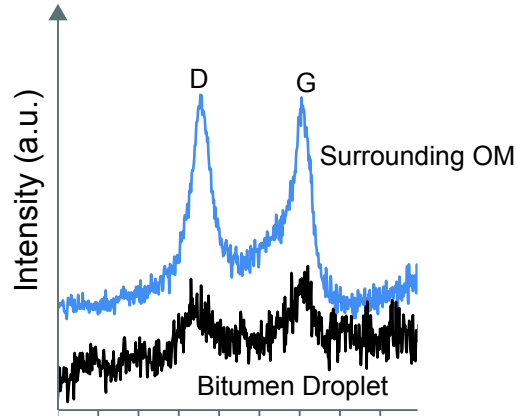




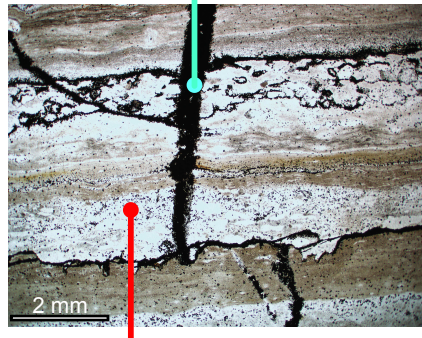
a. Surface degassing feature



b.



c. Hydrothermally altered OM



d.

