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► To cite this version:

Frédéric Delarue, Thanh Thuy Nguyen Tu, Rémi Duhamel, Céline Paris, François Baudin. Chemical degradation of thermally altered silicified organic matter during acid maceration: A case study from the Lower Devonian Rhynie chert. *Organic Geochemistry*, 2021, 156, pp.104246. 10.1016/j.orggeochem.2021.104246 . hal-03247567

HAL Id: hal-03247567

<https://hal.science/hal-03247567v1>

Submitted on 17 Nov 2021

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1 **Chemical degradation of thermally altered silicified organic matter during acid**
2 **maceration: a case study from the Lower Devonian Rhynie chert**

3

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16

17 **ABSTRACT**

18 The effect of standard acid maceration on organic matter (OM) from ancient silicified
19 sediments remains undocumented. Early silicification favours preservation of organic
20 moieties against thermal alteration over time. In this study, we investigated the effects of acid
21 maceration on the structure of OM isolated from the Lower Devonian Rhynie chert. The
22 structure of OM was investigated by combining Rock-Eval pyrolysis and Raman
23 spectroscopy. Besides a loss of thermolabile organic matter owing to solvent extraction,
24 Rock-Eval pyrolysis showed that standard acid maceration also causes a loss of C-H
25 emissions at high pyrolysis temperature ($> 500\text{ }^{\circ}\text{C}$). The standard acid maceration procedure
26 was also associated with the disappearance of the D4 and D5 Raman spectrum shoulders
27 assigned to C–H bonds in aliphatics and bitumens, respectively, entrapped in the
28 macromolecular network. Taken together, Rock-Eval pyrolysis and Raman spectroscopy
29 indicate that standard acid maceration can lead to the chemical degradation of syngenetic
30 hydro-carbonaceous moieties of OM isolated from ancient silicified and thermally altered
31 sediments. In sediments having experienced early silicification, which hampers bitumen
32 migration and favours pyrobitumen formation, we suggest that novel in situ molecular
33 analytical techniques are required to provide a thorough examination of the syngenetic
34 molecular content independent of the soluble/insoluble operational definition.

35

36 **1. Introduction**

37 The chemical composition of ancient organic matter (OM) attests to turning points in
38 the evolution of life during the history of the Earth (Summons et al., 1988; Edwards et al.,
39 1997; Love et al., 2008; Duda et al., 2016; Nguyen et al., 2019; Love et al., 2020). However,
40 investigating the structural and chemical compositions of ancient OM is still a challenging
41 issue as thermal alteration during geological times results in losses of pristine molecular and

42 elemental content. Since ancient sediments and metasediments are generally depleted in OM,
43 isolation procedures have typically been employed before applying analytical techniques to
44 investigate the chemical composition of ancient OM, notably at the molecular scale.
45 Historically, in the field of organic geochemistry, isolation of organic-insoluble and mineral-
46 free OM is performed through a standard acid maceration procedure involving maceration
47 followed by successive organic solvent extractions (e.g., dichloromethane [DCM] and
48 methanol [MeOH]) and demineralisation with acid (e.g., hydrochloric [HCl] and hydrofluoric
49 [HF]). This physical and chemical maceration procedure (HMM) yields kerogen, which is
50 defined as insoluble macromolecular OM (Durand, 1980; Vandenbroucke and Largeau,
51 2007). Several investigations have suggested that acid maceration does not significantly
52 modify the structure of kerogens from ancient rocks (Larsen et al., 1989; Vandenbroucke and
53 Largeau, 2007; Aboulkas and El Harfi, 2009). However, there is contrasting evidence that
54 acid maceration of coals can lead to either a rise in carbon structural order (Zhang et al., 2016)
55 or a decrease in hydrocarbon content (Tekely et al., 1987). Moreover, Kebukawa et al. (2019)
56 demonstrated the contrasting effects of acid maceration by comparing the chemical structure
57 of bulk chondrites to their corresponding insoluble OM fractions. Insoluble OM from type 3
58 chondrite was depleted in aliphatic moieties in comparison to the bulk type 3 chondrite
59 starting material. However, the effect of acid maceration varied among the different chondrite
60 groups studied (Kebukawa et al., 2019). Thus, according to current literature, it therefore
61 seems that the chemical stability of thermally altered OM to standard acid maceration cannot
62 simply be assumed.

63 Among ancient sedimentary rocks, silicified sediments are of interest as they are
64 essential geological archives of biological evolution throughout Earth's history. However,
65 there is often very little OM remaining in these sediments and acid maceration procedures are
66 required to concentrate it before studying its molecular content. Occurring prior to cell lysis

67 and early degradation of organic matter, rapid silicification leads to a closed chemical system
68 by reducing sediment porosity (Boyce et al., 2002; Ledevin et al., 2014), which favours
69 preservation of organic remnants against thermal alteration (Alleon et al., 2016). Using
70 geochemical micrometre-scale analysis tools, it was demonstrated that some silicified
71 Precambrian organic-walled microfossils are composed of significant amounts of carbonyl,
72 phenolic, carboxylic, hydroxyl, and amide functional groups, despite being subjected to peak
73 temperatures of up to 300 °C (Alleon et al., 2016). However, standard acid maceration
74 procedures applied to ancient silicified sediments have the potential to degrade syngenetic
75 OM through solvent extraction and acid hydrolysis of bitumens and chemically labile organic
76 moieties, respectively. Such degradation, if it occurs, implies that a substantial amount of the
77 initial molecular content depicting the evolution of life, past environmental conditions, and/or
78 thermal maturation may be lost in the process. Further investigations on the effect of standard
79 acid maceration on the chemical structure of ancient thermally altered silicified OM are
80 therefore required.

81 Our aim in this study was to investigate the effect of the standard acid maceration
82 procedure on the chemical structure of ancient silicified OM. We selected the iconic Lower
83 Devonian Rhynie chert, the earliest preserved terrestrial ecosystem owing to a rapid and
84 complete silicification through siliceous hot-spring deposits (Trewin, 2003; Preston and
85 Genge, 2010). Despite the exceptional preservation of fossil plants, fungi, insects, and other
86 organisms, the overall organic carbon content of Rhynie chert is very low (Summons et al.,
87 1996). It therefore typically requires acid maceration to access the molecular signature(s). The
88 Rhynie chert therefore constitutes a case study to evaluate the impact of standard acid
89 maceration on the chemical structure of ancient thermally altered silicified OM. To this end,
90 OM was isolated according to two acid maceration procedures: (1) a high-manipulation
91 maceration (HMM), which followed the standard treatments generally applied to geological

92 samples, and (2) a low-manipulation maceration (LMM), which minimized chemical
93 degradation by avoiding organic solvents and HCl. Rock-Eval pyrolysis and Raman
94 spectroscopy were used to assess the chemical structure of the OM isolated by each
95 procedure. Comparison of the so-obtained chemical structures allowed us to estimate the
96 minimum amount of chemical degradation imparted by HMM maceration.

97

98 **2. Material and methods**

99 *2.1. The Rhynie chert*

100 Situated in Aberdeenshire (Scotland), the Rhynie chert is a Konservat-Lagerstätte. It is
101 hosted by the Dryden Flags Formation, which is characterised by a succession of Lower
102 Devonian sedimentary and volcanic rocks (Rice et al., 2002). Pragian–earliest Emsian in age
103 (407.1 ± 2.2 Ma; Mark et al., 2011), the Rhynie chert is composed primarily of
104 microcrystalline silica and was deposited as siliceous sinter from subaerial hot springs
105 systems (Rice et al., 1995).

106

107 *2.2. High- and low-manipulation maceration procedures*

108 HMM and LMM procedures were performed on similar portions of the same rock
109 sample. HMM was performed on ~30 g of crushed rock. Solvent extraction was first
110 performed on rock powder using a mixture of DCM and MeOH (2:1; v:v). Carbonates were
111 then removed at room temperature using HCl (37%; reagent grade) to minimise the formation
112 of fluorides during subsequent HF/HCl maceration. Samples were then centrifuged and
113 washed with ultrapure water until reaching neutrality. Concentration of OM was achieved
114 through acid maceration at room temperature in a mixture of HF (40%, reagent grade) and
115 HCl (2:1, v/v; reagent grade). Samples were centrifuged and washed with ultrapure water to
116 reach neutrality. Finally, HCl (37%; reagent grade) at 60 °C (24 h) was used to degrade

117 neoformed fluorides. After an additional step of solvent extraction using a mixture of DCM
118 and MeOH (2:1, v/v), the isolated OM was again centrifuged/washed with ultrapure water
119 until reaching neutrality. Samples were then air-dried at 60 °C after final rinsing in acetone.
120 Hereafter, OM isolated by the HMM procedure is referred to as OHMM.

121 LMM was performed by first fragmenting ~30 g of rock samples into ~3 g rock chips.
122 Rock chips were cleaned using ultrapure water and a mixture of DCM and MeOH (2:1, v/v)
123 and were then placed directly in a Teflon vessel filled with HF (40%, reagent grade) at room
124 temperature. After 48 h, successive centrifugation and rinsing steps using ultrapure water
125 were performed until reaching neutrality. Samples were then air-dried at 60 °C. Hereafter,
126 OM isolated by the LMM procedure is referred to as OLMM.

127

128 *2.3. Rock-Eval pyrolysis*

129 OHMM and OLMM were analysed using Rock-Eval 6 (Vinci Technologies) following
130 the standard pyrolysis protocol described in Behar et al. (2001). Performed in a N₂
131 atmosphere, Rock-Eval pyrolysis comprises two steps: an isothermal phase held for 3 minutes
132 followed by a rise in pyrolysis temperature from 300 to 650 °C at a rate of 25 °C/min. After
133 pyrolysis, the residual material was then heated from 300 °C to 850 °C under purified air in an
134 oxidation oven in order to calculate total organic carbon (TOC) value (see Behar et al., 2001
135 for further details about calculation procedure). Released hydrocarbons (HC) were
136 continuously quantified by a flame ionisation detector (S1 and S2, for the first and second
137 pyrolysis steps, respectively, in mg HC/g of sample) while released CO and CO₂ were
138 continuously and simultaneously monitored by infrared detectors during both pyrolysis
139 (S3CO and S3CO₂) and combustion (S4CO and S4CO₂). Quantification of the amount of
140 effluents led to the determination of the TOC (wt%), of the Hydrogen Index (HI, defined as
141 $S2 \times 100 / \text{TOC}$, in mg HC/g of TOC) and of the Oxygen Index (OI; defined as $S3 \times 100 / \text{TOC}$, in

142 mg CO₂/g of TOC). The pyrolysis temperature associated with the maximum release of
143 hydrocarbons, called “TpK_{S2}”, was also determined.

144

145 *2.4. Raman spectroscopy*

146 Raman spectroscopy analysis was performed using a Renishaw inVia micro-
147 spectrometer equipped with a 532 nm argon laser. The spectrometer was first calibrated using
148 a silicon standard before each session. For each sample analysis, the laser was focused using a
149 Leica microscope with a ×50 objective and the spectra were recorded in the 1000–1900 cm⁻¹
150 first order spectral window including the defect (D) and graphite (G) peaks (Fig. 1). The laser
151 power at the sample surface was kept below 1 mW to prevent thermal alteration of isolated
152 OM (Everall et al., 1991). Spectra acquisition was achieved after two iterations using a time
153 exposure of 40 s. After linear correction of the baseline between 1000 and 1900 cm⁻¹ and
154 spectra normalization, we identified Raman peaks according to the nomenclature defined in
155 Romero-Sarmiento et al. (2014).

156 The heights of the sub-bands D1 (~1365 cm⁻¹), D4 (~1285 cm⁻¹), D5 (~1445 cm⁻¹) and
157 G+D2 (~1600 cm⁻¹; Fig. 1) were then determined to compute the I_{D1}/I_{G+D2} , I_{D4}/I_{G+D2} and
158 I_{D5}/I_{G+D2} , ratios. Slopes α_{D4} (determined between 1265 and 1300 cm⁻¹ Raman shift) and α_{D5}
159 (determined between 1415 and 1445 cm⁻¹ Raman shift) were determined to geometrically
160 evaluate the expression of D4 and D5 shoulders on the D band.

161

162 **3. Results and discussion**

163 The TOC of OHMM and OLMM samples was measured to determine the efficiency
164 of rock mineralization through HMM and LMM, respectively. The TOC in all OHMM and
165 OLMM samples was low (25.4% and 27.5% respectively; Table 1) suggesting that the
166 preservation and/or neoformation of substantial mineral content had occurred during both

167 procedures. The OI was approximately 15 mg and 59 mg CO₂/g TOC in OHMM and OLMM,
168 respectively (Table 1). The higher OI in OLMM is partially explained by the higher level of
169 CO₂ emissions during the first isothermal step, showing that they are mostly related to
170 desorbable OM (Fig. 2). Such a result is in line with previous investigations on coals
171 suggesting that acid maceration can lead to a rise in oxygen content resulting possibly from
172 the neoformation of carboxylic groups replacing carboxylate through ion exchange (Larsen et
173 al., 1989). Higher levels of CO₂ emissions were also recorded for OLMM during the rise in
174 pyrolysis temperature from 300 to 650 °C (Fig. 2). In this pyrolysis temperature range, CO₂
175 emissions appeared to be independent of hydrocarbon emissions suggesting that they do not
176 correspond to the thermal cracking of the macromolecular network.

177 OHMM and OLMM isolated from the Rhynie chert were characterised by a TpkS2 of
178 481 °C and 504 °C, respectively (Table 1). In every type of kerogen, these pyrolysis
179 temperatures are commonly assigned to OM that has been subjected to high thermal
180 alteration. Consistent with high TpkS2 values, pyrolysis of OHMM and of OLMM released
181 low amounts of HC as evidenced by HI of 46 HC/g TOC and 68 mg HC/g TOC, respectively.
182 Together, high TpkS2 and low HI imply that OM from the Rhynie chert falls at the transition
183 between the oil and gas windows registered by TpkS2 ranging between 470 °C and 505 °C in
184 analogous Type III kerogens (Espitalié et al., 1986). Hydrocarbon release during Rock-Eval
185 pyrolysis was higher in OLMM than in OHMM (Table 1). The S1 value for OLMM was
186 about 320% higher than for OHMM (Table 1), which suggests that thermolabile OM was
187 more abundant in OLMM than in OHMM. This is consistent with the fact that OLMM was
188 not subjected to organic solvent extractions, which have been shown to dramatically reduce
189 S1 values (Delvaux et al., 1990). Between 300 and 350 °C, no release of hydrocarbons was
190 observed suggesting a virtual absence of residual heavy oil and/or of pyrobitumen in both
191 OHMM and OLMM (Fig. 2; Clementz, 1979; Sanei et al., 2015). The S2 curves for OHMM

192 and OLMM differ at high pyrolysis temperature ($> 500\text{ }^{\circ}\text{C}$), at which point a broad shoulder
193 is only observed in OLMM (Fig. 2). The occurrence of this thermorecalcitrant OM in OLMM
194 mostly explains its higher HI, in the absence of solvent extractions and/or hydrochloric acid
195 hydrolysis (Table 1). In turn, this suggests that standard acid maceration can lead to a
196 modification of the macromolecular chemical structure in this ancient silicified OM by
197 promoting a loss of hydrocarbonaceous moieties.

198 Determined on 15 random targets in both OHMM and OLMM, Raman spectra
199 exhibited two broad D and G+D2 bands at around 1365 cm^{-1} and 1600 cm^{-1} in each
200 preparation (Fig. 1). The D band presents a complex structure resulting from the presence of
201 several sub-bands including here, the D4, D1, and D5 bands. In addition to the contribution of
202 amorphous carbon, the D band is dominated by the D1 sub-band corresponding to the
203 breathing mode of the sp^2 aromatic ring within polyaromatic clusters and is attributed to
204 defects in these aromatic structures (Ferrari and Robertson, 2000). The D2 band corresponds
205 to defects in aromatic structure but in contrast to the D1 band, does not include amorphous
206 carbon. A distinct D2 peak (usually centered at about 1620 cm^{-1}) is mainly observed in highly
207 mature OM (Kouketsu et al. 2014) and is not observed in OM studied here. Therefore, the
208 G+D2 band is mostly related to the G band corresponding to in-plane C-C bond stretching in
209 polyaromatic layers from thermally altered materials (Marshall and Marshall, 2014). As the
210 height of the D1 band increases with temperature, the $I_{\text{D1}}/I_{\text{G+D2}}$ ratio is often used to probe the
211 structural order of OM in the course of carbonization (Table 2; Wopenka and Pasteris, 1993;
212 Quirico et al., 2005; Kouketsu et al., 2014; Delarue et al., 2016). In this study, OHMM and
213 OLMM are characterized by $I_{\text{D1}}/I_{\text{G+D2}}$ ratios of 0.58 ± 0.02 and 0.52 ± 0.02 , respectively
214 (Table 2). This result would imply a higher carbon structural order in OHMM compared to
215 OLMM, which is in agreement with previous findings indicating that standard acid
216 maceration can yield a rise in carbon structural order (Zhang et al., 2016).

217 The D band also exhibits two shoulders corresponding to the D4 (1285 cm⁻¹) and D5
218 (1445 cm⁻¹) bands (Fig. 1). The D4 peak is generally assigned to C–H bonds in aliphatics as
219 C-H in aromatics does not seem to directly contribute to the D4 region (Ferralis et al., 2016).
220 The D5 band indicates the presence of hydrocarbons trapped within the organic porosity and
221 has been detected in a few oil and gas shale samples (Romero-Sarmiento et al., 2014;
222 Rouzaud et al., 2015). In the current study, α_{D4} and α_{D5} slopes in Raman spectra were lower in
223 OLMM than in OHMM, consistent with the more pronounced D4 and D5 shoulders in the
224 Raman line of OLMM (Fig. 1; Table 2). However, the more pronounced D4 and D5 shoulders
225 in OLMM were not associated with higher I_{D4}/I_{G+D2} and I_{D5}/I_{G+D2} ratios (Table 2). This could
226 be explained by the higher carbon structural order in OHMM implying a bias in the
227 determination of I_{D4}/I_{G+D2} and I_{D5}/I_{G+D2} ratios. The occurrence of more pronounced D4 and D5
228 shoulders in OLMM indicate that OLMM is indeed enriched in hydrocarbonaceous moieties,
229 due to the C-H bonds in aliphatics and other entrapped hydrocarbons, relative to OHMM. The
230 presence of entrapped hydrocarbons in the macromolecular network of OLMM likely explains
231 the broad shoulder cracking at high temperature (> 500 °C) as revealed by Rock-Eval
232 pyrolysis (Fig. 2). Both Raman spectroscopy and Rock-Eval pyrolysis suggest that standard
233 acid maceration results in a loss of hydrocarbons in OM isolated from the Rhynie chert. As
234 LMM does not involve the organic solvent extraction used in HMM, part of this hydrocarbon
235 loss is likely due to solvent-extractible OM, which is reflected by the respective S1 values. In
236 contrast to OHMM, OLMM did not involve extraction with HCl, which when mixed with HF
237 has been demonstrated to favour hydrolysis leading to a loss of aliphatic CH and/or CH₂
238 functional groups in coal (Tekely et al., 1987). Even though our experimental design did not
239 allow us to test the singular effect of HCl hydrolysis, such an effect can be hypothesized to
240 partly explain the loss in aliphatic moieties with HMM treatment.

241 Although the Raman spectroscopy results support the notion that hydrocarbons are lost
242 during HMM, it does not directly allow the extent of this loss to be determined. Following the
243 relationship between H/C and HI (Espitalié et al., 1977), we determined that H/C atomic
244 ratios were 0.53 and 0.57 in OHMM and OLMM, respectively (Table 1). Standard acid
245 maceration therefore led to a reduction of at least about 7–8% of the hydrocarbon content of
246 Rhynie OM. We use “at least” because chemical degradation of hydrocarbons occurring
247 during the isolation of OLMM cannot be straightforwardly excluded. To evaluate this point,
248 Raman spectra were also acquired on in situ OM from thin sections of Rhynie chert
249 (Supplementary information). These in situ Raman spectra were acquired with another Raman
250 spectroscope and on polished thin sections, which can modify the apparent carbon structural
251 order by yielding an increase in the D band (Ammar et al., 2011; Maslova et al., 2012). These
252 issues therefore prevent a straightforward comparison between Raman-derived ratios from in
253 situ OM and from OLMM/OHMM. Nonetheless, the α_{D4} and α_{D5} parameters are independent
254 of the height of the D band and can be used to track a potential effect of LMM procedure. In
255 situ OM presents a mean α_{D4} and α_{D5} of about 31 ± 4 and -24 ± 23 , respectively ($n = 10$),
256 indicating more pronounced D4 and D5 shoulders in the in situ OM compared to OLMM
257 (Supplementary information). This suggests that simple treatment with HF and water also led
258 to a slight loss in aliphatic content. In addition to these hydrocarbon losses related to acid
259 maceration procedures, the estimated 7–8% loss in hydrocarbons can also be considered as
260 minimum estimation because of thermolabile hydrocarbons (S1 parameter), which are not
261 taken into account in the calculation of HI and were more abundant in OLMM than in
262 OHMM.

263 Thermolabile hydrocarbons are tightly linked to soluble OM (Delvaux et al., 1990).
264 However, this soluble OM in ancient sediments is often ignored because its syngeneity can be
265 difficult to prove due to the potential for post-deposit contamination (Brocks et al., 2003a,

266 2003b; Derenne et al., 2008). However, silicified sediments can be seen as unconventional
267 dual source/reservoir rocks. Indeed, rapid silicification drastically reduces porosity leading to
268 a closed chemical system (Boyce et al., 2002; Ledevin et al., 2014). In such source/reservoir
269 rocks, migration of bitumens was very restricted implying that bitumens and/or pyrobitumens
270 coexisted in close proximity with residual kerogens (Vandenbroucke and Largeau, 2007).
271 Hence, in ancient silicified sediments, bitumens and pyrobitumens can be considered
272 syngenetic.

273 In contrast to soluble OM, insoluble OM is often considered less prone to late
274 contamination (Derenne et al., 2008). Involving no chemical treatment or low-manipulation
275 procedures, numerous studies have investigated the molecular structure of OM – at the scale
276 of plant fossils – to assess the effects of fossilization or to depict plant evolution and affinities
277 (Ewbank et al., 1996; Edwards et al., 1997; Abbott et al., 1998; Czaja et al., 2009; Quijada et
278 al., 2016). Because a large proportion of the hydrocarbon content of these samples is
279 preserved, these investigations minimized secondary hydrothermal and endolithic
280 contaminations – which can also yield insoluble OM – by studying insoluble OM directly
281 from plant fossils. To avoid contamination and to optimize the study of syngenetic
282 hydrocarbons that can be degraded in the course of acid maceration, the development of in
283 situ molecular micrometre-scale analyses techniques (e.g., time-of-flight secondary ion mass
284 spectrometry and laser micropyrolysis) are of interest. Such techniques have the potential to
285 directly probe the molecular structure of organic fossils independent of the soluble/insoluble
286 operational definition. In addition to insightfully assessing chemical heterogeneity within
287 macrofossils (Boyce et al., 2002; Abbott et al., 2018), in situ molecular micrometre-scale
288 analyses also offers the possibility to study the molecular composition of micrometric to sub-
289 micrometric diffuse particulate OM (Stout, 1993; Greenwood et al., 2001; Yoshioka and

290 Takeda, 2004; Silva et al., 2016). This includes remnants of microorganisms, such as organic-
291 walled microfossils, which are essential organic components of the early geological record.
292 In the specific context of silicified rocks – where silicification prevented migration of
293 bitumens and favoured formation of pyrobitumen in the close vicinity of the residual kerogen
294 – the use of in situ molecular micrometre-scale analyses offers promise in the investigation of
295 the molecular composition of early life found within Archean silicified sediments. Indeed, the
296 emergence of micrometre-scale *in situ* analyses have provided compelling evidence
297 supporting an unexpected and wide chemical heterogeneity among Archean putative organic-
298 walled microfossils (Delarue et al., 2017, 2020; Hickman-Lewis et al., 2020). Overlooked by
299 bulk extraction approaches, this chemical heterogeneity defines a chemically-well preserved
300 end product among the earliest traces of life. Therefore, the precise study of such geological
301 archives requires further development of in situ molecular micrometre-scale analyses Such
302 techniques may pave the way to document biological and abiotic processes and affinities of
303 the earliest putative remnants of life by: (i) focussing on chemically well preserved
304 specimens, (ii) without the use of chemical extraction and maceration techniques, which can
305 degrade aliphatic moieties preserved in sediments subjected to early and prompt silicification.

306

307 **4. Conclusions**

308 In this study, we investigated the impact of standard acid maceration on the chemical
309 structure of silicified OM from the Lower Devonian Rhynie chert. Using Rock-Eval pyrolysis
310 and Raman spectroscopy, we assessed the chemical structure of OM isolated by two different
311 physical and chemical manipulation procedures. Results from Rock-Eval pyrolysis and
312 Raman spectroscopy converged to demonstrate that the standard procedure of OM isolation
313 led to a significant and substantial degradation of hydrocarbons. These chemical alterations
314 indicate that a significant amount of molecular content is lost as a result of standard acid

315 maceration procedures, thus preventing a thorough examination of the molecular content of
316 organic remnants in thermally altered silicified sediments.

317

318 **Acknowledgements**

319 Authors are grateful to Andrew Ross (Department of Natural Sciences, National
320 Museum of Scotland, Edinburgh) for providing the Rhynie chert sample. We also thank F.
321 Savignac (ISTeP) for Rock-Eval pyrolysis and O. Belhadj (CRCC) for Raman spectroscopy.
322 We also acknowledge K. Liitschwager for proofreading the English writing of this
323 manuscript. J.K. Volkman, G.D. Abbott, anonymous reviewers and C.K. Boyce are
324 acknowledged for their constructive comments on the former versions of the manuscript.

325

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496

497 **Figure captions**

498

499 **Fig. 1.** (a) Typical Raman spectra measured on OHMM (black line) and OLMM (grey line).

500

501 **Fig. 2.** Emissions of (a) hydrocarbons and (b) CO₂ during Rock-Eval pyrolysis of OHMM

502 (black line) and OLMM (grey line). The red curve indicates the pyrolysis temperature

503 program. The green area in (b) indicates the temperature interval, for which CO₂ emissions

504 are included in the calculation of OI.

505

Table 1: Rock-Eval parameters determined in OHMM and OLMM. *H/C atomic ratio was estimated using the relationship between H/C atomic ratio and HI ($H/C = 0.0017 \times HI + 0.453$) published by Espitalié et al. (1977).

	S1 (mg HC/g)	S2 (mg HC/g)	TpkS2 (°C)	TOC (%)	HI (mg HC/g TOC)	OI (mg CO ₂ /g TOC)	H/C atomic ratio*
OHMM	0.59	11.76	481	25.4	46	59	0.53
OLMM	2.48	18.83	504	27.5	68	15	0.57

Table 2: Raman-derived parameters (mean value \pm S.D.) determined in OHMM and OLMM (n= 15; Wilcoxon rank test).

	I_{D1}/I_{G+D2}	I_{D4}/I_{G+D2}	I_{D5}/I_{G+D2}	α_{D4}	α_{D5}
OHMM	0.58 ± 0.02	0.38 ± 0.02	0.43 ± 0.04	359 ± 35	-288 ± 39
OLMM	0.52 ± 0.02	0.36 ± 0.02	0.31 ± 0.01	202 ± 37	-240 ± 28
<i>p</i> -value	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001



