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# Mudstones and embedded concretions show differences in lithology-related, but not source-related biomarker distributions

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## Highlights

- Biomarker distributions of concretions and embedding mudstones were similar.
- Only lithology related indices differed between concretions and mudstones.
- Biomarker composition of mud is preserved during concretion formation.
- Biomarker composition of Gogo nodules is related to the palaeoenvironment at time of deposition.

1 **Mudstones and embedded concretions show differences in lithology-related, but not source-**  
2 **related biomarker distributions**

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11

12 **Abstract**

13 The mudstones of the Western Australian Gogo Formation harbour numerous carbonate concretions  
14 which often contain preserved fossils of Lagerstätte-like quality. These are especially notable in  
15 places where the mudstone has eroded, giving way to nodule fields, where they are collected for the  
16 paleobiological records of great interest they afford. It is, however, a challenge to determine their  
17 paleoenvironmental context. Here, we analysed concretions from a core drilled in the Canning Basin  
18 Gogo Formation. At two different depths, concretions were compared to the surrounding mudstone  
19 found at the same depth. Electron microscopy and X-ray spectroscopy showed that the concretions  
20 were carbonate-rich and contained detrital fragments. Biomarker data showed that mudstone and  
21 concretions were very similar and presented marine biosignatures including indicators of anoxic  
22 depositional conditions, a stratified water column, and photic zone euxinia. The concretions contained  
23 higher amounts of C<sub>27</sub> steranes, indicating that more labile organic matter such as animal remains  
24 could have triggered concretion formation. Statistical analyses of the results showed that concretions  
25 and shales differed ( $p < 0.1$ ) in indices diagnostic for lithologies (and often related to maturity),

26 particularly in the sample recovered from the younger section of the core: the diasterane/sterane  
27 indices at each of the depths were 0.34 in the shale vs 0.12 in the concretion in the younger, and 0.21  
28 vs 0.19 in the older set of samples. The homohopane isomerisation indices of mudstone and  
29 concretion were 0.66 vs 0.58 and 0.62 vs 0.60 (47 and 54 m depth, respectively). Further, shales  
30 contained higher relative amounts of moretanes. Concretions also differed from the mudstone in their  
31 methylhopane distributions, with shales showing higher amounts of 3-methylhopanes. Conversely,  
32 when biomarker composition was compared at the two depths, they only differed significantly ( $p <$   
33 0.1) in 2-Methylhopane index, % C<sub>31</sub> Homohopanes, and hopane/sterane ratios ( $p <$  0.1). Our results  
34 show that the biomarker composition of the mudstone at the time of deposition is largely preserved in  
35 the concretions with only a minor overprint from diagenesis, bacterial communities involved in  
36 concretion formation, or the nucleus. It is therefore possible to use biomarker analysis on carbonate  
37 concretions to determine their provenance if found outside their immediate geological context.

38

## 39 **1. Introduction**

40 The vast stromatoporoid reefs of the Devonian Period (419.2–358.9 Ma) harboured complex and  
41 diverse ecosystems, to which formations such as those found in the Canning Basin in the North of  
42 Western Australia bear witness (Playford, 1980; Playford et al., 2009). The Gogo Formation is part of  
43 this fossil reef complex, and composed of basin facies stemming from the Frasnian to the Givetian. In  
44 the Gogo mudstone, the presence of carbonate concretions is notable, and preserved fossils of high  
45 quality, close to that of a Lagerstätte, can be found (Long and Trinajstić, 2010). Carbonate concretions  
46 have formed diagenetically since the Proterozoic, and are often associated with organic matter-rich  
47 sediments (shales, mudstones) and sandstones. It is generally accepted that deposition of organic  
48 matter in low oxygen conditions supports their growth and preservation (Berner, 1968; Allison, 1988;  
49 Briggs and Kear, 1993; Briggs, 2003; Long and Trinajstić, 2010). They often form as a result of  
50 bacterial activity in the anoxic muds, and grow concentrically or pervasively around a centre of  
51 decaying organic matter, where microbial sulfate reduction and methanogenesis cause changes in  
52 alkalinity (Raiswell and Fisher, 2000). These changes result in fast precipitation of

53 carbonates including calcite and dolomite, as cements in the pore spaces of unconsolidated sediment,  
54 and preservation of the original characteristics of the organic matter nucleus (Wolff et al., 1992). A  
55 large number of studies have shown excellent morphological fossil preservation in concretions  
56 spanning the entire Phanerozoic (e.g. Weeks, 1953; Marshall and Pirrie, 2013; Wilson and Brett,  
57 2013). Many of these concretions have been eroded out of their embedding rock, are found as large  
58 nodules fields in the Canning Basin, and their enclosed fossils, such as the Gogo fish, have afforded  
59 major paleobiological insights (Long and Trinajstić, 2010). Biomarker analyses of concretions has  
60 shown the preservation of biolipids in very immature stages (Kiriakoulakis et al., 2000; Marynowski  
61 et al., 2008; Melendez et al., 2013a, 2013b). Melendez et al. (2013b, 2013a) described the biomarker  
62 composition of a soft-tissue concretion from the Gogo Fm. and found exceptionally preserved  
63 biomarkers and biomolecules, including a diagenetic continuum of steroids. However, it is poorly  
64 understood how the biomarker composition of the Gogo nodules relate to that of the mudstone they  
65 are immediately embedded in. A recent comparison of concretions from the Toarcian with their  
66 surrounding shale (Posidonia shale, SW German Basin) showed that the biomarker composition of  
67 concretions was similar to those of the surrounding shales and thus to environmental conditions at  
68 time of formation in those pyritic, organic matter (OM) containing carbonate nodules from this  
69 location (Plet et al., 2016). However, this hypothesis requires testing in more settings. Here, we  
70 investigated the biomarker compositions of concretions from a core from the Gogo Formation and  
71 compared it to the embedding mudstone. The results could allow the use of the biomarker  
72 composition to place eroded nodules, such as those found in the North Western Australian nodule  
73 fields, in a confirmed paleoenvironmental context.

74

## 75 **2. Methods**

### 76 *2.1. Geological setting and core*

77 A core drilled at 18.4818°S 125.9768°E in 1983 by the East Pillara Joint Venture stored at the core  
78 repository of the Western Australian Geological Survey (ED20) was examined (Benn and Styles,  
79 1984). It stems from the Canning Basin and was in total 500 m long, of which the upper 110 m

80 spanned the Gogo Fm. (basin facies of the Givetian to Frasnian; Playford, 1980) consisting of  
81 laminated, alternating light and dark grey mudstone with little fauna and of low thermal maturity  
82 (Schwark, 2013). At two depths, 47.15–47.45 m, and at 54.56–54.86 m depth, carbonate concretions  
83 were found embedded in the mudstones; both were sampled for geochemical analysis. The concretion  
84 at 54 m depth was large and partially cored (Fig. S3), whereas the concretion at 47 m depth was a  
85 small round nodule of < 10 cm diameter.

## 86 *2.2 Scanning electron microscopy*

87 The small concretion, taken from the core section at 47 m depth, was cut, polished and coated with Pt  
88 using a Cressington 208HR. Scanning electron microscopy and energy-dispersive X-ray spectroscopy  
89 imaging was carried out with a Tescan Mira3 FESEM and an Oxford Instruments X-Max 150mm<sup>2</sup>  
90 and AZtec software at 15 mm working distance and 20 kV. X-ray diffraction (XRD) patterns of the  
91 powdered shales were collected on a D8 Advance diffractometer (Bruker AXS, Germany) using Cu  
92 K $\alpha$  radiation. The data were collected using a 2 $\theta$  step size of 0.015°, a count time of 0.5 s per step and  
93 a 2 $\theta$  range of 5°–120°. Rietveld modelling with the data was performed using Bruker AXS TOPAS  
94 version 5. A corundum (Al<sub>2</sub>O<sub>3</sub>) internal standard (10 wt.%) was used to facilitate quantitative  
95 analysis.

## 96 *2.3 Extraction, fractionation and derivatisation*

97 The concretions and mudstones were cleaned by 5 x 15 min sonication in dichloromethane /methanol  
98 1:1 (v:v), followed by grinding with a rock grinder using a ceramic bowl that had been baked at 450  
99 °C. The resulting powder was extracted via Soxhlet in dichloromethane (DCM) / methanol (MeOH)  
100 9:1 (v:v) for 72 hours. The extract was concentrated by rotary evaporation and weighed. Aliquots of  
101 the total lipid extracts were fractionated by elution over activated silica (SiO<sub>2</sub>) with 3 column volumes  
102 of hexane (saturate fraction), 3 column volumes of hexane/DCM (7:3, v:v, aromatic fraction) and 3  
103 column volumes of DCM/MeOH (1:1, v:v, polar fraction). For the concretions, the total lipid extract  
104 was used after derivatisation with N,O-Bis(trifluoro)acetamide (BSTFA) in pyridine for 1 h at 70 °C.  
105 A procedural blank of annealed sand was also processed in the same way. Only a few contaminants,

106 predominantly plasticizers, were identified in the blank. As the focus of this study was to obtain and  
107 describe the preserved biomarker fraction rather than determining the fatty acid composition of the  
108 concretions, HCl dissolution prior to extraction (Wolff et al., 1992; Pearson et al., 2005) was in this  
109 case not employed.

#### 110 *2.4 Biomarker identification*

111 The aromatic fraction of the mudstones, the total lipid extract (TLE) of the concretions and the  
112 procedural blank were analysed by gas-chromatography mass spectrometry (GC-MS) as described by  
113 Tulipani et al. (2015a) in order to evaluate the carotenoid pigment contents. The saturate fraction of  
114 the mudstones and the TLE of the concretions was analysed by gas-chromatography metastable  
115 reaction monitoring (GC-MRM) (Tulipani et al., 2015b) in order to determine the sterane and hopane  
116 biomarkers and ratios and compared to a Blina oil standard. Some C<sub>33</sub> 3-methylhopanes were  
117 tentatively identified by their retention behaviour according to Summons and Jahnke (1992).  
118 Additionally, as the biomarker concentrations in the concretions were low, they were analysed by GC-  
119 MRM using a DB-5 MS column, monitoring the transitions  $m/z$  554  $\rightarrow$  134 and  $m/z$  546  $\rightarrow$  134 and  
120 compared to Blina oil and oil from the Perth Basin in order to identify carotenoid pigments (French et  
121 al., 2015). Biomarker ratios were calculated from the areas of the MRM transition peaks as outlined in  
122 Peters et al. (2004). Statistical analysis on biomarker ratios was conducted in R using the FactoMineR  
123 package (Le et al., 2008).

124

### 125 **3 Results and discussion**

#### 126 *3.1. Inorganic Geochemistry*

127 QXRD analyses revealed similar mineralogy of both mudstones, which largely consisted of quartz  
128 and Muscovite (22 and 26%, Clay), and contained smaller amounts of brushite, pyrite and orthoclase.  
129 Electron microscopy of the concretion found at 47 m showed the heterogeneous structure of the  
130 concretion (Fig. 1). Elemental mapping confirmed that the main cement of the concretions was  
131 CaCO<sub>3</sub> (Fig. 1B, Site 1), with fragments of SiO<sub>2</sub> (Fig. 1B, Site 2) and other silicates (Fig. 1B, Site 3)

132 such as K-Feldspar (Fig. 1B, Site 4) and pyrite (Fig. 1B, Site 5). Maps of individual elements of an  
133 area containing a small vein (Fig. 1C) confirmed that it consisted of a silicate (Si, Al, O, C, Na, Fig.  
134 1D) and also showed the presence of pyrite (Fe, S, possibly framboidal, Fig. 1D), fragments of apatite  
135 (P, Fig. 1D) and albite (Na, Fig. 1D). No obvious preserved fossils or OM-rich areas were detected,  
136 suggesting that the concretions were formed around a very small organic nucleus, or that the nucleus  
137 had been completely replaced. The lithified carbonate in concretions stems from micro-  
138 environmental changes in pH and Ca or Mg ion concentrations by the microbial community involved  
139 in organic matter degradation (Wright and Oren, 2005), while the presence of pyrite is indicative of  
140 microbial sulphate reduction (MSR). The silicate fragments are probably detrital (Sugitani et al.,  
141 1995), although authigenic K-feldspar in carbonates has been reported previously and its formation  
142 attributed to sulfate reduction coupled to anaerobic methane oxidation (Jørgensen, 1981). This could  
143 provide an explanation for the appearance of silica-filled cracks (Fig. 1D), which could have formed  
144 during compression of the carbonate concretions during burial and filled with authigenic silica by  
145 either inorganic or microbially-mediated reactions. However, if these cracks were septarian fractures,  
146 these would normally be calcite-filled (Kiriakoulakis et al., 2000), and the features found here could  
147 rather present the remains of siliceous spicules of marine hexactinellids odemosponges (Uriz et al.,  
148 2003). These results confirm that the samples analysed were indeed post-depositional carbonate  
149 concretions.

### 150 *3.2 Biomarkers and derived indicators*

151 Pristane/phytane ratios were low for all samples, and amounted to 0.43 for the concretions and 0.47  
152 and 0.57 for the mudstone, indicating exceptionally low thermal maturity for material of this age. The  
153 aromatic fractions of the mudstones possessed small amounts of paleorenieratene and isorenieratene  
154 (Fig. 2AB), and GC-MRM analysis of the TLEs confirmed that they were also present in the  
155 concretions (Fig. 2CD), providing evidence for photic zone euxinia during deposition of the sediment  
156 (Grice et al., 1996; Sinninghe Damsté et al., 2001; Whiteside and Grice, 2016). All samples displayed  
157 a high proportion of C<sub>29</sub> steranes (Table 1, Fig. 3B, Supplementary. Fig. 1), which is common for  
158 marine sediments older than 350yr (Moldowan et al., 1985), and would thus be expected from



159 Devonian reef basin facies such as the Gogo Fm. However, the concretions contained slightly more  
160  $C_{27}$  steranes (Fig. 3B) and  $C_{27}$  diasteranes, while the mudstones contained more  $C_{29}$  steranes,  
161 indicating that part of the sterane complement contained in the concretions could stem from decaying  
162 animal remains providing labile organic matter acting as a nucleus for concretion formation.  $C_{27}$   
163 sterols, such as cholesterol, are typically present in higher abundances in animals. This observation  
164 has recently also been made for Toarcian nodules in which the  $C_{27}/C_{29}$  sterane ratio was slightly  
165 higher for the concretions than for the shales (Plet et al., 2016). Only small amounts of  $C_{30}$  steranes  
166 (*n*- and *isopropylcholestane*) were detected.  $C_{30}$  steranes, though present in higher abundances in e.g.  
167 the Cryogenian, have been reported to be scarce in samples from e.g. the Lower Paleozoic  
168 (Moldowan, 1984; Rohrssen et al., 2015; Gold et al., 2016). However, they are often present in  
169 Devonian settings, albeit sometimes in equally low relative proportions (e.g. Tulipani et al., 2015a).

170 The fractional abundances of all ( $17\alpha,21\beta + 17\beta,21\alpha + 17\beta,21\beta$ )  $C_{31-35}$  homohopanes, often used for  
171 fingerprinting, were very similar across all samples (Fig. 3A), with significant amounts of  $C_{35}$   
172 homohopane, the presence of which is generally associated with sulfidic depositional conditions  
173 (Sinninghe Damsté et al., 1989; Peters and Moldowan, 1991; Sinninghe Damsté et al., 1995). The  
174 similarity of the homohopane fingerprints between muds and concretions indicates that a bacterial  
175 community involved in concretion formation did either not produce extended hopanes different from  
176 the bacteria in the muds or overlying water column, or that the bacterial community was the same as  
177 in the surrounding sediment, and only activity was enhanced due to a localised high concentration of  
178 labile organic matter. . It is possible that preservation of the extended hopanes occurred by  
179 incorporation into kerogen, during early diagenesis in the presence of reduced-sulfur compounds  
180 (Kohnen et al., 1991; Sinninghe Damsté et al., 1995; Wakeham et al., 1995; Grice et al., 1998).

181 However, due to the small size of the concretions (< 10 cm) as sampled from the core, desulfurisation  
182 and hydrogen pyrolysis to analyse the sulfur-bound and kerogen-bound fractions could not be applied.  
183  $C_{29}/C_{30}$  hopane ratios were highest in the mudstone at 47 m depth, slightly lower in the corresponding  
184 concretion and even lower in both the mudstone and the concretion at 54 m, indicating a possible  
185 effect of either production of the  $C_{29}$  or preferential degradation of the  $C_{30}$  hopane during concretion

186 formation. All samples showed high gammacerane ratios (5.6–6.9, Table 1), indicating a stratified  
187 water column during deposition in agreement with recent studies of the paleoenvironmental  
188 conditions during the deposition of the muds of the Gogo Formation (Tulipani et al., 2015b). The  
189 ratios of diasteranes over steranes were low across all samples, indicating relatively low thermal  
190 maturity (0.12–0.34, Table 1). However, relative amounts of diasteranes were higher in the mudstones  
191 than in the concretions. This was expected, as the conversion from steranes to diasteranes is clay-  
192 catalysed and slower in carbonates than in mudstones (van Kaam-Peters et al., 1998; Nabbefeld et al.,  
193 2010). Hopane-derived maturity parameters such as  $C_{31-35} \text{ 22S}/(22\text{S}+22\text{R})$  homohopanes and  
194  $C_{29}\text{Ts}/(C_{29} \text{ hopane} + C_{29} \text{ Ts})$  did vary between concretions and muds, with the muds showing higher  
195 amounts of isomerisation of these compounds.  $\text{Ts}/(\text{Tm}+\text{Ts})$ , however did not vary as strongly:  
196 it ranged from 0.30 to 0.40, which is typical for anoxic marine, comparatively immature sediments.  
197 Isomerization indices in sulfur-rich sedimentary environments can sometimes vary between facies,  
198 and depend on side chain length (Köster et al., 1997). In agreement with this,  $22\text{S}/(22\text{S}+\text{SSR})$  were,  
199 overall, lower for the  $C_{31}$  hopanes (0.4) compared to the  $C_{32}$  to  $C_{35}$  homohopanes (0.6). Concretions  
200 also showed higher relative amounts of  $\beta\beta$   $C_{30}$  hopane (0.25 and 0.28 in concretions, vs 0.21 and 0.24  
201 in muds). The hopane/sterane ratio for all samples was between 0.17 and 0.19.

202 These results strongly suggest that the biomarker composition of the anoxic mud was preserved  
203 during concretion formation. Differences in sterane composition could indicate that part of those are  
204 derived from sterols from a former organic matter nucleus. Higher diasterane/sterane,  $22\text{S}/(22\text{S}+22\text{R})$   
205 hopane, and moretane ratios in the mudstone most likely reflect enhanced isomerisation in the  
206 presence of clays, which are naturally more abundant in mudstones than in the carbonate concretions.

### 207 *3.3 Methylhopanes*

208 Methylhopanes derive from bacterially produced 2- and 3-methylbacteriohopanepolyols and can thus  
209 be useful in the investigation of organic matter sources as well as bacterially mediated processes.  
210 MRM analysis of all samples showed abundant methylhopanes (Supplementary. Fig. 2) which were  
211 present in the muds and the concretions. The 2-methylhopane index ( $2\alpha$ -methyl- $17\alpha,21\beta$ - $C_{31}$ -hopane

212 / ( $2\alpha$ -methyl- $17\alpha,21\beta$ - $C_{31}$ -hopane +  $17\alpha,21\beta$ - $C_{30}$ -hopane) varied between concretions and muds.  
213 Concretions are also showing much lower relative amounts of  $3\beta$ - over  $2\alpha$ -methylhopanes than the  
214 muds (0.43 vs. 3.04 and 0.17 vs. 1.12 at 47 m; and 1.28 vs. 2.01 and 0.48 vs. 0.96 at 54 m; for  $C_{31}$  and  
215  $C_{32}$  methylhopanes, respectively). While 2-methylhopanes have been considered cyanobacterial  
216 biomarkers, it is now clear that a number of different bacteria have the potential to produce their  
217 precursors (Welander et al., 2010; Ricci et al., 2014). They are generally considered to be particularly  
218 prevalent in dysoxic environments (Dumitrescu and Brassell, 2005) and have been reported to be  
219 particularly abundant in cyanobacterial akinetes from nutrient-starved *Nostoc punctiforme* (Doughty  
220 et al., 2009). 3-Methylhopanes can be derived from intraaerobic methanotrophs, from acetic acid  
221 bacteria, and possibly a range of other sources (Neunlist and Rohmer, 1985; Simonin et al., 1994;  
222 Welander and Summons, 2012; Kool et al., 2014) and are generally observed to be elevated in  
223 alkaline, lacustrine source rocks (Farrimond et al., 2004). An explanation for the elevated 3-  
224 methylhopanes in the mudstones could be preferential preservation. It is also possible, that the anoxic  
225 muds were harbouring microorganisms such as *Acetobacter* sp. or *Methylomirabilis oxyfera* (Ettwig  
226 et al., 2010), who produce 3-methylhopanoids (Zundel and Rohmer, 1985; Kool et al., 2014) during  
227 burial, while the comparatively rapid microbial processes of concretion formation were not involving  
228 these microorganisms. This further confirms that the concretion formation occurred very quickly after  
229 burial.

### 230 3.4 Principal component analysis

231 Distinctive features confirmed by principal component analysis (PCA) revealed that the first  
232 component PC1 could explain differences between mud and concretions (63.10 %), while the second  
233 component could explain differences between different depths (23.90 %). Variables that correlated  
234 significantly ( $p < 0.1$ ) with PC1 were partly lithology- and partly source-related ratios (Table 2). The  
235 lithology-related indices that showed highest significance in their correlation ( $p < 0.1$ ) were the  
236 homohopane isomerisation index  $C_{31-35} S/(S+R)$ , the diasterane/sterane ratios, some moretane ratios,  
237 and the  $C_{29}Ts/(C_{29} \text{ hopane} + C_{29} Ts)$  ratio. These were all higher in the muds, most probably reflecting  
238 the higher clay content of the mudstones which catalysed stereochemical conversions. Previously,

239 differences in moretane/hopane ratios have been linked to clay contents (French et al., 2012). Other  
240 variables that were significantly correlated with PC1, and thus differentiated between concretions and  
241 shales were the relative amounts of C<sub>30</sub>, C<sub>29</sub> and C<sub>27</sub> steranes and C<sub>31</sub>/C<sub>30</sub> hopanes. As discussed in  
242 section 3.3, the higher relative amounts of 3β-methylhopanes in the muds than in the concretions (3β-  
243 Me αβ hopanes/2α-Me αβ hopanes) showed strong significance. In turn, variables which  
244 differentiated the samples from different depths (PC2) were sterane/hopane ratios, indicating different  
245 inputs of organic material or possibly a difference in benthic activity, 2-Methylhopane ratios and %  
246 C<sub>31</sub> homohopanes (Table 2, Supplementary. Fig. 1). Only negligible differences in clay content were  
247 present in this core, which is probably the reason for the strong similarities between lithology- or  
248 maturity related indicators between the two depths (Table S1). Only further studies including dating  
249 and paleoenvironmental studies of the core might allow conclusions about the origin of these  
250 differences.

251

#### 252 **4. Conclusions**

253 Biomarker indices determined from carbonate concretions and their surrounding mudstone in the core  
254 showed small differences between muds and concretions in those biomarker ratios that are indicative  
255 of clay-catalysed conversions in the muds. The stronger differences in source- or process-related  
256 biomarker ratios between the muds and the concretions were their methylhopane distributions, which  
257 could be due to preferential preservation, or to differences in bacterial processes during concretion  
258 formation compared to bacterial activity during burial of the muds; and their C<sub>27</sub> sterane abundances,  
259 which indicates that the concretion formed around labile organic matter such as animal remains.  
260 Generally, characteristic biomarker ratios were very similar between concretions and their  
261 surrounding muds. This confirms that the organic geochemistry of the carbonates of concretions  
262 found in a geologically less clear setting such as the eroded Gogo nodules can be used to place them  
263 in a paleoenvironmental context.

264

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274

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438

Table 1. Biomarker ratios for the mudstones and the embedded concretions.

Biomarker ratio	Mud 47	Nodule 47	Mud 54	Nodule 54
Pristane/phytane	0.57	0.43	0.47	0.43
% C <sub>27</sub> steranes	32	44	37	41
% C <sub>28</sub> steranes	17	17	15	15
% C <sub>29</sub> steranes	50	39	47	44
C <sub>30</sub> /(C <sub>27</sub> -C <sub>30</sub> )	0.03	0.01	0.02	0.02
Diasteranes/steranes	0.34	0.12	0.21	0.19
diaC <sub>27</sub> /(C <sub>27</sub> +C <sub>28</sub> +C <sub>29</sub> )	0.32	0.51	0.37	0.41
diaC <sub>28</sub> /(C <sub>27</sub> +C <sub>28</sub> +C <sub>29</sub> )	0.19	0.17	0.17	0.16
diaC <sub>29</sub> /(C <sub>27</sub> +C <sub>28</sub> +C <sub>29</sub> )	0.49	0.32	0.46	0.43
% C <sub>31</sub> homohopanes	36	29	28	36
% C <sub>32</sub> homohopanes	18	22	19	19
% C <sub>33</sub> homohopanes	24	17	25	21
% C <sub>34</sub> homohopanes	11	18	15	13
% C <sub>35</sub> homohopanes	11	14	13	11
C <sub>29</sub> /C <sub>30</sub> hopane	0.28	0.25	0.25	0.21
C <sub>31</sub> /C <sub>30</sub> hopane	0.22	0.16	0.17	0.16
10xGa/(Ga+C <sub>30</sub> hopane)	5.63	5.70	6.88	5.82
C <sub>31-35</sub> 22S/(22S+22R) homohopanes	0.66	0.58	0.62	0.60
C <sub>31</sub> 22S/(22S+22R) homohopane	0.37	0.46	0.42	0.44
C <sub>32</sub> 22S/(22S+22R) homohopane	0.69	0.62	0.64	0.62
C <sub>33</sub> 22S/(22S+22R) homohopane	0.68	0.57	0.63	0.61
C <sub>34</sub> 22S/(22S+22R) homohopane	0.67	0.60	0.64	0.62
C <sub>35</sub> 22S/(22S+22R) homohopane	0.67	0.59	0.65	0.64
C <sub>29</sub> Ts/(C <sub>29</sub> hopane + C <sub>29</sub> Ts)	0.27	0.14	0.25	0.21
Ts/(Tm+Ts)	0.32	0.40	0.36	0.30
ββ/(αβ+βα+ββ) C <sub>30</sub> hopane	0.21	0.25	0.24	0.28
ββ/(αβ+βα+ββ) C <sub>31</sub> hopane	0.05	0.05	0.04	0.07
ββ/(αβ+βα+ββ) C <sub>32</sub> hopane	0.06	0.03	0.06	0.05
Hopanes / steranes	0.19	0.18	0.17	0.19
2-Methylhopane index	0.12	0.30	0.39	0.15
2β-Me αβ C <sub>31</sub> hopane/2α-Me αβ C <sub>31</sub> hopane	1.59	1.02	1.75	1.25
2β-Me αβ C <sub>32</sub> hopane/2α-Me αβ C <sub>32</sub> hopane	1.53	0.94	1.98	1.10
2β-Me αβ C <sub>33</sub> hopane/2α-Me αβ C <sub>33</sub> hopane	1.16	0.96	1.54	0.89
3β-Me αβ C <sub>31</sub> hopane/2α-Me αβ C <sub>31</sub> hopane	3.04	0.43	2.01	1.28
3β-Me αβ C <sub>32</sub> hopane/2α-Me αβ C <sub>32</sub> hopane	1.12	0.17	0.96	0.48
<i>Moretane / hopane ratios</i>				
βα/(αβ + βα) 2α-Me C <sub>33</sub> hopane	0.15	0.18	0.38	0.19
βα/(αβ + βα) 2α-Me C <sub>32</sub> hopane	0.29	0.13	0.24	0.26
βα/(αβ + βα) 2α-Me C <sub>31</sub> hopane	0.26	0.13	0.25	0.17
βα/(αβ + βα) C <sub>29</sub> hopane	0.32	0.22	0.28	0.24
βα/(αβ + βα) C <sub>30</sub> hopane	0.13	0.09	0.12	0.07
βα/(αβ + βα) C <sub>31</sub> hopane	0.20	0.13	0.19	0.15
βα/(αβ + βα) C <sub>32</sub> hopane	0.18	0.09	0.14	0.14
βα/(αβ + βα) C <sub>33</sub> hopane	0.25	0.18	0.21	0.20
βα/(αβ + βα) C <sub>34</sub> hopane	0.20	0.17	0.19	0.18
βα/(αβ + βα) C <sub>35</sub> hopane	0.20	0.14	0.18	0.15

443 Table 2. Correlation coefficients with p-values for the ratios determining the first (PC1, 63.10 % of variability)  
 444 and second component (PC2, 23.90 % of variability).

<b>Biomarker ratio</b>	<b>Correlation</b>	<b>p-value</b>
PC1 (Mud vs Nodule)		
3 $\beta$ -Me $\alpha\beta$ C <sub>31</sub> hopane/2 $\alpha$ -Me $\alpha\beta$ C <sub>31</sub> hopane	0.997	0.003
$\beta\alpha$ /( $\alpha\beta$ + $\beta\alpha$ ) C <sub>34</sub> hopane	0.988	0.012
% C <sub>29</sub> steranes	0.988	0.012
3 $\beta$ -Me $\alpha\beta$ C <sub>32</sub> hopane/2 $\alpha$ -Me $\alpha\beta$ C <sub>32</sub> hopane	0.986	0.014
$\beta\alpha$ /( $\alpha\beta$ + $\beta\alpha$ ) C <sub>35</sub> hopane	0.981	0.019
C <sub>31-35</sub> 22S/(22S+22R) homohopanes	0.980	0.020
$\beta\alpha$ /( $\alpha\beta$ + $\beta\alpha$ ) C <sub>29</sub> hopane	0.977	0.023
C <sub>29</sub> Ts/(C <sub>29</sub> hopane + C <sub>29</sub> Ts)	0.975	0.025
$\beta\alpha$ /( $\alpha\beta$ + $\beta\alpha$ ) 2 $\alpha$ -Me C <sub>31</sub> <u>hopane</u>	0.975	0.025
$\beta\alpha$ /( $\alpha\beta$ + $\beta\alpha$ ) C <sub>31</sub> hopane	0.971	0.029
$\beta\alpha$ /( $\alpha\beta$ + $\beta\alpha$ ) C <sub>33</sub> hopane	0.955	0.045
Diasteranes/Steranes	0.952	0.048
$\beta\alpha$ /( $\alpha\beta$ + $\beta\alpha$ ) C <sub>32</sub> hopane	0.940	0.060
% C <sub>33</sub> homohopanes	0.921	0.079
$\beta\beta$ /( $\alpha\beta$ + $\beta\alpha$ + $\beta\beta$ ) C <sub>32</sub> hopane	0.918	0.082
C <sub>30</sub> /(C <sub>27</sub> -C <sub>30</sub> )	0.916	0.084
% C <sub>32</sub> homohopanes	-0.928	0.072
% C <sub>27</sub> steranes	-0.992	0.008
PC2 (47 vs 54 m)		
2-Methylhopane index	0.953	0.047
% C <sub>31</sub> homohopanes	-0.948	0.052
Hopanes / steranes	-0.982	0.018

445

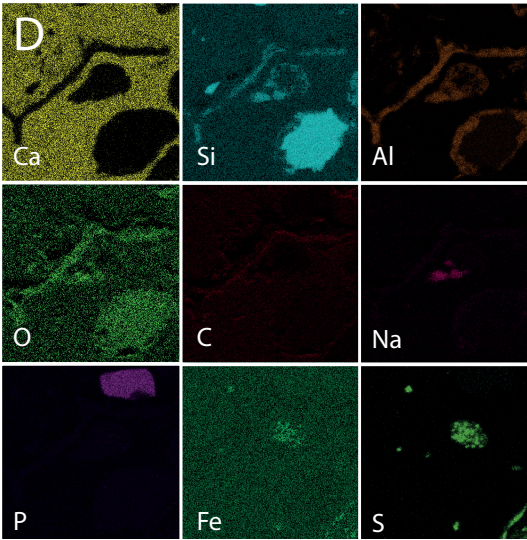
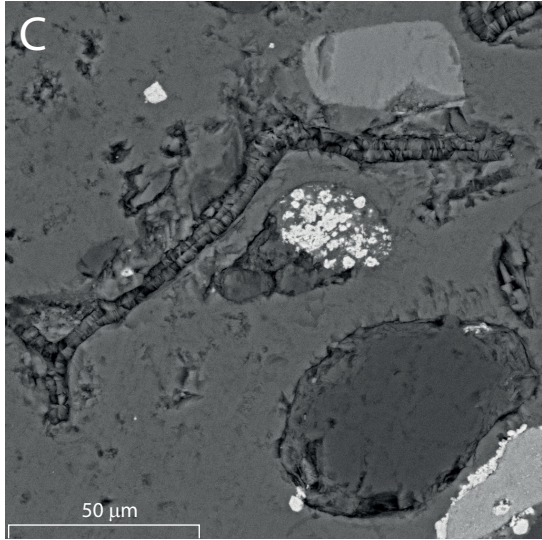
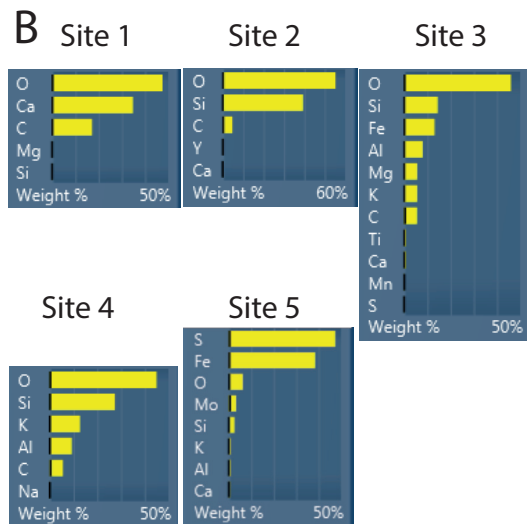
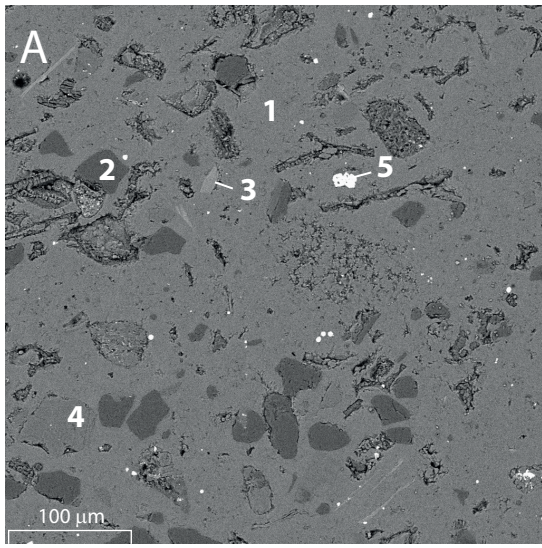
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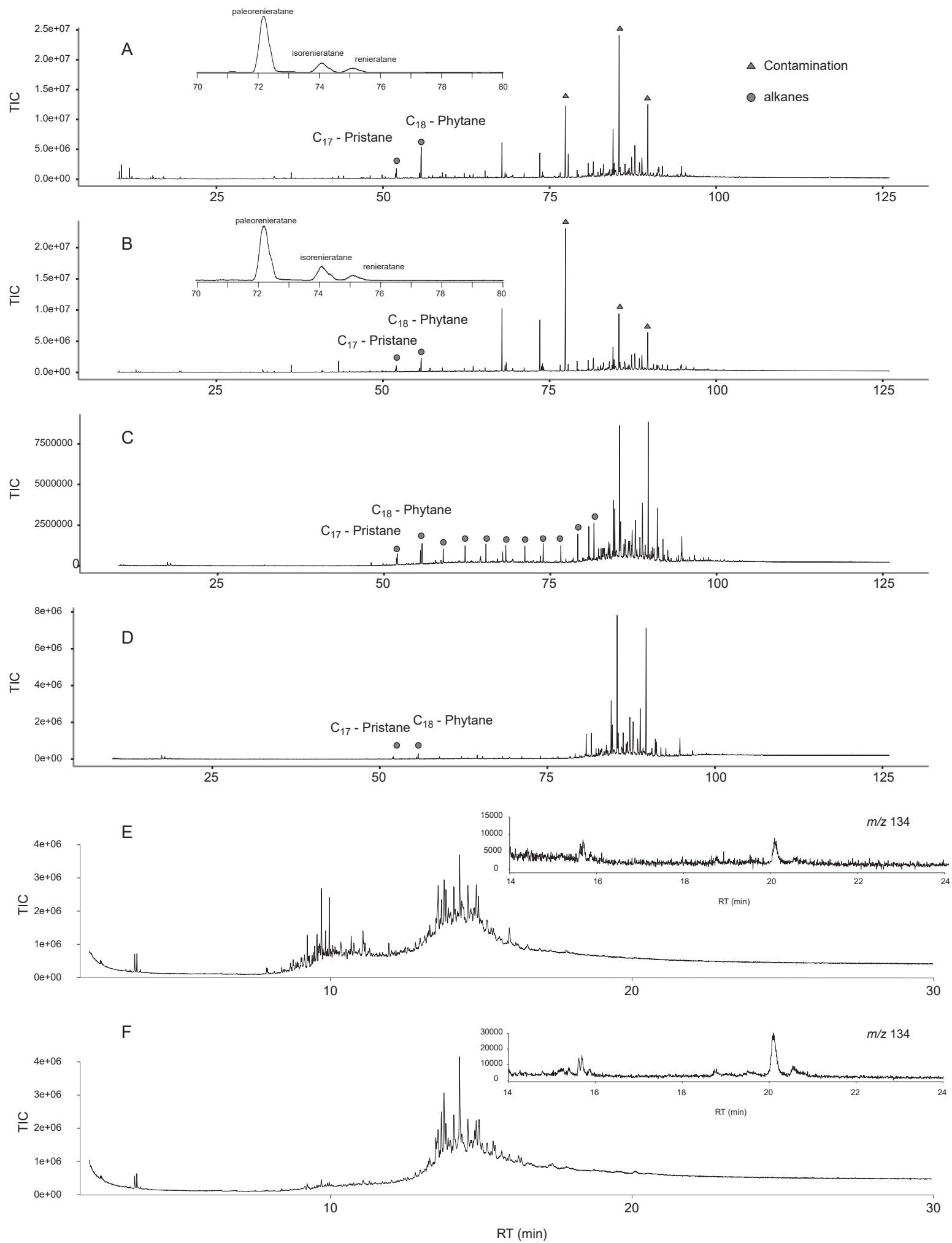
447 Figure captions.

448 **Figure 1.** Scanning electron microscopy images of one concretion. A shows a backscatter image, and B shows  
449 the elemental mapping results for the different types of mineral seen in the backscatter image. C shows a smaller  
450 section backscatter image, and D shows element abundances / K of the section shown in C.

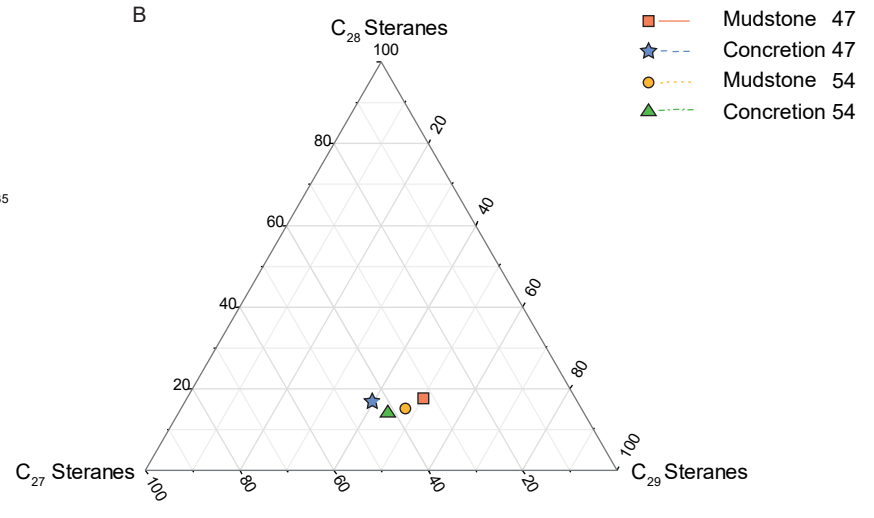
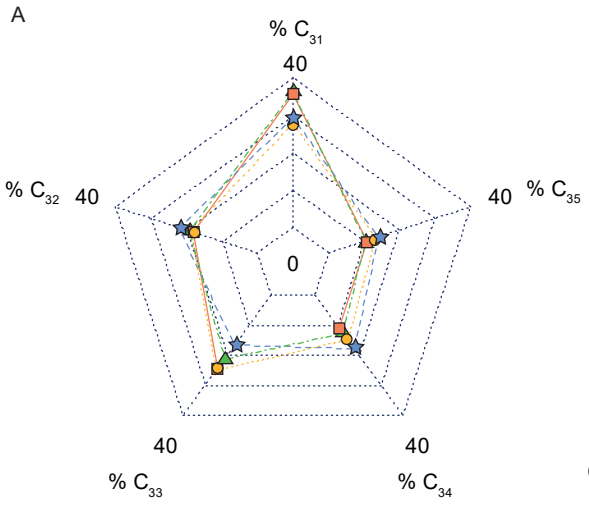
451 **Figure 2.** Chromatograms of TLEs and fractions. A BSTFA-derivatised TLE of the concretion at 47 m, B  
452 BSTFA-derivatised TLE of the concretion at 54 m. C Saturates fraction of the mudstone at 47 m, D Saturates  
453 fraction of the mudstone at 54 m, E Aromatic fraction of the mudstone at 47 m, F aromatic fraction of the  
454 mudstone at 54 m. Inserts in E and F show the extracted ion current at  $m/z$  134, while inserts in A and B show  
455 the GC-MRM results of the TLEs for transitions  $m/z$  546  $\rightarrow$  134 and the peaks identified by comparison to  
456 Blina-oil standard.

457 **Figure 3.** Biomarker ratios of the mudstones and concretions. Shown are % of homohopanes (A) and ternary  
458 diagram of sterane distributions (B).

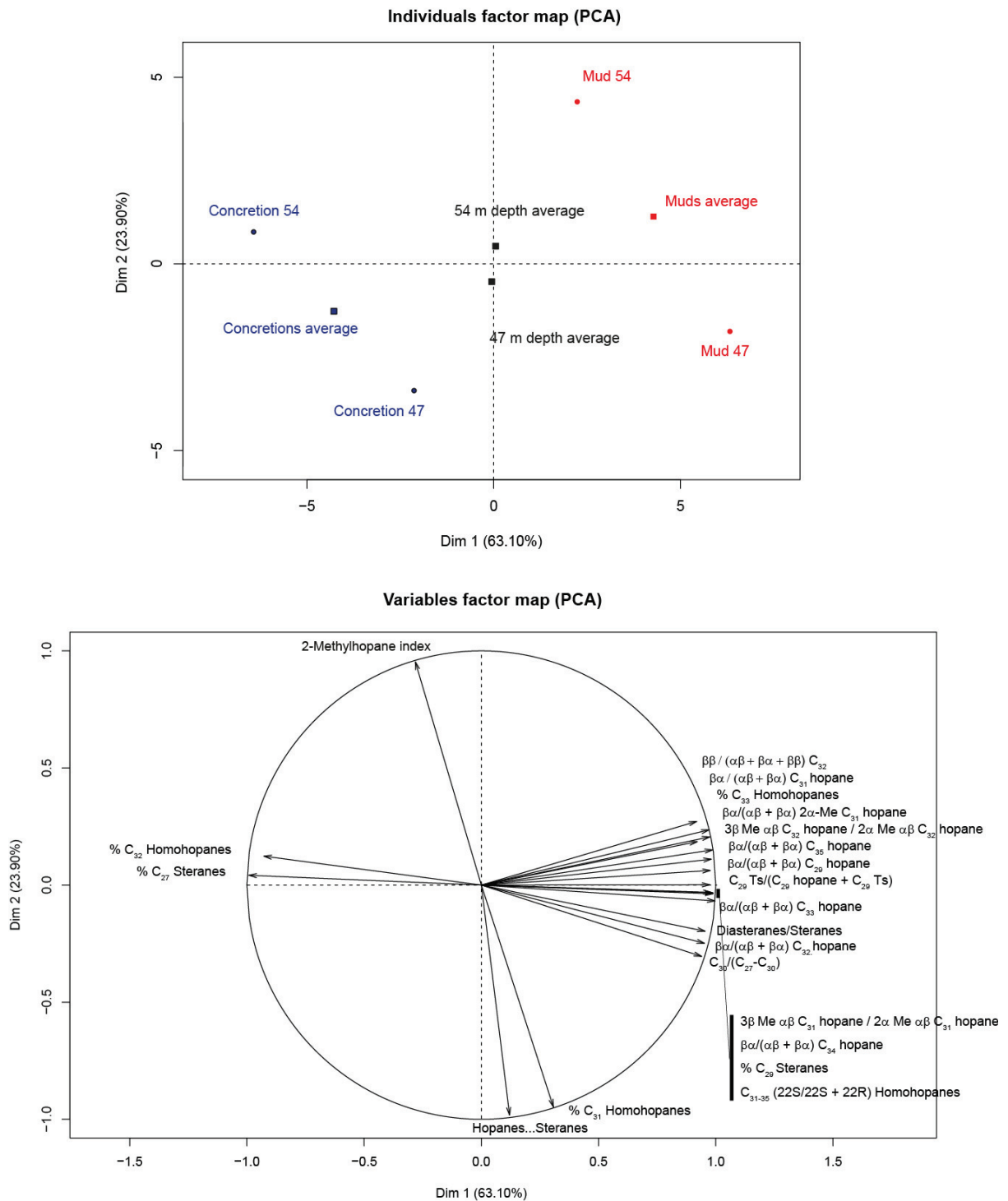




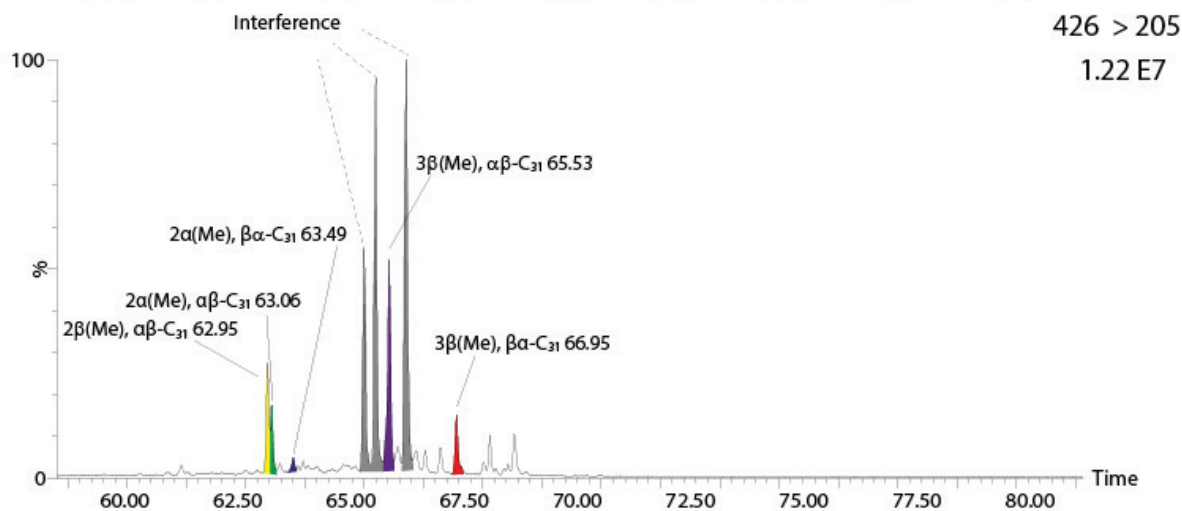
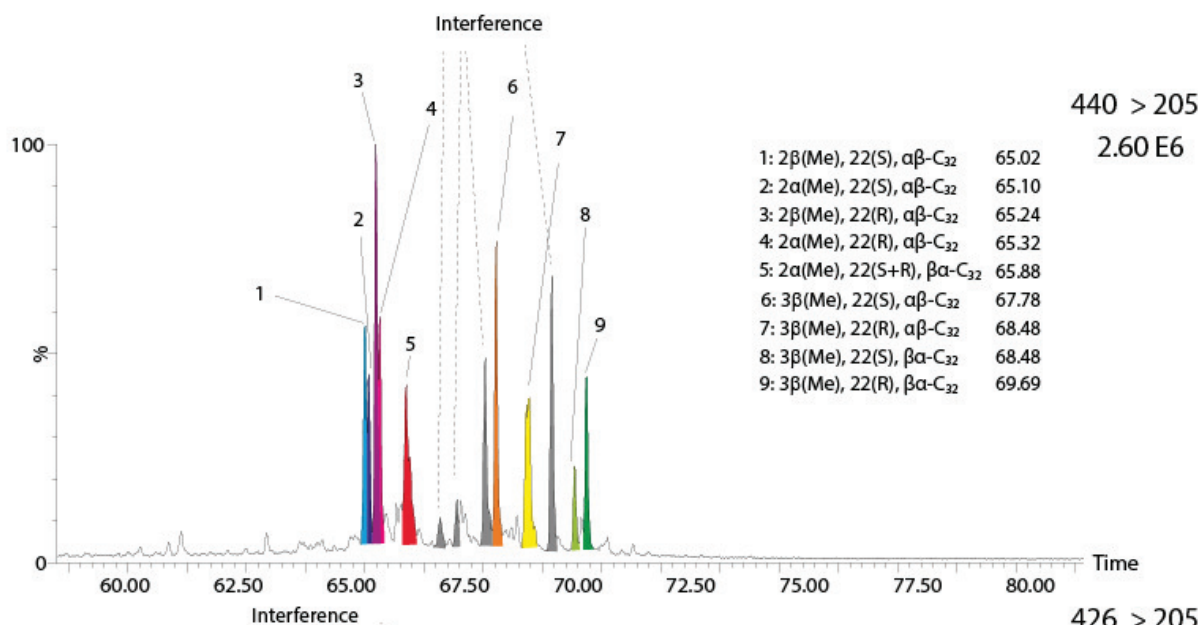
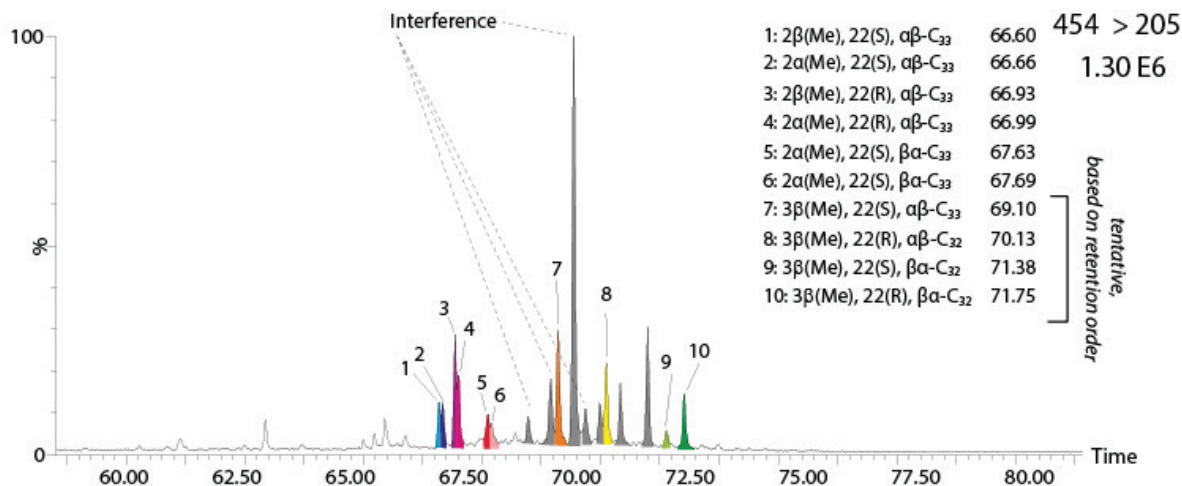




**Supplementary Material** to *Mudstones and embedded concretions show differences in lithology-related, but not source-related biomarker distributions* by Sabine K. Lengger, Ines M. Melendez, and Kliti Grice.



Supplementary Figure 1. Results of the principal component analysis (only significant factors included in the graph).



Supplementary Figure 2. Identified methylhopanes.



Supplementary Figure 3. Pictures of the mud and concretion. (A) 47 m depth (concretion), (B) 54 m depth (mudstones and concretion).

Supplementary Table 1. QXRD analysis results

	Quantitative analysis [ % w/w]	
	Mudstone 47.15 m	Mudstone 54.46 m
Amorphous content	4.6	6.9
Calcite	1.8	3.0
Pyrite	2.4	2.1
Orthoclase	9.5	10
Muscovite	22	27
Brushite	6.4	6.7
Quartz	53	44