Aromatic hydrocarbons provide new insight into carbonate concretion formation and the impact of eogenesis on organic matter

Authors:

Plet, C. [1,2], Grice, K.[1*], Scarlett, G. A.[1], Ruebsam, W.[3], Holman, I. A.[1], Schwark, L.[3]

[1] WA-OIGC, School of Earth and Planetary Sciences, Curtin University, Kent St, Bentley WA 6102, Australia

[2] CSIRO Mineral Resources, ARRC, 26 Dick Perry Avenue, Kensington WA 6151, Australia

[3]Department of Organic and Isotope Geochemistry, Institute of Geoscience, Christian Albrecht University, Kiel 24118, Germany

*corresponding author: K.grice@curtin.edu.au

Keywords: phytanyl toluene, phytanyl benzene, stable isotopes, GC×GC-ToF-MS, microbial eogenesis, PAHs

ABSTRACT

Investigation of aromatic biomarkers extracted from carbonate concretions can contribute to characterize the enhanced microbial activity that mediates carbonate concretion formation. This microbial footprint can be further inferred from the stable isotopic values of carbonate ($\delta^{13}C$) and pyrite ($\delta^{34}S$). Here, we used a combination of GC-MS and GC×GC-ToF-MS to compare the aromatic fractions of two Toarcian carbonate concretions from the *H. falciferum ammonite zone* of the Posidonia Shale (SW-Germany) and their host sediment. The results revealed that *n*-alkylated and phytanyl arenes were enhanced in the concretions relative to the host sediment. These findings support a very early diagenetic (eogenetic) microbial source for alkylated and phytanyl arenes derived from the microbial ecosystem mediating concretion formation. In contrast, aromatic

compounds formed by thermal maturation (e.g. polycyclic aromatic hydrocarbons, aromatic steroids, organic sulphur compounds) remained invariant in host rock and concretion samples. When combined with bulk sediment and concretion properties, the aromatic compounds composition indicates that eogenetic microbial activity upon concretion growth does not diminish organic matter quality.

1. INTRODUCTION

Carbonate concretions are a common geological feature that is encountered in sedimentary rocks throughout the geological record. They sometimes enclose exceptionally-preserved fossils (Grice et al., 2019; Long and Trinajstic, 2010; Martill, 1989, 1988; Williams et al., 2015). Carbonate concretions can also preserve information on the palaeoenvironment of deposition of their host sediments (Grice et al., 2019; Plet et al., 2016). Concretions have been the focus of a large number of studies, as highlighted in a review by Dietrich (2001)[1]. Early on, Berner (1968, 1967) performed laboratory experiments investigating the processes and timing involved in carbonate concretion. More recently, Yoshida et al. (2018, 2015) succeeded in growing carbonate concretions around tusk shells in a matter of weeks. In parallel to laboratory experiments, several studies have investigated the geochemistry and petrology of carbonate concretions, indicating a pivotal role of microorganisms, in particular, sulfate reducing bacteria and possibly archaea involved in the anaerobic oxidation of methane (Coleman and Raiswell, 1995; Dale et al., 2014; Marshall and Pirrie, 2013; Martill, 1989). The following microbially-mediated reactions are believed to play a crucial role in the formation of the carbonate with the product of each of these reactions utilised by other microbial processes or reacting with ions present in the immediate environment (Coleman, 1993; Coleman and Raiswell, 1995, 1980; Hendry et al., 2006; Lash and Blood, 2004):

[1] https://web.archive.org/web/20081202111650/http://www.cst.cmich.edu/users/dietr1rv/concretions/index.htm

Bacterial sulfate reduction (BSR)

$$2CH_2O + SO_4^{2-} \rightarrow 2HCO_3^- + H_2S$$

Methanogenesis

$$CH_3COOH \rightarrow CH_4 + CO_2$$

Anaerobic oxidation of methane

$$CH_4 + SO_4^{2-} \rightarrow HCO^{3-} + H_2S + OH^-:$$

Bacterial iron reduction (FeR)

$$4FeOOH + CH_2O + 7H^+ \rightarrow 4Fe^{2+} + HCO_3^- + 6H_2O.$$

In particular settings, such as at methane seeps in the Black Sea, Reitner et al.(2005) investigated the microbial mats surrounding carbonate concretions using molecular analyses (DNA). These analyses evidenced the abundant sulfate reducing bacteria and archaea, in particular ANME-1 believed to be active players in the anaerobic oxidation of methane (AOM). Unfortunately, accessible presently-forming carbonate concretions are rare (Boni et al., 1994; Coleman, 1993; Duan et al., 1996; Pye et al., 1990), and most carbonate concretions investigated come from the sedimentary record therefore challenging our understanding of microbial communities involved in concretion formation. Although, the exact microbial communities involved in concretion formation remain uncertain, models agree that carbonate concretions form around a centre of decaying organic matter (OM) harbouring complex microbial communities within anoxic to euxinic sediments (e.g. Coleman, 1993; Coleman and Raiswell, 1995).

Due to the labile nature of DNA molecules, DNA investigation of ancient carbonate concretions is limited (Briggs and Summons, 2014). However, since lipids are more resilient to geological time and processes, molecular studies of carbonate concretions can provide important insights into the genetic processes leading to concretions (Briggs and Summons, 2014; Grice et al., 2019). Lipids were

69 first studied in carbonate concretions by Wolff et al. in 1992. This study highlighted the presence of
70 distinct lipid compositions for the different mineralogical zones of the concretion. In the dolomitic
71 zone. the presence of pentamethyleicosane (PMI) and squalane at trace levels were attributed to
72 the presence of methanogenic archaea. Since then, a range of molecular studies on lipids from
73 concretions has been conducted revealing the occurrence of several biomarkers attributed to
74 archaea and sulfate reducing bacteria, but also information on thermal maturity and
75 palaeoenvironments, for instance. An overview of these findings is presented in Table 1.

76 The investigations of lipids have largely focused on aliphatic hydrocarbons and fatty acids whereas
77 aromatic fractions of carbonate concretions have received much less attention (Table 1). Yet,
78 aromatic compounds can provide insightful information on the catagenetic kerogen maturation
79 state *via* investigation of PAHs or aromatic steroids but also about eogenetic and
80 palaeoenvironmental conditions. Carotenoids, for instance isorenieratene and its degradation
81 products - i.e. isorenieratane and aryl isoprenoids, are indicative of photic zone euxinic conditions
82 (e.g. Grice et al., 1996). Few studies investigated these compounds in carbonate concretions.
83 Melendez et al. (2013b) reported a range of carotenoids and aryl isoprenoids from a Devonian
84 concretion, the occurrence of isorenieratane and aryl isoprenoids were also reported from the
85 concretions investigated here (Plet et al., 2016). In the present study, we aim to gain further insights
86 into the processes and micro-ecosystems involved in concretion formation by comparing the
87 aromatic hydrocarbon distributions from concretions and host sediments using traditional GC-MS
88 and comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GC×GC-
89 ToF-MS). This data was integrated with stable isotopic analyses of carbonate and sedimentary sulfur
90 ($\delta^{13}C$ of carbonate and $\delta^{34}S$ of mainly sulfide-bound S).

91

92 **2. GEOLOGICAL SETTING**

The Lower Toarcian (Early Jurassic; ~183 Ma) is marked by a global perturbation of the carbon cycle, characterised by a negative carbon isotopic excursion related to release of ^{12}C-enriched carbon to the ocean-atmosphere system and global warming (e.g. Gómez et al., 2016; Hesselbo et al., 2000; Kemp et al., 2005). These processes, which were potentially forced by changes in the Earth's solar orbit (Boulila and Hinnov, 2017; Kemp et al., 2005; Ruebsam et al., 2019), and were accompanied by marine transgressions (Haq, 2018). These events resulted in the accumulation of OM-rich sediments during a widespread oceanic anoxic event (OAE) in the Lower Toarcian. This OAE has been identified in Europe, North America, South America, Asia, Australia and Madagascar (Jenkyns, 1988).

During the Lower Jurassic, Europe was located on an extensive shallow epicontinental shelf (West Tethys shelf), which contained deeper sub-basins (Bassoulet et al., 1993; Röhl and Schmid-Röhl, 2005; Ziegler, 1990) . The SW Germany Basin, where the Posidonia Shale was deposited, is the focus of a number of detailed organic geochemical studies (Schouten et al., 2000; Röhl et al., 2001; Schmid-Röhl et al., 2002; Schwark and Frimmel, 2004). Deposition of early Lower Toarcian black shales was linked to warm climates, a high sea level and prolonged water column stratification (Frimmel et al., 2004; Hermoso et al., 2013; McArthur et al., 2008; Röhl et al., 2001). These conditions promoted a shift of the chemocline from the sediment to water column, which in some shelf areas led to the establishment of euxinic conditions (H_2S-rich waters) in the photic zone (photic zone euxinia) (Ruebsam et al., 2018; Schouten et al., 2000; Schwark and Frimmel, 2004) .

3. MATERIAL AND METHODS

3.1. Sampling location and preparation

The concretions and the host sediment Posidonia Shale studied herein were collected from the Holcim Cement quarry of Dotternhausen (SW-Germany) shortly after blasting. Although the exact stratigraphic position remains unknown due to blasting, Plet et al. (2016) established that these concretions derived from the lower *H. falciferum ammonite* zone, likely from above the Unterer Stein carbonate horizon based on the comparison of microfacies, lithology and geochemical

signatures from the concretions with previous reports (Frimmel et al., 2004; Röhl et al., 2001; Schwark and Frimmel, 2004). Both concretions have preserved a nucleus rich in OM (jet). The concretion body is darker than the concretion rim and sedimentary bedding is preserved. Here, we investigated sub-samples taken across bedding, however, the nuclei of the concretions were not studied. Three samples were taken from each concretion. For both concretions, sample one was taken from the inner concretion, sample two from the middle area of the concretion and sample three was taken from the outer pyritic rim (Figure 1). These concretion were previously analysed using microscopy and revealed micritic texture with dispersed small euhedral pyrite for sample one and two, whereas sample three was characterised by abundant and larger pyrite crystals agglomerated together (Plet et al., 2016).

3.2. Whole rock geochemistry

Elemental analyses of major and trace elements have been reported by Plet et al. (2016). Analyses were performed using inductively coupled plasma mass spectrometry (ICP-MS) by ACTLABS (Ancaster, Canada). Protocol information for the package Ultratrace 7 can be found on actlabs.com. The carbonate concentration was inferred from the loss of weight during HCl treatment (HCl concentration of 10% and 25%). Decalcified samples were analysed for their total organic carbon content (TOC_{cf}) using a CNS-Elemental Analyzer (Elementar ®). The total organic carbon content of the original sample (TOC) was then calculated by correcting the TOC_{cf} for carbonate concentration. Earlier mineralogical and SEM-EDS investigations revealed that these concretions exclusively contained calcite, pyrite and quartz (Plet et al., 2016). No other Fe-minerals commonly found in concretions (e.g. ankerite, siderite) were detected. Therefore, the pyrite content was established based on the assumption that the Fe is exclusively located in the pyrite of the concretions (Plet et al., 2016). The Fe content, which was determined by ICP-MS, was used to calculate the pyrite content. The Fe content was multiplied by 2.15 (stoichiometry of FeS_2). Finally, the residual input is considered to correspond to the siliciclastic input.

3.3. Stable isotope geochemistry

3.3.1. $\delta^{13}C$ of carbonate

$\delta^{13}C$ values of carbonate in ground samples were determined with a Kiel III carbonate preparation line connected to a Thermo Fisher 252 isotope ratio mass spectrometer (IRMS). The $\delta^{13}C$ values were reported in per mil (‰) relative to Vienna PeeDee Belemnite (VPDB). Standard deviations were <0.1‰.

3.3.2. $\delta^{34}S$ of bulk sediment

Stable sulfur isotopes ($\delta^{34}S$) were measured via combustion of the decalcified bulk-sample using a Thermo EA elemental analyzer coupled to a Thermo Finnigan Delta V isotope ratio mass spectrometer. Decalcification was achieved by HCl (10%) treatment and was carried out in order to increase sulfur abundances. Afterwards, samples were washed, neutralized with deionized water and dried in an oven at 40 °C (48 h). Sulfur isotope values were reported in conventional delta notation relative to VCDT (Vienna Canyon Diablo Troilite). Reproducibility of the analysis is better than 0.3‰. The $\delta^{34}S_{bulk}$ values reported here mainly reflect the isotopic composition of sulfide-bound sulfur species, as the carbonate associated sulfur fraction was removed during HCl-treatment.

3.4. Biomarkers

To remove surficial organic contaminants, each sample block was washed in a mixture of dichloromethane: methanol (DCM:MeOH) at 9:1 (v:v) for 15 mins in an ultrasonic bath. Samples were then manually crushed, and ground in a zircon mill using benchtop ring mill (BRM, Rocklabs) along with pre-annealed sand used as a procedural blank for lipid analyses. Procedures are reported in more detail in Plet et al. (2016).

3.4.1. Soxhlet extraction

Each ground sample was Soxhlet extracted using a 9:1 mixture of DCM:MeOH for 72 h and activated copper was added to remove elemental sulfur. Excess solvent was removed under a nitrogen purge

and concentrated total lipid extract (TLE) was adsorbed onto activated silica gel (160 °C, 24 h). TLE was separated into aliphatic hydrocarbons eluted with *n*-hexane, aromatic hydrocarbons eluted with a mixture of *n*-hexane:DCM (7:3) and polar compounds eluted with DCM:MeOH (1:1) using a large column (20 cm x 0.9 cm i.d.).

3.4.2. Gas chromatography mass spectrometry (GC-MS) analyses

Aromatic fractions were analysed on an Agilent 6890 gas chromatographs (GC) interfaced with an Agilent 5973 mass selective detector (MSD). The GC was equipped with a DB-5MS column [60 m × 0.25 mm coated with a 0.25 µm film thickness] and a split/splitless injector operated in splitless mode. The oven temperature was programmed from 40 °C to 325 °C (3 °C min^{-1}), with initial and final temperature hold for 1 min and 30 min, respectively. Ultra-high purity helium was used as a carrier gas at a constant flow of 1.1 mL min^{-1}. Electron ionisation mass spectra were acquired in full scan mode at 4 scans s^{-1} and at 70 *eV* electron energy.

3.4.3. GC×GC-ToF-MS

Aromatic fractions were analysed using a Leco Pegasus IV system equipped with dual stage cryogenic modulator (Leco, Saint Joseph, MI, USA). The primary column was a 60 m × 0.25 mm × 0.25 µm DB 5MS (Agilent, Santa Clara, CA, USA) coupled to a secondary 1.2 m × 0.15 mm × 0.15 µm BPX50 (SGE Analytical Science Pty Ltd, Ringwood, Victoria, Australia). The carrier gas was ultrahigh purity helium with constant flow of 1.5 mL min^{-1}. The inlet temperature was 310 °C with 1 µL injection. Conditions were: 50 °C (1 min isothermal), then 2.5 °C min^{-1} to 310 °C, (isothermal 15 min) and a modulation period of 3 s, with secondary oven offset of 10 °C and modulator offset of 15 °C. The mass spectrometer was operated at 70 *eV* electron energy*;* the ion source temperature was 250 °C and the transfer line 315 °C. The scan speed was 100 Hz with a range of 45–600 Daltons (Da). ChromaTOF (LECO) software package was used for instrument control and data analysis. Minimum acceptable signal to noise ratio was 30:1.

191

192 3.4.4. Gas chromatography isotope ratio mass spectrometry (GC-irMS) analyses

193 Compound specific stable isotope analyses were performed using a Thermo Delta Advantage isotope
194 ratio mass spectrometer couple to a Thermo Trace GC Ultra via a GC Isolink and Conflo IV. GC
195 conditions were similar to the ones previously described for the GC MS analyses. The $\delta^{13}C$ values
196 were determined by integration of the masses 44, 45 and 46 using Thermo Isodat software and
197 manually evaluated. Comparison of the samples to a mixture of *n*-alkanes with known $\delta^{13}C$ values
198 was used to calibrate the values to the VPDB scale. Samples were run in duplicate.

199 **4. RESULTS**

200 **4.1. Aromatic hydrocarbons**

201 4.1.1. Evaluation of the resilience of aromatic hydrocarbon compounds

202 All aromatic fractions were highly similar in their overall molecular composition (Figure 2). However,
203 the unresolved complex mixture (UCM) was relatively enhanced in the concretions compared to the
204 host sediment suggesting a slightly higher degree of biodegradation in the concretions (Trolio et al.,
205 1999). In addition, Plet et al. (2016) reported that the host sediment presents the highest hydrogen
206 index (HI) values (820 mgHC/gTOC), whereas the concretion samples revealed lower values (580 to
207 740 mgH/gTOC). In the present samples, which have a low maturity (R_0 ~ 0.5%, Frimmel et al., 2004),
208 the concretion samples show lower HI compared to the host sediment. The HI indicates a higher
209 degree of kerogen preservation in the host sediment than in the concretions .

210 Three compound classes were assessed for their resilience towards thermal maturation and
211 biodegradation: i) methyltrimethyltridecylchromans (MTTCs); ii) methylated phenanthrenes and
212 dibenzothiophenes (MP and MDBT, respectively) and iii) triaromatic steroids (TAS) (Figure 3). To
213 identify the most resilient compound group, we determined the degree of OM preservation using HI
214 values reported in Plet et al. (2016) and compared the relative evolution of the three compound

groups. We assumed that the most resilient compounds of the three groups would present a relative increase in the samples demonstrating the lowest HI values (Table 2) – i.e. concretion rim samples A3 and B3. Both MTTCs and TAS relatively increased in samples A3 and B3 (Figure 3). However, the relative increase of TAS was higher (~10 %) than that of MTTC (~5 %) from the sample presenting the greater HI –i.e. host sediment, and samples with the lower HI –i.e. concretion rims (A3 and B3). Therefore, all compounds presented here were normalised to TAS.

4.1.5. PAHs and organic sulphur compounds

Polycyclic aromatic hydrocarbons (PAHs) are relatively low in abundance in all samples (Figure 2). The aromatic hydrocarbon distribution is characterised by abundant methyldibenzothiophenes (MDBTs), mono-, di- and tri-MTTCs and aromatic steroids. In addition to these compounds, two large peaks **I** and **II** were identified as 1,1,7,8-tetramethyl-1,2,3,4-tetrahydrophenanthrene (Azevedo et al., 1992; Sinninghe Damsté et al., 1999) and C_3 alkylphenanthrene (Killops, 1991), respectively. Phenanthrene and mono- to tetra-methylated analogues as well as methylated naphthalene homologues were detected in all samples. However, larger unsubstituted ≥4rings PAHs are either present as trace (e.g. benzo[*ghi*]perylene) or were found to be below detection limits. Sulphur compounds, such as dibenzothiophene (DBT) as well as methyl- (MDBTs) and dimethyl- (DMDBTs) substituted homologues are abundant in all samples, whereas trimethyl-DBTs (TMDBTs) were only present in traces. Three benzonaphthothiophene (BNT) isomers were also present. The relative distribution of the sulphur-bearing compounds shows some strong similarities between the different samples. Methyl-substituted 1-MDBT is particularly abundant and constitutes one of the major peaks of the total ion chromatograms (Figure 1). The normalisation of aromatic compounds or compound classes to TAS suggests that DBT, MDBTs and DMDBTs compounds are relatively more abundant in the host sediment and the innermost concretion body samples and are less abundant in the concretion rims with exception of sample A2.

4.1.2. Alkylated and phytanyl arenes

240 Alkylated and phytanyl benzene and toluene were identified in all concretion samples using
241 traditional GC-MS analyses (Ostroukhov et al., 1983). Extracted ion chromatograms (m/z 92) of the
242 host sediment presented several minor peaks showing some degree of co-elution and no alkylated
243 benzene nor phytanyl benzene were identified (Figure 4). The low intensity coupled with some
244 coelution of these minor peaks prevented from comparison and challenged the interpretation.
245 Therefore, we used GC×GC-ToF-MS to overcome this issue by avoiding co-elution in the polar
246 dimension. For identification and relative quantification purposes, alkylated and phytanyl benzenes
247 were extracted using *m/z 91* and *m/z 92* whereas alkylated and phytanyltoluenes were measured on
248 *m/z 105* and *m/z 106*. The GC×GC-ToF-MS analyses revealed that alkylbenzenes and
249 phytanylbenzene were also present in the host sediment. The distribution of alkylated benzenes was
250 similar in all samples, maximizing at C_{18} and C_{20} and decreasing to trace level for compounds >C_{28}. To
251 compare the relative abundances of the alkylated benzenes and alklylated toluenes across the
252 different samples, we define the AlBr (alkylbenzene ratio=sum alkyl benzenes/sum C_{26}-C_{28} TAS) and
253 the AlTr (alkyltoluene ratio=sum alkyltoluenes/sum C_{26}-C_{28} TAS) ratios. The AlBr is 10 times greater in
254 both concretion samples than in the host sediment (Table 3). Phytanylbenzene is also present in
255 relatively low abundances in concretion samples (Table 3). The alkylated toluenes were detected in
256 all samples (Figure 4) and the newly defined AlTr ratio is 4 to 11 times greater in the concretion
257 samples than in the host sediment. Phytanyl toluene is also more abundant in the concretion
258 samples (Table 3) than in the host sediment. The ratio of phytanyl toluene to TAS is 3.5 to 13 times
259 greater in the concretion than in the host sediment (Table 3). In the two rim samples, A3 and B3,
260 $\delta^{13}C$ values of phytanyl toluene were measured. Sample A3 ($\delta^{13}C$= –36.1 ‰ ± 0.5) is slightly less ^{13}C-
261 depleted than sample B3 ($\delta^{13}C$= –38.1 ‰ ± 0.4).

262 In addition, the GC×GC-ToF-MS analyses showed the presence of a range of toluene compounds with
263 isoprenoid branching (supplementary Figure 1). These branched toluenes (C_{16} BrT, C_{18} BrT, C_{23} BrT,
264 C_{26} BrT) were identified in all samples (*m/z 106*), sometimes at trace levels only. To compare their
265 relative abundances across the sample set, the following ratio was defined: BrTr= sum C_{16}-C_{26} BrT *

1000 / sum C_{26}-C_{28} TAS. The BrTr shows that these compounds are relatively less abundant in the host sediment than in concretion samples, by as much as 20 times in sample B1 and as little as three times in sample A2 (Table 3).

4.1.3. Alkylated naphthalenes

Alkylated naphthalenes are present in all samples with side chain lengths comprised between C_3 and C_{21}, although only concretion samples (A1, A3 and B1) contain long alkylated homologues (side chain > C_{15}). All samples are maximizing at C_{17}-C_{18} (alkylated naphthalenes with a side chain of C_7-C_8). The ratios of alkylated naphthalene to TAS (sum AlkN /sum C_{26}–C_{28} TAS) highlight that alkylated naphthalenes are slightly more abundant in the concretion than in the host sediment (Table 3).

4.1.6. Aromatic hopanoids

The identification of aromatic hopanoids was performed based on comparison with published data [mass spectra and retention order; (Hussler et al., 1984; Killops, 1991)]. Although the GC-MS analyses suggested most aromatic *seco*hopanoid compounds reported in Killops (1991) were present in the concretion samples, GC×GC-ToF-MS analyses revealed that most of these compounds are co-eluting in the polar dimension with other compounds. C_{29}-D,E-aromatised-8,14-*seco*hopanoid (Supplementary Figure 2) and C_{29}-C_{30} D-ring aromatised 8,14-*seco*hopanoids were present (Supplementary Figure 3). In addition, benzohopanes (C_{31} – C_{35}) were also detected in all samples both by GC-MS and GC×GC-ToF-MS. C_{32} and C_{33} benzohopanes were the most abundant throughout the sample set and were integrated from the TIC using GC×GC-ToF-MS. To compare the relative abundances of these compounds across samples, the peak area normalisation of C_{29} D,E-ring aromatised 8,14-*seco*hopane (C_{29}DESHr) and C_{32}-C_{33} benzohopane (BHr) to TAS was performed on GC×GC-ToF-MS data (Table 3). These ratios revealed i) more abundant C_{29}-D,E-ring aromatised 8,14-*seco*hopanoid in the concretion than in the host sediment; ii) greater benzohopane content in the host sediment than in the concretion, iii) within the concretions, the benzohopane relative abundance increased towards the rim.

4.1.7. Aryl isoprenoids and MTTC

The identification of aryl isoprenoids within these concretions was previously reported in (Plet et al., 2016). In brief, isorenieratane and aryl isoprenoids with a 2,3,6-subsitution pattern are present in the host sediment, but were only detected in trace abundance in the carbonate concretions and the aryl isoprenoid ratio was consistent with persistent reductive environmental conditions (Schwark and Frimmel, 2004). MTTC are relatively abundant in all samples. MTTC ratio as defined by Sinninghe Damsté et al. (1993, 1988b) are remarkably constant for all samples (=0.63±0.01).

4.2. Whole rock geochemistry and stable isotope analyses

High proportion of carbonate cements in carbonate concretions (>70 %) can easily overprint the original signal inherited from the host sediment. This process, commonly referred to as carbonate dilution, can lead to the host sediment signature being too low to be detected. For instance, this carbonate dilution can explain why detrital components were not detected by powder XRD analyses reported in Plet et al. (2016), although quartz grains were observed using SEM analyses..

The variations in mineral abundances between the host sediment and the two carbonate concretions (bodies and rims) are presented in Table 2. In the host sediment, the siliciclastic and carbonate component are of similar relative abundance (~40 wt%, Table 2), and the pyrite and TOC proportions are also similar (~ 10 wt%). In contrast, all concretions samples are clearly dominated by carbonate: >95 wt% for the concretion body and >75 % for the concretion rim. The rim is also characterised by a greater pyrite component ~17.5 wt% in average than the concretion body (1 wt%) and the host sediment (7 wt%).

Pyrite is more ^{34}S-enriched in the concretion than in the host sediment (table 2). Moreover, the $\delta^{34}S_{bulk}$ and $\delta^{13}C_{carbonate}$ values in the concretions co-vary, displaying more negative values in the concretion body than in the concretion rim (Table 2).

5. DISCUSSION

5.1. Distribution of catagenetic aromatic hydrocarbons and microbial eogenesis: significance for kerogen quality

The HI indicates a better preservation of the organic matter in the host sediment compared to the concretion. This may appear contradictory given that carbonate concretions are known for their exceptional preservation of organic matter and fossils. Here, we attribute the low HI in concretion samples to the microbial eogenetic activity rather than burial diagenesis. We suggest that in a context of more mature settings such as the ones reported by Dong et al. (2008), the concretion actually protects the organic matter from further degradation related to burial diagenesis and catagenetic processes.

The majority of PAHs and aromatic steroids commonly form during late diagenesis, i.e. catagenetic processes, such as the cracking of sedimentary OM during sediment burial, which occurs at basin scale. In contrast, processes related to microbial eogenesis that occur during the very early stages of diagenesis can be highly localised. Microbial eogenesis includes the mineralisation of OM by microbial processes (e.g. sulfate reduction, iron reduction, methanogenesis and methanotrophy), which would decrease HI values,and can induce the precipitation of carbonate cement (e.g. Riding, 2000) as well as pyrite framboids (e.g. Wilkin and Barnes, 1997). In the present study, the concretion samples are characterised by high $CaCO_3$ content (up to 97 wt%, Table 2) with their overall carbonate content being twice as abundant as that of the host sediment (Table 2). During microbial degradation of the OM, organic carbon is mineralised into HCO_3^- which is, in turn, assimilated into the formation of $CaCO_3$ present in the concretion..

Yet, diagenetic compounds, commonly ≤4 ring PAHs such as naphthalenes, phenanthrene and homologues, DBT and methyl-substituted homologues, were detected in both the concretion and host shale samples. In addition, the overall distribution of aromatic steroids is similar for all samples; although the rim samples display a relative increase of triaromatic steroids compared to other aromatic compounds (Figure 3). The similarities in catagenetic compound distributions indicate that

the kerogen from which they derive was similar in both the concretions and in the host sediment, despite of the microbial metabolization of OM during carbonate concretion growth. Eogenetic concretion growth thus has not altered the kerogen´s potential for generation of aromatic hydrocarbons. These observations are in agreement with previous studies of biomarkers in carbonate concretions (Boni et al., 1994; Marynowski et al., 2007; Zatoń and Marynowski, 2004) and suggest that although the quantity of OM is affected by microbial metabolism involved in concretion growth, the petroleum formation potential of the OM has not suffered from these eogenetic processes. Formation of carbonate concretions in petroleum source rocks thus does not diminish their oil generation capacities.

5.2. Inferred microbial activity in the concretion from the variations of $\delta^{13}C_{carbonate}$ and $\delta^{34}S_{bulk}$

Stable carbon isotopic values are of importance to refine microbial processes in concretion genesis. In the present study, the stable carbon isotopic signatures of carbonate from the concretion samples are more ^{13}C-depleted than in the host sediment (^{13}C values from -17 ‰ to -8.3 ‰ in the concretions *versus* -1.8 ‰ in the host sediment). The $\delta^{13}C$ values, measured in the concretions, are in line with previous reports of Jurassic calcite concretions presenting a pyrite rim (e.g. Coleman and Raiswell, 1995, 1980). These studies attributed the ^{13}C-depletion of the carbonate from the concretion to the enhanced activity of sulfate reducing bacteria.

In addition, in anoxic sedimentary environment enhanced bacterial sulfate reduction may also be recorded in the sulfur stable isotopic composition of sedimentary pyrite (Berner et al., 2013; Borowski et al., 2013; Lin et al., 2016). In this study, $\delta^{34}S_{bulk}$ values are more positive in the concretion than in the host sediment (Table 2). However, $\delta^{34}S_{bulk}$ value of the host sediment is more positive than common values from marine environments (Werne et al., 2003; Wilkin and Arthur, 2001). According to Berner et al. (2013), such $\delta^{34}S_{pyrite}$ values for marine sediments could be related

to the accumulation of sedimentary pyrite under sulfate limitation within the SW-German sub-basin, which had restricted connection to the open ocean.

Variations in stable isotopic composition were also measured within a single concretion. Although the values were not identical for both concretions, a similar trend was observed. Concretion A and concretion B revealed an increase in $\delta^{13}C_{carbonate}$ and $\delta^{34}S_{bulk}$ values in the rim (Table 2). This increase coincides with a rise in pyrite content (from ~1 wt% up to ~ 22 wt % in concretion B). Such variations in Jurassic pyritiferous carbonate concretions were previously reported in association with a change from framboidal pyrite, in the concretion body, to euhedral pyrite in the concretion rim. They were also attributed to either a temporal or spatial control on concretion growth, with a strong contribution of sulfate reducing bacteria to the carbonate and sulfide pool (Coleman, 1993; Coleman and Raiswell, 1995).

Here, the concretion contained dominantly euhedral pyrite in both concretion body and rim (Plet et al., 2016), which suggest a high rate of microbial sulfate reduction generating sulfide more rapidly than the iron was supplied to the system from external sources (Coleman and Raiswell, 1995). In the present samples, the preservation of an OM-rich nucleus also indicates a rapid isolation from the surrounding environment, either by the precipitation of a carbonate cement (Martill, 1989), the formation of Ca soap (Berner, 1968; Thiel and Hoppert, 2018), or the entombment within a microbial mat (Reitner et al., 2005).

In this closed system, we hypothesise that the degradation of OM by microbial sulfate reduction was such that microbes consumed all light ^{12}C and ^{32}S isotope available and therefore, had to rely on the heavier isotope (^{13}C and ^{34}S) to sustain their activity. This would have resulted in an increasingly heavier carbon and sulfide pool through time. This hypothesis suggests that the heavier stable isotopic composition of the concretion rim reflects an outward concretion growth, i.e. formation of the mineral in the concretion body followed by the concretion rim.

An alternative explanation, however, could be a simultaneous formation of concretion body and rim with distinct dominant microbial communities forming each of them. The carbonate cement with the greatest ^{13}C-depletion along with lowest pyrite content observed in the concretion body could indicate a greater contribution of anaerobic methane oxidisers (archaea), whereas a greater pyrite content along with more ^{34}S-enriched pyrite in the rim would point to greater input from bacterial sulfate reduction. Generally, studies of calcium carbonate concretions attribute most of the carbonate production to microbial sulfate reduction, although the activity of micro-organisms involved in the methane cycle – i.e. methanogenesis and anaerobic oxidation of methane – is also mentioned (Coleman and Raiswell, 1995; Curtis et al., 1987; Duan et al., 1996; Huggett, 1994; Raiswell and Fisher, 2000; Scotchman, 1991). Concretionary carbonate presently forming at methane seeps in the Black Sea revealed the presence of microbial mats able to perform both sulfate reduction and anaerobic oxidation of methane (Reitner et al., 2005). Although methane seeps are not a prerequisite for the formation of carbonate concretions, the study by Reitner et al. (2005) revealed how organisms involved in methanogenesis and anaerobic oxidation of methane are both actively contributing to the microbial ecosystem leading to concretion formation, along with sulfate-reducing bacteria.

Both a temporal decrease in light stable isotopes available (Rayleigh distillation) and a spatial change in the microbial ecosystem could result in the pyrite content as well as the stable isotopic variations observed, and these hypotheses are not necessarily exclusive. Although the exact mechanisms of carbonate concretion formation remain to be fully understood, evidence of exceptional preservation of fossils (e.g. Martill, 1989, 1988; Plet et al., 2017; Williams et al., 2015) and biomolecules (Melendez et al., 2013a; Plet et al., 2017) indicate a system rapidly isolated from the surrounding environment. This is also confirmed by laboratory experiments (Berner, 1968, 1967; Yoshida et al., 2018, 2015) and dating studies (Yoshida et al., 2019).

5.3. **Alkylated and phytanyl arenes distribution and significance**

An additional aspect of this study relates to the alkylated and phytanyl arenes (supplementary Figure 4). Alkylated benzenes are common laboratory contaminants due to their use in detergents. In order to be confident that all the monoaromatic compounds identified in the samples were not artefacts resulting from the work-up procedures, repeated extractions were performed using multiple procedural blanks. When analysed by GC-MS and GCxGC-TOFMS, none of the blanks contained any of compounds reported herein and are therefore authentic biomarkers of the concretions.

These compounds, particularly phytanyltoluene, show high relative abundance in the concretion samples in comparison to the host sediment. Such an elevated relative abundance indicates that the source organisms of these compounds thrive in concretion-forming ecosystems. Although alkylated and phytanyl arenes have been widely reported in sedimentary OM and oils (e.g. Grotheer et al., 2017; Sinninghe Damsté et al., 1993, 1988b; Williams et al., 1988; Zhang et al., 2014), their origin presently remains unclear (Grotheer et al., 2017 and references therein). Amongst the different hypotheses proposed, the direct biosynthesis by hypersaline archaeal communities (Sinninghe Damsté et al., 1993, 1988b) is of interest here. As discussed above, it has been suggested that archaea could be major contributors to concretion-forming microbial ecosystems (De Boever et al., 2009; Hendry et al., 2006; Lash and Blood, 2004; Reitner et al., 2005; Wolff et al., 1992; Woo and Khim, 2006). In order to further test this hypothesis in the present context and determine the degree of salinity during concretion formation, the MTTC ratio was calculated (Sinninghe Damsté et al., 1993, 1988a). This ratio provides insight into palaeosalinity with low values (<0.4) reflecting hypersaline conditions (Sinninghe Damste et al., 1987, 1988a, 1993; Grice et al., 1998; Tulipani et al., 2015). Here, the MTTC ratio is not representative of hypersaline conditions and is remarkably constant for all samples (=0.63 ±0.01). This value for the MTTC ratio coincides with normal marine conditions at the time of concretion formation. Our results therefore do not indicate that alkylated and phytanyl arenes originate from halophilic archaea. These observations are supported by a previous study on the Permian-Triassic Boundary (~252 Ma) which also reported abundant phytanyl arenes despite an absence of paleo-hypersaline conditions (Grotheer et al., 2017).

Stable carbon isotopic composition of phytanyltoluene can be used to further determine the origin of this compound. In the rim samples, $\delta^{13}C_{PT}$ values are up to 3.4 ‰ more negative than previously reported values of *n*-alkanes from the same concretions (Plet et al., 2016). Interestingly, an inverse trend is usually observed for aromatic compounds: aromatics are commonly more ^{13}C-enriched than *n*-alkanes from a similar sediment or oil sample (Holman and Grice, 2018).

Here, the $\delta^{13}C_{PT}$ values, –36.1 ‰ and –38.1 ‰ for concretion A and concretion B, respectively, are more ^{13}C-enriched than common biomarkers of archaea involved in methane cycling (e.g. Hinrichs and Boetius, 2002). Moreover, no additional archaeal biomarker was detected in any of the samples. The greater relative abundance of alkylated and phytanyl arenes, along with the C_{29} D,E-ring diaromatic secohopanoid, a potential bacterial marker, in the concretion suggests that phytanyl and *n*-alkylated arenes probably derive from a type of bacteria particularly active in the microbial ecosystem leading to concretion formation. Benzohopanoids also increase in the rim compared to the concretion body, however they are relatively more abundant in the host sediment. This benzohopane distribution suggests a different bacterial source that is not particularly abundant in the micro-ecosystem of the concretion.

To better constrain the origin of the alkylated and phytanyl arenes in carbonate concretion, correlation coefficients were calculated. The correlations coefficients were determined both including and excluding the host sediment sample to highlight the differences and the likely origin of the *n*-alkylated and phytanyl arenes compounds (Figure 5). PTr and PBr showed a high correlation coefficient (Figure 5A) when the host sediment was included r^2=0.9 (n=7). However, a slightly higher correlation was achieved when the host sediment sample was excluded (r^2=0.93, n=6). This strong correlation, although on a small dataset, supports a common source for these compounds in the concretions. Grotheer et al. (2017) detected phytanylbenzene and phytanyltoluene along with C_{33} *n*-alkyl cyclohexane (C_{33} *n*-ACH) compounds in black shale samples from the Permian-Triassic Boundary. The authors reported a very strong correlation (r^2=0.99) between phytanylbenzene and

464 phytanyltoluene, indicating a common source for these compounds in samples from high latitude
465 environments. However, the compounds were not detected in samples from carbonate-rich low
466 latitude environments (Grotheer et al., 2017). Here, no C_{33} *n*-ACH was detected, supporting this
467 biomarker is characteristic of samples from the Permian-Triassic crisis (Grice et al., 2005). In
468 addition, the concretions were formed in warm, mid-latitude climate (Gómez et al., 2016; Rodrigues
469 et al., 2019) , indicating that the source organism is not exclusive to cooler environment but thrives
470 in concretion-forming microbial ecosystem. Correlation coefficients between AlkBr and AlkTr, AlkBr
471 and PBr, and AlkTr and PTr (all with $r^2<0.9$, n=7, Figure 5B-D) are lower than for phytanyl compounds
472 ($r^2>0.9$; Figure 5A) and decrease when the host sediment sample is excluded from the dataset. In
473 particular, the correlation coefficients of AlkBr/PBr and AlkTr/PTr (r^2 values of 0.66 and 0.37,
474 respectively) in the carbonate concretion highlight a different source for alkylated v*ersus* phytanyl
475 compounds.

476 **6. CONCLUSIONS**

477 The detailed examination of the aromatic fractions from carbonate concretions and their host
478 sediment highlights microbial processes involved in carbonate concretion formation. In addition to
479 bulk stable isotopes supporting enhanced and complex microbial activity, the present study
480 demonstrates that:

481 • Stable isotopic values of calcite and sedimentary sulfur (mainly pyrite) ($\delta^{13}C$ and $\delta^{34}S$,
482 respectively) co-vary. The ^{13}C-depleted carbonate cement from the concretion body results
483 from microbial activity relying on a ^{13}C-depleted source.
484 • The increase in $\delta^{34}S$ values in the rim associated with greater pyrite content indicates that
485 microbial sulfate reduction under successively higher ^{32}S-depletion of the sulfate pool is
486 largely responsible for pyritic rim genesis.
487 • Phytanylbenzene and phytanyltoluene share a similar biological source, thriving in
488 concretion-forming microbial ecosystem.

- *n*-alkylated and phytanyl arenes do not share a common source in concretion-forming ecosystem. Although a clear origin for these compounds was not identified, it is likely that, in this specific setting, halophilic archaea were not the source organisms.

Our study of two Toarcian carbonate concretions along with their host sediment indicates that *n*-alkylated and phytanylbenzenes and toluenes could provide some insight into the processes of carbonate concretion formations. Constraining the source of these compounds could improve our understanding of ancient microbial ecosystems forming these concretions. Furthermore, it would provide clues to unravel how the kerogen quality remained unaffected by the enhanced microbial activity during carbonate concretion formation.

ACKNOWLEDGMENTS

This research was supported by a Discovery Grant from the Australian Research Council (ARC-DORA-Kliti Grice, DP130100577) and DFG grants Schw554/23 and Schw554/29. Peter Hoper is thanked for GC-MS technical support. Marieke Sieverding is thanked for $\delta^{34}S$ technical support. CP thanks Curtin University and The Institute of Geoscience Research for a PhD and a Top-up scholarship. The authors wish to acknowledge Anais Pages for constructive criticisms that contributed to the improvement of an earlier version of this paper. We thank two anonymous reviewers for their constructive comments.

REFERENCES

Azevedo, D.A., Aquino Neto, F.R., Simoneit, B.R.T., Pinto, A.C., 1992. Novel series of tricyclic aromatic terpanes characterized in Tasmanian tasmanite. Org. Geochem. 18, 9–16. https://doi.org/10.1016/0146-6380(92)90138-N

Bassoulet, J.P., Elmi, S., A.P., Cecca, F., Bellion, Y., Guiraud, R., Baudin, F., 1993. Mid-Toarcian, in: Dercourt, J., Ricou, L.E., Vrielynck, B. (Eds.), Atlas Tethys Paleoenvironmental Maps. BEICIP —

513 FRANLAB, Rueil-Malmaison, pp. 63–84.

514 Baumann, L.M.F., Birgel, D., Wagreich, M., Peckmann, J., 2016. Microbially-driven formation of
515 Cenozoic siderite and calcite concretions from eastern Austria. Austrian J. Earth Sci. 109.
516 https://doi.org/10.17738/ajes.2016.0016

517 Berner, R.A., 1968. Calcium carbonate concretions formed by the decomposition of organic matter.
518 Science (80-.). 159, 195–197.

519 Berner, R.A., 1967. Rate of concretion growth. Geochim. Cosmochim. Acta 32, 477–483.

520 Berner, Z.A., Puchelt, H., Nöltner, T., Kramar, U., 2013. Pyrite geochemistry in the Toarcian Posidonia
521 Shale of south-west Germany: Evidence for contrasting trace-element patterns of diagenetic
522 and syngenetic pyrites. Sedimentology 60, 548–573. https://doi.org/10.1111/j.1365-
523 3091.2012.01350.x

524 Boni, M., Simoneit, B.R.T., Leif, R.N., Mckenzie, J.A., 1994. 15 . Organic Matter and Carbon Isotope
525 Composition of Carbonate Nodules and Associated Sediments From Middle Valley , Leg 139 1.
526 Proc. Ocean Drill. Program, Sci. Results 139.

527 Borowski, W.S., Rodriguez, N.M., Paull, C.K., Ussler, W., 2013. Are 34S-enriched authigenic sulfide
528 minerals a proxy for elevated methane flux and gas hydrates in the geologic record? Mar. Pet.
529 Geol. 43, 381–395. https://doi.org/10.1016/j.marpetgeo.2012.12.009

530 Boulila, S., Hinnov, L., 2017. A review of tempo and scale of the early Jurassic Toarcian OAE:
531 implications for carbon cycle and sea level variations. Newsletters Stratigr. 50, 363–389.

532 Briggs, D.E.G., Summons, R.E., 2014. Ancient biomolecules: their origins, fossilization, and role in
533 revealing the history of life. Bioessays 36, 482–90. https://doi.org/10.1002/bies.201400010

534 Coleman, M.L., 1993. Microbial processes: Controls on the shape and composition of carbonate
535 concretions. Mar. Geol. 113, 127–140. https://doi.org/10.1016/0025-3227(93)90154-N

536 Coleman, M.L., Raiswell, R., 1995. Source of carbonate and origin of zonation in pyritiferous
537 carbonate concretions: evaluation of a dynamic model. Am. J. Sci. 295, 282–308.

538 Coleman, M.L., Raiswell, R., 1980. Carbon , oxygen and sulphur isotope variations in concretions
539 from the Upper Lias of N . E . England. Geochim. Cosmochim. Acta 45, 329–340.

540 Curtis, C., Building, B., Sheffield, S., 1987. Mineralogical consequences of organic matter degradation
541 in sediments : inorganic / organic, in: Leggett, J.K., Zuffa, G.G. (Eds.), Marine Clastic
542 Sedimentology. pp. 108–123.

543 Dale, A., John, C.M., Mozley, P.S., Smalley, P.C., Muggeridge, A.H., 2014. Time-capsule concretions:
544 Unlocking burial diagenetic processes in the Mancos Shale using carbonate clumped isotopes.
545 Earth Planet. Sci. Lett. 394, 30–37. https://doi.org/10.1016/j.epsl.2014.03.004

546 De Boever, E., Birgel, D., Thiel, V., Muchez, P., Peckmann, J., Dimitrov, L., Swennen, R., 2009. The
547 formation of giant tubular concretions triggered by anaerobic oxidation of methane as revealed
548 by archaeal molecular fossils (Lower Eocene, Varna, Bulgaria). Palaeogeogr. Palaeoclimatol.
549 Palaeoecol. 280, 23–36. https://doi.org/10.1016/j.palaeo.2009.05.010

550 de Craen, M., Swennen, R., Keppens, E.M., Macaulay, C.I., Kiriakoulakis, K., 1999. Bacterially
551 mediated formation of carbonate concretions in the Oligocene Boom Clay of Northern Belgium.
552 https://doi.org/10.2110/jsr.69.1098

553 Dong, J., Zhang, S., Jiang, G., Zhao, Q., Li, H., Shi, X., Liu, J., 2008. Early diagenetic growth of
554 carbonate concretions in the upper Doushantuo Formation in South China and their
555 significance for the assessment of hydrocarbon source rock. Sci. China Ser. D Earth Sci. 51,
556 1330–1339. https://doi.org/10.1007/s11430-008-0107-3

557 Duan, W.M., Hedrick, D.B., Pye, K., Coleman, M.L., White, D.C., 1996. A preliminary study of the
558 geochemical and microbiological characteristics of modern sedimentary concretions. Limnol.
559 Oceanogr. 41, 1404–1414. https://doi.org/10.4319/lo.1996.41.7.1404

560 Frimmel, A., Oschmann, W., Schwark, L., 2004. Chemostratigraphy of the Posidonia Black Shale, SW
561 Germany I. Influence of sea-level variation on organic facies evolution. Chem. Geol. 206, 199–
562 230. https://doi.org/10.1016/j.chemgeo.2003.12.007

563 Gómez, J.J., Comas-Rengifo, M.J., Goy, A., 2016. Palaeoclimatic oscillations in the Pliensbachian
564 (Early Jurassic) of the Asturian Basin (Northern Spain). Clim. Past 12, 1199–1214.
565 https://doi.org/10.5194/cp-12-1199-2016

566 Grice, K., Gibbison, R., Atkinson, J.E., Schwark, L., Eckardt, C.B., Maxwell, J.R., 1996. Maleimides (1H-
567 pyrrole-2,5-diones) as Molecular Indicators of Anoxygenic Photosynthesis in Ancient Water
568 Columns. Geochim. Cosmochim. Acta 60, 3913–3924. https://doi.org/10.1016/0016-
569 7037(96)00199-8

570 Grice, K., Holman, A.I., Plet, C., Tripp, M., Grice, K., Holman, A.I., Plet, C., Tripp, M., 2019. Fossilised
571 Biomolecules and Biomarkers in Carbonate Concretions from Konservat-Lagerstätten. Miner.
572 2019, Vol. 9, Page 158 9, 158. https://doi.org/10.3390/MIN9030158

573 Grice, K., Schouten, S., Nissenbaum, A., Charrach, J., Sinninghe Damsté, J.S., 1998. Isotopically heavy
574 carbon in the C21 to C25 regular isoprenoids in halite-rich deposits from the Sdom Formation,
575 Dead Sea Basin, Israel. Org. Geochem. 28, 349–359. https://doi.org/10.1016/S0146-
576 6380(98)00006-0

577 Grice, K., Twitchett, R.J., Alexander, R., Foster, C.B., Looy, C., 2005. A potential biomarker for the
578 Permian–Triassic ecological crisis. Earth Planet. Sci. Lett. 236, 315–321.
579 https://doi.org/10.1016/j.epsl.2005.05.008

580 Grotheer, H., Le Métayer, P., Piggott, M.J., Lindeboom, E.J., Holman, A.I., Twitchett, R.J., Grice, K.,
581 2017. Occurrence and significance of phytanyl arenes across the Permian-Triassic boundary
582 interval. Org. Geochem. 104, 42–52. https://doi.org/10.1016/j.orggeochem.2016.12.002

583 Haq, B.U., 2018. Triassic eustatic variations reexamined. GSA Today 28, 4–9.

584 https://doi.org/10.1130/GSATG381A.1

585 Hendry, J.P., Pearson, M.J., Trewin, N.H., Fallick, A.E., 2006. Jurassic septarian concretions from NW
586 Scotland record interdependent bacterial, physical and chemical processes of marine mudrock
587 diagenesis. Sedimentology 53, 537–565. https://doi.org/10.1111/j.1365-3091.2006.00779.x

588 Hermoso, M., Minoletti, F., Pellenard, P., 2013. Black shale deposition during Toarcian super-
589 greenhouse driven by sea level. Clim. Past 9, 2703–2712. https://doi.org/10.5194/cp-9-2703-
590 2013

591 Hesselbo, S., Grocke, D., Jenkyns, H.C., Bjerrum, C.J., Farrimond, P., Morgans Bell, H., Green, O.,
592 2000. Massive dissociation of gas hydrate during a Jurassic oceanic anoxic event. Nature 406,
593 392–395. https://doi.org/10.1038/35019044

594 Hinrichs, K., Boetius, A., 2002. The anaerobic oxidation of methane : new insights in microbial
595 ecology and biogeochemistry, in: Van Weering, T. (Ed.), Ocean Margin Systems. Springer, berlin
596 Heidelberg, pp. 457–477.

597 Holman, A.I., Grice, K., 2018. δ13C of aromatic compounds in sediments, oils and atmospheric
598 emissions: A review. Org. Geochem. 123, 27–37.
599 https://doi.org/10.1016/j.orggeochem.2018.06.004

600 Huggett, J.M., 1994. Diagenesis of Mudrocks and Concretions from the London Clay Formation in the
601 London Basin. Clay Miner. 29, 693–707. https://doi.org/10.1180/claymin.1994.029.4.22

602 Hussler, G., Connan, J., Albrecht, P., 1984. Novel families of tetra- and hexacyclic aromatic hopanoids
603 predominant in carbonate rocks and crude oils. Org. Geochem. 6, 39–49.
604 https://doi.org/10.1016/0146-6380(84)90025-1

605 Kemp, D.B., Coe, A.L., Cohen, A.S., Schwark, L., 2005. Astronomical pacing of methane release in the
606 Early Jurassic period. Nature 437, 396–399. https://doi.org/10.1038/nature04037

607 Killops, S.D., 1991. Novel aromatic hydrocarbons of probable bacterial origin in a Jurassic lacustrine
608 sequence. Org. Geochem. 17, 25–36. https://doi.org/10.1016/0146-6380(91)90037-K

609 Kiriakoulakis, K., Marshall, J.D., Wolff, G.A., 2000. Biomarkers in a Lower Jurassic concretion from
610 Dorset (UK). J. Geol. Soc. London. 157, 207–220. https://doi.org/10.1144/jgs.157.1.207

611 Lash, G.G., Blood, D., 2004. Geochemical and textural evidence for early (shallow) diagenetic growth
612 of stratigraphically confined carbonate concretions, Upper Devonian Rhinestreet black shale,
613 western New York. Chem. Geol. 206, 407–424. https://doi.org/10.1016/j.chemgeo.2003.12.017

614 Lengger, S.K., Melendez, I.M., Summons, R.E., Grice, K., 2017. Mudstones and embedded
615 concretions show differences in lithology-related, but not source-related biomarker
616 distributions. Org. Geochem. 113, 67–74. https://doi.org/10.1016/j.orggeochem.2017.08.003

617 Lin, Z., Sun, X., Peckmann, J., Lu, Y., Xu, L., Strauss, H., Zhou, H., Gong, J., Lu, H., Teichert, B.M.A.,
618 2016. How sulfate-driven anaerobic oxidation of methane affects the sulfur isotopic
619 composition of pyrite: A SIMS study from the South China Sea. Chem. Geol. 440, 26–41.
620 https://doi.org/10.1016/j.chemgeo.2016.07.007

621 Long, J.A., Trinajstic, K., 2010. The Late Devonian Gogo Formation Lägerstatte of Western Australia:
622 Exceptional Early Vertebrate Preservation and Diversity. Annu. Rev. Earth Planet. Sci. 38, 255–
623 279. https://doi.org/10.1146/annurev-earth-040809-152416

624 Marshall, J.D., Pirrie, D., 2013. Carbonate concretions-explained. Geol. Today 29, 53–62.
625 https://doi.org/10.1111/gto.12002

626 Martill, D.M., 1989. The Medusa effect: instantaneous fossilization. Geol. Today 5, 201–205.
627 https://doi.org/10.1111/j.1365-2451.1989.tb00671.x

628 Martill, D.M., 1988. Preservation of fish in the Cretaceous Santana Formation of Brazil.
629 Palaeontology 31, 1–18.

630 Marynowski, L., Zatoń, M., Simoneit, B.R.T.T., Otto, A., Jedrysek, M., Grelowski, C., Kurkiewics, S.,
631 Jędrysek, M.O., Grelowski, C., Kurkiewicz, S., 2007. Compositions, sources and depositional
632 environments of organic matter from the Middle Jurassic clays of Poland. Appl. Geochemistry
633 22, 2456–2485. https://doi.org/10.1016/j.apgeochem.2007.06.015

634 McArthur, J.M., Algeo, T.J., van de Schootbrugge, B., Li, Q., Howarth, R.., 2008. Basinal restriction,
635 black shales, Re-Os dating, and the Early Toarcian (Jurassic) oceanic anoxic event.
636 Paleoceanography 23.

637 Melendez, I., Grice, K., Schwark, L., 2013a. Exceptional preservation of Palaeozoic steroids in a
638 diagenetic continuum. Sci. Rep. 3, 2768. https://doi.org/10.1038/srep02768

639 Melendez, I., Grice, K., Trinajstic, K., Ladjavardi, M., Greenwood, P., Thompson, K., 2013b.
640 Biomarkers reveal the role of photic zone euxinia in exceptional fossil preservation: An organic
641 geochemical perspective. Geology 41, 123–126. https://doi.org/10.1130/G33492.1

642 Ogihara, S., 1999. Geochemical characteristics of phosphorite and carbonate nodules from the
643 Miocene Funakawa Formation, western margin of the Yokote Basin, northeast Japan.
644 Sediment. Geol. 125, 69–82. https://doi.org/10.1016/S0037-0738(98)00136-5

645 Ogihara, S., Ishiwatari, R., 1998. Unusual distribution of hydrocarbons in a hydrothermally altered
646 phosphorite nodule from Kusu Basin, northern Kyushu, Japan. Org. Geochem. 29, 155–161.
647 https://doi.org/10.1016/S0146-6380(98)00052-7

648 Ostroukhov, S.B., Aref'yev, O.A., Zabrodina, M.N., Petrov, A.A., 1983. C12-C30 petroleum
649 alkylbenzenes with regular isoprenane chains. Pet. Chem. USSR 23, 217–226.

650 Pearson, M.J., Hendry, J.P., Taylor, C.W., Russell, M.A., 2005. Fatty acids in sparry calcite fracture fills
651 and microsparite cement of septarian diagenetic concretions. Geochim. Cosmochim. Acta 69,
652 1773–1786. https://doi.org/10.1016/j.gca.2004.09.024

653 Pearson, M.J., Nelson, C.S., 2005. Organic geochemistry and stable isotope composition of New

654 Zealand carbonate concretions and calcite fracture fills. New Zeal. J. Geol. Geophys. 48, 395–
655 414. https://doi.org/10.1080/00288306.2005.9515122

656 Plet, C., Grice, K., Pagès, A., Ruebsam, W., Coolen, M.J.L., Schwark, L., 2016. Microbially-mediated
657 fossil-bearing carbonate concretions and their significance for palaeoenvironmental
658 reconstructions: A multi-proxy organic and inorganic geochemical appraisal. Chem. Geol. 426,
659 95–108. https://doi.org/10.1016/j.chemgeo.2016.01.026

660 Plet, C., Grice, K., Pagès, A., Verrall, M., Coolen, M.M.J.L., Ruebsam, W., Rickard, W.D.A., Schwark, L.,
661 2017. Palaeobiology of red and white blood cell-like structures, collagen and cholesterol in an
662 ichthyosaur bone. Sci. Rep. 7, 13776. https://doi.org/10.1038/s41598-017-13873-4

663 Pye, K., Dickson, J.A.D., Schiavon, N., Coleman, M.L., Cox, M., 1990. Formation of siderite-Mg-calcite-
664 iron sulphide concretions in intertidal marsh and sandflat sediments, north Norfolk, England.
665 Sedimentology 37, 325–343. https://doi.org/10.1111/j.1365-3091.1990.tb00962.x

666 Raiswell, R., Fisher, Q.J., 2000. Mudrock-hosted carbonate concretions: a review of growth
667 mechanisms and their influence on chemical and isotopic composition. J. Geol. Soc. London.
668 157, 239–251. https://doi.org/10.1144/jgs.157.1.239

669 Reitner, J., Peckmann, J., Blumenberg, M., Michaelis, W., Reimer, A., Thiel, V., 2005. Concretionary
670 methane-seep carbonates and associated microbial communities in Black Sea sediments.
671 Palaeogeogr. Palaeoclimatol. Palaeoecol. 227, 18–30.
672 https://doi.org/10.1016/j.palaeo.2005.04.033

673 Riding, R., 2000. Microbial carbonates: the geological record of calcified bacterial-algal mats and
674 biofilms. Sedimentology 47, 179–214.

675 Rodrigues, B., Silva, R.L., Reolid, M., Filho, J.G.M., Duarte, L.V., 2019. Sedimentary organic matter
676 and δ13CKerogen variation on the southern Iberian palaeomargin (Betic Cordillera, SE Spain)
677 during the latest Pliensbachian–Early Toarcian. Palaeogeogr. Palaeoclimatol. Palaeoecol. 534.

678 Röhl, H.-J., Schmid-Röhl, A., 2005. Lower Toarcian (Upper Liassic) Black Shales of the Central
679 European Epicontinental Basin: A Sequence Stratigraphic Case Study from the Sw German
680 Posidonia Shale. Depos. Org. Sediments Model. 165–189.
681 https://doi.org/10.2110/pec.05.82.0165

682 Röhl, H., Schmid-Röhl, A., Oschmann, W., Frimmel, A., Schwark, L., 2001. The Posidonia Shale (Lower
683 Toarcian) of SW-Germany : an oxygen-depleted ecosystem controlled by sea level and
684 palaeoclimate. Palaeogeogr. Palaeoclimatol. Palaeoecol. 165, 27–52.

685 Ruebsam, W., Mayer, B., Schwark, L., 2019. Cryosphere carbon dynamics control early Toarcian
686 global warming and sea level evolution. Glob. Planet. Change 172, 440–453.
687 https://doi.org/10.1016/j.gloplacha.2018.11.003

688 Ruebsam, W., Müller, T., Kovács, J., Pálfy, J., Schwark, L., 2018. Environmental response to the early
689 Toarcian carbon cycle and climate perturbations in the northeastern part of the West-Tethyl
690 shelf. Gondwana Res. 59, 144–158.

691 Schmid-Röhl, A., Röhl, H., Oschmann, W., Frimmel, A., 2002. Palaeoenvironmental reconstruction of
692 Lower Toarcian epicontinental black shales (Posidonia Shale , SW Germany): global versus
693 regional control. Geobios 35, 13–20.

694 Schouten, S., Van Kaam-Peters, H.M.E., Rijpstra, W.I.C., Schoell, M., Sinninghe Damste, J.S., 2000.
695 Effects of an oceanic anoxic event on the stable carbon isotopic composition of early Toarcian
696 carbon. Am. J. Sci. 300, 1–22.

697 Schwark, L., Frimmel, A., 2004. Chemostratigraphy of the Posidonia Black Shale, SW-Germany II.
698 Assessment of extent and persistence of photic-zone anoxia using aryl isoprenoid distibutions.
699 Chem. Geol. 206, 231–248. https://doi.org/10.1016/j.chemgeo.2003.12.008

700 Scotchman, I.C., 1991. The geochemistry of concretions from the Kimmeridge Clay Formation of
701 southern and eastern England. Sedimentology 38, 79–106. https://doi.org/10.1111/j.1365-

3091.1991.tb01856.x

Sinninghe Damsté, J.P., Kock-Van Dalen, A.C., De Leuuw, J.W., Schenck, P.A., Brassell, S.C., 1987. The identification of mono-, di- and trimethyl 2-methyl-2-(4,8,12-trimethyltridecyl)chromans and their occurrence in the geosphere. Geochim. Cosmochim. Acta 5, 2393–2400.

Sinninghe Damsté, J.S., De Leeuw, J.W., Schenck, P. a, 1988a. Organically-Bound Sulphur in the Geosphere: a Molecular Approach. Tech. Univ. Delft PhD., 287.

Sinninghe Damsté, J.S., Keely, B.J., Betts, S.E., Baas, M., Maxwell, J.R., De Leeuw, J.W., 1993. Variations in abundances and distributions of isoprenoid chromans and long-chain aikylbenzenes in sediments of the Mulhouse Basin : a molecular sedimentary record of palaeosalinity *. Org. Geochem. 20, 1201–1215.

Sinninghe Damsté, J.S., Kock-van Dalen, A.C., de Leeuw, J.W., 1988b. Identification of long-chain isoprenoid alkylbenzenes in sediments and crude oils. Geochim. Cosmochim. Acta 52, 2671–2677. https://doi.org/10.1016/0016-7037(88)90035-X

Sinninghe Damsté, J.S., Köster, J., Baas, M., Ossebaar, J., Dekker, M., Pool, W., Geenevasen, J.A.J., 1999. A sedimentary tetrahydrophenanthrene derivative of tetrahymanol. Tetrahedron Lett. 40, 3949–3952. https://doi.org/10.1016/S0040-4039(99)00618-8

Thiel, V., Hoppert, M., 2018. Fatty acids and other biomarkers in two Early Jurassic concretions and their immediate host rocks (Lias δ Buttenheim clay pit, Bavaria, Germany). Org. Geochem. 120, 42–55. https://doi.org/10.1016/j.orggeochem.2018.02.010

Trolio, R., Grice, K., Fisher, S.J., Alexander, R., Kagi, R.I., 1999. Alkylbiphenyls and alkyldiphenylmethanes as indicators of petroleum biodegradation. Org. Geochem. 30, 1241–1253. https://doi.org/10.1016/S0146-6380(99)00099-6

Tulipani, S., Grice, K., Greenwood, P.F., Haines, P.W., Sauer, P.E., Schimmelmann, A., Summons, R.E., Foster, C.B., Böttcher, M.E., Playton, T., Schwark, L., 2015. Changes of palaeoenvironmental

conditions recorded in Late Devonian reef systems from the Canning Basin, Western Australia: A biomarker and stable isotope approach. Gondwana Res. 28, 1500–1515. https://doi.org/10.1016/j.gr.2014.10.003

Werne, J.P., Lyons, T.W., Hollander, D.J., Formolo, M.J., Sinninghe Damsté, J.S., 2003. Reduced sulfur in euxinic sediments of the Cariaco Basin: Sulfur isotope constraints on organic sulfur formation. Chem. Geol. 195, 159–179. https://doi.org/10.1016/S0009-2541(02)00393-5

Wilkin, R.T., Arthur, M.A., 2001. Variations in pyrite texture , sulfur isotope composition , and iron systematics in the Black Sea : Evidence for Late Pleistocene to Holocene ... Geochemica Cosmochim. Acta 65, 1399–1416. https://doi.org/10.1016/S0016-7037(01)00552-X

Wilkin, R.T., Barnes, H.L., 1997. Formation processes of framboidal pyrite. Geochemica Cosmochim. Acta 61, 323–339.

Williams, J.A., Dolcater, D.L., Torkelson, B.E., Winters, J.C., 1988. Anomalous concentrations of specific alkylaromatic and alkylcycloparaffin components in West Texas and Michigan crude oils. Org. Geochem. 13, 47–60. https://doi.org/10.1016/0146-6380(88)90024-1

Williams, M., Benton, M.J., Ross, A., 2015. The Strawberry Bank Lagerstätte reveals insights into Early Jurassic life. J. Geol. Soc. London. 2014–144. https://doi.org/10.1144/jgs2014-144

Wolff, G.A., Rukin, N., Marshall, J.D., 1992. Geochemistry of an early diagenetic concretion from the Birchi Bed (L. Lias, W. Dorset, U.K.). Org. Geochem. 19, 431–444. https://doi.org/10.1016/0146-6380(92)90010-U

Woo, K.S., Khim, B.K., 2006. Stable oxygen and carbon isotopes of carbonate concretions of the Miocene Yeonil Group in the Pohang Basin, Korea: Types of concretions and formation condition. Sediment. Geol. 183, 15–30. https://doi.org/10.1016/j.sedgeo.2005.09.005

Yoshida, H., Asahara, Y., Yamamoto, K., Katsuta, N., Minami, M., Metcalfe, R., 2019. 87Sr/86Sr age determination by rapidly formed spherical carbonate concretions. Sci. Rep. 9, 1003.

https://doi.org/10.1038/s41598-019-38593-9

Yoshida, H., Ujihara, A., Minami, M., Asahara, Y., Katsuta, N., Yamamoto, K., Sirono, S., Maruyama, I., Nishimoto, S., 2015. Early post-mortem formation of carbonate concretions around tusk-shells over week-month timescales. Sci. Rep. 1–7. https://doi.org/10.1038/srep14123

Yoshida, H., Yamamoto, K., Minami, M., Katsuta, N., Sin-Ichi, S., Metcalfe, R., 2018. Generalized conditions of spherical carbonate concretion formation around decaying organic matter in early diagenesis. Sci. Rep. 8, 1–10. https://doi.org/10.1038/s41598-018-24205-5

Zatoń, M., Marynowski, L., 2004. Konzentrat-Lagerstätte-type carbonate concretions from the uppermost Bajocian (Middle Jurassic) of the Czêstochowa area , South-Cental Poland. Geol. Q. 48, 339–350.

Zhang, S., Huang, H., Su, J., Liu, M., Zhang, H., 2014. Organic Geochemistry Geochemistry of alkylbenzenes in the Paleozoic oils from the Tarim. Org. Geochem. 77, 126–139. https://doi.org/10.1016/j.orggeochem.2014.10.003

Ziegler, P.A., 1990. Geological Atlas of Western and Central Europe. Shell Internationalle Petroleum Mij. B. V. and Geological Society, London.

FIGURE CAPTIONS

Figure 1. Concretions A and B showing the positions and labelling of subsamples investigated. Subsample 1 being the most internal and subsample 3 corresponding to the concretion rim.

Figure 2. GC-MS total ion chromatogram (TIC) of the host sediment compared to body and rim samples of concretion A (left) and B (right). Vertical exaggeration was applied on the chromatograms to reveal the compounds of interest. DBT: dibenzothiophene; IS: internal standard; mDBT: methyldibenzothiophene; PT: phytanyl toluene; MTTC: methyltrimethyltridecylchromans. Peaks labelled I and II are tentatively identified as 1,1,7,8-tetramethyl-1,2,3,4-tetrahydrophenanthrene and a C_3 alkylphenanthrene.

Figure 3. Relative distribution of MTTCs, MPs + MDBTs, and C_{26}-C_{28} TAS within all samples studied. Most concretion samples show a higher TAS proportion than the host sediment (PS).

Figure 4. Both concretions showed similar extracted ion chromatograms, here represented by the chromatograms from concretion B. GC-MS and GC×GC-ToF-MS chromatograms of extracted ions m/z 92 for alkylated benzenes (AlkB) and phytanyl benzene (PB) on the left and m/z 106 for alkylated toluene (AlkT) and phytanyl toluene (PT) on the right. Comparison of the distribution from the host sediment and concretion B (representative of both concretion). Vertical exaggeration has been reported for the GC-MS data in order to facilitate the comparison.

Figure 5. Correlation between phytanyl and n-alkylated arenes in the sample set.

TABLES AND TABLE CAPTIONS

787 *Table 1. Compilation of publications reporting lipid biomarkers in carbonate concretions and main findings based on biomarker analyses.*

Age	Location	Reported mineralogy	lipids investigated	Main highlights from lipids & biomarkers	reference
Lower Lias	UK	calcite, (Fe)dolomite	aliphatic hydrocarbons, fatty acids	Mineralogical zonation derived from different microbial communities. Microbial activity involved: sulfate reduction, methanogenesis, iron and manganese-reducing activity	(Wolff et al., 1992)
Present	UK	Calcite, siderite, iron monosulfide	polar lipid fatty acids	Two sulfate reducing bacteria genera: Desulfovibrio sp. > Desulfobacter sp.	(Coleman, 1993)
Present	Middle Valley, Juan de Fuca Ridge	calcite-cemented soft mud, silt and pyrite	hydrocarbons	Biomarkers reflect high thermal maturity providing information on the geological history	(Boni et al., 1994)
Present	UK	siderite, calcite, fluorapatite, rhodochrosite, quartz, clay minerals, pyrite	Fatty acids, phospholipid fatty acids (PLFA)	Variations of lipid biomarker distributions within a single concretion, between individual concretions and between concretions and host sediments Great diversity of sulfate-reducing bacterial biomarker Biomarker for *Desulfovibrio* sp capable of iron-reduction	(Duan et al., 1996)
Pleistocene	Japan	carbonate fluorapatite	aliphatic hydrocarbons and fatty acids	Non-altered phosphorite nodule: high hydrocarbon maturity Altered phosphorite nodule: hydrocarbons derived from microbial activity under hydrothermal condition.	(Ogihara and Ishiwatari, 1998)
Miocene	Japan	calcite, phosphorite, dolomite	aliphatic hydrocarbons, ketones	Low maturity and high hopanoid content. P concentration and apatite precipitation mediated by bacteria in sulfate reduction zone.	(Ogihara, 1999)

Oligocene	Belgium	calcite with framboidal pyrite +detrital minerals in minor amount	aliphatic hydrocarbons and fatty acids	Large terrigenous input and low algal steroidal markers Abundant markers of sulfate-reducing bacteria in the concretion Presence of methanogenic archaeal markers in the concretion.	(de Craen et al., 1999)
Lower Lias	UK	calcite, dolomite	aliphatic hydrocarbons and fatty acids	Biomarkers indicative of sulfate-reducing bacteria in calcite core	(Kiriakoulakis et al., 2000)
Middle Jurassic	Poland		hydrocarbons, fatty acids	Thermally immature OM Predominance of terrestrial biomarkers in host sediment and concretions Diasterene > sterenes> steranes suggest early and shallow formation of carbonate concretions No evidence for water column stratification and anoxia	(Zatoń and Marynowski, 2004)
Late Jurassic	UK	calcite	fatty acids	Different fatty acids distribution between calcite septaria and concretion body Differences attributed to the low aqueous solubility of long chain fatty acids	(Pearson et al., 2005)
Jurassic, Cretaceous,Paleocene, Eocene, Miocene	New Zealand, UK	calcite, siderite, Fe-dolomite	aliphatic hydrocarbons, fatty acids	Concretion septaria: the fatty acids incorporated into septarian calcite during crystal formation Concretions matrix: fatty acids are kerogen derived Input from terrestrial vegetation Strong maturity differences between cracks and concretions	(Pearson and Nelson, 2005)
Present	Black Sea	calcite	Aliphatic hydrocarbons, alcohols	Combined DNA and biomarker analyses on microbial mats and carbonate at methane seep Evidence of archaea and sulfate reducing bacteria, algae and higher plant biomarkers Confirmation of pivotal role for archaea and sulfate-reducing bacteria during carbonate concretions formation in methane seep environments	Reitner 2005
Middle Jurassic	Poland	Siderite, rhodochrosite, calcite, dolomite	hydrocarbons, fatty acids	Comparison of biomarker from host sediment and concretion: similar hydrocarbon distribution but different fatty acid distribution Unsaturated fatty acids higher in concretions than host sediment No sulfate-reducing bacterial marker detected	(Marynowski et al., 2007)
Lower Eocene	Bulgaria	Calcite with detrital grains (quartz, feldspar)	alcohols, Fatty acids	Release of carbonate-bound and ester bound biomarkers Abundant archaeal biomarkers, bacterial markers and eukaryotic markers	(De Boever et al., 2009)

Devonian	Australia	Calcite	aliphatic and aromatic hydrocarbons	^{13}C-depleted *n*-alkane distribution attributed to sulfate reducing bacteria High cholestane with distinct ^{13}C signature attributed to fossil crustacean Aromatic hydrocarbon showed evidence of photic zone euxinia during concretion formation	(Melendez et al., 2013b)
Devonian	Australia	Calcite	steroids	Fossil preserved in concretion revealed presence of a steroid continuum (from sterols to triaromatic steroids) Oldest intact sterols reported in the rock record	(Melendez et al., 2013a)
Upper Miocene	Austria	Siderite, calcite	hydrocarbons, fatty acids	Low overall content of bacterial biomarkers	(Baumann et al., 2016)
Toarcian	Germany	Calcite, pyrite	aliphatic hydrocarbons, aryl isoprenoids	Similar biomarker distribution between two concretions and their host sediment indicate biomarker signature inherited from host sediment ^{13}C depletion of *n*-alkanes in the concretions compared to host sediment related to sulfate reducing bacterial activity	(Plet et al., 2016)
Toarcian	Germany	Calcite, pyrite	steroids	Preservation of intact sterols in the fossil vertebra embedded in a concretion Sterols δ^{13}C composition revealed two sources of sterols: C_{27} sterol largely derived from the ichthyosaur diet, C_{29} sterol derived from primary activity in the water column	(Plet et al., 2017)
Devonian	Australia	Calcite cement with pyrite and detrital grain	total lipid extract (focus on aliphatic hydrocarbons)	Aliphatic hydrocarbons of concretions similar to host sediment: aliphatic distribution inherited during concretion formation Variations exist in biomarker indices related to lithology (carbonate *vs.* mudstone)	(Lengger et al., 2017)
Toarcian	Germany	siderite, calcite, fluorapatite, rhodochrosite, quartz, clay minerals, pyrite	fatty acids, hydrocarbons	Evidence of enhanced preservation or selective accumulation mechanism of fatty acids and diacids in the concretions compared to the host sediment	(Thiel and Hoppert, 2018)

788

*Table 2. Proportions of TOC, $CaCO_3$, pyrite and siliciclastic component of each samples (in %). $\delta^{34}S_{bulk}$ for each sample. * is an average of two PS samples. ‡ values published in Plet et al., 2016.*

	HI ‡ (mg HC / gTOC)	**TOC** (wt%)	**$CaCO_3$**‡ (wt%)	**Pyrite** (wt%)	**Siliciclastic** (wt%)	**$\delta^{34}S_{bulk}$**	**$\delta^{13}C_{carbonate}$**‡
PS	820	9.4	40	7	43.4	**-21.9***	–1.8
A1	740	1.0	95	1	3.1	**--17.0**	–14.5
A2	750	1.0	95	1	3.1	**--15.5**	–14.4
A3	580	1.0	83	13	2.8	**-8.4**	–12.6
B1	700	0.9	96	1	2.3	**-11.7**	–10.2
B2	720	0.8	95	1	3.3	**-15.5**	–14.2
B3	590	2.1	70	22	6.5	**-8**	–8.3

*Table 3. Normalisation of compounds and groups of compounds to the sum of C_{26}-C_{28} TAS. *indicates ratios determined based on GC×GC-ToF-MS analyses. AlkBr: alkylbenzene ratio; PBr: phytanyl benzene/C_{26}-C_{28} TAS; AlkTr: alkyltoluene ratio;PTr: phytanyl toluene/C_{26}-C_{28} TAs; C_{18} BrTr= C_{18} BrT*1000/sum C_{26}-C_{28} TAS; BrTr= sum C_{16}-C_{26} BrT*1000/ sum C_{26}-C_{28} TAS; DBTr: DBT/C_{26}-C_{28}; MDBTr: sum MDBT/C_{26}-C_{28} TAS; DMDBTr: sum DMDBT/sum C_{26}-C_{28} TAS, BNTr: sum BNT/C_{26}-C_{28} TAS; AlkNr: sum alkyl naphthalene/C_{26}-C_{28} TAS; C_{29}DESHr: C_{29}DESH*1000/C_{26}-C_{28}TAS; BHr: sum C_{32}-C_{33} benzohopanes/C_{26}-C_{28} TAS.*

	Host sediment	**Concretion A**			**Concretion B**		
ratios	PS	A1	A2	A3	B1	B2	B3
AlkBr*	0.06	0.90	0.17	0.88	1.75	1.10	1.02
PBr *	<0.01	0.01	<0.01	0.04	0.04	0.03	0.02
AlkTr*	0.31	2.53	1.33	1.95	3.24	2.87	2.04
BrTr*	16	259	58	227	356	265	171
PTr*	0.06	0.53	0.26	0.81	0.77	0.73	0.69
DBTr	0.16	0.15	0.10	0.10	0.21	0.13	0.11
MDBTr	0.47	0.38	0.26	0.22	0.61	0.42	0.31
DMDBTr	0.41	0.32	0.20	0.29	0.56	0.41	0.29
BNTr	0.09	0.06	0.04	0.06	0.12	0.09	0.06
AlkNr	3.77	6.69	4.48	4.87	9.76	6.82	4.83
C_{29}DESHr*	1.8	3.77	3.78	3.72	4.31	4.71	5.99
BHr*	202	116	n.d.	202	178	141	248