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## Organic matter deposition in the Ghadames Basin (Libya) during the Late Devonian-A multidisciplinary approach

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1 **Organic matter deposition in the Ghadames Basin (Libya) during the Late Devonian—a**  
2 **multidisciplinary approach**

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21  
22  
23 **Abstract**

24 The organic rich deposits of Late Devonian age are the second most important  
25 petroleum source rocks in the Ghadames Basin (Libya). From available stratigraphy, the peak  
26 of organic matter deposition, corresponding to a level of radioactive shales easily recognized  
27 in gamma ray logs, occurred at the Frasnian-Famennian transition. The present study was  
28 focused on samples from borehole D1-26, located in the central part of the Ghadames Basin,  
29 belonging to the Aouinet Ouenine III and IV formations (Frasnian to Famennian). The  
30 mineral and organic content of the rocks were analyzed in order to determine the origin of  
31 organic matter accumulation and estimate if the organic matter enrichment could be related to

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32 the well-known Upper Kellwasser event. The results indicate that during the Frasnian, the  
33 planktonic primary productivity was moderate, but anoxic conditions reaching the euphotic  
34 zone were frequent and allowed efficient preservation of the organic matter. At the Frasnian-  
35 Famennian transition, the deposition of the radioactive shales level can be related to a eustatic  
36 rise, which allowed incursion of nutrient-rich water in the basin, leading to increase in  
37 primary productivity and photic zone anoxia. During the Famennian, the conditions changed,  
38 associated with a relative sea level fall and/or a progradation of detrital sediments originating  
39 from the south. Photic zone anoxia was only episodic and plankton-derived organic matter  
40 was poorly preserved. Nevertheless, the important influx of organic matter of terrestrial origin  
41 allowed significant enrichment of the sediment in organic matter. Several indications suggest  
42 the radioactive shales interval could be coeval with the Upper Kellwasser level, nevertheless  
43 further stratigraphic work is needed to confirm this hypothesis.

44

#### 45 **Keywords**

46 Biomarkers, palynofacies, major and trace elements, Frasnian-Famennian

47

#### 48 **1. Introduction**

49 The Late Devonian was a period of extensive organic matter (OM) deposition along  
50 continental margins (Ulmishek and Klemme, 1990). The reasons for such widespread  
51 deposition of OM within oceanic realm is still a matter of discussion but a combination of  
52 several favorable factors has been proposed, including: (1) an overall rise of the sea level and  
53 a warmer climate favoring water stratification (Ulmishek and Klemme, 1990; Bond and  
54 Wignall, 2008; Riquier et al., 2010); (2) a tectonic context marked by the onset of the  
55 Variscan orogeny inducing both an increase of the nutrient supply from continents and the  
56 reduction of sea-water communications along the former Paleotethysian seaways  
57 (Tribovillard et al., 2004; Averbuch et al., 2005); (3) the development of root systems in  
58 terrestrial plants during this interval that may have also contributed to an increase in nutrient  
59 delivery to oceanic basins, promoting planktonic productivity (Algeo and Scheckler, 1998).  
60 The maximum convergence of these favoring conditions resulted in several anoxic events  
61 associated with biotic crises, the most famous of which, called the Kellwasser event, occurred  
62 at the Frasnian-Famennian boundary; it is characterized by the widespread deposition of two  
63 organic-rich levels respectively called the Lower and Upper Kellwasser levels (Buggisch,  
64 1991; Joachimski and Buggisch, 1993; House, 2002; Bond et al., 2004; Racki, 2005; Riquier  
65 et al., 2006; Becker et al., 2012). Though considered as one of the major extinction events in

66 Earth history, affecting both marine and continental faunas (see McGhee et al., 2013 for a  
67 recent review), the exact timing, causes and consequences of the Kellwasser event is still a  
68 matter of active research (Racki, 2005; Becker et al., 2016). The resultant massive organic  
69 carbon burial may have had a major impact on the global carbon cycle thereby enhancing a  
70 significant drop of the CO<sub>2</sub> atmospheric content and a global cooling trend in Late Devonian  
71 times (Algeo et al., 1995; Joachimski and Buggisch, 2002; Godderis and Joachimski, 2004;  
72 Averbuch et al., 2005; Riquier et al., 2010).

73 North Africa is characterized by the presence of several large to giant petroleum  
74 systems associated with Paleozoic source rocks (Boote et al., 1998; Craig et al., 2008). In well  
75 logging, the organic-rich intervals are recognizable by their high radioactivity in gamma ray  
76 logs, and are qualified as “radioactive shales” or “hot shales”. The dominant source rocks in  
77 North African petroleum systems are of Silurian age, in particular the Tanezzuft Formation in  
78 Algeria Tunisia and Libya, which base shows a characteristic hot shales interval (Boote et al.,  
79 1998; Craig et al., 2008). Organic-rich deposits of Late Devonian age are also widespread in  
80 North Africa and represent the second most important source rocks (Boote et al., 1998;  
81 Echikh, 1998; Lüning et al., 2003). From available stratigraphic correlations, the age of the  
82 Upper Devonian hot shales nevertheless varies from the early Frasnian to the early  
83 Famennian, from one basin to the other (Lüning et al., 2003). In the Ghadames Basin (Libya  
84 and Tunisia, Fig. 1), the Upper Devonian organic-rich level corresponds to a radioactive  
85 shales and limestones interval of late Frasnian age, sometimes referred to as the Cues  
86 limestones Horizon (Massa, 1988; Weyant and Massa, 1991). This interval well recognized in  
87 gamma ray logs (Weyant and Massa, 1991; Boote et al., 1998) could therefore be coeval to  
88 the Upper Kellwasser horizon (Joachimski and Buggisch, 1993; Bond et al., 2004). The two  
89 Kellwasser levels are well known in Morocco (Riquier et al., 2005), and Soua (2014)  
90 proposed that the two late Frasnian hot-shale intervals detected in South Tunisia were coeval  
91 to the Kellwasser levels.

92 This paper presents the results of a multidisciplinary study of a Frasnian-Famennian  
93 section in the Libyan part of the Ghadames Basin. The aim of the study was to determine the  
94 factors which favored OM deposition in this basin during the Late Devonian, and potentially  
95 relate it to the general context of the extensive Kellwasser environmental crisis.

96

## 97 2. Materials and methods

### 98 2.1 Studied interval

99 This study is based on samples from borehole D1-26 (30° 29' 21" N, 10° 46' 28" E)  
100 cored in 1960-61 by the Oasis Oil Company in Libya, in the central part of the Ghadames  
101 Basin (Fig. 1). Samples were taken from cores 6, 7 and 8 in the Aouinet Ouenine (or Awaynat  
102 Wanin) formations III and IV (AO III and AO IV, Fig. 2) and were labeled according to their  
103 depth in the core, originally given in feet. In the studied borehole, the AO III and AO IV  
104 formations mostly consist in grey to dark grey, finely laminated and micaceous shales to silty  
105 shales (Fig. 2). The upper part of the AO III Fm. is more calcareous and passes to alternating  
106 shales and fossiliferous limestones in the lower part of the AO IV Fm. (Fig. 2). This latter  
107 interval should correspond to the "Cues Limestone Horizon" and associated radioactive shales  
108 (Weyant and Massa, 1991). Sandy levels appear and become more abundant in the upper part  
109 of the AO IV Fm. (Fig. 2). Biostratigraphic constraints, based on palynomorphs and  
110 conodonts, and gamma ray correlations with other cores from the Ghadames Basin (Loboziak  
111 and Streel, 1989; Weyant and Massa, 1991; Spina et al., 2017), indicate that the samples from  
112 core 8 are of late Frasnian age, likely within the *Palmatolepis rhenana* conodont Zone (Streel,  
113 2009), while those from core 6 are of late Famennian age (Fig. 2), likely within the  
114 *Siphonodella praesulcata* conodont Zone (Streel, 2009). Core 7 was collected in so-called  
115 radioactive shales (Massa, 2005, personal communication). This radioactive shale interval  
116 generally is considered of late Frasnian age (Massa, 1988; Boote et al., 1998). Nevertheless,  
117 Weyant and Massa (1991) analyzed the conodont content of two samples of unknown depth  
118 from core 7, and proposed an early Famennian age, in the Middle to Upper *Palmatolepis*  
119 *triangularis* Zone, or *Palmatolepis crepida* Zone.

120

### 121 2.2 Palynology

122 Eighteen core samples from the Aouinet-Ouenine III and IV formations (samples 7813  
123 to 7081, 2381.4 m to 2158.3 m) were processed and analyzed. About 20-30 g of sample have  
124 been initially treated in hydrochloric acid (37 %), followed by digestion in hydrofluoric acid  
125 (50 %) and by treatment in 30% boiling hydrochloric acid to remove fluorosilicates. Residues  
126 were then subjected to density separation using zinc bromide solution in order to separate OM  
127 from heavy minerals. Finally, the organic-rich residues were sieved with acid resistant 50 and  
128 15 µm sieves. No oxidation by nitric acid was performed. A minimum of three palynological

129 strew-slides were mounted for each sample using Eukitt as mounting medium. Palynological  
130 slides were examined using transmitted light microscopes, commonly with  $\times 20$  (dry) and  
131  $\times 100$  (oil immersion) objectives. Palynological slides are stored in the collection of the UMR  
132 8198 Evo-Eco-Paleo, Université de Lille-CNRS, Villeneuve d'Ascq (France). For  
133 palynofacies analysis, 300 particles were counted in each level, in order to estimate the  
134 proportions of the organic constituents. The organic constituents from D1-26 borehole were  
135 grouped according to Whitaker (1984) classification, modified to emphasize the organic  
136 components useful for palaeoenvironmental observations in the Devonian time span. The  
137 allochthonous fraction, of continental origin, includes the palynomaceral group (plant debris)  
138 and sporomorphs. The palynomaceral (PM) group is divided in PM1, orange to dark brown  
139 fragments, translucent, partially oxidized; PM2, cell-structured orange to dark-brown  
140 fragments, moderately oxidized; PM4, black opaque fragments, strongly oxidized. PM4 is the  
141 most stable palynomaceral and can be transported for a long distance before being degraded.  
142 Sporomorphs mostly correspond to cryptospores (Strother, 1991) and miospores (Steemans,  
143 1999). The autochthonous fraction, of marine origin, comprises acritarchs, prasynophycean  
144 cysts, chitinozoans and amorphous organic matter (AOM). Acritarchs are organic-walled  
145 microfossils of uncertain biological affinity (Evitt, 1963), but mostly representing marine  
146 phytoplankton (Tappan, 1980; Martin, 1993; Colbath and Grenfell, 1995). In the Aouinet  
147 Ouenine sediments, prasynophycean cysts mainly correspond to *Tasmanites* (Tasmanaceae).  
148 This type of algal microfossil occurs in many marine facies from Cambrian to Miocene  
149 (Martín-Closas, 2003). Abundance of *Tasmanites* is often observed in marine (shelf and  
150 oceanic) organic-rich sediments (Tyson, 1995). Chitinozoans are organic-walled microfossil  
151 of uncertain affinity, but most probably representing marine microzooplankton (Paris and  
152 Nölvak, 1999). AOM is the degradation product of benthic and pelagic cyanobacteria and  
153 sulfur bacteria in oxygen deficient environments. Being the most dissolvable OM, it can be  
154 preserved only in oxygen-deprived (suboxic to anoxic) environments, where it is not  
155 destroyed and biodegraded by consumers and decomposers or by the oxidizing processes  
156 (Hart, 1986). The quantity of this latter was established on unfiltered palynological residues,  
157 counting only particles larger than 50  $\mu\text{m}$ .

158

### 159 2.3 Bulk geochemistry

160 Twelve samples in the 2158.3 m to 2381.4 m interval (samples 7081 to 7813) were  
161 analyzed for bulk geochemistry. Rock-Eval analyses were performed on 100 mg of ground

162 bulk rock at the Institut Français du Pétrole-Energies Nouvelles using a Rock-Eval 6  
163 apparatus and standard analytical conditions (Behar et al., 2001). The main parameters  
164 obtained are total organic carbon content (TOC, in weight %), Hydrogen index (HI, mg HC/g  
165 TOC), oxygen index (OI, mg CO<sub>2</sub>/g TOC), that are proportional to the H/C and O/C ratio of  
166 the kerogen, respectively, and Tmax, an indicator of OM maturity. The sulfur content was  
167 determined by elemental analysis of the sediment with a FlashEA 1112 Elemental Analyser  
168 (Thermo). The analysis was performed on 1.5 to 2 mg of ground bulk rock added to  
169 approximately 5 mg of vanadium pentoxide, used as a combustion catalyst. 2.5-Bis(5-tert-  
170 butyl-benzoxazol-2-yl)thiophene (BBOT) was used as standard.

171 Major, minor, trace and rare earth elements (REE) concentrations were determined on  
172 ground bulk rock by inductively coupled plasma optical emission spectrometry (ICP-OES)  
173 and inductively coupled plasma mass spectrometry (ICP-MS), at Activation Laboratories Ltd.  
174 (Ancaster, Canada). Samples were mixed with a flux of lithium metaborate (LiBO<sub>2</sub>) and  
175 lithium tetraborate (Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>), and fused in an induction furnace. Molten sample was  
176 immediately poured into a solution of 5% nitric acid (HNO<sub>3</sub>) containing an internal standard,  
177 and mixed continuously until completely dissolved. The analytical accuracy and precision are  
178 found to be better than 1–2% for major elements, 5% for REE and 5–10% for the other  
179 elements, as checked by international standards and analysis of replicate samples. The  
180 enrichment factors were calculated for trace elements often enriched biogenically or  
181 authigenically, as follows:  $X_{EF} = [(X/Al)_{\text{sample}} / (X/Al)_{\text{PAAS}}]$ , where X and Al represent the  
182 weight % concentrations of element X and Al, respectively. Samples were normalized using  
183 the Post Archean Average shale (PAAS) compositions (McLennan, 1989). An enrichment  
184 factor larger than 1 theoretically points to the enrichment of the element relative to the PAAS  
185 ; in other words it indicates whether an element is biogenically or authigenically enriched  
186 compared to what its concentration would be, if it were of merely clastic origin. Practically,  
187 enrichment factors are taken into consideration when they out pass the value of 3. Full results  
188 are provided in Table S1. For calculation purpose, concentrations below the detection limit  
189 (Table S1) were taken as half the value of the detection limit.

190

#### 191 2.4 Biomarker analysis

192 For biomarker analysis, rock fragments were extracted (24 h) with dichloromethane  
193 (DCM) in a refrigerator to remove possible contamination from the sample surface. The  
194 fragments were then crushed to extract the lipids from inside the rock. Ca. 30 g pulverized

195 sample were extracted using a soxhlet apparatus with DCM (24 h). Elemental sulfur was  
196 removed by addition of activated copper to the recovered extracts. The solvent was removed  
197 by means of rotary evaporation and the residue re-dissolved in cyclohexane. The  
198 cyclohexane-soluble fraction (maltenes) was further separated by means of column  
199 chromatography. A mixture of standard compounds (2,2,4,4,6,8,8-heptamethylnonane, Dr  
200 Ehrenstorfer-GmbH; anthracene D10, Dr Ehrenstorfer-GmbH; nonadecan-2-one, Sigma-  
201 Aldrich) was added to the maltenes prior to fractionation. The aliphatic fraction was  
202 recovered from the maltenes by elution with cyclohexane on an activated silica column.  
203 Elution with a mixture of cyclohexane/DCM (9/1, v/v) recovered the aromatic fraction, after  
204 which the polar fraction was recovered by elution with DCM/MeOH (1/1, v/v). The aliphatic  
205 and aromatic fractions were analyzed by way of gas chromatography-mass spectrometry  
206 (GC-MS) using either a Trace GC 2000 gas chromatograph equipped with a DB5ht column  
207 (30 m × 0.25 mm i.d.; 0.1 µm film thickness). The oven temperature program was: 100 °C (1  
208 min) to 310 °C (held 16.5 min) at 4 °C/min. Helium was used as carrier gas. The mass  
209 spectrometer conditions were as follow: ionization energy 70 eV for electron ionization (EI)  
210 with a mass range m/z 50–700. Alternatively, samples were analyzed with a Perkin Elmer  
211 Clarus 680 GC equipped with a DB5MS ultra inert column (30 m × 0.25 mm i.d.; 0.25 µm  
212 film thickness). The oven temperature program was: 60 °C (1 min) to 100°C at 15°C/min,  
213 from 100°C to 200°C at 3°C/min, from 200 °C to 310 °C (held 20 min) at 4 °C/min. Helium  
214 was used as carrier gas. The mass spectrometer was operated at 70 eV for electron ionization  
215 (EI) with a mass range m/z 50–550 (full scan). Compounds were identified by comparison of  
216 mass spectra and elution order with published data.

217

### 218 **3. Results and interpretation**

#### 219 **3.1 Palynofacies**

220 The palynofacies of the studied samples shows variable proportions of palynomorphs as well  
221 as AOM (Fig. 3). The palynofacies of the first levels from the AO III Fm. (base of core 8,  
222 samples 7813 to 7809, Fig. 3) shows high abundances of acritarchs and prasinophycaean  
223 cysts (tasmanaceans) representing about 40% of the entire palynofacies. AOM is abundantly  
224 present in this interval, reaching up to ~40% of the palynofacies. Partially oxidized  
225 palynomacerals (e.g. PM1+PM2) and sporomorphs are scarcely present. Chitinozoans are  
226 relatively abundant (5-7 %). In the overlying levels of the AO III Fm. (samples 7802 to 7780,

227 Fig. 3), the palynofacies is dominated by the same marine elements but the proportion of  
228 acritarchs and tasmanaceans increases (up to 60 %) while the AOM content is reduced (0 to  
229 10 %). At the base of AO IV Fm. (core 7, Fig.3), corresponding to the "radioactive shales",  
230 AOM in high proportion, acritarchs and prasynophycean cysts characterize almost all the  
231 entire palynofacies. Sporomorphs and chitinozoans are very rare to absent. The acritarch  
232 fauna is well diversified in the samples from cores 8 and 7. A distinctive change in the  
233 palynofacies composition marks the uppermost levels (core 6) of AO IV Fm. (samples 7100  
234 to 7081, Fig. 3). Strongly oxidized palynomacerals (PM4) and partially oxidized  
235 palynomacerals (PM1 + PM2) are abundant as well as well-preserved sporomorphs. This  
236 latter group reaches abundance around 35% in the levels close to the boundary with the  
237 overlying Tahara Fm. Microplankton here mainly consists of acritarchs (10 to 15 %).  
238 *Tasmanites* are uncommon ( $\leq 10$  %). AOM and chitinozoans are very rare or absent.  
239

## 240 3.2 Bulk geochemistry

### 241 3.2.1 Organic matter and sulfur

242 Total organic carbon (TOC) contents of the analyzed samples vary between 0.8 and  
243 2.8 % (average 1.75 %, Table 1). Tmax values range between 431 and 440 °C. Average Tmax  
244 value in the uppermost samples is 435 °C indicating the beginning of the oil window. The  
245 average Tmax value is slightly higher in the samples from core 8 (438 °C) indicating a  
246 slightly higher thermal maturity.

247 HI values are between 60 and 319 mg HC/g TOC (av. 132 mg HC/g TOC) while OI  
248 values range between 0 and 47 mg CO<sub>2</sub>/g TOC. In a pseudo van Krevelen (HI-OI) as well as  
249 in the HI-Tmax diagram (Fig. 4A), the samples plot in the area of Type II-III OM. TOC/N  
250 atomic ratios vary between 14 and 44 (Table 1). In average, higher values are observed in the  
251 samples from core 6 (av. 38) than in samples from cores 7 and 8 (av. 18). Higher values of the  
252 C/N ratio in the samples from the top of AO IV Fm. (samples 7100 to 7081) suggest a higher  
253 contribution from woody organic matter (Meyers, 1997), which is consistent with  
254 palynofacies observations.

255 The sulfur content of the sediment is relatively high, with an average value of 2.8 %.  
256 In a S vs TOC plot (Fig. 4B), most samples plot above the "normal marine" line (Berner,  
257 1982), having a slope of 2 for the Devonian (Berner and Raiswell, 1983). It can be argued that  
258 this feature could result from a TOC loss upon maturation and petroleum expulsion, since

259 Rock Eval production index (PI) values between 0.10 and 0.48 are compatible with oil  
260 expulsion (Table 1). Nevertheless, considering an initially doubled TOC values does not  
261 significantly change the S-TOC relationship as most samples would remain above this  
262 “normal marine” line (Fig. 4C). This S-TOC behavior is often considered as indicating  
263 deposition under strongly reducing to euxinic conditions (Leventhal, 1983).

264

### 265 3.2.2 Productivity (Ba, Ni, Cu) and redox proxies (Mo, U, V, Ni, Cu, Zn, Co, Cr, Ce\*)

266 In order to be valid as productivity or redox proxies, elements must not be positively  
267 correlated with the Si (quartz) and/or Al (clay) content of the sediment. In the studied  
268 samples, Si and Al are negatively correlated, suggesting that the clay and silica content vary  
269 in opposite proportions. Most productivity and redox-sensitive elements in D1-26 samples are  
270 neither correlated with Si nor Al, except for Cr which is positively correlated with Al ( $r =$   
271  $0.818$ ,  $n=12$ ) and Ba which is positively correlated with Si ( $r = 0.933$ ,  $n=12$ ). The latter  
272 correlation might indicate the presence of silica of biogenic origin. The average value of the  
273 Ge/Si ratio of  $8.1 \cdot 10^{-6}$  however points for a mainly detrital origin of the silica in D1-26  
274 samples, therefore corresponding to detrital quartz (Tribovillard, 2013). This indicates that Cr  
275 and Ba have a dominant detrital origin and cannot be considered as environmental proxies.

276 The average enrichment factors (EF) of the different elements which are not  
277 influenced by the detrital supply range between 0.5 and 3 (Fig. 5A), pointing for no  
278 significant authigenic enrichment in these sediments. In detail, most elements do not show a  
279 marked temporal trend except for molybdenum. The  $Mo_{EF}$  curve shows values generally  
280 above 1 in the lowermost samples and a maximum value (22) in sample 7712. Above this  
281 sample, Mo is below the detection limit (Table S1) so that  $Mo_{EF}$  values are below 1. The  
282 cerium anomaly (Ce\*), though potentially influenced by changes in the detrital flux and sea  
283 level variations (Wilde et al., 1996), is negative for all the samples (average -0.048). The  
284 temporal variations of Ce\* are somehow opposite to Mo variations, the lowest values being  
285 observed in the lowermost samples, while higher values are observed in the upper part of the  
286 studied interval (Fig. 5B). Overall, these data point for only moderately reducing conditions  
287 during deposition of the two formations. The most reducing conditions, as indicated by the  
288 highest enrichment in molybdenum, are observed in the sample 7712, corresponding to the  
289 base of the organic-rich, radioactive clays. The AO III Fm. overall appears deposited in  
290 slightly more reducing conditions than the AO IV Fm.

291

### 292 3.2.3 Detrital proxies

293 In addition to Si and Al, elements mostly associated with detrital minerals comprise K  
294 (feldspar and/or illitic clay minerals), Ti (rutile, titanite or ilmenite), Zr (zircon) and rare earth  
295 elements (REE, which can be associated with several heavy minerals; Mongelli, 1995; Cullers  
296 and Podkovyrov, 2002). When normalized to the Al content, the concentration of these  
297 elements is a good indicator of changes in the detrital flux.

298 The geochemical composition of the lowermost five samples is relatively constant  
299 (Fig. 6). Only REE ratios show slight variations in this part (Fig. 6B). From sample 7780  
300 upwards the geochemical composition is more variable, with overall higher element/Al ratios  
301 for Ti, Hf, Th and Zr (Fig. 6A). The REE profiles also are more variable as indicated by the  
302  $(La/Lu)_N$  and  $(Gd/Yb)_N$  ratios (Fig. 6B). For major and trace elements a maximum in the Al-  
303 normalized content is observed in the sample 7087 (Fig. 6A). This sample is also  
304 characterized by a PAAS-normalized REE pattern markedly different from that of the other  
305 samples (Fig. 7).

306 Increase and variability of Al-normalized concentration of the different elements  
307 considered here mainly indicate a change from an argillaceous AO III Fm. to a more silty or  
308 more sandy AO IV Fm. The relative stability of REE patterns in the studied samples —except  
309 for sample 7087— suggests that these changes are mainly due to grain sorting rather than  
310 from changes in the origin of the detrital grains. In the case of sample 7087, the REE pattern  
311 of which is markedly different, the higher Zr/Al and Hf/Al ratios indicate a higher proportion  
312 of heavy minerals in the sediment. Such characteristics are observed in sediments deposited  
313 by turbidity currents (e.g. Riboulleau et al., 2014) and can be related to the increased  
314 proportion of sandy layers in the upper part of the AO IV Fm., reflecting a relative sea-level  
315 fall during the deposition of this formation (Massa, 1988; Carr, 2002).

316

## 317 3.3 Biomarkers

### 318 3.3.1 Saturated fraction

319 The saturate fraction is dominated by a series of linear alkanes (*n*-alkanes). Hopanes,  
320 steranes, linear isoprenoids and cycloalkanes are present in lesser proportion.

321 *n*-Alkanes range from C<sub>13</sub> to C<sub>37</sub> with a maximum in C<sub>16</sub> or C<sub>17</sub> (Fig. 8A). The  
322 contribution from long chain *n*-alkanes is generally low, as indicated by the low value of the  
323 terrestrial to aquatic *n*-alkane ratio (TAR; Bourbonniere and Meyers, 1996; TAR values 0.06-

324 0.52). Only the sample 7085 shows a higher contribution of long-chain alkanes (TAR = 0.74).  
325 No marked even or odd predominance is observed, as indicated by the CPI values close to 1  
326 (Bray and Evans, 1961). The highest CPI values (1.2) are observed in the two uppermost  
327 samples (7087 and 7085). Linear isoprenoids range from C<sub>14</sub> to C<sub>23</sub>, maximum in C<sub>19</sub>. The  
328 Pr/Ph ratio ranges from 1.0 to 2.2. This highest value is obtained for the two uppermost  
329 samples.

330 The distribution of bicyclic and tricyclic terpenoids is similar in all the samples.  
331 Bicyclic sesquiterpenoids range from C<sub>14</sub> to C<sub>16</sub> and are dominated by *ent*-8β(H)-  
332 homodrimane followed by a C<sub>15</sub> compound (Fig. 8B). *Ent*-8β(H)- drimane is also present in  
333 lesser amount. Three C<sub>19</sub> tricyclic terpanes are also present in low abundance in all the  
334 samples. From its mass spectrum, the first eluting compound corresponds to a 13α(methyl)-  
335 tricyclic terpane previously as described by Wang and Simoneit (1995). No other element  
336 from this series is apparently present. The following compounds correspond to compounds B  
337 and C of Greenwood and George (1999). A series of regular tricyclic terpanes (cheilantanes)  
338 ranging from C<sub>19</sub> to C<sub>26</sub> (max C<sub>23</sub>) is also observed in all the samples (Fig. 8C).

339 Hopanoids are present in all the samples but are relatively more abundant in the two  
340 uppermost samples. Hopanoids are dominated by a series of C<sub>27</sub> to C<sub>34</sub> regular αβ hopanes  
341 (Fig. 8C). βα Moretanes ranging from C<sub>29</sub> to C<sub>34</sub> are present in low abundance. In addition,  
342 several series of rearranged hopanes are observed: C<sub>24</sub> and C<sub>26</sub> 17,21-secohopanes (Lu et al.,  
343 2009), C<sub>29</sub> and C<sub>30</sub> 17α(H)-diahopanes, C<sub>27</sub> to C<sub>30</sub> 18α(H)-neohopanes (Ts series) and C<sub>29</sub>-C<sub>32</sub>  
344 early eluting series (Moldowan et al., 1991; Farrimond and Telnæs, 1996). Norgammacerane  
345 and gammacerane are also detected in low amounts, mostly in the two uppermost samples.

346 Steroids are present in all the samples, but in very low abundance. They are slightly  
347 more abundant in the two uppermost samples. The distribution of compounds is comparable  
348 in all the samples with a few variations, and comprises the dia- and regular series, dominated  
349 by the C<sub>27</sub> and C<sub>29</sub> compounds (Fig. 8D, Table 2). Diasteroids are relatively less abundant in  
350 the two uppermost samples (Table 2). Methylsteranes and dinosterane isomers were not  
351 detected. Short chain steroids C<sub>21</sub> to C<sub>23</sub> are also observed in all the samples (Fig. 8D). They  
352 are generally present in relatively low abundance compared to the longer C<sub>27</sub>-C<sub>29</sub> compounds.  
353

354 3.3.2 *Aromatic fraction*

355 This fraction is dominated by polycyclic aromatic hydrocarbons (PAHs) among which  
356 naphthalenes and phenanthrenes. Aromatic biomarkers mostly correspond to triaromatic  
357 steroids and arylisoprenoids.

358 Triaromatic steroids are observed in all the samples (not shown). They range from C<sub>20</sub>  
359 to C<sub>28</sub> and are dominated by the C<sub>26</sub> to C<sub>28</sub> compounds. Short chain compounds (C<sub>20</sub>-C<sub>22</sub>) are  
360 however more abundant in the lower samples. The distribution is dominated by the C<sub>28</sub>  
361 compounds for all the samples, however, the uppermost 2 samples show a higher contribution  
362 of the C<sub>26</sub> compounds. 3-Methyl and 4-methyltriaromatic steroids are also present in minor  
363 proportion in all the samples, however no triaromatic dinosteroids were identified.

364 Aromatic compounds derived from hopanoids were detected in very low proportions  
365 in the two uppermost samples. They mostly correspond to a C<sub>24</sub> ABCD-tetraaromatic  
366 hopanoid and des-E-D:C-friedo-25-norhopa-5,7,9-triene identified by Hauke et al. (1993).  
367 Cadalene is present in trace amounts in all the samples. Retene and the aromatic abietanoids  
368 were not detected.

369 A series of 2,3,6-trimethyl-arylisoprenoids ranging from C<sub>13</sub> to C<sub>31</sub> (max C<sub>18</sub>) is  
370 observed in all the samples (Fig. 9). This series of compounds is well known as the product of  
371 degradation of isorenieratene (Requejo et al., 1992). A second series corresponding to 3,4,5-  
372 trimethyl-arylisoprenoids is also observed (Fig. 9). These compounds derived from the  
373 degradation of the aromatic carotenoid palaerenieratene (Brown et al., 2000) are present in all  
374 the samples except the two uppermost samples (7087 and 7085). Isorenieratane was detected  
375 in low amount in all the samples while palaerenieratane is observed in the four lowest  
376 samples (7812 to 7712). Several other diagenetic/catagenetic products of isorenieratene  
377 previously described by Koopmans et al. (1996) were also detected in all the samples, where  
378 they show a similar distribution: a series of diaromatic isoprenoids with a biphenyl head  
379 characterized by a m/z 237 fragment ranging from C<sub>19</sub> (max) to C<sub>22</sub>, and C<sub>21</sub> to C<sub>24</sub> diaromatic  
380 compounds characterized by a m/z 133 fragment (compounds I to III, Fig. 9).

381 Alkylated di-, tri-, tetra-, and pentaaromatics are detected in abundance in all the  
382 samples. Naphtalene and methylated counterparts from C<sub>1</sub> to C<sub>6</sub> are present in all the samples.  
383 They are dominated by the C<sub>2</sub> or C<sub>3</sub> isomers. Phenanthrenes from C<sub>0</sub> to C<sub>4</sub> are observed in all  
384 the samples. Phenanthrene is the most abundant compound. Dibenzofurans are present in all  
385 the samples, but their proportion is higher in the uppermost two samples. They range from C<sub>0</sub>  
386 to C<sub>2</sub> and are dominated by the C<sub>1</sub> isomers. Dibenzothiophenes (DBT) from C<sub>0</sub> to C<sub>3</sub> are  
387 observed in all the samples. Their relative abundance is however lower in the two uppermost

388 samples. Their distribution is dominated by DBT or by 4-methyl-DBT. Fluoranthene, pyrene  
389 and methylated counterparts from C<sub>1</sub> to C<sub>2</sub> are detected in all the samples, however, their  
390 relative abundance is higher in the two uppermost samples. Triphenylene, chrysene their  
391 methylated counterparts from C<sub>1</sub> to C<sub>4</sub> are present in all the samples. The relative abundance  
392 of the C<sub>0</sub> counterparts and relative distribution of methylated homologs however differs  
393 between the lower four and upper two samples. In particular, a large dominance of the non-  
394 methylated counterparts is observed in the two uppermost samples. Isomer distribution ratios  
395 of selected PAHs are presented in Table 2.

396 Highly condensed PAH's such as benzo[e]pyrene, benzo[ghi]perylene or coronene are  
397 observed only in the uppermost two samples. They are not observed in the lowermost four  
398 samples, even by selective ion detection.

399

## 400 **4 Discussion**

### 401 4.1 Organic matter maturity

402 From the Rock-Eval Tmax values (Fig. 4A), the studied samples are located at the  
403 beginning of the oil window, with slightly higher maturity for samples from core 8 than for  
404 samples from core 6. This range of maturity is also indicated by the color and state of  
405 preservation of the miospores, acritarchs and *Tasmanites* in the samples (Spina et al., 2017).  
406 Using average correlation between biomarker isomerization ratios and thermal maturity  
407 (Peters et al., 2005), the ratio obtained in the studied samples (Table 2) tends to indicate a  
408 higher maturity than Rock-Eval Tmax, samples from core 8 having reached the peak of oil  
409 generation while samples from core 6 would be slightly less mature. Methylphenanthrene  
410 isomerization ratios indicate even more maturity with calculated vitrinite reflectance values  
411 higher than 0.7 % (Table 2). Hrouda (2004) previously observed a relatively poor correlation  
412 between molecular maturity indicators, vitrinite reflectance and Rock Eval in the Upper  
413 Devonian formations of the Ghadames Basin. Nevertheless, the relatively low maturity  
414 indicated by the Rock Eval data is supported by vitrinite reflectance measurements of 0.51 to  
415 0.59 performed by Underdown et al. (2007) on the same depth interval. These maturities are  
416 also consistent with those obtained by Hrouda (2004) for Upper Devonian formations in  
417 nearby cores from the Ghadames Basin. This low maturity allows interpret further the  
418 biomarker distribution in the analyzed samples.

419

## 420 4.2 Organic matter source

421 Based on palynofacies analysis, TOC/N ratio, and biomarker content, the OM in the  
422 Aouinet Ouenine Fm. shows a mixed contribution from continental and marine fractions. The  
423 palynofacies content and TOC/N ratio allow to clearly distinguish the lower samples (AO III  
424 Fm. and radioactive shales) dominated by marine elements from the upper part of AO IV Fm.,  
425 where the contribution from continental OM is more significant. Such distinction is less  
426 obvious basing on the biomarkers, since terrestrial plant biomarkers are almost absent from  
427 the record. Terrestrial plants in the Late Devonian were mostly restricted to bryophytes and  
428 early tracheophytes (Taylor et al., 2009). Earliest plants have not been so far related to an  
429 abundance of diversified biomarkers (Versteegh and Riboulleau, 2010), nevertheless a few  
430 higher plant terpenoids were previously identified in Devonian rocks, including in sediments  
431 of the Ghadames Basin (Kashirtsev et al., 2010; Romero-Sarmiento et al., 2011). Devonian  
432 plants already possessed a waxy coating made of long chain *n*-alkanes, typical of plant  
433 cuticles (Eglinton and Hamilton, 1967; Versteegh and Riboulleau, 2010). The dominance of  
434 short chain *n*-alkanes (<C<sub>20</sub>) in the samples is typical of sedimentary OM dominated by an  
435 autochthonous algal input (Gelpi et al., 1970). Nevertheless, the increased proportion of long  
436 *n*-alkanes in samples from core 6, as indicated by the higher TAR values (Table 2), is  
437 consistent with an increased contribution of OM of terrestrial origin. Contribution from land-  
438 derived OM in the two samples from core 6 (7087 and 7085) is also indicated by the PAH  
439 distribution, showing a high proportion of dibenzofurans, which have been related to  
440 dehydration of plant cellulose and polysaccharides (Sephton et al., 1999) and the contribution  
441 of unsubstituted highly condensed PAH such as coronene, which have been related to  
442 wildfires (Marynowski and Simoneit, 2009).

443 The sterane distribution, dominated by the C<sub>29</sub> and C<sub>27</sub> isomer (Table 2), is typical of  
444 OM of marine origin. Methylated counterparts, in particular 4-methyl isomers are generally of  
445 algal origin. Dinosteroids and 4-methyl steroids are often assigned to dinoflagellates and/or  
446 acritarchs. Though dinosteroids are absent from the extracts of D1-26 samples, the methylated  
447 steroids can be related to the marine algal input. In particular, several studies of Paleozoic  
448 rocks and petroleum have related these compounds to acritarchs (Moldowan et al., 1996;  
449 Moldowan and Talyzina, 1998).

450 Hopanoids and their diagenesis products, as well as drimane and homodrimane are  
451 related to bacterial inputs (Ourisson et al., 1979; Alexander et al., 1983). The sterane/hopane  
452 ratio is often used as an indicator of the proportion of bacterial biomass compared to the  
453 eukaryotic one. The highest values of this ratio are observed in the samples from the AO IV

454 Fm. and therefore suggest higher contribution from eukaryotes in these samples, while a  
455 higher contribution from bacterial biomass is observed in the lowermost four samples.

456 Though their origin is still debated, tricyclic terpanes (cheilantanes) have been mostly  
457 related to the contribution from prasinophytes and in particular tasmanaceans (Aquino Neto et  
458 al., 1992; Dutta et al., 2006). This is consistent with the frequent observation of *Tasmanites* in  
459 the palynofacies of D1-26 samples (Fig. 3). High relative abundances of cheilantanes,  
460 indicated by the tricyclic/17 $\alpha$  hopane ratio are observed in the four lower samples (7812 to  
461 7712, Table 2). The upper two samples (7087 and 7085) show lower relative abundance of  
462 cheilantanes (Table 2), which can be related to the lower relative abundance of *Tasmanites* in  
463 the palynofacies (Fig. 3). Abundance of prasinophytes in general or of *Tasmanites* in  
464 particular, has also been related to an increase of the C<sub>28</sub>/C<sub>29</sub> sterane ratio (Schwark and Empt,  
465 2006). This is for instance the case at the Frasnian-Famennian transition in the famous  
466 Kowala section in Poland, where prasinophytes represent 80 to 90% of palynomorphs  
467 (Filipiak, 2002; Schwark and Empt, 2006). No relationship is observed between the C<sub>28</sub>/C<sub>29</sub>  
468 sterane ratio and the relative abundance of *Tasmanites* in the palynofacies of D1-26 samples  
469 (Table 2, Fig. 3), which could be related to the fact that prasinophytes rarely account for more  
470 than 40% of palynomorphs in these samples.

471

#### 472 4.3 Redox conditions

473 Isorenieratene is a pigment synthesized by green sulfur bacteria (*Chlorobiaceae*),  
474 obligate anaerobes requiring light and free sulfides for living (Liaaen-Jensen, 1978;  
475 Overmann, 2008). In particular, *Chlorobiaceae* have been observed in the water column of  
476 the Black Sea (Overmann et al., 1992). For this reason, the observation of isorenieratene  
477 derivatives in sediment extracts is often used as an indicator of photic zone anoxia (Summons  
478 and Powell, 1986). The source of palaerenieratene is unknown but several arguments suggest  
479 this compound originates from extinct organisms related to *Chlorobiaceae* (Hartgers et al.,  
480 1994). A recent review of the occurrence of palaerenieratene in oils and sediments confirms  
481 this compound is almost restricted to the Paleozoic (French et al., 2015). When present,  
482 palaerenieratene is often more abundant than isorenieratene (Requejo et al., 1992; Behrens et  
483 al., 1998; Clifford et al., 1998; Joachimski et al., 2001; Armstrong et al., 2009; Bushnev,  
484 2009; Maslen et al., 2009; Racka et al., 2010; Marynowski et al., 2012; Melendez et al., 2013;  
485 Tulipani et al., 2015). Changes in the proportion of palaerenieratene vs. isorenieratene  
486 derivatives in relation to paleoenvironments are rarely reported in the literature. Nevertheless,  
487 in the Middle Devonian Keg River Fm., Behrens et al. (1998) observed that while both

488 palaerenieratane and isorenieratane and their derivatives were present in transgressive facies,  
489 the regressive facies of this formation only showed the presence of isorenieratane and its  
490 derivatives.

491 The total concentration of isorenieratene and palaerenieratene derivatives in the  
492 extracts of D1-26 generally decreases up-section through the studied interval, with the  
493 maximum value observed in the lowermost sample and the minimum value in the uppermost  
494 sample (Fig. 10A). When plotted in the Pr/Ph ratio versus the aryl isoprenoid ratio (AIR\*)  
495 modified from Schwark and Frimmel (2004), the lowermost four samples from D1-26 plot in  
496 a sector of relatively persistent photic-zone anoxia and reducing sediment, while the  
497 uppermost two plot in an area of oxygenated sediment with more episodic photic-zone anoxia  
498 (Fig. 10C). Location of D1-26 samples in this plot are also consistent with previous  
499 observations in the Posidonia black shale, regarding relative sea-level variations (Schwark  
500 and Frimmel, 2004): samples from AO III Fm. and radioactive shales, deposited in a rising  
501 sea level plot in the “intermediate sea level” sector, while samples from the higher part of AO  
502 IV Fm., deposited in a regressive context, plot in the “high sea level” and “low sea level”  
503 sectors. The ratio of the 3,4,5-trimethyl- to 2,3,6-trimethyl-arylisoprenoids (palaerenieratene  
504 to isorenieratene derivatives ratio, PIR) slightly increases from the base to the middle part of  
505 the series and falls to 0 in the uppermost two samples (Fig. 10B). The disappearance of  
506 palaerenieratane and its derivatives in the regressive, highest part of AO IV Fm. is consistent  
507 with the previous observations of Behrens et al. (1998).

508 The abundance of prasinophytes in the palynofacies of D1-26 samples shows a good  
509 parallel with the relative abundance of isorenieratene and palaerenieratene and their  
510 derivatives in the extracts (Figs. 3, 10): present in significant proportion in AO III Fm. and the  
511 radioactive shales, they become minor in the upper part of AO IV Fm. This observation fully  
512 supports the proposition of Prauss (2007), who suggested that prasinophyte abundance in  
513 sediments is controlled by, and therefore is an indicator of, reducing conditions in the photic  
514 zone.

515 Based on redox-sensitive trace metal concentration, the studied Devonian sediments  
516 from borehole D1-26 appear deposited under mainly oxic conditions. This appears  
517 inconsistent with the occurrence of *Chlorobiaceae* biomarkers and of *Tasmanites*, in all the  
518 samples. The only sample showing enrichment in redox-sensitive trace metals is sample 7712,  
519 belonging to the very base of the radioactive shales. Its enrichment in uranium remains  
520 modest (EF = 2) while a more notable enrichment is observed for molybdenum (EF=21). The  
521 contrasted enrichments in Mo and U, respectively suggest molybdenum enrichment

522 associated with redox cycling of manganese or iron oxyhydroxides, at the sediment water-  
523 interface or within the water column (Algeo and Tribovillard, 2009). It means that the water  
524 column would have been regularly oxygenated but the redox-cline would have been lying at  
525 short distance beneath the sediment-water interface, thence an anoxic sediment. High  
526 enrichment in trace elements in the radioactive shales is reported by Weyant and Massa  
527 (1991), nevertheless these authors did not indicate from which boreholes or outcrops these  
528 data originated, moreover, no data are available for the rest of the Aouinet Ouenine group.

529 The discrepancy between molecular and inorganic redox proxies could result from a  
530 so-called “reservoir effect” (Algeo, 2004; Algeo and Lyons, 2006). When a basin is poorly  
531 connected with the open sea, scavenging of molybdenum and other redox-sensitive trace  
532 metals by the precipitation of authigenic minerals may overcome the inflow of these elements  
533 to the basin. This process results in the progressive depletion of these elements in the water  
534 column (Algeo, 2004; Algeo and Lyons, 2006). Sediments deposited below such depleted  
535 water column will not be enriched in trace elements, even if they are organic-rich and/or  
536 anoxic (Algeo, 2004; Tribovillard et al., 2008). During the Devonian, the North African  
537 domain was structured into several basins separated by topographic highs (Lüning et al.,  
538 2003; Guiraud et al., 2005; Wendt et al., 2006; Frizon de Lamotte et al., 2013). Poor  
539 connections of the bottom part of these basins with the open sea are suggested by the  
540 widespread deposition of organic-rich sediments in the various North African basins (Lüning  
541 et al., 2003; Wendt et al., 2006). Such configuration might therefore have favored progressive  
542 depletion of the water column in trace elements, leading to the poor enrichment observed in  
543 the studied samples from borehole D1-26.

544

#### 545 4.4 Organic matter deposition and relationships with the F/F events

546 The studied samples from the Aouinet Ouenine Group where the TOC content was  
547 measured do not include the “radioactive shales” and are not very organic rich (Table 1).  
548 Nevertheless, the TOC values from 1 to 2% are consistent with previous studies of the  
549 Aouinet Ouenine Group in nearby boreholes (Hrouda, 2004).

550 The different methods used here indicate that in the Frasnian AO III Fm., OM mainly  
551 originates from an algo-bacterial biomass. The biomarker content and the significant  
552 contribution of *Tasmanites* in the palynofacies indicate that conditions in the sediment and  
553 water column were frequently reducing (Fig. 11A). The notable proportion of AOM in the  
554 palynofacies (Fig. 3) points to efficient OM preservation under reducing conditions. The  
555 moderate TOC values of the sediment despite recurrent anoxia, the notable proportion of

556 land-derived OM, and the abundant and well-diversified fauna of acritarchs in the  
557 palynofacies, nevertheless suggest that planktonic productivity was moderate (Fig. 11A).  
558 Consistent, Massa (1988) indicates that the facies in the AO III Fm. is confined and that the  
559 macrofauna are impoverished.

560 The palynofacies content and biomarkers in the radioactive shales from D1-26  
561 borehole only moderately differ with those of the AO III Fm., indicating a dominantly algo-  
562 bacterial OM and frequently anoxic conditions in the sediment and water column (Fig.  
563 11B,C). The high TOC content documented in the radioactive shales (Massa, 1988) is  
564 however a major difference with the AO III Fm., which, added to the low proportion of  
565 terrestrial OM in the palynofacies, suggests increased planktonic productivity and eutrophic  
566 conditions during deposition (Fig. 11B,C). Chitinozoans have been recently shown to be  
567 produced by relatively shelfal epiplanktonic organisms (Vandenbroucke et al., 2010). Their  
568 decreased abundance in the palynofacies of the radioactive shales compared to AO III Fm. as  
569 well as the absence of sporomorphs are consistent with a more pelagic setting, and therefore  
570 an increased sea level (Fig. 11B,C).

571 Eutrophication leading to the deposition of the radioactive shales could have resulted  
572 from the input of land-derived nutrients in the basin (Algeo et al., 1995; Averbuch et al.,  
573 2005), however, the Late Devonian was dominantly a period of subsidence and not of uplift  
574 around the Ghadames Basin (Craig et al., 2008). Moreover, though the detrital elements  
575 suggest a change in the detrital flux between AO III and AO IV formations (Fig. 6), this  
576 change appears to be modest (Fig. 7) and is already observed in sample 7780, several meters  
577 below the radioactive shales. The present data therefore do not support an increased supply of  
578 land-derived nutrients in the Ghadames Basin. Since depositional conditions were already  
579 reducing in the Ghadames Basin during the deposition of AO III Fm. (Fig. 11A), nutrients  
580 could either have been recycled from the water-column by more frequent water-column  
581 mixing (Murphy et al., 2000), or originate from incursions of nutrient-rich water from the  
582 Paleotethys. On the one hand, we do not have arguments regarding more frequent water-  
583 column mixing. On the other hand, incursions of water from the open sea were likely favored  
584 by the sea level rise, and are supported by the Mo/Al ratio of the samples (Fig. 5). As  
585 previously discussed, the redox-sensitive trace elements suggest that the water column of the  
586 Ghadames Basin was relatively depleted in dissolved trace metals during deposition of AO III  
587 Fm. The enrichment in molybdenum observed in sample 7712 was therefore only possible  
588 because of Mo inputs, refuelled by the ingression of « new » sea water into the basin (Algeo,  
589 2004; Algeo and Lyons, 2006).

590 The ambiguity on the age of samples from core 7 compels us to consider several  
591 scenarios relating the radioactive shales with the Frasnian-Famennian transition events. Massa  
592 (1988; pers. comm., 2005) suggested that the radioactive shales were of latest Frasnian age. If  
593 so, the radioactive shales of the Ghadames Basin might be equivalent to the Upper Kellwasser  
594 level. The two Kellwasser levels are well known in Morocco (Riquier et al., 2005), and the  
595 Frasnian radioactive shales have been related to the upper Kellwasser level in the Berkhine  
596 area in Algeria (Lüning et al., 2004) and in southern Tunisia (Soua, 2014). The deposition of  
597 the upper Kellwasser level and of the radioactive shales from the Ghadames Basin were both  
598 related to a Late Frasnian second-order sea-level high-stand (Carr, 2002; Chen and Tucker,  
599 2003; Dardour et al., 2004; Bond and Wignall, 2008). The eutrophication and possible  
600 development of more reducing conditions during the Upper Kellwasser event could result  
601 from the incursion of nutrient-rich and anoxic waters into the Ghadames Basin originating  
602 from the Paleotethys (Fig. 11B). This option would give support to the scenarios relating the  
603 deposition of the Kellwasser level to widespread oceanic eutrophication and development of  
604 anoxia in marginal basins (Joachimski and Buggisch, 1993; Bond et al., 2004; Averbuch et  
605 al., 2005; Riquier et al., 2006; Carmichael et al., 2014).

606 Alternately, if the radioactive shales were of early Famennian age (Weyant and Massa,  
607 1991), their deposition could be related to the early Famennian sea-level rise documented in  
608 several basins (Sandberg et al., 2002; Haq and Schutter, 2008). Though sea-level variations  
609 around the Frasnian-Famennian are still a matter of discussion (Bond and Wignall, 2008), this  
610 could correspond to T-R cycle IIe of Johnson et al. (1985). Deposition of black shales in  
611 basinal settings during the early Famennian have been described in Poland, France, Morocco  
612 and Eastern North America (Wendt and Belka, 1991; Bond et al., 2004; Schieber and Lazar,  
613 2004; Riquier et al., 2005) and may be related to this sea-level rise. For instance, in the  
614 Illinois Basin, the lowermost deposits of Famennian age in the New Albany shales show a  
615 more basal facies and more eutrophic conditions than late Frasnian deposits (de la Rue et  
616 al., 2007). The radioactive shales would then correspond to a model of « transgressive black  
617 shales », where connection with the open sea allows the entrance of nutrient-rich water and  
618 eutrophication (Fig. 11C), as observed in the Cariaco Basin (Venezuela) tuned to Quaternary  
619 sea-level oscillations (Peterson et al., 2000).

620 In addition to its well known  $\delta^{13}\text{C}$  excursion (Joachimski and Buggisch, 1993), recent  
621 studies indicate the Upper Kellwasser level could be characterized by molecular signatures:  
622 increase of the  $\text{C}_{28}/\text{C}_{29}$  sterane ratio (Schwark and Empt, 2006) related to the prominence of  
623 prasinophytes and low values of the hopane/sterane ratio, indicating high relative input of

624 eukaryotes (Haddad et al., 2016). The radioactive shales of borehole D1-26 show a slight  
625 decrease of the  $C_{28}/C_{29}$  sterane ratio compared to the other samples (Table 2). The  
626 hopane/sterane ratio is lower in the radioactive shales than in the samples from the AO IV  
627 formation (Table 2). Nevertheless, similarly low hopane/sterane ratios are observed in the  
628 samples from AO III Fm. (Table 2). None of these parameters therefore allows clarify the  
629 ambiguity on the age of samples from core 7.

630 The highest part of AO IV Fm. is characterized by a change in sedimentary facies  
631 compared to underlying levels. The proportion of sand increases (Fig. 2, 6), indicating a more  
632 proximal depositional setting. This lithological evolution is related to a third- or second-order  
633 relative sea-level fall (Carr, 2002; Dardour et al., 2004; Fig. 11D). Consistent, the OM content  
634 changes and is dominated by land-derived material (Fig. 3). The lower sea-level and restricted  
635 conditions could have favored oligotrophic conditions in the Ghadames Basin (Fig. 11D).  
636 Palynofacies and biomarkers point to relatively oxidative conditions in the sediment (Fig.  
637 11D), with only episodic photic zone anoxia. Though conditions were less prone to OM  
638 preservation, the highest part of the AO IV Fm. shows TOC values comparable to the AO III  
639 Fm. OM enrichment in this interval therefore appears to be related to an increased  
640 contribution of relatively resistant and less oil-prone terrestrial OM (Fig. 11D).

641

642

## 643 **5. Conclusions**

644 The multidisciplinary analysis of the Frasnian-Famennian Aouinet Ouenine III and IV  
645 formations in borehole D1-26, located in the Ghadames Basin (Libya) allowed to better  
646 understand the factors of OM enrichment in this important petroleum system. Our data  
647 indicate that during the Late Frasnian the Ghadames Basin was restricted and subject to  
648 frequent episodes of photic-zone anoxia. These conditions allowed a good preservation of  
649 OM derived from a moderate phytoplanktonic productivity. The beginning of OA IV Fm. is  
650 marked by the deposition of a radioactive shale interval, well known in core loggings of the  
651 Ghadames Basin, and corresponds to an episode of increased primary productivity and photic-  
652 zone anoxia. Though ambiguity remains on the exact age of this radioactive shale interval, our  
653 data suggest eutrophication was favored by the entrance of nutrient-rich waters into the  
654 Ghadames Basin. The upper part of OA IV Fm. is marked by a facies change associated with  
655 the Famennian regression. Photic zone anoxia was less frequent but the sediment is still  
656 organic-rich because of increased delivery of terrestrial OM.

657 The Late Devonian was a period of important changes in the carbon cycle marked by  
658 several episodes of oceanic anoxia and biotic crisis. While detailed and high-resolution  
659 studies of Late Devonian events in European, Asian and North-American successions are  
660 numerous, similar studies in North Gondwana remain rare and are mainly restricted to  
661 Morocco and Algeria, where the sediments present relatively proximal depositional facies.  
662 The present study demonstrates that the Ghadames Basin, in addition to its important  
663 petroleum interest, contains a rich sedimentary succession prone to future high-resolution  
664 studies of the Late Devonian events in North Gondwana.

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1024

1025 **Figure captions**

1026

1027 Figure 1: Location map of the Ghadames Basin showing the location of borehole D1-26.

1028

1029 Figure 2: Lithological and stratigraphic description of the Upper Devonian formations in  
1030 borehole D1-26, with sonic and resistivity (ILD) curves (unavailable scale). Compilation of  
1031 data from Oasis oils Company (1961), Canaple (1963) Loboziak and Streel (1989), Weyant  
1032 and Massa (1991) Spina et al. (2017). The peaks in the ILD curve (grey area) underline an  
1033 alternance of shale and limestones corresponding to the radioactive shales and Cues  
1034 Limestone horizon.

1035

1036 Figure 3: Palynofacies observations of the samples from borehole D1-26. A) Particle  
1037 counting; B,C) Prasinophycean cysts, AOM and acritarchs (B: slide 7802; C: slide 7780); D)  
1038 Prasinophycean cysts and AOM (slide 7704); E) miospores, Prasinophycean cysts and  
1039 palynomacerals (slide 7083). Photographs show the >50 $\mu$ m palynological residue. Legend of  
1040 the log as in fig. 2.

1041

1042 Figure 4: Rock-Eval and bulk geochemistry of samples from borehole D1-26. A) Hydrogen  
1043 index (HI) *versus* Tmax plot showing the type and maturity of the organic matter. B) Total  
1044 sulfur *versus* total organic carbon (TOC) of the sediment. The dotted line corresponds to the  
1045 relationship observed in “normal marine” shales (Berner, 1982; Berner and Raiswell, 1983).  
1046 C) Same as B after doubling the TOC content in order to account for thermal loss of organic  
1047 matter.

1048

1049 Figure 5: Mineral redox proxies in the samples from borehole D1-26. A) Enrichment factor  
1050 (EF) of the main redox-sensitive trace elements. B) Cerium anomaly. The grey interval  
1051 corresponds to the Cues Limestone horizon and radioactive shales.

1052

1053 Figure 6: Detrital proxies in the samples from borehole D1-26. A) major and trace element  
1054 content normalized to the aluminum content. B) Rare earth element ratios and europium  
1055 anomaly. The grey interval corresponds to the Cues Limestone horizon and radioactive shales.

1056

1057 Figure 7: Rare earth element content in the samples from borehole D1-26 normalized to the  
1058 Post Archean Average Shale (PAAS, McLennan, 1989).

1059

1060 Figure 8: Representative fragmentograms showing the biomarker distribution in the aliphatic  
1061 fraction of the extracts from borehole D1-26 samples. A) *n*-alkanes and linear isoprenoids  
1062 (m/z 57; sample 7087). B) Di- and tri-cyclic terpenoids (m/z 123; sample 7087). C)  
1063 Cheilantanes and hopanoids (m/z 191; sample 7085). D) Steroids and diasteroids (m/z 217;  
1064 sample 7780). Numbers above symbols indicate carbon number.

1065

1066 Figure 9: Example of distribution of isorenieratene and palaerenieratene derivatives in the  
1067 aromatic fraction of the extracts from borehole D1-26 samples (m/z 133+134; sample 7810).

1068

1069 Figure 10: Molecular indicators of redox conditions in the extracts from D1-26 samples. A)  
1070 Total concentration of isorenieratene and palaerenieratene derivatives in the extracts. B) C<sub>16</sub>-  
1071 C<sub>31</sub> palaerenieratene to isorenieratene derivatives ratio (PIR). The grey interval corresponds to  
1072 the Cues Limestone horizon and radioactive shales. C) Pristane to phytane ratio (Pr/Ph) versus  
1073 the modified aryl isoprenoid ratio (AIR\*). Scheme from Schwark and Frimmel (2004)

1074

1075 Figure 11: Depositional model for organic matter in the Ghadames Basin during the Frasnian  
1076 to upper Famennian interval. See text for explanations.

1077

#### 1078 **Supplementary material**

1079 Table S1: major, trace and rare earth element content in samples from borehole D1-26.

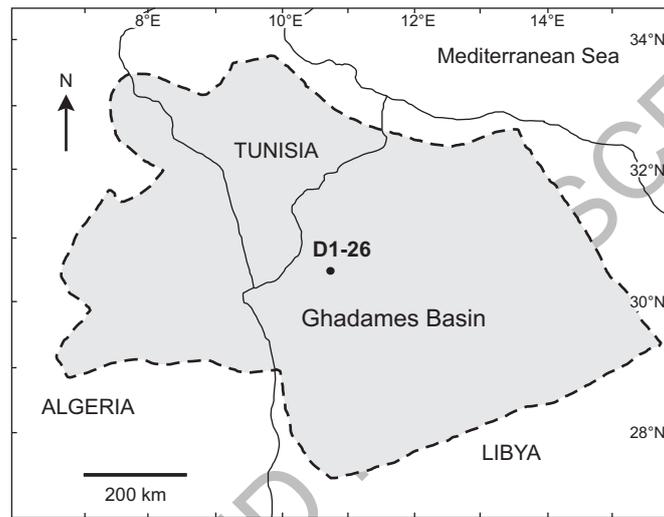


Figure 1

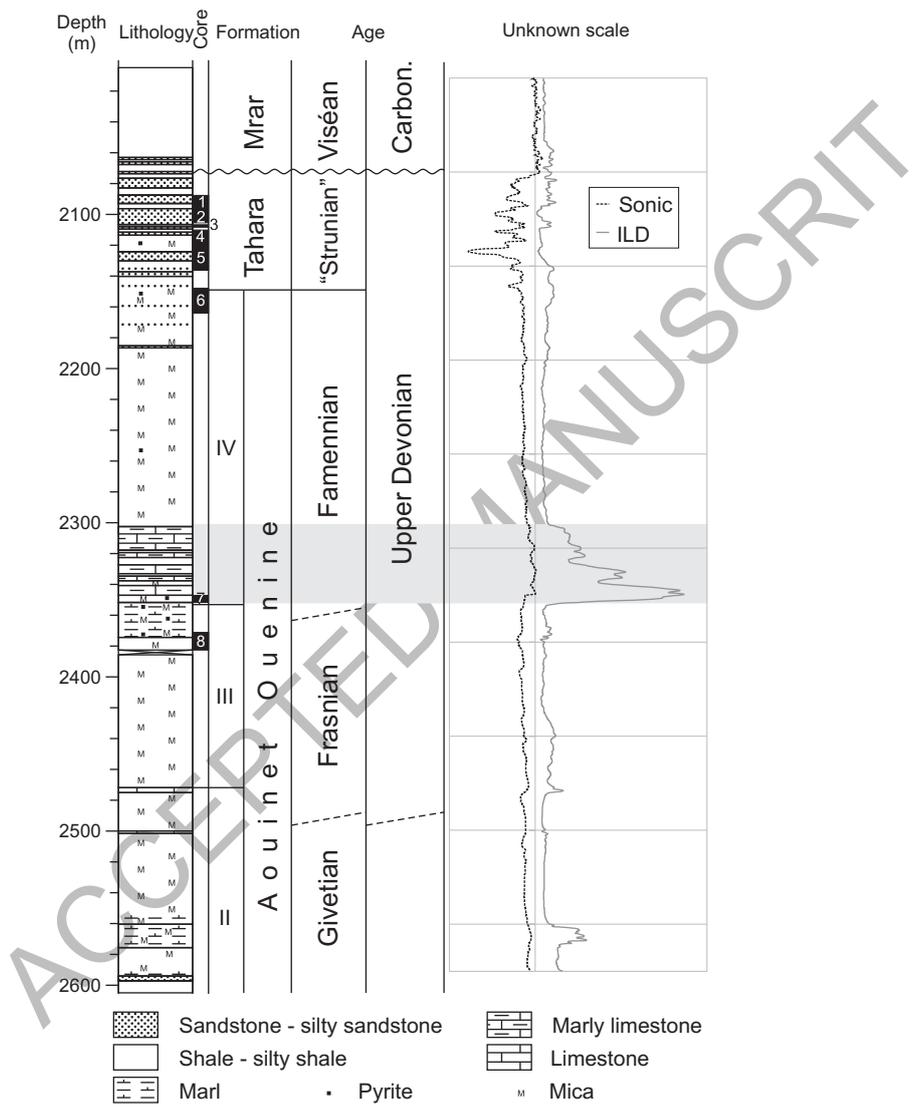


Figure 2

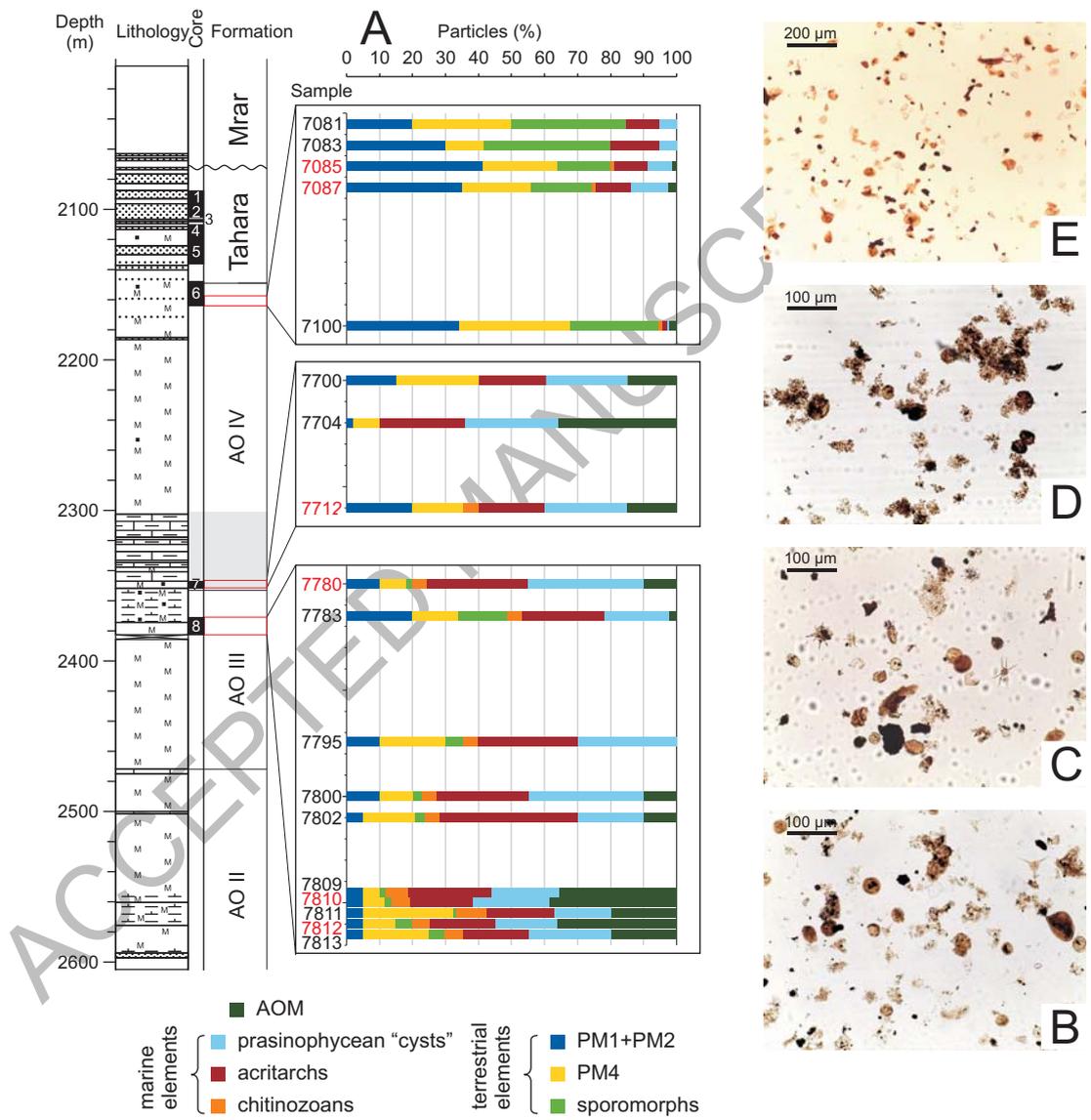


Figure 3

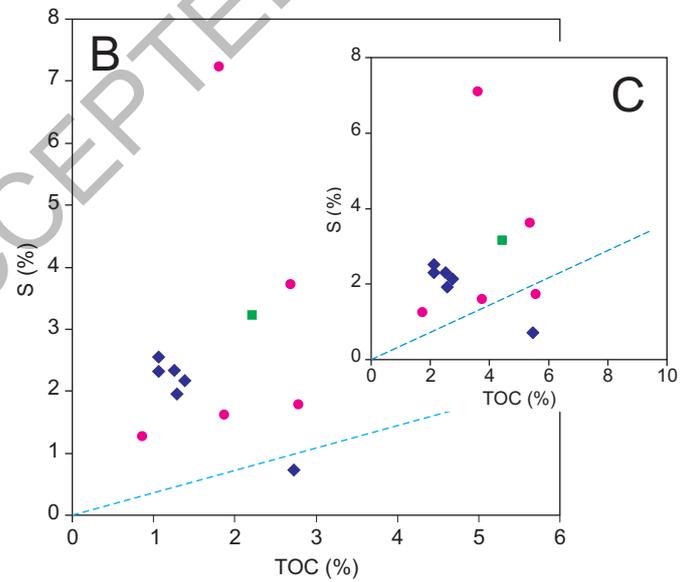
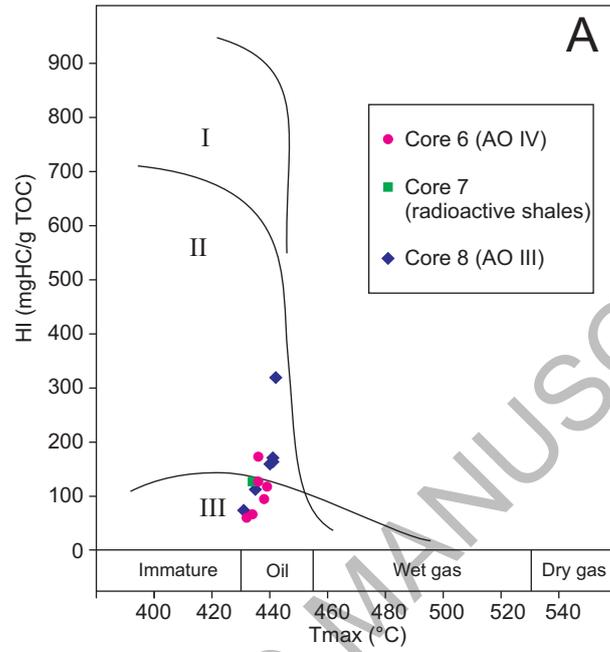


Figure 4

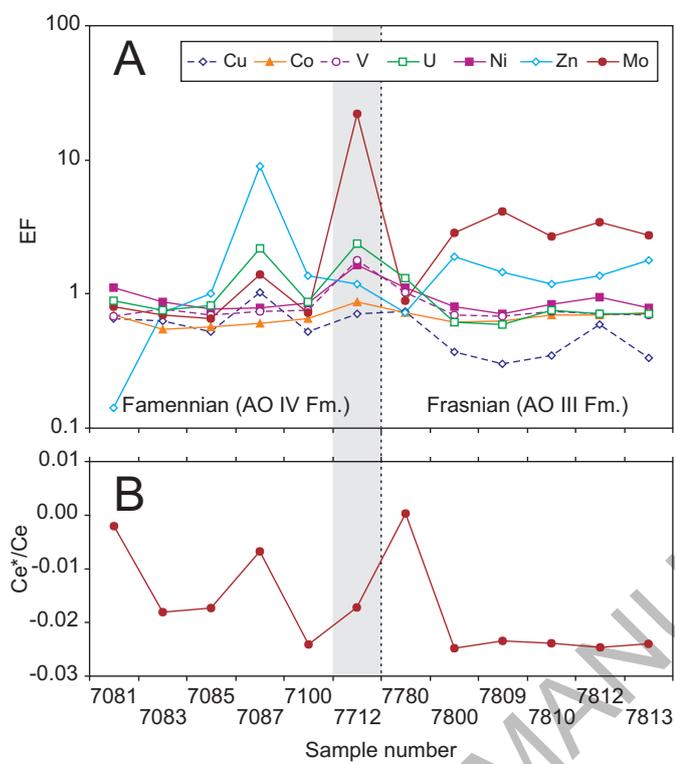


Figure 5

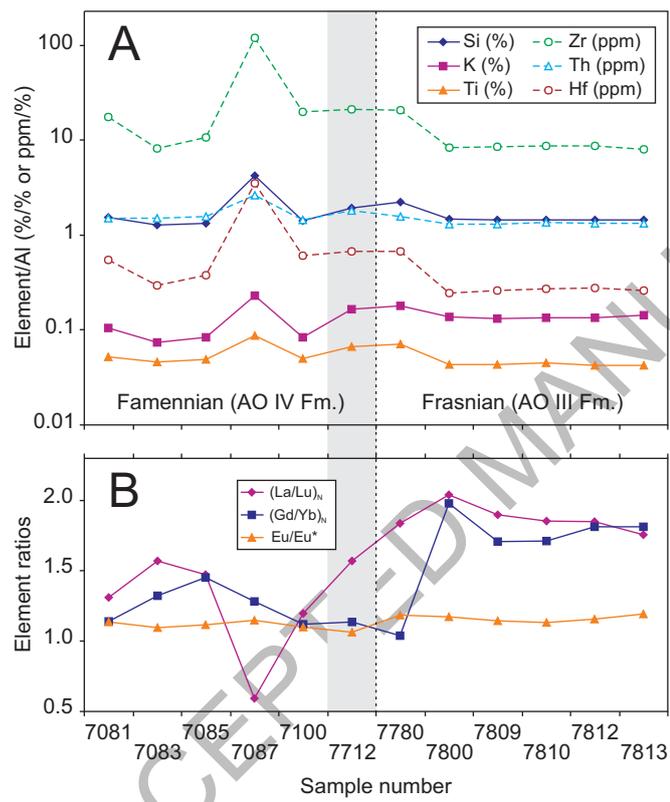


Figure 6

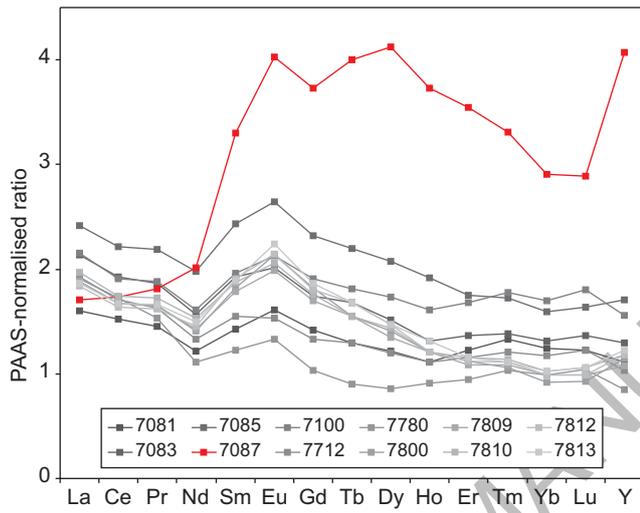


Figure 7

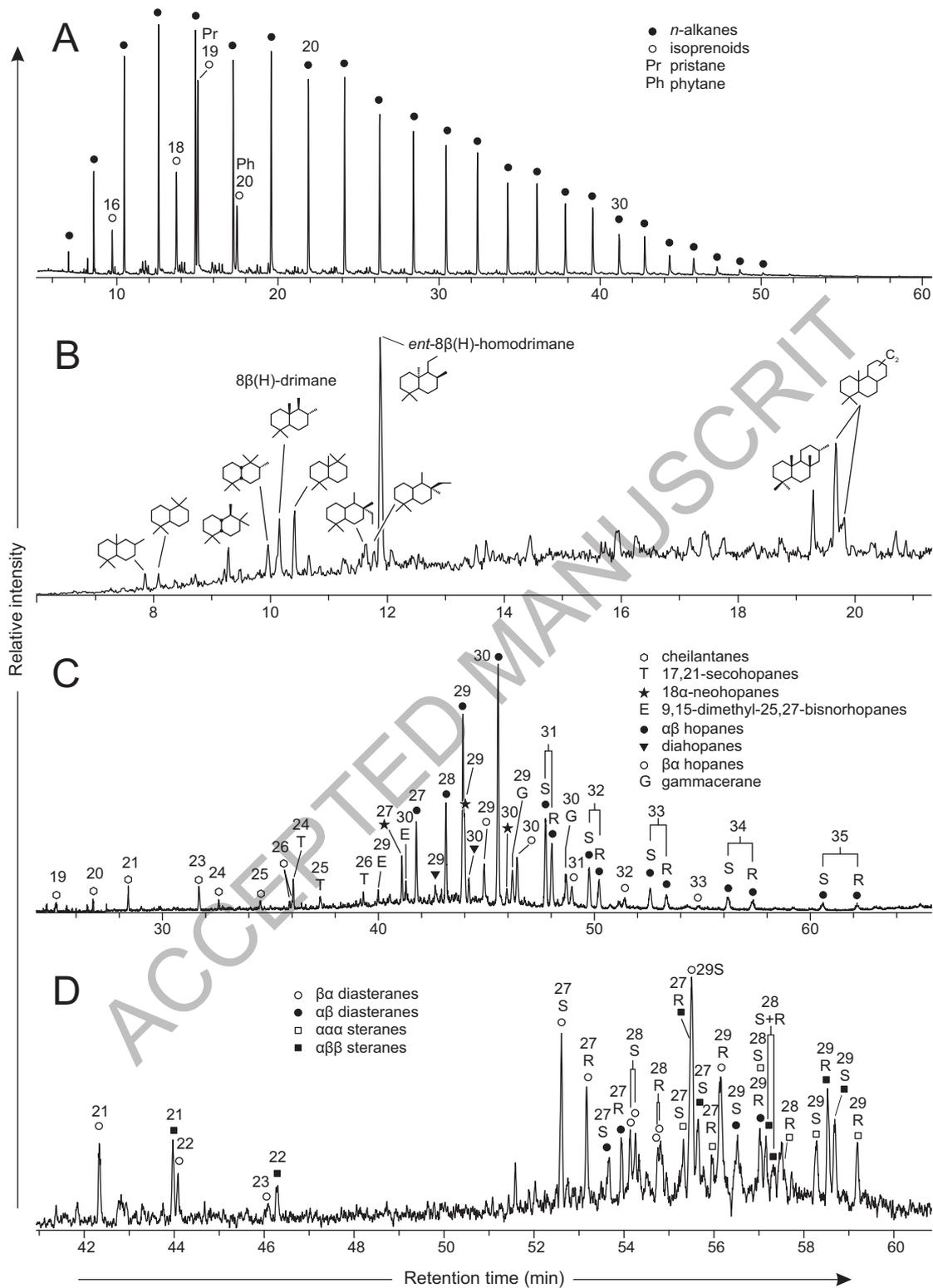


Figure 8

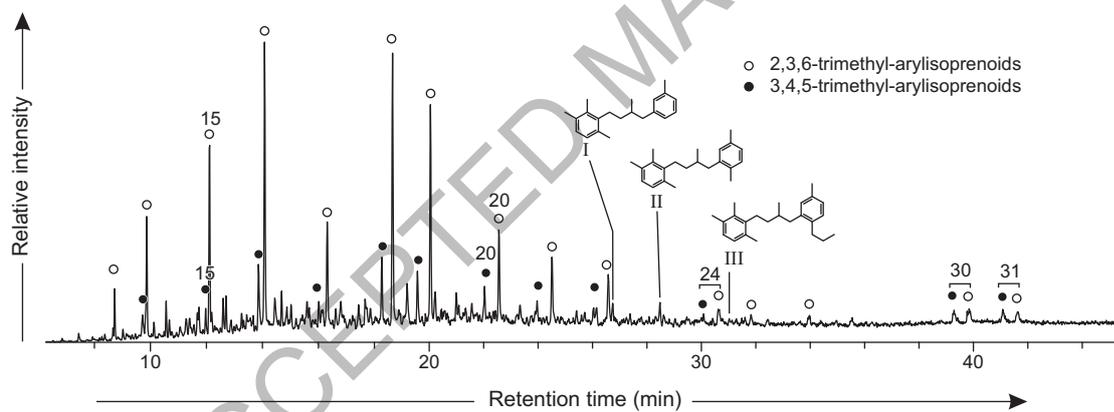


Figure 9

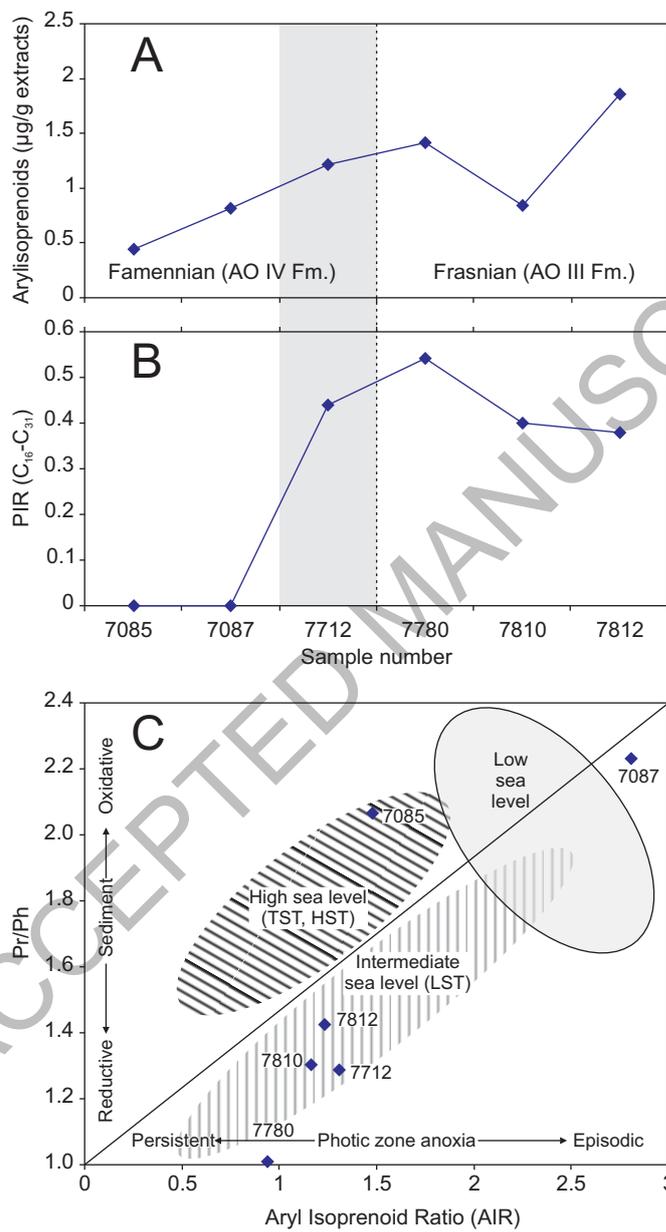


Figure 10

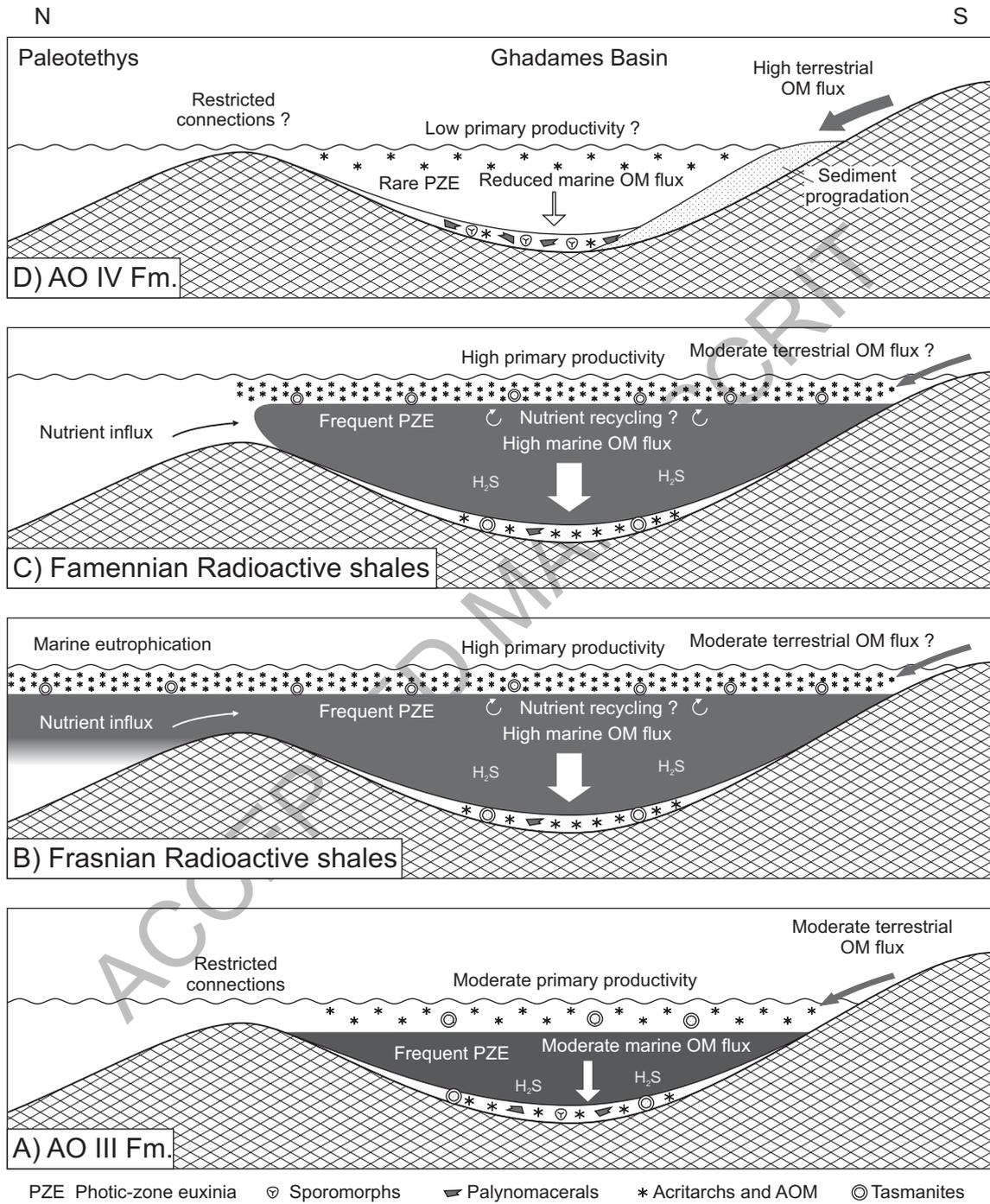


Figure 11

## Tables

Table 1: Rock Eval and elemental analysis results of the samples from borehole D1-26.

Sample	S1 <sup>1</sup>	S2 <sup>1</sup>	Tmax °C	TOC %	PI <sup>2</sup>	HI <sup>3</sup>	OI <sup>4</sup>	C <sub>min</sub> (%)	S (%)	N (%)	TOC/N
7081	0.19	1.08	432	1.8	0.15	60	0	0.1	7.23	0.06	35
7083	0.24	1.78	434	2.68	0.12	66	0	0.14	3.73	0.08	39
7085	0.36	3.53	436	2.78	0.09	127	8	0.12	1.79	0.08	41
7087	0.15	1.01	439	0.86	0.13	117	48	0.96	1.27	0.03	33
7100	0.2	1.76	438	1.87	0.1	94	22	0.86	1.63	0.05	44
7712	0.85	2.8	434	2.21	0.23	127	5	0.16	3.23	0.12	21
7780	1.55	8.7	442	2.73	0.15	319	2	0.14	0.73	0.13	25
7800	0.7	0.77	431	1.06	0.48	73	27	0.13	2.55	0.07	18
7809	0.65	1.19	435	1.06	0.35	112	0	0.05	2.32	0.09	14
7810	0.78	2.2	441	1.29	0.26	171	12	0.09	1.95	0.1	15
7812	0.86	2.05	441	1.26	0.29	163	0	0.1	2.33	0.09	16
7813	0.73	2.2	440	1.38	0.25	159	4	0.12	2.17	0.08	20

<sup>1</sup> mgHC/g

<sup>2</sup> Production index:  $PI = S1 / (S1 + S2)$

<sup>3</sup> Hydrogen index in mgHC/gTOC

<sup>4</sup> Oxygen index in mgCO<sub>2</sub>/gTOC

Table 2: Biomarker ratios in the extracts of samples from borehole D1-26.

Sample	7085	7087	7712	7780	7810	7812
Source/environment						
Pr/Ph	2.07	2.23	1.29	1.01	1.30	1.42
Pr/C <sub>17</sub>	0.82	1.03	0.65	0.76	0.77	0.74
Ph/C <sub>18</sub>	0.43	0.53	0.51	0.69	0.66	0.57
CPI <sup>1</sup>	1.19	1.22	0.97	1.05	1.07	0.93
TAR <sup>2</sup>	0.96	0.41	0.07	0.39	0.2	0.52
tricyclic/17 $\alpha$ hopanes <sup>3</sup>	0.11	0	0.43	0.3	0.5	0.46
Hop/ster <sup>4</sup>	3.6	3.24	1.41	1.32	1.27	1.22
%C <sub>27</sub> <sup>5</sup>	26.6	27.8	34.6	30.9	22.5	23.6
%C <sub>28</sub> <sup>5</sup>	23.5	17.3	14.2	17.5	22.9	30.2
%C <sub>29</sub> <sup>5</sup>	49.9	54.9	51.2	51.6	54.6	46.2
AIR* <sup>6</sup>	2.22	1.02	0.84	0.4	0.86	1.26
Maturity						
Diasterane S/(S+R) <sup>7</sup>	0.58	0.59	0.55	0.59	0.6	0.62
Sterane C <sub>29</sub> S/(S+R) <sup>8</sup>	0.43	0.45	0.48	0.5	0.48	0.33
Sterane C <sub>29</sub> $\beta\beta$ /( $\beta\beta$ + $\alpha\alpha$ ) <sup>9</sup>	0.34	0.41	0.61	0.61	0.66	0.67
Hopane C <sub>32</sub> 22S/(22S+22R)	0.6	0.59	0.62	0.56	0.6	0.56
Hopane C <sub>30</sub> $\beta\alpha$ /( $\beta\alpha$ + $\alpha\beta$ )	0.17	0.15	0	0.13	0.15	0.16
Ts/(Ts+Tm)	0.35	0.36	-	0.72	0.81	0.82
MPI <sup>10</sup>	0.62	0.73	0.61	0.66	0.73	0.81
MPR <sup>11</sup>	1.36	1.48	0.81	0.88	0.96	0.94
Vitrinite reflectivity Rc <sup>12</sup>	0.77	0.84	0.77	0.79	0.84	0.89

<sup>1</sup> *n*-Alkanes Carbon Preference Index:

$$CPI = \{ [(C_{25} + C_{27} + C_{29} + C_{31} + C_{33}) / (C_{26} + C_{28} + C_{30} + C_{32} + C_{34})] + [(C_{25} + C_{27} + C_{29} + C_{31} + C_{33}) / (C_{26} + C_{28} + C_{30} + C_{32} + C_{34})] \} / 2$$

(Bray and Evans, 1961).

<sup>2</sup> *n*-Alkanes Terrestrial to aquatic ratio: TAR = (C<sub>27</sub> + C<sub>29</sub> + C<sub>31</sub>) / (C<sub>15</sub> + C<sub>17</sub> + C<sub>19</sub>) (Bourbonniere and Meyers, 1996).

<sup>3</sup>  $\Sigma(C_{21}-C_{29})$  cheilantanes /  $\Sigma(C_{29}-C_{35})$   $\alpha\beta$  hopanes

<sup>4</sup> Calculated using the sum of dia- and regular steroids and the sum of all hopanoids (diahopanes, TS series, hopanes and moretanes).

<sup>5</sup> Relative percentage of C<sub>27</sub>, C<sub>28</sub> and C<sub>29</sub> regular steranes, determined on the  $\alpha\alpha\alpha$ R isomers.

<sup>6</sup> Modified arylisoprenoid ratio: AIR\* = (C<sub>13</sub>-C<sub>17</sub>) / (C<sub>18</sub>-C<sub>22</sub>) arylisoprenoids using both the 2,3,6- and 3,4,5-trimethyl-aryl isoprenoids on m/z 133+134 fragmentogram.

<sup>7</sup> Calculated using C<sub>27</sub>  $\beta\alpha$  diasteranes.

<sup>8</sup> Calculated using C<sub>29</sub>  $\alpha\alpha$  steranes.

<sup>9</sup> Calculated using C<sub>29</sub> R and S stereoisomers.

<sup>10</sup> Methylphenanthrene index MPI = 1.5[3-MP+2-MP] / [P+9-MP+1-MP] (Radke and Welte, 1983).

<sup>11</sup> Methylphenanthrene ratio MPR = [2-MP] / [1-MP] (Radke et al., 1982).

<sup>12</sup> Rc = 0.6 \* MPI + 0.4 (Radke and Welte, 1983)

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