

2017-01-15

Bulk-carbonate and belemnite carbon-isotope records across the Pliensbachian-Toarcian boundary on the northern margin of Gondwana (Issouka, Middle Atlas, Morocco)

Ait-Itto, F-Z

<http://hdl.handle.net/10026.1/8648>

10.1016/j.palaeo.2016.11.014

Palaeogeography, Palaeoclimatology, Palaeoecology

Elsevier BV

All content in PEARL is protected by copyright law. Author manuscripts are made available in accordance with publisher policies. Please cite only the published version using the details provided on the item record or document. In the absence of an open licence (e.g. Creative Commons), permissions for further reuse of content should be sought from the publisher or author.

1 Carbon isotope stratigraphy and belemnite isotope records across the Pliensbachian-
2 Toarcian boundary, of the Northern Margin of Gondwana, Issouka, Middle Atlas,
3 Morocco

4
5 Ait-Itto F.-Z^a, Ait Addi A^a, Price G.D.^b, Samar, L. ^c, Chafiki D.^a, Mannani, I. ^a

6
7 ^a*Cadi Ayyad University, Faculty of Sciences and Techniques, Geosciences and Environmental*
8 *research's Laboratory, P.O. Box 549, Marrakech-Morocco. Emails: f.aititto@gmail.com;*
9 *aitaddiabdellah@gmail.com*

10 ^b*School of Geography, Earth and Environmental Sciences Plymouth University, Plymouth, Devon, PL4*
11 *8AA, UK*

12 ^c*SONATRACH, Algeria*

13
14 **ABSTRACT**

15 The data presented here provide the first high resolution investigation of carbon isotope
16 and geochemical analyses derived from the Pliensbachian-Toarcian boundary, of Issouka, Middle
17 Atlas, Morocco. The isotope data recorded in micrite reveal a stepwise negative carbon isotope
18 excursion with values dropping to -1.8‰ within the Polymorphum Zone. This excursion coincides
19 with major marine biological changes and extinctions and corresponds with European records
20 supporting the assertion that the excursion is global in origin. The Issouka section is relatively
21 expanded compared to other well-studied European sections. The excursion at the Pliensbachian-
22 Toarcian boundary also shows several similarities with the negative Early Toarcian event. In
23 contrast, carbon isotope values derived from coeval belemnites show positive values. The

24 belemnite $\delta^{13}\text{C}$ data presented here suggests spatial heterogeneity in the Early Jurassic ocean.
25 Overturning or upwelling of a stratified water mass, is inconsistent with our data, as it requires the
26 belemnites to have lived elsewhere and only later migrated into the Middle Atlas area where they
27 became fossilized. The oxygen isotope values from belemnite calcite show no distinct trend across
28 the event, indicative of either no significant change in temperatures or change in seawater $\delta^{18}\text{O}$.
29 We suggest the introduction of any light carbon (e.g. a volcanogenic) source must have resulted in
30 spatial variability in the $\delta^{13}\text{C}$ of the dissolved inorganic carbon of seawater. Alternatively, a regional
31 change in the source of the carbonate carrying the isotope signal, could lead to a negative shift in
32 the $\delta^{13}\text{C}_{\text{micrite}}$ signature without any relation to variations in the global carbon isotope trend.

33

34 *Keywords*

35 Palaeoenvironment, stratigraphy, Early Jurassic, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$

36

38 **1. Introduction**

39 The Early Jurassic was marked by extreme environmental changes (Cohen et al., 2004; 2007;
40 Hesselbo et al., 2007), characterized by major marine biological changes and extinctions at a global
41 scale (Little and Benton, 1995; Harries and Little, 1999; Cecca and Macchioni, 2004; Wignall and
42 Bond, 2008), and pronounced negative carbon isotope shifts recorded in marine carbonates and
43 organic matter, brachiopods, biomarkers and fossil wood (Hesselbo et al., 2000; 2007; Suan et al.,
44 2008, Hermoso et al., 2009; Littler et al., 2010; Sandoval et al., 2012; Montero–Serrano et al., 2015;
45 Krencker et al., 2015). The increasing number of high resolution studies has led to smaller scale
46 events being recognised during the Early Sinemurian (Porter et al., 2014) and at the Pliensbachian–
47 Toarcian boundary (Bodin et al., 2010; Littler et al., 2010). In order to further document these
48 palaeoenvironmental changes, the Late Pliensbachian–Early Toarcian of the Middle Atlas rift basin
49 of Morocco, was investigated. Previous investigations in the region have mainly focused on the
50 platform drowning event observed in the Middle Atlas Basin at the Pliensbachian–Toarcian
51 boundary (Benshili, 1989; Ruget and Nicollin, 1997; Blomeier and Reijmer, 1999; Lachkar et al.,
52 2009; Dera et al., 2009), and a few studies have characterized palaeoenvironmental change using
53 benthic foraminiferal assemblages (Bejjaji, 2007, Bejjaji et al., 2010; Reolid et al., 2013).

54 The aim of this research is to present a new high–resolution investigation of carbon isotopes
55 from the Middle Atlas in order to contribute to an understanding of the palaeoceanographic
56 conditions during the Pliensbachian–Toarcian boundary in the deeper water zones of the Tethyan
57 realm. A concurrent analysis of the oxygen– and carbon–isotope analysis of belemnites has also
58 been undertaken. Analysis of the isotopes of belemnites is used to as a means of investigating
59 temperature variation as well as carbon cycling, both of which can be related to our high–resolution

60 carbon isotope stratigraphy as well as help elucidated the mechanisms behind the purported
61 isotope event.

62

63 **2. Geological Setting**

64 Both the opening of the north Atlantic and western Tethys during the early Mesozoic and
65 the collision of Africa and Europe during the middle Cenozoic (Michard, 1976) influenced the
66 geological history of Morocco. These two geological events formed the Atlas System as well as the
67 Rif Mountains. Crustal extension was initiated in the Late Triassic and lasted until the earliest
68 Jurassic. This was followed by renewed crustal extension in Toarcian times (Laville et al., 2004)
69 which led to the formation of the fault–bounded mosaic of Middle and High Atlas troughs (Studer
70 and Du Dresnay, 1980). The Middle Atlas of Morocco is structurally dominated by four NE–SW
71 trending anticlines and is mainly constituted of Lower and Middle Jurassic formations (Du Dresnay,
72 1971; Benshili, 1989; Bejjaji, 1994; Sabaoui, 1998, Souhel et al., 2000, El hammichi et al., 2008;
73 Bejjaji et al., 2010). The Pliensbachian–Toarcian transition coincides with a dislocation of the Lower
74 Jurassic carbonate platform (Blomeier and Reijmer, 1999; Lachkar et al., 2009, Dera et al., 2009;
75 Bodin et al., 2016) with Toarcian deposits dominated by marls lying upon Upper Pliensbachian
76 shallow marine limestones and calcareous marls. At the top of the sequence, these deposits are
77 overlain by Aalenian–Lower Bajocian marls and calcareous marls (Bejjaji et al., 2010).

78 The palaeogeography of the Middle Atlas consists of relatively deep marine conditions
79 (Fig.1) in the center and shallows towards the northern and southern basin margins (Du Dresnay,
80 1971; Souhel et al., 2000; Bodin et al., 2010). The study area during the Early Toarcian was located
81 at a palaeolatitude of $\sim 20^{\circ}\text{N}$ (Bassoulet et al., 1993). The sedimentary evolution and
82 palaeogeographic differentiation is controlled by tectonic activity, combined with the rate of
83 sedimentation and global eustatic variations (Benshili, 1989; Ruget and Nicollin, 1997). The rapid

84 transition from shallow marine carbonates to hemipelagic marls has been taken to reflect a major
85 deepening phase across the entire Middle and High Atlas area (Ettaki et al. 2000; El Arabi et al.
86 2001; Wilmsen and Neuweiler 2008). This drowning episode is linked with the eustatic sea-level
87 rise of the Early Toarcian in Europe and Africa, described by many workers (e.g. Hallam, 1997;
88 Hardenbol et al., 1998). Coincident with this drowning episode, a substantial increase of seawater
89 temperatures in the Early Toarcian has been inferred, reaching a maximum during the Falciferum
90 Zone, documented using the oxygen isotope composition and the Mg/Ca ratio of belemnites and
91 brachiopods from NW European regions (e.g. Jenkyns et al., 2002; Rosales et al., 2004 ; Suan et al.,
92 2010; Dera et al., 2011; Harazim et al., 2013; Ferreira et al., 2015).

93

94 **3. Methods**

95

96 The samples for this study were obtained from the Late Pliensbachian–Early Toarcian
97 Issouka section, within the Middle Atlas, Morocco (Figs. 1, 2). The studied section was logged and
98 samples for analysis were collected from selected intervals throughout the section. Bulk samples
99 were dominated by wackestone and carbonate mudstones (Fig. 3). Bulk carbonate analyses are
100 therefore considered to represent the total biogenic carbonates, i.e. foraminifers and calcareous
101 nanofossils and exported neritic carbonate mud, predominantly reflecting a surface water signal.
102 Samples were recovered from up to 15 cm below the surface, to minimize the effects of surface
103 weathering. Bulk samples (and belemnites) were analysed at Plymouth University for carbon and
104 oxygen stable isotopes. Using 200 to 300 micrograms of carbonate, stable isotope data were
105 generated on a VG Optima mass spectrometer with a Gilson autosampler. Isotope ratios were
106 calibrated using NBS19 standards and are given in δ notation relative to the Vienna Pee Dee

107 Belemnite (VPDB). Reproducibility was generally better than 0.1 ‰ for samples and standard
108 materials. Selected samples were also analyzed at SONATRACH (Algeria), for Total Organic Carbon
109 (TOC). The calcium carbonate (CaCO₃) content for each bulk carbonate sample was performed using
110 Bernard calcimeter at Cadi Ayyad University, Morocco.

111 A number of belemnite samples were also analysed. These were typically somewhat
112 fragmentary, making the identification of genera represented problematic. Where identifiable,
113 ?*Passaloteuthis* was present, consistent with Sanders et al. (2013). Polished thin sections were used
114 to undertake initial diagenetic screening using a MK5 CITL cathodoluminescence (CL) instrument
115 (Fig. 4). The preservation of the belemnite rostra was also assessed using trace element analysis
116 (Ca, Sr, Mg, Fe and Mn concentrations). The belemnites were prepared for stable isotope and trace
117 element analysis by first removing the areas of the rostrum typically most prone to diagenesis (the
118 rostrum exterior, apical region, alveolus and observable cracks/fractures). The remaining calcite
119 was then fragmented, washed in pure water and dried in a clean environment. Fragments were
120 subsequently picked under a binocular microscope to secure those judged to be best preserved,
121 which were then analyzed for oxygen and carbon isotopes. The sub-samples taken for trace
122 element analysis were digested in HNO₃ and analysed by Inductively Coupled Plasma-Atomic
123 Emission Spectrometer (ICP-AES) using a PerkinElmer 3100 at Plymouth University. Based upon
124 analysis of duplicate samples reproducibility was better than ± 3% of the measured concentration
125 of each element. Repeat analyses of standards JLS-1 and BCS CRM 393 was within 2% of the
126 certified values for Sr, Mn, Ca and Mg and 10% for Fe.

127

128 **4. Results**

129 *4.1. Lithology and stratigraphy*

130

131 The Issouka section is situated near the village of Issouka, ~ 25 km southwest of Immouzer
132 Marmoucha, in the Middle Atlas (N 33°26'55.56" ; W 4°20'33.83") (Fig.2). The section begins with
133 centimeter thick of limestone–marl alternations (equivalent of the Ouchbis Formation of the High
134 Atlas). The limestone beds are typically wackestone–packstones, and contain a rich ammonite
135 fauna, with also belemnites, echinoids and brachiopods. Foraminifera (Bejjaji, 2007; Bejjaji et al.,
136 2010) suggested a Late Pliensbachian age. The Lower Toarcian succession starts with green marls
137 and marl–limestone alternations, rich in foraminifera, belemnites, echinoids and gastropods. The
138 limestone beds are mudstone–wackestones (Figs. 3, 4). The Toarcian deposits are generally
139 hemipelagic and correspond to basin environments (Reolid et al., 2013). The biostratigraphic
140 framework of the Issouka section and the Middle Atlas has been established with ammonites
141 (Benshili, 1989; Sabaoui, 1998; El Hammichi et al., 2008) and benthic foraminifera (Bejjaji, 2007;
142 Bejjaji et al., 2010). For example, the occurrence of the benthic foraminifera *Lenticulina sublaevis* in
143 the Middle Atlas is correlated by Bejjaji et al., (2010) to the Emaciatum ammonite zone of the
144 Pliensbachian, whilst *Lenticulina bochari* and *Lenticulina toarcense* are correlated with the
145 Toarcian Polymorphum Zone and *Lenticulina obonensis* with the Serpentinus Zone. With respect to
146 ammonites of the Middle Atlas, *Emaciatoceras emaciatum* of the Emaciatum Zone, *Dactyloceras*
147 *polymorphum* of the Toarcian Polymorphum Zone and *Hildaites levisoni* and the Semicelatum Zone
148 have also been identified (e.g. Benshili, 1989; El Hammichi et al., 2008; Bejjaji et al., 2010).
149 Importantly, the lowermost Toarcian Polymorphum Zone is recognized, which has been taken as
150 age equivalent to the Tenuicostatum Zone of NW Europe (e.g. Hesselbo et al., 2007; Reolid et al.,
151 2012).

152

153 4.2 Geochemistry

154

155 The bulk carbon isotope data range from -1.8 to $+2.0$ ‰. The carbon isotope curve shows a large (4
156 ‰) negative (stepwise) shift in the lower part of the section (Fig. 5), across the Upper
157 Pliensbachian–Lower Toarcian boundary. The most negative value (-1.8 ‰) is seen within the lower
158 part of Polymorphum Zone. The sediment thickness recording this negative excursion is 15m.
159 Thereafter the bulk carbon isotope values return to pre–excursion values, around $+1.0$ ‰, in the
160 upper part of the Polymorphum Zone and into the Serpentinus Zone. The oxygen isotope data
161 derived from the limestone and marls of the Pliensbachian and Toarcian show negative values that
162 vary between -2.3 to -6.5 ‰. Whilst the preservation of primary $\delta^{13}\text{C}$ values during carbonate
163 diagenesis is quite typical, fluid–rock interactions commonly result in a change in oxygen isotope
164 ratios leading to relatively light $\delta^{18}\text{O}_{\text{carbonate}}$ values (Hudson, 1977). Hence, with respect to the
165 oxygen isotope data, a diagenetic overprint affecting the samples analysed is more likely. The
166 oxygen isotope data are therefore not considered any further. The CaCO_3 content shows values near
167 100% within the latest Pliensbachian and drop to 15-40 % in the lowermost Toarcian, before increasing
168 again in the upper part of Polymorphum Zone. The TOC data (Fig. 5) reveal low absolute values
169 between 0.1% to 0.7% TOC.

170 Oxygen and carbon isotope ratios derived from the belemnites can also be seen in Figure 5
171 as well as in Table 1. Elemental concentrations were as follows: Sr (665 to 1194ppm); Mn (4 to 460
172 ppm); Mg (1210 to 3475 ppm) and Fe (10 to 2859 ppm) and Ca (26.7 to 45.4%). The geochemical
173 study of the belemnites reveals that they are typically well preserved, consistent with CL images,
174 which show that the belemnites sampled in this study were largely non–luminescent (Fig. 4). Some
175 areas were revealed to be Mn–rich and partial replacement by diagenetic calcite was observed
176 particularly along the outermost growth bands and adjacent to the alveolar region. Despite some
177 high values observed for Fe and Mn (these data have been excluded from further analysis, see

178 Table 1), reliable isotopic data from non–recrystallized shells of belemnites from the High Atlas are
179 presented, showing little effects of substantial diagenetic changes associated with burial (cf.
180 Lachkar et al., 2009). Positive carbon isotope values are recorded from the lowermost part of the
181 section up to +2.8 ‰. No marked shift towards lower carbon isotope values is seen across the
182 boundary Pliensbachian–Toarcian. The positive values derived from the belemnites are seen within
183 the lower part of Polymorphum Zone (and coincident with the negative carbon values derived from
184 bulk analyses). The oxygen isotope data derived from the Pliensbachian belemnites range from (–
185 1.2 to 0.0 ‰). These data are considerably more positive than those data derived from the bulk rock
186 analysis.

187 **5. Discussion**

188 *5.1. Correlation of the negative carbon isotope excursion at Issouka with other sections*

189

190 In accord with existing Jurassic carbon isotope curves, the Pliensbachian–Toarcian boundary
191 is characterized by a negative excursion within the Polymorphum Zone (Hesselbo et al., 2007; Littler
192 et al., 2010; Suan et al., 2011; Reolid et al., 2012), recorded in marine bulk–rock carbonates,
193 brachiopods, wood and organic matter. This excursion coincides with major marine biological
194 changes and extinction (Wignall et al., 2005; Wignall and Bond, 2008; Mattioli et al., 2009; Dera et
195 al., 2010, Reolid et al., 2012) and an increase in temperature (e.g. Jenkyns et al. 2002; Rosales et al.,
196 2004 ; Dera et al., 2011) culminating in the Falciferum Zone.

197 The negative excursion seen in Issouka is characterized by a large ~3.6 ‰ negative shift, and
198 shows some noteworthy similarities with data from the Amellago section (Bodin et al., 2016) and
199 Bou Oumardoul/Toskine sections, Dades Valley (Krencker et al., 2015) also from the High Atlas (Fig.
200 6). In contrast, Bodin et al. (2016) show that the uppermost Pliensbachian is characterised by a

201 gentle decreasing trend in $\delta^{13}\text{C}_{\text{org}}$ values, followed by an overall positive trend within the
202 Polymorphum Zone. The Issouka section is relatively expanded compared to the well-studied
203 European sections. Within the European sections where the Pliensbachian–Toarcian boundary
204 excursion is observed e.g. the Hawsker Bottoms section, Yorkshire, England (Littler et al., 2010), the
205 Mochras Farm Borehole (Jenkyns and Clayton, 1997) and Peniche, Portugal (Hesselbo et al., 2007)
206 the negative excursion is typically $\sim 2\%$. As shown by Littler et al. (2010), this negative shift is
207 recorded within a relatively thin interval (Fig. 6). This could be the result of a short-lived episode or
208 alternatively sedimentary condensation. Littler et al. (2010) for example noted the abrupt onset of
209 the isotope excursion at Hawsker Bottoms and the initiation of an extinction step near the same
210 level, supporting the notion of a catastrophic event such as release of methane hydrate.
211 Alternatively it could equally be argued that the sections in Yorkshire and Peniche are
212 stratigraphically condensed (Fig. 6) or incomplete at this level. Nevertheless, the duration and pace
213 of onset of the event is unclear (Littler et al., 2010). Bodin et al. (2011), however, recorded the
214 event in an interval from the Amellago section of a few 10's of meters. They suggested the duration
215 is likely to be similar to the Early Toarcian Event and the Pliensbachian–Toarcian boundary negative
216 excursion was inadequately recorded in the more condensed sediments in Europe. The greater
217 magnitude of the event at Issouka is considered to be related to the expanded nature of the section
218 (e.g. when compared to the Europe sections) allowing sampling of the full magnitude of the event
219 as well as the stepwise character of the excursion. This stepwise character is certainly reminiscent
220 of the Toarcian event (e.g. Kemp et al., 2005; Hesselbo and Pieńkowski, 2011).

221

222 *5.2. Comparison between the Pliensbachian-Toarcian boundary and Early Toarcian Event*

223

224 The similarities of the Pliensbachian–Toarcian boundary negative excursion and the Early
225 Toarcian Event have been noted elsewhere (e.g. Suan et al., 2008; Krencker et al., 2015). An
226 extinction among different faunal groups has also been associated with both events. Carbon–
227 isotope records across the Late Pliensbachian to Early Toarcian interval show similarities between
228 the Middle and High Atlas and Peniche (Hesselbo et al., 2007) and Hawsker Bottoms sections
229 (Littler et al., 2010), in materials ranging from organic–matter, fossil–wood and bulk carbonate has
230 been taken to strongly suggest that the carbon cycle perturbation is at least a regional (e.g. Bodin et
231 al., 2010). Indeed, Hesselbo et al. (2007) suggested that the fossil–wood record from Peniche
232 indicates that the perturbation must have affected the atmospheric as well as the marine carbon
233 reservoir (c.f. Bodin et al., 2016).

234 As the excursion at the Pliensbachian–Toarcian boundary is similar to the negative Early
235 Toarcian event, proposed mechanisms to explain the latter may also be relevant to the boundary
236 event. The various models put forward to explain the Early Toarcian event have included the
237 overturning or upwelling of a stratified water mass (‘the Küspert model’, Küspert 1982), a
238 dissociation of methane clathrates and or the thermal metamorphism of organic rich sediments
239 (McElwain et al, 2005; Hesselbo et al., 2007; Suan et al., 2008; Harazim et al., 2013). The belemnite
240 carbon isotope record from the Late Pliensbachian–Early Toarcian interval, of this study, can
241 possibly be used to unravel which mechanism is applicable to this event. As noted above, markedly
242 positive carbon isotope values derived from the belemnites within the lower part of Polymorphum
243 Zone are coincident with the negative carbon values derived from bulk analyses. A similar, 2 ‰
244 carbon isotope shift to higher values is also recorded belemnites from the Polymorphum Zone in
245 Spain (Gomez et al., 2008). The Küspert model, within which isotopically light respired CO₂ is
246 recycled in a restricted basin, is potentially inconsistent with the absence of light values derived
247 from the belemnite record, as presumably if the belemnites were nektonic they would have

248 recorded light isotope values or if they were surface dwellers they would recorded the isotopic
249 composition of the overturning of a stratified water mass. To resolve this inconsistency the
250 belemnites need to inhabit waters characterised by a DIC with 'normal' carbon–isotope
251 compositions, and they only later migrate into the Middle Atlas area where they became fossilised.
252 Alternatively, the belemnites flourished during brief events, and so captured a record of conditions
253 only during these times, whilst the longer term oceanic conditions is represented by the sediment
254 in which they are buried. These sediments carry a different isotopic record. It is difficult to
255 determine whether a clear carbon isotope excursion across the Late Pliensbachian–Early Toarcian
256 interval is seen in other macrofossil records. For example, the brachiopod data of Suan et al. (2010)
257 showed a range of positive and negative values associated with the boundary interval, whilst
258 belemnites precisely coinciding with the negative excursion at Peniche have yet to be isotopically
259 analysed (Littler et al., 2010). A possible hint of a negative carbon isotope excursion across the Late
260 Pliensbachian–Early Toarcian interval is also seen in the belemnite–derived data of Korte and
261 Hesselbo (2011) from Yorkshire, UK.

262 The palaeotemperature record from the Late Pliensbachian–Early Toarcian interval could be
263 used to inform which mechanism is applicable to the boundary event. The oxygen isotope values
264 from the belemnite calcite show, however, no distinct trend across the event, indicative of either
265 no significant change in temperatures or a change in seawater $\delta^{18}\text{O}$. Since upwelling should lead to
266 cooler temperatures and a massive methane dissociation should be associated with a temperature
267 maximum, the belemnite ^{18}O data support neither of these mechanisms. Likewise, $\delta^{18}\text{O}_{\text{belemnite}}$
268 records from Spain show a gradual decrease in oxygen isotope values in the latest Pliensbachian–
269 earliest Toarcian, which indicates warming (e.g. Rosales et al. 2004). The oxygen isotope data of
270 brachiopods from Peniche of Suan et al. (2010) also showed lighter values associated with the

271 boundary possibly linked to warming. Other studies, however, have showed the opposite trend
272 (Harazim et al., 2013), which could be interpreted as falling temperatures.

273 Notably Littler et al. (2010) considered the release of isotopically light thermogenic methane
274 (McElwain et al., 2005) as a possible mechanism driving the Late Pliensbachian–Early Toarcian
275 carbon isotope excursion. As peak lava emplacement for the Karoo region coincided with the
276 Pliensbachian–Toarcian boundary it is possible that a pulse of thermogenic methane from this
277 region could be partly responsible for the excursion (Littler et al., 2010). Bearing in mind the
278 positive carbon values derived from the belemnites, any effect of the explosive release of
279 metamorphic thermogenic methane needs to have resulted in spatial variability in the $\delta^{13}\text{C}$ of the
280 DIC of seawater. The surface ocean $\delta^{13}\text{C}_{\text{DIC}}$ is required to drop, possibly owing to relatively slow
281 vertical mixing, whilst deeper sea $\delta^{13}\text{C}_{\text{DIC}}$ remains constant ('normal'), as reflected in the positive
282 carbon values derived from the belemnites. Although the atmosphere and surface ocean carbon
283 reservoirs would have responded almost immediately to an initial release of light carbon, because
284 of the slower mixing time of the deep ocean (~1,500 years), it should take several thousands of
285 years for the full magnitude of the carbon isotope excursion to be manifested in the deeper ocean
286 water masses. Given the likely duration of the Polymorphum Zone (0.9–1.0 myr, Martinez et al.,
287 2016), mixing and equilibration should, however, have taken place prior to when those more
288 belemnites recording the most positive carbon isotopes lived and were deposited.

289 Alternatively, Bodin et al. (2016) have recently suggested a lithological, rather than
290 oceanographical control on $\delta^{13}\text{C}$ trends, whereby neritic $\delta^{13}\text{C}_{\text{micrite}}$ signatures show more positive
291 values than carbonate ooze produced by planktonic organisms (e.g. Swart and Eberli, 2005). Hence
292 the loss of exported neritic mud, for example during the earliest Toarcian, could lead to a negative
293 shift in the $\delta^{13}\text{C}_{\text{micrite}}$ signature without any relation to variations in the global carbon isotope trend
294 (Bodin et al., 2016, see also Martinez et al., 2016). Given the correlation between CaCO_3 content

295 and the $\delta^{13}\text{C}_{\text{micrite}}$ shift across the Pliensbachian–Toarcian boundary (Fig. 5) a loss of exported
296 neritic mud, as a result of platform drowning could lead to the negative shift observed in the
297 $\delta^{13}\text{C}_{\text{micrite}}$. The belemnite record in this setting reflects the DIC of more open-ocean water masses.
298 Bodin et al. (2016) go on to suggest that given that their $\delta^{13}\text{C}_{\text{org}}$ record from the High Atlas is
299 mostly derived from continental organic matter, it reflects genuine changes in the atmospheric
300 carbon cycle. The $\delta^{13}\text{C}_{\text{belemnite}}$ record of this study appearing to correlate with the Bodin et al.
301 (2016) $\delta^{13}\text{C}_{\text{org}}$ record (Fig. 6), raises the possibility that belemnite carbon isotope data are also
302 tracking the atmosphere carbon cycle. Nevertheless, this scenario is difficult to reconcile with data
303 from more distal locations (e.g. Yorkshire, UK, Littler et al., 2010)

304

305

306 **6. Conclusions**

307 The carbon isotope curve obtained from the Issouka section (Middle Atlas, Morocco)
308 displays a distinct negative shift at the Pliensbachian–Toarcian. This excursion coincides with a
309 change in sedimentation and major marine biological changes and extinctions. This shift is
310 correlated to the ones observed in well–documented European sections and thus further confirms,
311 the supra–regional nature of perturbation in the oceanic carbon cycle. A regional change in the
312 source of the carbonate carrying the isotope signal, could lead to a negative shift in the $\delta^{13}\text{C}_{\text{micrite}}$
313 signature without any relation to variations in the global carbon isotope trend. However, as fossil–
314 wood records also showed the excursion the perturbation is considered to have affected the
315 atmospheric as well as the marine carbon reservoir. If the belemnite records of this study can be
316 replicated elsewhere it may suggest that the entire water column was not affected by these carbon
317 cycle changes, as would be anticipated if methane hydrate release was the mechanism. Likewise,

318 overturning or upwelling of a stratified water mass requires the belemnites to have lived elsewhere
319 and only later migrated into the Middle Atlas area where they became fossilized. Nevertheless, the
320 belemnite $\delta^{13}\text{C}$ data presented here suggests a more complex pattern and some spatial
321 heterogeneity.

322

323 **Acknowledgements**

324 We would like to thank Nino Mariotti (Sapienza University) for the confirmation of
325 belemnite identification. This paper greatly benefited from 2 constructive reviews of Guillaume
326 Suan and Stéphane Bodin.

327

328 **References**

- 329 Bassoulet, J., Elmi, S., Poisson, F., Cecca, F., Belion, Y., Guiraud, R., Baudin, F., 1993. Mid Toarcian.
330 In: Dercourt, J., Ricou, L.E., Vrielynck, B. (Eds.) Atlas Tethys, Paleoenvironmental Maps:
331 Becip–Franlab, Rueil–Malmaison, France. 63–80.
- 332 Bejjaji, Z., 1994. Les foraminifères du Toarcien du Moyen Atlas Central(Maroc), micropaléontologie
333 et paléoenvironnements. Thèse 3ème cycle, Univ. Mohammed V, Rabat (Thèse 3ème
334 cycle,Univ. Mohammed V,) 231.
- 335 Bejjaji, Z., 2007. Biostratigraphie, paléoenvironnements et paléoécologie des foraminifères
336 toarciens du Moyen Atlas. PhD Thesis Université Mohammed V, Rabat 1–231.
- 337 Bejjaji, Z., Chakiri, S., Reolid, M., Boutakiout, M., 2010. Foraminiferal biostratigraphy of the Toarcian
338 deposits (Lower Jurassic) from the Middle Atlas (Morocco). Comparison with western
339 Tethyan areas. Journal of African Earth Sciences 57, 154–162.

340 Benschili, K., 1989. Lias–Dogger du Moyen Atlas plissé (Maroc) sédimentologie, biostratigraphie et
341 évolution paléogéographique. Documents des Laboratoires de Géologie Lyon 106, 1–285.

342 Blomeier, D.P.G., Reijmer, J.J.G., 1999. Drowning of a Lower Jurassic Carbonate Platform: Jbel Bou
343 Dahar, High Atlas, Morocco. *Facies* 41, 81–110.

344 Bodin, S., Mattioli, E., Fröhlich, S., Marshall, J.D., Boutib, L., Lahsini, S., Redfern, J., 2010. Toarcian
345 carbon isotope shifts and nutrient changes from the Northern margin of Gondwana (High
346 Atlas, Morocco, Jurassic): Palaeoenvironmental implications. *Palaeogeography,*
347 *Palaeoclimatology, Palaeoecology* 297, 377–390.

348 Bodin, S., Fröhlich, S., Boutib, L., Lahsini, S., Redfern, J., 2011. Early Toarcian source–rock potential
349 in the Central High Atlas Basin (central Morocco): Regional distribution and depositional
350 model. *Journal of Petroleum Geology* 34, 345–364.

351 Bodin, S., Krencker, F., Kothe, T., Hoffmann, R., Mattioli, E., Heimhofer, U., Kabiri, L., 2016.
352 Perturbation of the carbon cycle during the late Pliensbachian – Early Toarcian: New
353 insight from high–resolution carbon isotope records in Morocco. *Journal of African Earth*
354 *Sciences* 116, 89–104.

355 Cecca, F., Macchioni, F., 2004. The two Early Toarcian (Early Jurassic) extinction events in
356 ammonoids. *Lethaia* 37, 35–56.

357 Charriere, A., 1990. Héritage hercynien et évolution géodynamique alpine d'une chaîne
358 intracontinentale: le Moyen Atlas au SE de Fès(Maroc). Thèse d'Etat, Univ.Paul
359 Sabatier,ToulouseIII (Sciences),2 tomes 589.

360 Cohen, A.S., Coe, A.L., Harding, S.M., 2004. Osmium isotope evidence for the regulation of
361 atmospheric CO₂ by continental weathering. *Geology* 32, 157–160.

362 Cohen, A.S., Coe, A.L., Kemp, D.B., 2007. The Late Palaeocene–Early Eocene and Toarcian (Early
363 Jurassic) carbon isotope excursions: a comparison of their time scales, associated

364 environmental changes, causes and consequences. *Journal of the Geological Society of*
365 *London* 164, 1093–1108.

366 Dera, G., Pellenard, P., Neige, P., Deconinck, J.–F., Pucéat, E., Dommergues, J.–L., 2009. Distribution
367 of clay minerals in Early Jurassic Peritethyan seas: Palaeoclimatic significance inferred
368 from multiproxy comparisons. *Palaeogeography, Palaeoclimatology, Palaeoecology* 271,
369 39–51.

370 Dera, G., Neige, P., Dommergues, J.–L., Fara, E., Laffont, R., Pellenard, P., 2010. High resolution
371 dynamics of Early Jurassic marine extinctions: the case of Pliensbachian–Toarcian
372 ammonites (Cephalopoda). *Journal of Geological Society of London* 167, 21–33.

373 Dera, G., Brigaud, B., Monna, F., Laffont, R., Pucéat, E., Deconinck, J.–F., Pellenard, P., Joachimski,
374 M., Durlet, C., 2011. Climatic ups and downs in a disturbed Jurassic world. *Geology* 39,
375 215–218.

376 Du Dresnay, R., 1971. Extension et developement des phenomenes recifaux Jurassique dans le
377 domaine Atlasique Marocain, particulierement au Lias moyen. *Bulletin de la Société*
378 *Géologique de France* 13, 46–56.

379 El Arabi, H., Ouahhabi, B., Charrière, A., 2001. Les séries du Toarcien–Aalénien du SW du Moyen–
380 Atlas (Maroc): précisions stratigraphiques et signification paléogéographique. *Bulletin de*
381 *la Société Géologique de France* 172, 723–736.

382 El Hammichi, F., Benshili, K., Elmi, S. 2008, Les faunes d’Ammonites du Toarcien-Aalénien du Moyen
383 Atlas sud-occidental (Maroc). *Revue de Paléobiologie*, 27, 429–447. Ettaki, M., Chellai,
384 E.H., Milhi, A., Sadki, D., Boudchiche, L., 2000. Le passage Lias moyen–Lias superieur dans
385 la region de Todrha–Dades: environnements bio–sedimentaires et geodynamiques (Haut
386 Atlas central, Maroc) . *Comptes Rendus de l'Academie des Sciences – Series IIA* 331, 667–
387 674.

388 Ferreira, J., Mattioli, E., Pittet, B., Cachão, M., Spangenberg, J.E., 2015. Palaeoecological insights on
389 Toarcian and lower Aalenian calcareous nannofossils from the Lusitanian Basin (Portugal):
390 Palaeogeography, Palaeoclimatology, Palaeoecology, 436, 245–262.

391 Hallam, A., 1997. Estimates of the amount and rate of the of sea level change across the Rhaetian–
392 Hettangian and Pliensbachian–Toarcian boundary (latest Triassic to Early Jurassic) .
393 Journal of the Geological Society of London 154, 773–779.

394 Harazim, D., van de Schootbrugge, B., Sorichter, K., Fiebig, J., Weug, A., Suan, G., Oschmann, W.,
395 2013. Spatial variability of watermass conditions within three European epicontinental
396 seaways during the Early Jurassic (Pliensbachian–Toarcian). Sedimentology 60, 359–390.

397 Hardenbol, J., Thierry, J., Farley, M.B., Jacquin, T. de Graciansky, P.C., Vail, P., 1998. Mesozoic and
398 Cenozoic sequence chronostratigraphic framework of European basins, in P.C.
399 Graciansky, et al. (eds) Mesozoic and Cenozoic Sequence Stratigraphy of. European
400 Basins: SEPM Special Publication 60, 3–13.

401 Harries, P.J., Little, C.T.S., 1999. The Early Toarcian (Early Jurassic) and the Cenomanian–Turonian
402 (Late Cretaceous) mass extinctions: similarities and contrasts. Palaeogeography
403 Palaeoclimatology Palaeoecology 154, 39–66.

404 Hermoso, M., Le Callonnec, L., Minoletti, F., Renard, M., Hesselbo, S.P., 2009. Expression of the
405 Early Toarcian negative carbon–isotope excursion in separated carbonate microfactions
406 (Jurassic, Paris Basin). Earth and Planetary Science Letters 277, 194–203.

407 Hesselbo, S.P., Gröcke, D.R., Jenkyns, H.C., Bjerrun, C.J., Farrimond, P., Morgans Bell, H.S., Green,
408 O.R., 2000. Massive dissociation of gas hydrate during a Jurassic oceanic anoxic event.
409 Nature 406, 392–395.

410 Hesselbo, S.P., Jenkyns, H.C., Duarte, L.V., Oliveira, L.C.V., 2007. Carbon–isotope record of the Early
411 Jurassic (Toarcian) Oceanic Anoxic Event from fossil wood and marine carbonate
412 (Lusitanian Basin, Portugal). *Earth and Planetary Science Letters* 253, 455–470.

413 Hesselbo, S.P., Pienkowski, G., 2011. Stepwise atmospheric carbon isotope excursion during the
414 Toarcian Oceanic Anoxic Event (Early Jurassic, Polish Basin). *Earth and Planetary Science*
415 *Letters* 301, 365–372.

416 Hudson, J.D., 1977. Stable isotopes and limestone lithification. *Journal of the Geological Society of*
417 *London* 133, 637–660.

418 Jenkyns, H.C., Clayton, C.J., 1997. Lower Jurassic epicontinental carbonates and mudstones from
419 England and Wales: chemostratigraphic signals and the early Toarcian anoxic event.
420 *Sedimentology* 44, 687–706.

421 Jenkyns H.C., Jones, C., Gröcke, D., Hesselbo S.P., 2002. Chemostratigraphy of the Jurassic System:
422 applications, limitations and implications for palaeoceanography. *Journal of Geological*
423 *Society of London* 159, 351–378.

424 Kemp, D.B., Coe, A.L., Cohen, A.S., Schwark, L., 2005. Astronomical pacing of methane release in the
425 Early Jurassic period. *Nature* 437, 396–399.

426 Krencker, F.–N., Bodin, S., Suan, G., Heimhofer, U., Kabiri, L., Immenhauser, A., 2015. Toarcian
427 extreme warmth led to tropical cyclone intensification. *Earth and Planetary Science*
428 *Letters* 425, 120–130.

429 Küspert, W., 1982. Environmental changes during oil shale deposition as deduced from stable
430 isotope ratios, in *Cyclic and Event Stratification*. G. Einsele and A. Seilacher. (Eds)
431 Springer, Berlin 482–501.

432 Lachkar, N., Guiraud, M., El Harfi, A., Dommergues, J.–L., Dera, G., Durllet, C., 2009. Early Jurassic
433 normal faulting in a carbonate extensional basin: characterization of tectonically driven

434 platform drowning (High Atlas rift, Morocco) . Journal of Geological Society of London
435 166, 413–430.

436 Laville, E., Pique, A., Amrhar, M., Charroud, M., 2004. A restatement of the Mesozoic Atlasic Rifting
437 (Morocco). Journal of African Earth Sciences 38, 145–153.

438 Little, C.T.S., Benton, M.J., 1995. Early Jurassic mass extinction: a global long–term event. Geology
439 23, 495–498.

440 Littler, K., Hesselbo, S.P., Jenkyns, H.C., 2010. A carbon–isotope perturbation at the Pliensbachian–
441 Toarcian boundary: evidence from the Lias Group, NE England. Geological Magazine
442 147,181–192.

443 Martinez, M., Krencker, F.-N., Mattioli E., Bodin, S. 2016. Orbital chronology of the Pliensbachian –
444 Toarcian transition from the Central High Atlas Basin (Morocco). Newsletters on
445 Stratigraphy,

446 Mattioli, E., Pittet, B., Petitpierre, L., Mailliot, S., 2009. Dramatic decrease of pelagic carbonate
447 production by nanoplankton across the Early Toarcian Anoxic Event (T–OAE). Glob.
448 Planet. Change 65, 134–145.

449 McElwain, J. C., Wade–Murphy, J., Hesselbo S.P., 2005. Changes in carbon dioxide during an oceanic
450 anoxic event linked to intrusion into Gondwanan coals. Nature 435,479–482.

451 Michard, A., 1976. Eléments de géologie Marocaine. Notes et Mémoires du Service Géologique 252,
452 408.

453 Montero–Serrano, J.C., Föllmi, K., Adatte T., Spangenberg J.E., Tribovillard, N., Fantasia, A., Suan, G.,
454 2015. Continental weathering and redox conditions during the early Toarcian Oceanic
455 Anoxic Event in the northwestern Tethys: Insight from the Posidonia Shale section in the
456 Swiss Jura Mountains. Palaeogeography, Palaeoclimatology, Palaeoecology 429, 83–99.

- 457 Porter, S.J., Smith, P.L., Caruthers, A.H., Pengfei, H., Gröcke, D.R., Selby, D. 2014. New high
458 resolution geochemistry of Lower Jurassic marine sections in western North America: A
459 global positive carbon isotope excursion in the Sinemurian? *Earth and Planetary Science*
460 *Letters* 397, 19–31.
- 461 Reolid, M., Martínez–Ruiz, F. 2012. Comparison of benthic foraminifera and geochemical proxies in
462 shelf deposits from the Upper Jurassic of the Prebetic (southern Spain). *Journal of Iberian*
463 *Geology* 38, 449–465.
- 464 Reolid, M., Chakiri, S., Bejjaji, Z., 2013. Adaptative strategies of the Toarcian benthic foraminiferal
465 assemblages from the Middle Atlas (Morocco): Palaeoecological implications. *Journal of*
466 *African Earth Sciences* 84, 1–12.
- 467 Rosales, I., Robles, S., Quesada, S., 2004. Elemental and oxygen isotope composition of early
468 Jurassic belemnites: Salinity vs. temperature signals. *J. Sediment. Res* 74,342–354.
- 469 Ruget, Ch., Nicollin, J.P., 1997. Les petites foraminifères benthiques dégagés. In: Cariou, E.,
470 Hantzpergue, P. (Eds.), *Biostratigraphie du Jurassique Ouest–European et Mediterranen*,
471 *Bull. Centre Rech. Elf Explor. Prod. Mem*, 17, 281–291.
- 472 Sabaoui, A., 1998. Rôle des inversions dans l'évolution Méso–Cénozoïques du Moyen Atlas
473 septentrional (Maroc). L'exemple de la transversale El Menzel–Ribat El Khayr–Bou Iblane.
474 PhD Thesis, Université Mohammed V Rabat, 1–432.
- 475 Sandoval, J., Bill, M., O'Dogherty, L., Rivas, P., Morard, A., Guex, J. 2012. The Toarcian in the
476 Subbetic basin (southern Spain): bioevents (ammonite and calcareous nannofossils) and
477 carbon–isotope stratigraphy. *Palaeogeography Palaeoclimatology, Palaeoecology* 342–
478 434, 40–63.

479 Sanders, M.T., Bardin, J., Benzaggagh, M., Cecca, F., 2013. Early Toarcian (Jurassic) belemnites from
480 northeastern Gondwana (South Riffian ridges, Morocco). *Paläontologische Zeitschrift*,
481 DOI 10.1007/s12542-013-0214-0

482 Souhel, A., Canerot, J., El Bchari, F., Chafiki, D., Gharib, A., El Hariri, K., Bouchouata, A., 2000. The
483 Liassic carbonate platform on the western part of the Central High Atlas (Morocco):
484 stratigraphic and palaeogeographic patterns. In: Crasquin-Soleau, S., Barrier, E. (Eds.),
485 Peri-Tethys Memoir 5: new data on Peri-Tethyan sedimentary. Paris 39–56.

486 Studer, M., Du Dresnay, R., 1980. Deformations synsedimentaires en compression pendant le Lias
487 superieur et le Dogger, au Tizi n'Irhil (Haut Atlas central de Midelt, Maroc). *Bulletin de la*
488 *Société Géologique de France*, 22, 391–397.

489 Suan, G., Pittet, B., Bour, I., Mattioli, E., Duarte, L.V., Mailliot, S., 2008. Duration of the Early
490 Toarcian carbon isotope excursion deduced from spectral analysis: consequence for its
491 possible causes. *Earth and Planetary Science Letters* 267, 666–679.

492 Swart, P.K., Eberli, G.P., 2005. The nature of the $\delta^{13}\text{C}$ of periplatform sediments: Implications for
493 stratigraphy and the global carbon cycle. *Sediment. Geol.* 175, 115–129.

494 Suan, G., Mattioli, E., Pittet, B., Lécuyer, C., Suchéras-Marx, B., Duarte, L.V., Philippe, M., Reggiani,
495 L., Martineau, F., 2010. Secular environmental precursors to Early Toarcian (Jurassic)
496 extreme climate changes. *Earth and Planetary Science Letters* 290, 448–458.

497 Suan, G., Nikitenko, B.L., Rogov, M.A., Baudin, F., Spangenberg, J.E., Knyazev, V.G., 2011. Polar
498 record of Early Jurassic massive carbon injection. *Earth and Planetary Science Letters* 312,
499 102–113.

500 Wignall, P.B., Newton, R.J., Little, C.T.S., 2005. The timing of paleoenvironmental change and
501 cause-and-effect relationships during the early Jurassic mass extinction in Europe.
502 *American Journal of Science* 305, 1014–1032.

- 503 Wignall, P.B., Bond, D.P.G., 2008. The end–Triassic and Early Jurassic mass extinction records in the
504 British Isles. *Proceedings of the Geologists' Association* 119, 73–84.
- 505 Wilmsen, M., Neuweiler, F., 2008. Biosedimentology of the Early Jurassic postextinction carbonate
506 depositional system, central High Atlas rift basin, Morocco. *Sedimentology* 55, 773–807.
- 507
- 508

509 **Figure Captions**

510

511 Figure 1. (a) Toarcian palaeogeographic map, Western Tethyan realm (modified after Bassoulet et
512 al., 1993), with localities; 1–Issouka, 2–Peniche, 3–Mochras Farm (b) Simplified structural map of
513 Morocco, with position of the Issouka section and the Amellago section (of Bodin et al., 2010) and
514 Bou Oumardoul section (of Krencker et al., 2015) (modified after Lachkar et al., 2009). Grey inset
515 box shows location of Figure 2.

516

517 Figure 2. Geological map of the Middle Atlas and section locality (modified from Bejjaji et al., 2010)

518

519 Figure 3. The different facies in the Issouka section. (a). Limestones of the Late Pliensbachian with
520 fauna (sponges and brachiopods). (b). Photomicrograph of limestone from the Pliensbachian
521 showing abundance of microfauna – wackestone texture. (c) The Lower Toarcian, characterized by
522 grey marls at the boundary and limestone intercalation. (d) Photomicrograph showing the marls of
523 the Lower Toarcian – a mudstone texture with quartz grains.

524

525 Figure 4 (a) CL and (b) PPL photomicrographs of belemnite rostrum (Sample IS8) exhibiting a minor
526 degree of luminescence associated with central apical zone (c) CL and (d) photomicrographs of
527 belemnite rostrum (IS6B1) exhibiting a modest luminescence associated with central apical zone (e)
528 CL and (f) PPL photomicrographs of belemnite margin (sample IS3) showing highly luminescence
529 mudstone adjacent to the rostrum margin exhibiting minor luminescence.

530

531 Figure 5. CaCO₃, TOC data and isotopic results from the Issouka section. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}_{\text{micrite}}$ (grey
532 and black circles) $\delta^{13}\text{C}$ and $\delta^{18}\text{O}_{\text{belemnite}}$ (open and grey squares). The ammonite zonation is after
533 (Benshili, 1989; Sabaoui, 1998; El Hammichi et al., 2008).

534

535 Figure 6. Carbon isotope stratigraphies at the Pliensbachian–Toarcian boundary from the Issouka
536 section compared with the Amellago (Bodin et al., 2010; Bodin et al., 2016) and the Bou
537 Oumardoul sections, High Atlas (Krencker et al., 2015; Bodin et al., 2016); the Peniche section,
538 Portugal (Hesselbo et al., 2007; Littler et al. 2010) and the Mochras Farm borehole (Wales; Jenkyns
539 and Clayton, 1997).

540

541 Table 1 Isotopic and elemental compositions of belemnites analysed in this study.