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

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

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## ABSTRACT

The data presented here provide the first high resolution investigation of carbon isotope and geochemical analyses derived from the Pliensbachian-Toarcian boundary, of Issouka, Middle Atlas, Morocco. The isotope data recorded in micrite reveal a stepwise negative carbon isotope excursion with values dropping to  $-1.8\text{‰}$  within the Polymorphum Zone. This excursion coincides with major marine biological changes and extinctions and corresponds with European records supporting the assertion that the excursion is global in origin. The Issouka section is relatively expanded compared to other well-studied European sections. The excursion at the Pliensbachian-Toarcian boundary also shows several similarities with the negative Early Toarcian event. In 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 ~20°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 nannofossils 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  $\delta$  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 (CaCO<sub>3</sub>) 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 HNO<sub>3</sub> 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, *Dactylioceras*  
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  $\text{CaCO}_3$  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

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

## 5. Discussion

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

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

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

gentle decreasing trend in  $\delta^{13}\text{C}_{\text{org}}$  values, followed by an overall positive trend within the Polymorphum Zone. The Issouka section is relatively expanded compared to the well-studied European sections. Within the European sections where the Pliensbachian–Toarcian boundary excursion is observed e.g. the Hawsker Bottoms section, Yorkshire, England (Littler et al., 2010), the Mochras Farm Borehole (Jenkyns and Clayton, 1997) and Peniche, Portugal (Hesselbo et al., 2007) the negative excursion is typically  $\sim 2\text{‰}$ . As shown by Littler et al. (2010), this negative shift is recorded within a relatively thin interval (Fig. 6). This could be the result of a short-lived episode or alternatively sedimentary condensation. Littler et al. (2010) for example noted the abrupt onset of the isotope excursion at Hawsker Bottoms and the initiation of an extinction step near the same level, supporting the notion of a catastrophic event such as release of methane hydrate. Alternatively it could equally be argued that the sections in Yorkshire and Peniche are stratigraphically condensed (Fig. 6) or incomplete at this level. Nevertheless, the duration and pace of onset of the event is unclear (Littler et al., 2010). Bodin et al. (2011), however, recorded the event in an interval from the Amellago section of a few 10's of meters. They suggested the duration is likely to be similar to the Early Toarcian Event and the Pliensbachian–Toarcian boundary negative excursion was inadequately recorded in the more condensed sediments in Europe. The greater magnitude of the event at Issouka is considered to be related to the expanded nature of the section (e.g. when compared to the Europe sections) allowing sampling of the full magnitude of the event as well as the stepwise character of the excursion. This stepwise character is certainly reminiscent 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 CO<sub>2</sub> 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  $^{18}\text{O}$  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  $\text{CaCO}_3$  content

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

## 6. Conclusions

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

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327

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## Figure Captions

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

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

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

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

531 Figure 5. CaCO<sub>3</sub>, 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.