

# Early Jurassic climatic trends in the south-Tethyan margin

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#### Early Jurassic climatic trends in the south-Tethyan margin

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#### **Abstract**

The Early Jurassic period was characterized by extreme environmental changes, as reflected by major global carbon isotope anomalies and abrupt changes in oxygen isotope and elemental records of marine organisms. Available data suggest an overall warm Early Jurassic climate interrupted by periods of severe cooling, with a climatic optimum during the early Toarcian. Available geochemical studies, however, have mainly focused on the northern margin of the Tethys Ocean, so that the extent of these environmental perturbations, palaeogeographic palaeotemperature gradients and climate belt boundaries remain poorly constrained. Here we report the first stable isotope records of brachiopod shells ( $\delta^{13}$ C and  $\delta^{18}$ O values) from the Upper Sinemurian-Middle Toarcian interval in the southern margin of the Tethys Ocean (northwest Algeria). These data were used to better constrain the palaeoenvironmental evolution of the North Gondwana margin during the Early Jurassic, which likely played an important role on supra-regional climate. The diagenetic history of the analysed brachiopod shells was monitored using scanning electron microscopy, and elemental (manganese and strontium) compositions. The brachiopod  $\delta^{13}$ C and  $\delta^{18}$ O data show very similar trends as those reported for various Tethyan regions, and record negative carbon and oxygen isotope excursions near the Sinemurian-Pliensbachian and Pliensbachian-Toarcian transitions and during the Toarcian oceanic anoxic event (T-OAE). Despite these similarities, the carbon and oxygen isotope records are systematically offset towards more positive  $\delta^{13}$ C values

(average +0.5‰) and more negative δ<sup>18</sup>O values (-1.0‰) compared to those obtained from sites of higher palaeolatitudes in the northern Tethyan margin. These offsets suggest a spatial heterogeneity in the stable isotope composition of dissolved inorganic carbon in the Early Jurassic Ocean and a marked latitudinal temperature gradient between the southern and northern margins of the Tethys.

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40 Keywords: Carbon and Oxygen stable isotopes, Early Jurassic, NW Algeria,41 Palaeoclimate

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## 1. Introduction

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The Early Jurassic period (~ 200-175 Ma) has been intensively studied because it was a key time interval for the environmental evolution of the western Tethys. Indeed, this time interval is characterized by extreme climate fluctuations, with possible glacial interludes occurring within an interval of general greenhouse conditions (Price, 1999). This interval is marked by major events in the large igneous provinces of the Central Atlantic and Karoo-Ferrar (e.g., Wignall, 2001), and the gradual disintegration of the Pangea supercontinent (Olsen, 1997). Severe perturbations of the carbon cycle are reflected by large fluctuations of the stable carbon isotope composition ( $\delta^{13}$ C) of marine and terrestrial material. Severe biotic crises, such as the first-order extinction of the end-Triassic (Wignall, 2001) or the Toarcian oceanic anoxic event (T-OAE; Jenkyns, 1988) produced marked floral and faunal turnovers (Harries and Little, 1999; Macchioni and Cecca, 2002; Mattioli et al., 2008; Suan et al., 2008a, 2010). Numerous studies have focused on the palaeoenvironmental and biological perturbations in sites from the northwestern Tethys (e.g., Harries and Little, 1999; Hesselbo et al., 2000a; Jenkyns et al., 2002; Gomez et al. 2008; Harazim et al., 2013; Ruebsam et al., 2018). However, climate conditions during the Early Jurassic in the Tethyan southern margin are very poorly known (Bodin et al., 2010, 2016; Reolid et al., 2012; Krencker et al., 2014; Ait-Itto et al., 2017). The North Gondwana is considered to be characterized by a more arid climate with respect to the NW Tethys (Aberhan, 2001; van de Schootbrugge et al., 2005). The carbon and oxygen isotope trends have been documented for bulk carbonate, belemnites and brachiopods from uppermost Pliensbachian and Toarcian strata of Morocco (Bodin et al., 2010; Krencker et al., 2014; Ait-Itto et al., 2017). High-resolution carbon isotope records of bulk carbonate and associated organic matter in micrite samples from the upper Pliensbachian and lower Toarcian intervals in three sections from the Central High Atlas Basin in Morocco were presented and discussed by Bodin et al. (2016). Apart from these records, there is a desperate lack of information about the climate and environmental evolution in North Gondwana during most of the Early Jurassic interval. The distribution of climate belts and the role played by North Africa in Early Jurassic climate evolution remain therefore poorly understood.

This study presents new carbon and oxygen isotope measurements of brachiopod shell calcite from sections in NW Algeria, which was a marginal part of the NW Gondwana. The data set spans the Early Jurassic interval, from the Upper Sinemurian to the Middle Toarcian. Well-preserved articulate brachiopod shells are considered as some of the most pertinent materials for geochemical analyses, as modern representatives are strictly sessile and benthic organisms that precipitate their calcite shell in close chemical and isotopic equilibrium with ambient seawater (e.g., Veizer et al., 1999). Therefore, their stable isotope record can safely be interpreted in terms of temperature and changes in the isotopic composition of the dissolved inorganic carbon (DIC) pool through time. The isotope data obtained in NW Algeria are here compared to the isotopic records from various NW Tethys settings in order to discriminate between local *versus* global fluctuations of environmental parameters during the early Jurassic.

## 2. Geological background

The samples studied in this paper were collected from five different sites, all located in NW Algeria, which in the Jurassic was part of the south-west part of the western Tethys (Fig. 1A). These sites are separated longitudinally by a distance of a few hundred kilometres, but were approximately situated at the same palaeolatitude (Fig. 1). Most of the brachiopod samples come from the Alméras collection (Almeras et al., 2007), hosted in the Collections de Géologie de Lyon. These specimens are stratigraphically well-constrained at the ammonite Zone to Subzone level, and come from 22 sections in the Traras, Rhar Roubane, Saïda, Ouarsenis and Nador Mountains (Fig. 1B). These regions are part of the Tello-Rifain chains, which constitute the western Mediterranean part of the Alpine chain and are separated from the Sahara craton by a narrow, tectonic corridor extending eastwards from Morocco (Agadir) to Tunisia (Gabes; Wildi, 1983).

- 102 Within the Tlemcen Domain, the Traras Mountains are bounded to the north by the
- 103 Mediterranean Sea, to the east by the Mio-Pliocene and Quaternary basin of Tafna, to
- the west by the Beni Snassen Massifs (Eastern Morocco), and to the south by the
- 105 Maghnia depression. The Traras mountains are subdivided into at least three
- subbasins (or "umbilici") separated by structural highs in the Early Jurassic (Ameur,
- 107 1999; Elmi et al., 2006). The slope-basin transition occurred in the eastern Traras
- 108 Mountains (Benhamou, 1983) (Fig. 1B).
- 109 A field mission was realized in 2017 in the Mellala section (Traras Mountains) to collect
- brachiopod specimens from the Pliensbachian-Toarcian transition where brachiopod
- specimens were scarce in the Alméras collection (Table 1). This section exposes an
- exceptionally thick (~50 m) succession of interbedded argillaceous limestones and
- calcareous marls that are well-constrained biostratigraphically by assemblages of
- ammonites, brachiopods (Elmi et al., 2006), and calcareous nannofossils (Baghli et al.,
- 115 in prep.).
- The Rhar Roubane mountains are limited to the north by the Maghnia Plain, to the
- south by the Oran High Plains, to the east by the Tlemcen Mountains, and to the west
- by the Oujda Mountains. The Lower Jurassic facies associations are representative of
- protected carbonate ramp, slope and basin depositional environments (Mekahli, 1988)
- 120 (Fig. 1B).
- 121 The Saïda Mountains are located in an intermediate region comprised between the
- Tell to the north, the Oran High Plains to the south, to the west by the transform fault
- of Ain-Sefra, and to the east by the high-plains of Sersou. Facies associations in Saïda
- Mountains are representative of deep-external platform environments, in contrast to
- the Traras Mountains and to the Rhar Roubane area, which represent shallower, more
- proximal environments. It was part of a protected transitional zone during most of the
- 127 Early Jurassic, which opened towards the marine domain in the latest part of the middle
- Toarcian substage (Elmi and Almeras, 1984; Elmi et al., 1985).
- In the southern part of the Tell, the Ouarsenis massif is bounded to the north by the
- 130 Chelif valley, to the south by the Sersou plateau, to the west by the Beni-Chougrane
- and Mina Mountains, and to the east by the Bibans. During the Early Jurassic, this
- region corresponded to an internal platform evolving into an external platform,
- connected to the open sea and showing a deepening trend (Benhamou et al., 2000).
- 134 The Nador Mountains correspond to a SW-NE alignment of the reliefs located along
- the southern edge of the Sersou plateau. The Djebel Nador constitutes an intermediate

zone between the Tellian area to the north and the high-plains to the southwest, resulting from the collapse of a Sinemurian-Pliensbachian carbonate platform. Sedimentation in this area indicates a neritic environment to the west and an epi-oceanic environment to the east.

#### 3. Materials and methods

## 3.1. Brachiopod shell material and preparation

A total of 156 brachiopod shells from NW Algeria, ranging in age from the upper Sinemurian to the middle Toarcian, were analysed for their carbon and oxygen isotope composition. The isotopic data were obtained from a composite of different articulate brachiopod taxa, including Rhynchonellida (*Homoeorhynchia*, *Soaresirhynchia*; Table 1) and Terebratulida (*Telothyris*, *Lobothyris*; Table 1). The sediment matrix was mechanically removed from brachiopod specimens using stainless dental tools, and the shell surface was thoroughly washed with deionized water in an ultrasonic bath (three times for 10-min with renewed water), rinsed with MQ water (obtained from a Direct-Q Millipore® purification system), and dried at 50°C for 48 h. The outermost layer of the brachiopod shells was carefully removed with a dental tool under a Stereomicroscope (Leica M125) at 80 X. Powders for stable isotope measurements were obtained by scraping the pristine long and thin fibrous textures lying in the innermost secondary layer of the anterior shell (Fig. 2).

## 3.2. Analyses

- The preservation of calcite fibres of all brachiopod shells was assessed under the optical microscope and scanning electron microscope (SEM) using a PHENOM G2 PRO instrument in backscatter mode (Phenom-World B.V., Dillenburgstraat 9T, 5652 AM, Eindhoven, The Netherlands) before stable isotope measurements.

  The carbon and oxygen isotope measurements were performed using a Thermo Fisher Scientific (Bremen, Germany) Gas Bench II carbonate preparation device, connected
  - Scientific (Bremen, Germany) Gas Bench II carbonate preparation device, connected to a Delta Plus XL isotope ratio mass spectrometer at the Institute of Earth Surface Dynamics of the University of Lausanne. The CO<sub>2</sub> extraction was done by reaction of 100–200 µg of powdered carbonate sample with anhydrous phosphoric acid at 70°C.

The carbon and oxygen isotope ratios are reported in the delta ( $\delta$ ) notation as the per mil (‰) deviation relative to the Vienna Pee Dee belemnite standard (VPDB). The standardization of the  $\delta^{13}C$  and  $\delta^{18}O$  values relative to VPDB was done by replicate analysis of the in-house working standard Carrara marble (UNIL-CM,  $\delta^{13}C = 2.05$  ‰,  $\delta^{18}O = -1.70$  ‰) within the analytical sequences. The  $\delta^{13}C$  and  $\delta^{18}O$  values of the reference CO<sub>2</sub> gas and the UNIL-CM standard were obtained by normalization with the international reference materials NBS-19 limestone, NBS-18 carbonatite and LSVEC lithium carbonate using the values reported in Brand et al. (2014). Analytical uncertainty (1 $\sigma$ ), monitored by replicate analyses of NBS-19 and UNIL-CM was not greater than  $\pm 0.05$  ‰ for  $\delta^{13}C$  and  $\pm 0.1$  ‰ for  $\delta^{18}O$ .

Trace element analysis was performed at the Laboratoire de Géologie de Lyon, on the fibrous secondary layer of selected brachiopods. A total of 57 specimens were selected for element analysis, including those sample that had apparently anomalous  $\delta^{13}C$  and  $\delta^{18}O$  values, and also some samples with isotopic ratios in the range of marine carbonates. For each brachiopod specimen, 1 mg of powdered sample was digested in 10 ml of HNO<sub>3</sub> solution (5% v/v) for 24 h. An aliquot of 1 ml from each stock solution was then diluted in a solution of 9 ml of HNO<sub>3</sub> (2% v/v) and Indium (2 µg/l). Each solution was analysed for Sr and Mn by an inductively plasma mass spectrometer (ICP MS), Agilen Technologies 7500 Series.

#### 3.3. Data treatment

A numerical age was attributed to each analysed brachiopod, based on available stratigraphic information (i.e., ammonite zone and subzone). The ages of each biozone were derived from the timescale of Gradstein et al., (2012). The stable isotope data ( $\delta^{13}$ C and  $\delta^{18}$ O values) were smoothed to better highlight the long-term trends. Two methods for smoothing data by locally weighted regression were implemented, the LOESS smoothing function using the software PAST 3.18 (Hammer et al., 2001), and the lowess algorithm (Cleveland, 1981). Lowess is a linear polynomial smoother, whereas the LOESS procedure uses a quadratic polynomial to avoid over-fitting and excessive twisting and bending (e.g., Faber and Rajko, 2007). The smoothing factor applied to the whole data is 0.1. Such a small factor was chosen in order to highlight short-term fluctuations in the considered time interval.

The LOESS smoothing with a factor of 0.1 was also applied to the data available in the literature from different Tethyan regions. For each region, the smoothed isotopic data were computed, plotted against absolute age, and compared to the LOESS values obtained for NW Algeria. One-way ANOVA analyses were used to determine the significance (probability value P) of the observed differences (offsets). The difference between two groups is considered to be statically significant at the 95% level when  $P \leq 0.05$ .

#### 4. Results

## 4.1. Optical microscopy and SEM images

All the brachiopod specimens were screened under SEM and optical microscope before C and O isotope analyses. The textures observed vary from well-preserved, when calcite fibres are long and thin, without any clear trace of overgrowth (Fig. 2C), to mediumly-preserved material showing slightly overgrown fibres (Fig. 2B). Few brachiopod specimens have shown very poorly preserved calcite fibres, almost completely overgrown. The ultra-structure of the inner layers of the shell of all the brachiopod under SEM (Fig. 2) allowed us to discard specimens showing a variable but strong degree of post-depositional alteration that resulted in marked textural changes compared to that of modern specimens. These changes are expressed by a loss of pristine microstructures, ranging from slight dissolution of calcite fibres to almost complete obliteration of any fibrous structure (Bates and Brand, 1991). Such specimens were not processed for geochemical analyses. After this screening by optical microscopy and SEM analysis, 156 brachiopod shells were retained for  $\delta^{13}$ C and  $\delta^{18}$ O measurements.

## 4.2. Carbon and oxygen isotope data and trace element concentrations

The  $\delta^{13}$ C and  $\delta^{18}$ O values of well-preserved brachiopod shells are given in Appendix A (Supplementary data). The  $\delta^{13}$ C- $\delta^{18}$ O scatterplot shows a large dispersion of data (Fig. 4), with  $\delta^{13}$ C values ranging from 0 to 5.0 % and  $\delta^{18}$ O values from –5.0 to –1.0 %. Few samples record anomalously negative  $\delta^{13}$ C (down to –4.8 %) and  $\delta^{18}$ O (down

to -7.6 %) compared to the Mesozoic and modern brachiopod records, which are strongly suggestive of strong post-mortem diagenetic overprint. No clear  $\delta^{13}$ C- $\delta^{18}$ O relationship was observed for 95% of the brachiopod specimens, even when considering the different localities separately (Fig. 4). The relative stratigraphic position of brachiopods in the different sections was respected and vertical bars on the isotope curves (Fig. 5) indicate the stratigraphic extension of brachiopod ages according to ammonite zones and sub-zones. The main differences in the isotopic composition of the brachiopod shells occur between localities and are likely due to the record of various time spans in the different study areas (Appendix B). Nonetheless, the relatively large variability of the composite specimen samples is certainly attributable to the presence of peculiar environmental conditions in a given area or to different water-depths that likely affect the isotope results (Fig. 5). The  $\delta^{13}$ C trends reveal several events across the studied interval, which are more clearly visible in the LOESS smoothing curve (Fig. 5). The earliest event is recorded at the Sinemurian/Pliensbachian boundary, where a pronounced ~2.5 % negative excursion, with  $\delta^{13}$ C values as low as -4.0 % mark the Raricostatum-Jamesoni interval. According to the original study of Alméras et al. (2007), the analysed brachiopods belong to an assemblage characteristic of the Sinemurian/Pliensbachian boundary. Importantly, the samples showing positive values were collected in the lower part of the section, the brachiopods showing negative values were collected in the upper part of the same section (see Supplementary material). In the lbex zone and in the lower part of the Davoei zone,  $\delta^{13}$ C values are around 1.0 %. In the upper part of the Davoei zone, more positive values reach up to 4.0 \%. The  $\delta^{13}$ C values return close to ~1.0 % near the transition between the Lavinianum-Algovianum Zones, and show a ~1.0 % negative excursion in the uppermost Pliensbachian (Emaciatum Zone). Towards the lowermost part of Tenuicostatum zone, the  $\delta^{13}$ C values become more positive with a +2.0 % shift, and decrease upwards to -1.0 % in the basal part of the Serpentinum Zone. After this event, a large shift toward positive values (up to 4.5 %) characterizes the middle part of the Serpentinum zone, followed by some less pronounced fluctuations until the Bifrons zone with an average value of 3.0 %. At the Sinemurian/Pliensbachian boundary, the  $\delta^{18}$ O values range between -5.2 %. and -3.0 % (on average  $-4.3 \pm 0.68$  %). The  $\delta^{18}$ O values increase considerably in the Ibex zone (lower Pliensbachian) and at the base of the Davoei zone, both with average

values of -1.9 ‰. In the upper part of the Davoei zone, the  $\delta^{18}$ O values decrease again

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to an average of -4.0 ‰. Up to the beginning of the Emaciatum zone, the oxygenisotope values are rather stable with an average at -3.0 ‰. Passing from the Emaciatum zone to the Pliensbachian/Toarcian boundary, the  $\delta^{18}$ O values record a negative excursion of almost 2.0 ‰ attaining an average of -4.0 ‰ at the boundary. A positive 2.0 ‰ shift characterizes the base of the Toarcian with average values of -2.0 ‰ towards the middle part of the Tenuicostatum zone. This isotopic change is followed by a second negative excursion ending in the lower part of the Serpentinum zone, with average  $\delta^{18}$ O values of -3.8 ‰. In the aftermath, small isotopic rebounds to less negative values (of  $\sim 0.8$  ‰) are recorded, after which  $\delta^{18}$ O values, although fluctuating, enter a  $\sim 2.0$  ‰ long term trend toward more negative values extending from the middle part of the Serpentinum zone to the middle part of the Bifrons zone and lasting around 2 Myrs.

- The trace element contents of the selected samples revealed Sr contents varying between 130 and 1000 ppm, with most samples exceeding 450 ppm (on average 524
- $\pm$  260) (Fig. 3). Mn contents range between 3 to about 80 ppm (on average 64  $\pm$  58).
- Half a dozen samples are depleted in Sr and enriched in Mn (Supplementary data).
- Ten samples show anomalously negative  $\delta^{13}C$  and  $\delta^{18}O$  values, or anomalous
- contents in both Mn (< 80 ppm) and Sr (> 450 ppm) with respect to modern brachiopod
- shells secreted in equilibrium with ambient water (e.g., Brand and Veizer, 1980; Brand
- 289 et al., 2003). These samples were hence excluded from the LOESS calculation, but
- are presented in the chemostratigraphic profiles in Figures 5 to 7.
- 291 The comparison of LOESS smoothing data from NW Algeria and from different
- 292 Tethyan regions shows an offset of 1 ‰, which, according to the one-way ANOVA
- analyses, is statistically significant (P = 1E-05; permutation n = 99999).

## 5. Discussion

A certain degree of variability is observed both for carbon and oxygen isotopes (Fig. 5). Such variability is higher than that observed by Suan et al. (2010) in brachiopods of comparable age from the Portuguese Peniche section in Portugal. However, this can be partly due to the different environmental origin of the brachiopods sampled in five different regions of the NW Algeria. The water depth differences between the studied regions in Algeria are not important, as samples belong to outer platform, slope or shallow-basin settings. Furthermore, these five regions were located almost at the

same palaeolatitude. Thus, apart from the data dispersion (Fig. 5) also reported from brachiopod isotope composition in other time intervals (e.g., Giraud et al., 2016), some prominent excursions are observed in the present work for  $\delta^{13}$ C and  $\delta^{18}$ O values from NW Algeria (i.e., Sinemurian-Pliensbachian boundary, Pliensbachian-Toarcian boundary, early Toarcian Anoxic Event). These excursions can likely be related to palaeoclimatic and palaeoceanographic events, once proven the primary nature of the isotopic signal. The palaeoenvironmental significance and interpretations of these isotopic records can then be safely compared with analogous records from other Tethys regions.

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#### 5.1. Preservation of brachiopods shells

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Present-day articulate brachiopods (Rhynchonellida, Terebratulida) are strictly benthic and sessile organisms that generally precipitate their secondary shell layer in isotopic equilibrium with the ambient waters (Brand et al., 2003; Brand et al., 2013), and incorporate trace elements and stable isotopes from the surrounding environments (Brand and Veizer, 1980). In the case of exposure of this carbonate phase to meteoric waters, it might undergo partial or total dissolution, exchange trace elements and stable isotopes with those of interstitial water, and finally re-precipitate as diagenetic calcite (Brand and Veizer, 1980). In modern brachiopod species, the outermost primary layer, which is characterized by a thickness of about 50 µm and a granular texture, is most probably secreted out of isotopic equilibrium with sea water (Carpenter and Lohmann, 1995; Auclair et al., 2003; Brand et al., 2003). Specialized structures (mainly located in the posterior part of the shell) and the uppermost part of the secondary shell were excluded from analysis as, in modern brachiopod species, these parts may also have an isotope signature out of the expected values for calcite precipitated in isotopic equilibrium with environmental water (Carpenter and Lohmann, 1995; Curry and Fallick, 2002; Auclair et al., 2003). The stable isotope analyses were performed on powders obtained from the outermost layer of the brachiopod shells (see section 3.1). SEM images were used to evaluate the preservation of the microstructures of the secondary layer, the shell microstructures are considered to be well preserved when smooth fibrous surfaces of secondary layer occur, similarly to those observed in living specimens (Brand et al., 2003; Suan et al., 2008a). Diagenetically-altered structures of the secondary layer of brachiopod shells are identified by the poor individualization

of calcite fibres (Suan et al., 2008a; Giraud et al., 2016). In specimens showing a good preservation of the calcite fibres of the secondary layer under SEM, the primary character of the stable carbon and oxygen isotope composition of the brachiopod shells was tested using the concentrations of strontium and manganese, which are known to be sensitive to diagenetic alteration (Brand and Veizer, 1980; Brand et al., 2003). Although it has been shown that there were variations in the concentrations of these elements through the Phanerozoic in relation with episodes of aragonite and calcite seas (Steuber and Veizer, 2002), it is widely acknowledged that the Sr concentration of low-magnesium calcite in the well-preserved secondary brachiopod layer varies between 450 and 1900 ppm at middle-to-low latitudes, while Mn values vary between 0 ppm and about 80 ppm (Brand and Veizer, 1980; Korte et al., 2003), even in modern brachiopods (Brand et al., 2003). The Sr and Mn contents of almost all the brachiopod shells are in the range of unaltered fossil brachiopod calcite mentioned above, with the exception of few specimens that are plotted with different symbols along non-altered samples in figure 3, but excluded from our isotopic interpretations and thus not discussed in the following. In some cases, the anomaly only concerns a single trace element (i.e., Mn or Sr), and the  $\delta^{13}$ C and  $\delta^{18}$ O values are well within those expected for primary marine carbonates. Mn contents outside the range for low-Mg calcite are probably due to seasonal conditions that may influence the Mn contents of sea-water, with a decrease in winter and an increase in spring (Dromgoole and Walter, 1990). Alternatively, redox conditions may also affect the trace element concentrations (Vander Putten et al., 2000). The Sr content in calcite of modern bivalve species appears to be greatly controlled by kinetic and metabolic effects (Freitas et al., 2005; Vander Putten et al., 2000), a possible minor temperature and salinity influence may occur (Beck et al., 1992; Elderfield and Ganssen, 2000). In the brachiopods we analysed, no difference in Sr and Mn concentrations between specimens and species from the same stratigraphic level were observed. Our results show that the Mn content is similar between two analysed genera and varying Sr contents between genera, if any, could probably reflect particular metabolic effects (Table 1). A  $\delta^{13}C_{\text{brachiopod}}$  versus  $\delta^{18}O_{\text{brachiopod}}$  scatterplot provided further information on the eventual diagenetic modification by meteoric waters (Fig. 4). A 95% ellipse data concentration shows that most of the values obtained in this paper are in the range of

"normal" marine carbonates. Sedimentary diagenesis involves recrystallization

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(dissolution and precipitation) and/or overgrowth on primary carbonate minerals, resulting in a depletion in  $^{13}$ C and  $^{18}$ O of the secondary carbonate phases (Burdett et al., 1990; Bates and Brand, 1991; McConnaughey et al., 1997; Auclair et al., 2003), and therefore generating a positive linear  $\delta^{13}$ C- $\delta^{18}$ O correlation. The large dispersion of our results in the  $\delta^{13}$ C- $\delta^{18}$ O scatterplot and the absence of clear correlation between values suggest that the isotopic composition of brachiopod shells did not suffered major diagenetic overprint. However, the  $\delta^{13}$ C and  $\delta^{18}$ O values of samples from the different localities seem to form distinct clusters (Fig. 4). This is mainly related to the fact that the studied localities correspond to different stratigraphic intervals, recording distinct temporal changes of the  $\delta^{13}$ C and  $\delta^{18}$ O values. Conversely, the differences in isotopic compositions between genera, species or specimens sampled within a given stratigraphic level are relatively small, ranging from 0 to about 1 % for both  $\delta^{13}$ C and  $\delta^{18}$ O values (Table 1), in line with the inter-specimen variability of modern brachiopod or bivalve specimens collected from the same localities (Carpenter and Lohmann (1995) and Vander Putten et al. (2000).

## 5.2. Late Sinemurian - Early Pliensbachian interval

In spite of the broad stratigraphic range of the brachiopod specimens analysed in this study that have been assigned to the Raricostatum to Jamesoni zones, the new data from NW Algeria sites show a prominent negative carbon isotope excursion (CIE) and a 1.0 % negative shift in oxygen isotopes that might correspond to the Sinemurian/Pliensbachian interval. Previous studies have shown that the negative CIE at the Sinemurian/Pliensbachian interval has a supra-regional nature (Figs. 6 and 7). The CIE is recorded in Spain (Rosales et., 2006), Portugal (Suan et al., 2010; Duarte et al., 2014), and the UK (Jenkyns et al., 2002; Korte and Hesselbo, 2011; Price et al., 2016). Some authors interpreted this negative  $\delta^{13}$ C excursion as reflecting the massive injection of isotopically light carbon into the ocean-atmosphere reservoirs (Korte and Hesselbo, 2011; Price et al., 2016). Several sources have been proposed for similar events recorded in the Phanerozoic, such as methane release from clathrates, wetlands, thermal metamorphism, kerogen maturation, or decomposition of fossil organic matter (e.g., Scholle and Arthur, 1980; Dickens et al., 1995; Kump and Arthur, 1999; Higgins and Schrag, 2006). However, it is unclear which of these mechanisms is the most likely to have occurred at the Sinemurian-Pliensbachian interval. In the

case of NW Algeria, and in several other cases, the negative CIE at the 406 407 Sinemurian/Pliensbachian boundary appear to be as a sharp  $\delta^{13}$ C-excursion. This can be explained either by the presence of a sedimentary condensation or a hiatus, or by 408 409 the occurrence of a sudden event. The second hypothesis is the most plausible, considering the abruptness of the  $\delta^{13}$ C decrease in several localities, such as in the 410 stratotype for the base of the Pliensbachian (Robin Hood's Bay, NE England), which 412 is known to be only slightly or not affected by condensation or hiatuses (Hesselbo et 413 al., 2000b). 414 Oxygen isotope data can help understanding the perturbations of the carbon cycle across the Sinemurian/Pliensbachian transition. The variations in the  $\delta^{18}$ O values of 415 416 the brachiopod shell reflect mainly changes in ambient temperature and seawater 417 oxygen isotope composition, which indirectly reflect changes in salinity (Brand et al., 418 2013). The oxygen isotope fractionation between calcite and water is temperature dependent, and warmer waters lead to <sup>18</sup>O depleted calcite (Lowenstam, 1961; O'Neil 419 420 et al, 1969). Although a certain dispersion is observed in Upper Sinemurian-Lower Pliensbachian  $\delta^{18}$ O values, a trend to more negative  $\delta^{18}$ O values in the brachiopod 421 422 shells is observed. This trend has revealed to be statistically significant after an 423 ANOVA test and most probably indicates a sudden temperature increase. This 424 temperature increase would support the hypothesis of a massive injection of 425 isotopically light carbon in the ocean-atmosphere system, because enhanced 426 emissions of CO<sub>2</sub> and CH<sub>4</sub> might have produced an increased greenhouse effect. 427 Furthermore, the oxygen isotope data of the studied areas do not show more positive 428  $\delta^{18}$ O values than the northern localities, as it would be expected in case of higher 429 seawater salinity (Epstein and Mayeda, 1953). High evaporation rates should have 430 occurred in NW Algeria, which occupied the southern Tethys arid margin during the Early Jurassic (Turner and Sherif, 2007). A positive  $\delta^{18}$ O shift is conversely reported 431 432 across the Sinemurian-Plienbachian boundary (Korte and Hesselbo, 2011). However, 433 this shift is likely produced by a bottom water cooling related to a deepening phase in 434 the Cleveland Basin (Korte and Hesselbo, 2011). This cooling might be the expression 435 of local conditions rather than a climatic deterioration. 436 In the Davoei zone, another isotope event is recognized despite the relatively low data 437 resolution in this interval. The  $\delta^{13}$ C values in the NW Algeria sections show a positive 438 excursion similar to that observed in other regions (Silva et al., 2011; Franceschi et al., 439 2014; Gómez et al., 2016) (Fig. 6), suggesting that this event was a supra-regional

phenomenon; it is also marked by a drop in the ammonite species richness in the Mediterranean and NW European provinces (Dommergues et al., 2009). At the Davoei zone, also a prominent negative  $\delta^{18}$ O-excursion indicates warmer conditions (Fig. 5). This event was a relatively hot, humid phase, as shown in NW European sediments by kaolinite enrichment and a high  ${}^{87}$ Sr/ ${}^{86}$ Sr values caused by enhanced continental weathering (Jones and Jenkyns, 2001; Dera et al., 2009).

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## 5.3. Late Pliensbachian – Early Toarcian interval

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In the Late Pliensbachian, the  $\delta^{13}$ C values settle between 1 and 2% in the Lavinianum-Algovianum zones (time equivalent of the Margaritatus zone of the Boreal Realm). This trend has been reported in coeval strata from several localities in Europe (Jenkyns and Clayton, 1986; Bailey et al., 2003; Rosales et al., 2006; Suan et al., 2010; Korte and Hesselbo, 2011), and is accompanied in some sections, as those in Portugal and Spain by the occurrence of black shales in the Margaritatus Ammonite Zone (Rosales et al., 2006; Suan et al., 2010; Silva et al., 2015). A trend towards higher  $\delta^{18}$ O values in the Late Pliensbachian (Fig. 5) most probably indicates a trend to cooler seawater culminating in the Emaciatum (or Spinatum) zone, as it was suggested for similar  $\delta^{18}$ Otrends in coeval belemnites and brachiopods from France, Germany, England, Spain or Portugal (e.g., Mcarthur et al., 2000; Rosales et al., 2004a; van de Schootbrugge et al., 2005; Oliveira et al., 2006; Harazim et al., 2013). Several studies have discussed the possible causes of this cooling event. Guex et al. (2001) interpreted this cooling as the result of a decreased insolation following the repeated volcanogenic SO<sub>2</sub> emissions in the Karoo-Ferrar Large Igneous Province. Similarly, Jourdan et al. (2008) inferred a temporal correspondence between the earliest pulses of the Karoo-Ferrar LIP and the beginning of the climate cooling in the upper Pliensbachian. However, this interpretation remains speculative given the short-term residence time in the atmosphere of sulphur aerosols (~10 years) (Wignall, 2001), while the cooling event lasted longer than 1 Myrs according to recent astronomical calibration of Upper Pliensbachian strata from the Mochras borehole in Wales (Ruhl et al., 2016). This cooling episode could also be ascribed to a global drawdown of atmospheric CO2 (inverse greenhouse effect) caused by a widespread burial of isotopically light organic carbon ensuing the accumulation of organic matter-rich sediments in the Margaritatus Zone (Jenkyns and Clayton, 1997; Silva et al., 2015).

Across the Pliensbachian/Toarcian boundary, the negative  $\delta^{13}$ C excursion in Algeria correlates remarkably well with that recorded in coeval sites in NW Europe, which was interpreted as reflecting another pulse of massive injection of  $^{13}$ C-depleted carbon into the oceans and the atmosphere (Hesselbo et al., 2007; Suan et al., 2008a). This hypothesis is consistent with the marked  $\delta^{18}$ O negative excursion in biogenic carbonates at the same level in Algeria (Fig. 5), Spain and Portugal (Fig. 7), which has been interpreted in the latter localities as the evidence of a sharp increase in temperature (Suan et al., 2008b) more or less directly linked to a pulse of the activity in the Karoo-Ferrar LIP (Jourdan et al., 2008; Littler et al., 2009; Pálfy and Smith, 2000; Percival et al., 2015, 2016). At the end of this Pliensbachian/Toarcian event, a relatively small positive rebound of  $\delta^{13}$ C values is noticed in almost all the sites in the lower part of the Tenuicostatum Zone (Fig. 6), which correlates with a trend toward higher  $\delta^{18}$ O values (Fig. 7) and can be interpreted as a temporary cooling event.

## 5.4. Early-Middle Toarcian environmental evolution

A marked shift towards lower  $\delta^{13}$ C values is recorded in NW Algeria in the basal Serpentinum zone, followed by a gradual return to higher values. We interpret this shift as the expression of the well-documented negative CIE often used to define the base of the T-OAE interval. Again, this CIE is classically interpreted as being derived from the massive and rapid injection of <sup>13</sup>C-depleted carbon to the ocean-atmosphere reservoirs, possibly as the result of the release of methane from continental margins (Hesselbo et al., 2000a; 2007; Kemp et al., 2005), of enhanced CO<sub>2</sub> emissions during a renewed peak activity of the Karoo-Ferrar LIP (Suan et al., 2008a; Burgess et al., 2015), of thermogenic methane related to the LIP emplacement, or due to the combined effects of all these processes (Beerling and Brentnall, 2007). These hypotheses are consistent with the coeval negative  $\delta^{18}$ O values recorded in NW Algeria (Fig. 5) which, although less intense that observed in in other areas (Fig. 7), suggests warm conditions during the T-OAE (e.g., Suan et al., 2010; Korte and Hesselbo, 2011; Svensen et al., 2007). In the aftermath of the T-OAE, a marked 2.0 % positive  $\delta^{13}$ C excursion at the Serpentinum zone is recorded in NW Algeria as well as in many other localities (e.g., Jenkyns et al., 2002). This positive  $\delta^{13}$ C excursion is considered to reflect the global burial of excess organic carbon, which in turn likely caused a climate cooling through 508 CO<sub>2</sub> drawdown, as an inverse greenhouse effect (e.g., Jenkyns et al., 2002; Hermoso and Pellenard, 2014; Xu et al., 2017). This scenario is supported by the relatively large 509 positive shift toward higher  $\delta^{18}$ O values recorded in the same interval and most likely 510 511 reflecting a period of cooling (Fig. 7). 512 513 5.5. Differences between C- and O-isotope records from NW Algeria and western 514 Tethys 515 516 The new brachiopod C- and O-isotope profiles show some interesting similarities but 517 also differences with previously published data from different NW Tethys regions 518 based on measurements of belemnite or brachiopod calcite. The possible causes of 519 these differences are discussed in the following sections. 520 521 5.5.1. Trends in  $\delta^{13}C$  values 522 523 The  $\delta^{13}$ C curve of NW Algeria sections shows the main excursions recorded in other 524 European settings, as well as a similar steady trend during the mid-Pliensbachian 525 stage. In particular, the Sinemurian/Pliensbachian negative excursion, the Davoei 526 positive excursion, the Pliensbachian/Toarcian negative excursion, the basal 527 Toarcian positive shift and the Early Toarcian negative excursion are all recorded in 528 NW Algeria. Importantly, the comparison of the different sections shows that the 529 belemnite  $\delta^{13}$ C data from NW Europe are systematically offset towards more 530 negative values than those of North Africa, with an overall offset of ~0.5 % (Fig. 6). 531 This offset of the LOESS-smoothed  $\delta^{13}$ C values is statistically significant, and may 532 suggest that the C-isotope composition of the dissolved inorganic carbon (DIC) in 533 shallow shelf waters of the Western Tethys were spatially heterogeneous during the 534 Early Jurassic. 535 This offset could be explained by differences in ecology, physiology and modes of life 536 of brachiopods and belemnites. In fact,  $\delta^{13}$ C values of DIC decrease with increasing 537 depth due to the remineralisation of  $^{13}$ C-depleted organic matter. The lower  $\delta^{13}$ C 538 values recorded in belemnites suggest that they secreted their calcite rostra in deep waters, more enriched in free <sup>13</sup>C-depleted DIC (Wierzbowski and Joachimski, 2007; 539 540 Dutton et al., 2007). Such differences could also explain why belemnite  $\delta^{13}$ C values 541 from Peniche in Portugal (Jenkyns et al., 2002; Hesselbo et al., 2007) are more negative than those obtained for brachiopods (Suan et al., 2010) from the same site (Fig. 6). The higher amplitude of the  $\delta^{13}$ C-excursions measured in NW Europe can be tentatively interpreted as the result of a greater supply of freshwater by rivers to the epi-continental N-Tethyan basins. In fact, the oceanic DIC is fed by freshwaters enriched in oxidized organic matter thus have a  $^{13}$ C-depleted DIC. This leads to the precipitation of biogenic carbonates with more negative  $\delta^{13}$ C values (Clayton and Degens, 1959). It has been also suggested that higher productivity at higher latitudes led to a  $^{13}$ C enrichment of the DIC in surface waters (e.g., the Cleveland Basin, Harazim et al., 2013). Episodes of higher productivity in western European sites or transient migrations of belemnites toward higher latitudes may have intensified changes in belemnite  $\delta^{13}$ C records.

The tectono-climatic regime of North Africa might also have influenced the C-isotope signals. Following the Triassic rift phase related to the opening of the North Atlantic and of the Neo-Tethys (Favre and Stampfli, 1992), restricted continental basins would have developed under arid climates in the Lower Jurassic northern part of Gondwana (Bracène and Frizon de Lamotte, 2002). High evaporation in such palaeo-lakes would have produced substantial  $^{13}$ C and  $^{18}$ O enrichment as the production of light isotopes is favoured in water vapour. The resulting covariance between  $\delta^{18}$ O and  $\delta^{13}$ C is hence generally considered as an evidence of hydrological closure in palaeo-lakes deposits. Accordingly, in the case of continental runoff of such palaeo-lake basins, the  $\delta^{13}$ C signal in adjacent marine basins should be significantly shifted towards more positive values (Talbot, 1990; Deocampo and Jones, 2014). However, the measured  $\delta^{13}$ C values in NW Algeria sections are in the range of "normal" marine carbonates, and do not show such very positive values. It seems therefore unlikely that the NW Algeria basins have been under the influence of continental runoff from surrounding arid lakes.

#### 5.5.2. Trends in $\delta^{18}$ O values

Although the carbon isotope records in NW Algeria show the main events reported in other Tethys settings, the oxygen isotope data show an important difference. Systematically, the  $\delta^{18}$ O values are 1.5 to 2.0 % lower compared to those from NW Tethys sections (e.g., N Spain, France, England), where isotope data mainly derive from belemnite calcite. The offset of the LOESS-smoothed  $\delta^{18}$ O values is statistically significant. The relatively low  $\delta^{18}$ O values in NW Algeria samples are, however, in the

same range as those obtained by Krencker et al. (2014) on brachiopods from Toarcian shelf sediments in Morocco. This offset was partly expected, since these two regions were both located at lower palaeo-latitudes, and therefore were likely to have experienced warmer seawater temperatures (i.e., warm subtropical region; Aberhan, 2001) than European sites. Interpreting the  $\delta^{18}$ O records solely in terms of temperature and considering available  $\delta^{18}$ O-temperature equations (Epstein et al., 1953; Anderson and Arthur, 1983), this 1.5 to 2.0 % offset would suggest that seawater temperatures were about 6 to 8°C warmer in Northern Gondwana than in NW Europe, which appears unrealistic for the relatively low palaeo-latitudinal range implied (~5 to 20°; Fig. 1). In  $\delta^{18}O$ values addition, high belemnite recently reported for Pliensbachian/Toarcian boundary of Issouka in the Central Atlas of Morocco (0 to -1.0 %; Aït-Itto et al., 2017) are almost identical to those obtained for most European belemnites of the same interval (Fig. 7). This similarity suggests that there was no difference in seawater temperature between these various areas, an interpretation that is at odds with the new data set. As discussed above for  $\delta^{13}$ C records (section 4.5.1), however, the difference in material used for geochemical investigations, namely brachiopods in this study *versus* belemnites in most other published works, may introduce a substantial ecological and physiological bias in the comparison of the  $\delta^{18}$ O records (Ullmann et al., 2016). Indeed, several studies have suggested that belemnites precipitate their calcite in deeper waters than brachiopods. This hypothesis is supported by the  $\delta^{18}$ O record of belemnites from Portugal (Jenkyns et al., 2002; Hesselbo et al., 2007), which are ~0.5 to 1.0 % higher than stratigraphically equivalent brachiopods (Suan et al., 2010) sampled from the same site (Fig. 7). It is thus perhaps safer to compare  $\delta^{18}$ O records obtained on the biogenic calcite of organisms with similar ecology and physiology to avoid such palaeoecological complications. The new  $\delta^{18}$ O brachiopod data from Algeria are still 0.5 to 1.0 % lower than brachiopod  $\delta^{18}$ O data from Portugal, suggesting a more reasonable difference in temperature of about 2 to 4°C between bottom water masses of these two areas. It is very likely that the recorded spatial changes in  $\delta^{18}$ O values of biogenic carbonates also reflect spatial changes in seawater  $\delta^{18}$ O values, as a result of different hydrological regime between the N and S Tethys margins and thus indirectly related changes in seawater salinity. The northern margin of Gondwana was characterized from the Middle-Late Triassic to the Early Jurassic by the development of a number of

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basins along the northern margin of the Saharan craton. As the opening of Tethys ocean proceeded and the relative sea level increased, these basins were flooded and turned to be evaporitic (Turner et al., 2001). Lithostratigraphic studies of continental basins in Eastern Algeria (e.g., Berkine Basin; Turner and Sherif, 2007) show a succession of lower Sinemurian-Pliensbachian halite deposits, and lower Pliensbachian-upper Toarcian sulphate/halite deposits. In Morocco, similar evaporitic basins are reported (Van Houten, 1977; Peretsman, 1988). This attests for the extent of evaporitic environments along the North Africa margin in the Lower Jurassic, with a vast assemblage of evaporitic basins (Le Roy and Piqué, 2001; Courel et al., 2003; Turner and Sherif, 2007), where Sabkha-type environments developed (Elmi and Benshilil, 1987). Given the proximity of these evaporitic basins to the study area, any continental water input to the marine environment would have drained these evaporitic basins. According to studies on current Sabkha environments, salinity may vary, according to the seasons, between 50 % and 250 % (Amarouayache et al., 2018). Since  $\delta^{18}$ O would change by about 0.2 % per unit change in salinity (Sharp, 2017), a 5.0 % fluctuation in salinity would be accompanied by a 1.0 % change in the  $\delta^{18}$ O value in the ocean shallow-waters (Sharp, 2017). In the case of runoff of these waters into the ocean, a large  $\delta^{18}$ O positive offset would be expected. As we observe, conversely, a negative  $\delta^{18}$ O offset with respect to other Tethys settings, we can exclude the effects related to Sabkha environment runoff. Besides that, brachiopods are known to be intolerant to important salinity changes, which would result from a strong evaporation or from saline lake drainage (Ager, 1967). Higher evaporation at southern latitudes is thus very unlikely to be the main cause of the observed offset of  $\delta^{18}$ O values of NW Algeria and the  $\delta^{18}$ O data from NW Europe. We cannot rule out, however, that the isotopic offset between the N and S margin of Tethys is somehow mitigated by such differences in evaporation. In the meantime, more intense precipitations, the combined impact of melting ice and the input of freshwaters by river systems should have produced lower  $\delta^{18}$ O values in the northernmost basins (Rosales et al., 2004b; Dera and Donnadieu, 2012), which may explain the anomalously low belemnite  $\delta^{18}$ O values in the UK compared to all other belemnites records (Fig. 7). The Pliensbachian-Toarcian record from England (Cleveland Basin) is also singular in that it shows an opposite trend for oxygen isotopes compared to NW Algeria, as well as with respect to other localities (Fig. 7). Indeed, the basal Tenuicostatum Zone is marked in England by a distinct positive shift toward higher values, while a wide

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negative shift is recorded in NW Algeria (this work) and in Portugal (Suan et al., 2010). Some authors explain this trend by a deepening of sea-level near the Pliensbachian/Toarcian, which is indeed marked by a supra-regional marine transgression (Hardenbol et al., 1998; Pittet et al., 2014). Due to this sea-level rise, belemnites would have migrated in deeper and cooler waters (Korte and Hesselbo, 2011). However, one may ask why the same effect was not recorded by belemnites during the T-OAE interval, which recorded an even more important sea-level rise, while belemnites display a negative excursion that can be interpreted as an evidence for warming. Korte and Hesselbo (2011) and Ullmann et al., (2014) attributed this variable response of belemnite  $\delta^{18}$ O record relative to sea-level changes to bottom water anoxia, which forced belemnites to secrete their calcite rostrum in shallower waters during the T-OAE. Similarly, substantial differences in spatial trends in  $\delta^{18}$ O recorded by belemnite rostra and bivalve shells have been documented for several other intervals, such as during the lower Bajocian, the middle Oxfordian, and Lower Tithonian cooling (Dera et al., 2011), and attributed to metabolic and ecological factors. In this regard, our new record emphasizes differences in life habitats, namely the depth in the water column belemnites thrived, as a crucial parameter to consider. Brachiopods conversely were sessile organisms, generally inhabiting shallow-water depth, making them more susceptible to record temperature fluctuations and changes in evaporation-precipitation budgets than belemnites. In summary, all these observations indicate that the  $\delta^{18}$ O trends in brachiopod shell in NW Algeria reflect mainly temperature fluctuations, and suggest that a latitudinal temperature gradient of around 2 to 4°C existed between bottom water masses of the

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## 6. Summary and conclusions

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We produced a continuous record of carbon and oxygen stable isotope for Upper Sinemurian-Middle Toarcian successions in NW Algeria based on brachiopod calcite. This fills an important gap in the palaeolatitudinal record of carbon and oxygen stable isotopes, which is essential for our understanding of Jurassic climatic belts. The  $\delta^{13}$ C and  $\delta^{18}$ O excursions documented in NW Algeria confirm the main climate and environmental changes previously documented in the NW Tethys, although slight differences can be seen because of the peculiar paleogeographic context of the

central and southern part of the western Tethys during the Early Jurassic.

studied area. The negative  $\delta^{13}$ C excursion near the Sinemurian/Pliensbachian boundary in NW Algeria, previously documented in England and Portugal, is accompanied by a decrease of  $\delta^{18}$ O values, supporting the hypothesis of a greenhouse-forced warming during this interval. The Pliensbachian/Toarcian boundary negative CIE is well marked on the S-Tethys margin and the coeval shift toward lower  $\delta^{18}$ O values is also interpreted as reflecting a transient warming. Also, the well-known T-OAE CIE is documented in NW Algeria along with an intense warming phase, as shown by a coeval decrease of  $\delta^{18}$ O values.

The new NW Algerian records are also valuable in that they reveal a systematic positive offset of ~0.5 % for  $\delta^{13}$ C values and negative offset of ~1.5 % for  $\delta^{18}$ O values compared to European sections. We interpret these offsets as mainly reflecting higher seawater temperatures along the southern margin of Tethys. This was previously interpreted on the basis of the sedimentary record of widespread carbonate platforms and of evaporitic environments in coastal areas of N-Africa settings. We bring for the first-time quantitative data on the existing temperature gradient. This gradient can further explain the distribution of marine (Bucefalo Palliani and Riding, 2003; Mattioli et al., 2008) or continental organisms (Philippe and Thevenard, 1996), which show significant differences in terms of assemblage composition between the S and the N of the Tethys. These new data should be integrated in future climate models to constrain Early Jurassic climate belt distribution and their latitudinal fluctuations during times of environmental perturbations.

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#### Legend of figures

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Fig. 1. A. Location of Western Algeria in the frame of an Early Jurassic palaeogeographic map (modified after Thierry et al., 2000). The main current circulation pattern is reported, as well as the main climatic modes (i.e., arid and wet) for the Northern and Southern Tethys margin, respectively (after Dera and Donnadieu, 2012). B. Palaeogeographical map of western Algeria during the Toarcian (modified after Elmi and Benshili, 1987).

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Fig. 2. Scanning electron micrographs showing the ultra-structures of brachiopod shells (A and C) *Cuersithyris provincialis*; (B) *Lobothyris hispanica*; (D) *Soaresirhynchia tamazirta*.

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Fig. 3. The relationships between  $\delta^{18}$ O values and Mn, Sr concentrations in brachiopod shells. The arrows indicate the shift produced by diagenetic incorporation in Mn and Sr in brachiopod calcite.

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Fig. 4. Cross Plot of  $\delta^{13}$ C *versus*  $\delta^{18}$ O values of brachiopod shell calcite. Coloured dots represent the different studied localities. The dashed circle corresponds to the 95% concentration of data points.

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Fig. 5. C and O isotope compositions of brachiopod calcite from the Upper Sinemurian to the Middle Toarcian in north-western Algeria. Numerical ages are derived from "The Geologic Time Scale 2012" (Gradstein et al., 2012). The relative stratigraphic position of brachiopods in the different sections was respected and vertical bars on the isotope curves indicate the stratigraphic extension of brachiopod ages according to ammonite zones and sub-zones. The colours of the symbols correspond to the region where the samples come from. A LOESS Smoothing with a 0.1 factor was applied using Past

3.18. Square symbols show samples recording anomalous Sr or Mn contents and therefore not considered for the LOESS smoothing.

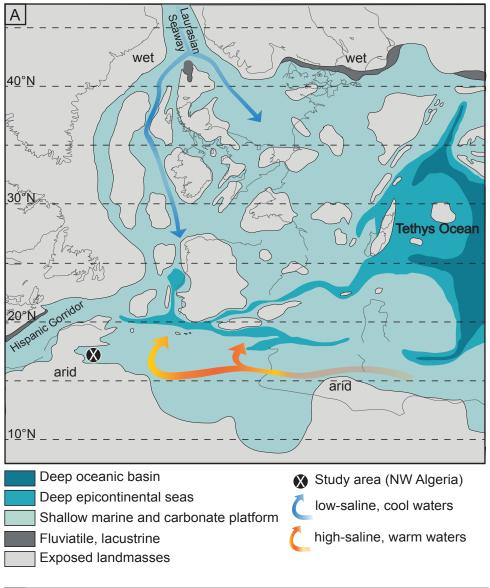
Fig. 6. C-isotope comparisons and chemo-stratigraphy correlation between sections studied in Algeria: Traras, Rhar Roubane, Ouarsenis, Saïda, and Nador Mountains (this work); in England: Cleveland Basin (Hesselbo et al., 2000b; Mcarthur et al., 2000; Jenkyns et al., 2002; Bailey et al., 2003; Korte and Hesselbo, 2011; Li et al., 2012); in France: Grands Causses Basin, Sud-Est Basin and Paris Basin (Dera et al., 2011; Harazim et al., 2013); in Spain: Iberian Range, Asturias, and Basque-Cantabrian Basin (Rosales et al., 2004a; Schootbrugge et al., 2005; Gómez et al., 2008; Armendáriz et al., 2012); in Portugal: Lusitanian Basin (Jenkyns et al., 2002; Suan et al., 2010). All of the data have been measured on belemnite calcite, except in Portugal (Suan et al., 2010) and in NW Algeria (this work) where C isotopes have been measured on brachiopod calcite. Light red and blue shaded areas respectively indicate warming and cooling events.

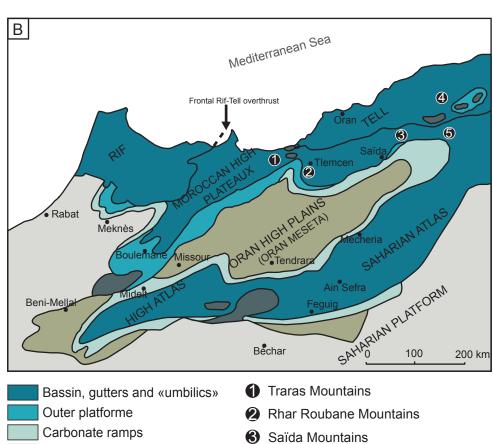
Fig. 7. O-isotope comparisons and chemo-stratigraphy correlation between sections studied in Algeria: Traras, Rhar Roubane, Ouarsenis, Saïda, and Nador Mountains (this work); in England: Cleveland Basin (Hesselbo et al., 2000b; Mcarthur et al., 2000; Jenkyns et al., 2002; Bailey et al., 2003; Korte and Hesselbo, 2011; Li et al., 2012); in France: Grands Causses Basin, Sud-Est Basin and Paris Basin (Dera et al., 2011; Harazim et al., 2013); in Spain: Iberian Range, Asturias, and Basque-Cantabrian Basin (Rosales et al., 2004a; Schootbrugge et al., 2005; Gómez et al., 2008; Armendáriz et al., 2012); in Portugal: Lusitanian Basin (Jenkyns et al., 2002; Suan et al., 2010). All of the data have been measured on belemnite calcite, except in Portugal (Suan et al., 2010) and in NW Algeria (this work) where O isotopes have been measured on brachiopod calcite. Light red and blue shaded areas indicate the warming or, conversely, cooling events.

**Supplementary data** (Appendix A) List of all the brachiopod specimens analysed for carbon and oxygen isotopic composition and strontium and manganese contents. Most of these brachiopods come from Alméras collection (Alméras et al., 2007), which is curated at the Collections de Géologie de Lyon. FSL numbers are provided along with the section and the locality where they have been collected. Brachiopods from Melalla section were sampled by the authors. A numerical age has been attributed to each

specimen according to their stratigraphic position and corresponding ammonite biozonation calibrated against the timescale of Gradstein et al. (2012).

Supplementary data (Appendix B) Synthetic stratigraphic logs with the position of the brachiopod samples analysed for carbon and oxygen isotope composition. These logs have been redrawn after Benhamou (1983, 1996); Elmi et al. (1985); Kharroubi (1987); Mekahli (1988).





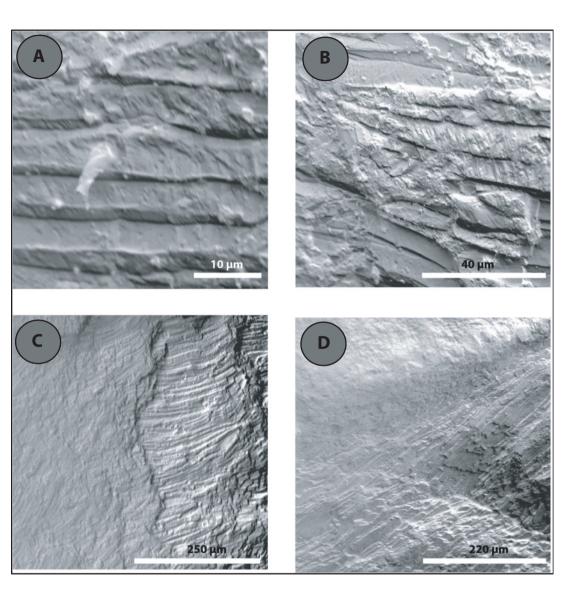
Ouarsenis Mountains

Nador Mountains

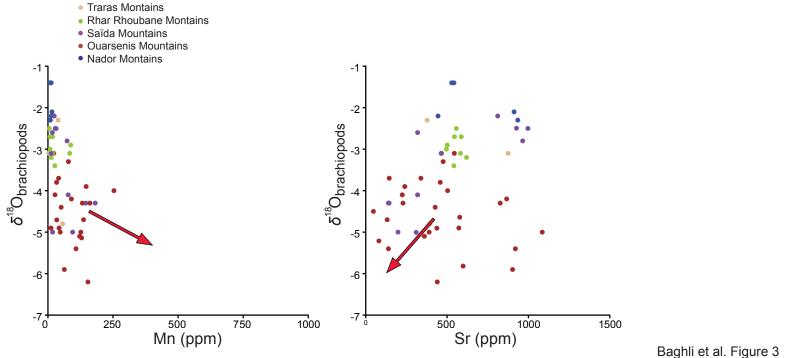
Shoals and importants gaps

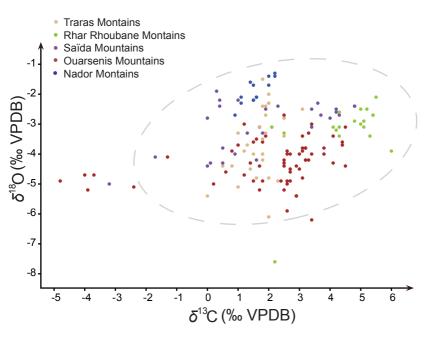
Sabkha confined facies

Probably emergent areas



Baghli et al. Figure 2





Baghli et al. Figure 4

