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Late Valanginian–Barremian (Early Cretaceous) palaeotemperatures inferred from belemnite stable isotope and Mg/Ca ratios from Bersek Quarry (Gerecse Mountains, Transdanubian Range, Hungary)

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ABSTRACT

A high resolution stable isotope study of Upper Valanginian–Barremian (Early Cretaceous) belemnites from Bersek Quarry (Gerecse Mountains, Transdanubian Range, Hungary) is presented. Over 190 belemnite rostra (including Hibolithes subfusiformis, Duvalia dilatata and Conohibolites gladiiformis) have been analysed for oxygen and carbon isotopes and for trace element geochemistry. The obtained carbon isotope curve shows a long term decrease from ~1.2% in the Upper Valanginian to ~-0.5% in the Upper Hauterivian followed by more variable values in the Early Barremian. Superimposed on this trend are a number of possible shorter term peaks. This pattern broadly follows published carbon isotope curves for the same interval and is therefore thought to reflect a global rather than a regional signal. The oxygen isotopes show the most positive values in the uppermost Valanginian and become increasingly more negative through the Hauterivian into the Barremian. Such changes are interpreted as an increase in marine temperatures through the section. The Mg/Ca data paralleling the oxygen isotope trend confirms our temperature interpretation. The oxygen isotope ratios are generally more negative and therefore allow us to infer warmer temperatures, than those derived from belemnites from time equivalent sections in Germany and Speeton, UK, consistent with the more southerly latitudinal position of the Gerecse Mts. within the Tethys Ocean. The oxygen isotope and Mg/Ca data also reveal habitat differences for the different belemnite groups analysed. Vaunagites pistilliformis, "Belemnites" pistilliformis and Hibolithes typically have more negative oxygen isotope values than Pseudobelus and *Duvalia* and are therefore interpreted to have lived in warmer and/or shallower parts of the water column, consistent with previous interpretations.

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1. Introduction

The relationship between Early Cretaceous δ^{13} C excursions, oceanographic and climate change has been the subject of much discussion (e.g. Weissert, 1989; Föllmi et al., 1994; Weissert et al., 1998; Price et al., 2000; 2008; van de Schootbrugge et al., 2000; Wortmann and Weissert, 2000; Gröcke et al., 2005; Godet et al., 2006; McArthur et al., 2007a; Malkoč and Mutterlose, 2010; Price and Nunn, 2010). For example, certain oceanographic events such as the Faraoni event close to the Hauterivian–Barremian boundary are less than obvious in the δ^{13} C record. Much of the data testing such relationships have been derived from the Boreal realm and the western Tethys. Data

* Corresponding author. *E-mail address:* g.price@plymouth.ac.uk (G.D. Price). presented from more eastern Tethyan sites (e.g. Melinte and Mutterlose, 2001; Fisher et al., 2005; Gröcke et al., 2005; Főzy et al., 2010) are consistent with the data from these regions although, importantly, also highlight some key differences. Herein, we provide new data regarding the temporal record of isotope variation of the west-central Tethys region and improve the time constraints on episodes of temperature variation and carbon cycling. Utilising stable isotopes derived from well-preserved belemnites as a potential palaeoceanographic and stratigraphic tool (e.g. van de Schootbrugge et al., 2000; Price and Mutterlose, 2004) permits a δ^{13} C profile to be directly compared with an oxygen isotope-derived palaeotemperature signal. Because of the relative diversity of the belemnites analysed in this study, we have also been able to examine some recent inferences regarding the palaeoecology and palaeobiology of belemnites in terms of depth habitats and agility (e.g. Mutterlose and Wiedenroth, 2008; Price et al., 2009a, b; Rexfort and Mutterlose, 2009).

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2. Geological setting

The samples of this study are derived from the Lower Cretaceous sedimentary strata of Bersek Quarry, Bersek Hill in the Gerecse Mountains, close to the Danube River (Fig. 1) south of the village of Lábatlan in north-central Hungary. This location was at a palaeolatitude of ~35°N, (e.g. Smith et al., 1994) during the Early Cretaceous. The palaeogeographic map of Bulot et al. (2000) for the Early Hauterivian suggests a palaeolatitude of ~32°N. The samples form a part of the Fölöp Collection that was gathered in 1963–1964, by a team from the Hungarian Geological Institute. The largest part of the collected fauna comprises more than 10,000 ammonites which now provides a precise biostratigraphic control (e.g. Főzy and Fogarasi, 2002; Főzy and Janssen, 2009) but it also contains belemnites and benthic fossils, such as bivalves, brachiopods, solitary corals and trace fossils. These biostratigraphic studies build upon the earlier ammonite biostratigraphic data of Nagy (1967, 1968, 1969).

The Gerecse Mountains belong to the Transdanubian Range, which in turn forms part of the Alcapa terrane, a distinctive tectonostratigraphic unit of the Alpine–Carpathian orogen (Csontos and Vörös, 2004). The major part of the Bersek Quarry comprises monotonous, grey marlstones (Bersek Marl Formation; Császár, 1996). The lower part is Valanginian in age, and is very poor in megafossils, whereas the upper ~15 m of the marl is relatively rich in cephalopods. This part of the succession is purplish in colour, composed of calcareous and argillaceous bed couplets and represents the Hauterivian (Fülöp, 1958; Főzy and Fogarasi, 2002; Főzy and Janssen, 2009). These sediments were deposited on a mud and silt-dominated submarine slope (Fogarasi, 1995). The overlying Lábatlan Sandstone Formation (Császár, 1996) forms a coarsening-upward sequence of turbiditic origin and yielded Barremian fossils (Fülöp, 1958; Főzy and Fogarasi, 2002; Janssen and Főzy, 2005). The Lábatlan Sandstone Formation begins with slumped beds, and its base is marked by a hardground. Apart from this single bed at 15.6 m above the base, the studied section records continuous sedimentation, with no obvious signs of condensation or gaps. Zonal resolution ammonoid biostratigraphy provides independent evidence for a complete stratigraphic succession.

3. Materials and methods

The belemnite samples have been derived from five sections within the quarry. The location of each sample and section with respect to ammonite zones and lithology was clarified by Fozy and Janssen (2009). Sections A, B, C and D are located within 20 m of each other. The fifth section (Section E), yielding Barremian fossils, was sampled further west in the neighbouring quarry yard (Főzy and Janssen, 2009). The order of sections from the oldest to the youngest is C, B, A, D. Section E overlaps in age with A and D. The belemnite specimens forming a part of the Fülöp Collection have been fully described and identified at the species level, wherever possible (see Janssen and Főzy, 2004, 2005; Főzy and Janssen, 2009). Specimens identifiable at the genus level only are labelled as sp. Some specimens could only be assigned to the family Mesohibolitidae. The genus referred to as "Mesohibolites" is used in the sense of Janssen and Főzy (2005), denoting a taxon in need of a revision and formal description as a new genus. The species *pistilliformis* and *marginatus* are of unknown affinity, hence we chose to use the informal generic name "Belemnites". The belemnites examined include "Mesohibolites" bakalovi, "Belemnites" marginatus, "B." pistilliformis, Conohibolites gladiiformis, Duvalia dilatata, Duvalia grasiana, D. maioriana, Duvalia silesica, Hibolithes aff. krimholzi, H. carpaticus, H. inae, H. jaculiformis, H. longior, H. targovishtensis, Mesohibolitidae, Pseudobelus brevis, Pseudoduvalia and Vaunagites pistilliformis. Of note is that these belemnites display a broad range of morphologies (Fig. 2). "Belemnites" pistilliformis and Hibolithes sp. for



Fig. 1. Location map of Bersek Quarry, Bersek Hill in the Gerecse Mountains and Tethyan palaeogeography modified from Ziegler (1988) and Smith et al. (1994). The location of time equivalent sections in Hannover, northern Germany and Speeton, UK is also shown.



Fig. 2. Early Cretaceous (Upper Valanginian–Upper Barremian) belemnites from Bersek Quarry (Gerecse Mts, Transdanubia, Hungary). All figures are in original size. (1) Duvalia silesica, lateral view; (2a, b) Duvalia aff. gagrica, lateral and dorsal views; (3) Adiakritobelus sp., ventral view; (4) "Mesohibolites" aff. elegans, ventral view; (5) Hibolithes jaculiformis, lateral view; (6) Conohibolites escragnollensis, ventral view; (7a, b) Duvalia dilatata, lateral and dorsal views; (8) "Belemnites" pistilliformis, ventral view; (9a, b, c) Duvalia grasiana, lateral, ventral and dorsal views; (10) Conohibolites ex gr. gladiiformis, ventral view. Note the morphological differences between groups with slender, hastate and flattened rostra.

example have a hastate, spear-like morphology whilst *Duvalia*, have a laterally flattened rostrum.

Trace element geochemistry in conjunction with thin section petrography and cathodoluminescence (CL) was used to determine the state of preservation of the belemnites examined (Figs. 3 and 4). The use of Mg/Ca ratios may offer an additional means for detecting temperature changes (e.g. Bailey et al., 2003; Rosales et al., 2004; McArthur et al., 2007a; Price, 2010). Laboratory experiments have documented a strong correlation of seawater temperature with Mg/Ca ratios whilst salinity is only weakly reflected in skeletal Mg/Ca ratios (Klein et al., 1996). In general, high Mg/Ca ratios have been associated with warmer seawater temperatures.

Prior to drilling for chemical and isotopic analysis those areas of each belemnite deemed most susceptible to diagenetic alteration (predominantly chalky opaque parts and the exterior of each rostra), were removed or avoided. Because of the historic origin of the belemnites (forming a part of the Fölöp Collection), excessive drilling of the specimens had to be avoided, thus a small number of samples provided insufficient drilled powders for chemical analysis. Isotopes were determined on a VG Instruments Optima Isotope Ratio Mass Spectrometer with a Multiprep Automated Carbonate System (at the University of Plymouth) using 200–300 µg of carbonate. Isotopic results were calibrated against NBS-19. Reproducibility for both δ^{18} O and δ^{13} C was better than 0.1‰, based upon multiple sample analysis. Isotope results are reported in δ values relative to the Vienna Pee Dee Belemnite (VPDB) international standard. Sub-samples of belemnites for chemical analysis (Fe, Mn, Mg, Sr) weighing 100–200 mg were dissolved in concentrated nitric acid and analysed using ICP-AES. Based upon analysis of duplicate samples, reproducibility was better than 4% of the measured concentration of each element.

4. Results

Although many belemnites sampled in this study were translucent, numerous samples exhibited prevalent cloudy and opaque areas particularly around the margins of the rostra and the apical region (Fig. 3). These areas tended to be Mn-rich as revealed by cathodoluminescence (CL). As noted above, such areas were either removed prior to or avoided during subsampling. The determined elemental ranges of belemnite rostra (Fig. 4, Table 1 of Appendix 1) were as follows: Sr (327–2035 ppm); Mn (11–1193 ppm); Mg (1394– 5419 ppm) and Fe (11–1848 ppm). The average Ca concentration was 38.9%. Those samples where Fe concentrations were >200 ppm and Mn concentrations >100 ppm (cf. Wierzbowski, 2004; Price et al., 2009a) totalled 55 (29%) and were considered likely to have undergone some isotopic exchange registered by the precipitation



Fig. 3. (a) Plane polarised photomicrograph of *Mesohibolites* (sample 2004.113.1–3) showing acute mottling and opaque cloudy texture. Scale bar is 1 mm. (b) CL photomicrograph of *Hibolithes carpaticus* (sample 2005.21D) showing luminescence picking out growth banding and a cross cutting luminescent spar vein. Scale bar is 1 mm. (c and d) *Hibolithes gr. jaculiformis* (sample 2004.93.1–7A) exhibiting a highly luminescent margin and mottling and opaque cloudy in plane polarised light. Scale bars are 0.5 mm. (e and f) *Hibolithes gr. jaculiformis* (sample 2004.93.1–7A) showing cloudy texture and luminescence adjacent to the apical region. Scale bars are 1 mm. (g) *Hibolithes jaculiformis* (sample 2004.150.1–11B) showing generally clear calcite and growth lines with more opaque calcite around the apical region. Scale bar is 1 mm. (h) *Hibolithes targovishtensis* (sample 2005.83B) showing mottling and opaque cloudy texture. Scale bar is 1 mm.



Fig. 4. Cross-plot of Mn and Fe concentration (in ppm) derived from the belemnites. For clarity a sample with >1190 ppm Fe is not included. Dashed line shows diagenetic screening cut-off values.

of post-depositional diagenetic calcite and were hence excluded from any further analysis. No tendency for a particular belemnite species to show elevated levels of Fe and/or Mn and hence possibly be more susceptible to diagenetic alteration, was noted (Fig. 4). Low Sr concentrations in some belemnite rostra may also be an indicator of diagenetic alteration (Veizer, 1974; Rosales, et al., 2004).

Although the δ^{18} O data do show a certain amount of scatter, it also reveals some meaningful trends (Fig. 5). The oxygen isotope data show the most positive values (-2.7 to 0.9% VPDB) in the uppermost Valanginian and become increasingly more negative through the Hauterivian into the Barremian (-5.9 to -0.8% VPDB). Individual species data also follow this overall trend. Of note is the increasing spread of data seen in the upper part of the section with a number of relatively negative δ^{18} O values observed. These negative values are not restricted to a single belemnite species but include Mesohibolitidae, *D. grasiana* and *Hibolithes targovishtensis*. These negative data cannot be excluded on the basis of diagenesis detected through petrographic or geochemical means. The carbon isotope curve similarly shows a long term decrease from $\sim 1.2\%$ in the Upper Valanginian to $\sim -0.5\%$ in the Upper Hauterivian. More variable δ^{13} C values (-3.1 to 4.3\% VPDB) are seen in the Barremian.

Also illustrated in Fig. 5 are the Mg/Ca ratios derived from the belemnites. The data follow the oxygen isotope trend whereby increasingly high Mg/Ca ratios (associated with warmer seawater temperatures) are observed upwards through the succession. A differentiation (as identified by the 5-point running means) between the *Duvalia/Pseudobelus* data and *V. pistilliformis/"Belemnites" pistilliformis/Hibolithes* data is also maintained.

5. Discussion

The oxygen isotope values of diagenetically screened belemnite rostra have been considered by many as a reliable tool to be used to calculate seawater palaeotemperatures (e.g. van de Schootbrugge et al., 2000; McArthur et al., 2004; Price, 2010). Equilibrium fractionation during the precipitation of belemnite calcite is supported by the fact that *Sepia* and *Spirula*, which are regarded to be the closest living analogues of belemnites, are considered not to exert a vital fractionation effect with respect to oxygen isotopes (Bettencourt and Guerra, 1999; Price et al., 2009b).

In determining palaeotemperatures, the equation of Epstein et al. (1953) as modified by Anderson and Arthur (1983), has been used, as

it was based primarily on molluscan isotope data. This equation utilizes the oxygen isotopic composition of the water, δ_{water} , directly relative to the standard mean ocean water (SMOW):

$$T(^{\circ}C) = 16.0 - 4.14(\delta_{calcite} - \delta_{water}) + 0.13(\delta_{calcite} - \delta_{water})^{2}$$

where $\delta_{calcite}$ equals the oxygen isotopic composition of the calcite with respect to the VPDB international standard and δ_{water} equals the oxygen isotopic composition of the water from which the calcite was precipitated with respect to the SMOW standard. Estimations of seawater δ^{18} O are complex because of such variables as the input of freshwater and/or evaporation. The presence of glacial ice (inferred for parts of the Cretaceous, e.g. Price, 1999) provides a further complication as this also influences global seawater δ^{18} O values. A globally invariant seawater δ^{18} O value of -1.0% is often used (as suggested by Shackleton and Kennett, 1975) although may well represent an oversimplification. A more realistic estimate value might be based upon latitudinal position which takes into account increased evaporation relative to precipitation in sub tropical latitudes (e.g. Zhou et al., 2008). In this study at a palaeolatitude of ~35°N, (e.g. Smith et al., 1994) a seawater δ^{18} O range of -0.5 to 0.0% (VSMOW) may be more realistic (e.g. Zhou et al., 2008). Using a mean of this δ^{18} O range (-0.25%), the resultant belemnite palaeotemperature curve reveals temperatures typically ranging from 11-25 °C for the Upper Valanginian, and 13-32 °C in the Hauterivian. The Mg/Ca data paralleling the $\delta^{18}\text{O}$ data suggest that the overriding control on the oxygen isotope trends is indeed temperature. Taking into account the palaeogeography of central Tethys Ocean during the Hauterivian (~35°N), these temperatures are not unrealistic. Our findings therefore support the view that the Late Hauterivian-Early Barremian in particular represents a warm episode within the Cretaceous, possibly attributed to high levels of atmospheric CO₂. Of note is that inferred temperatures equal the low latitude sea-surface temperature estimates of the mid-Cretaceous (e.g. Moriya et al., 2007). The δ^{18} O is generally more negative (i.e. implying warmer temperatures) than belemnites from the time equivalent sections in northern Germany (east and southeast of Hannover) and Speeton, UK (e.g. Price et al., 2000; McArthur et al., 2004; Malkoč and Mutterlose, 2010), consistent with the more southerly latitudinal position of the Gerecse Mountains within the Tethys Ocean. Furthermore, existing Tethyan palaeotemperature curves (e.g. van de Schootbrugge et al., 2000; McArthur et al.,



Fig. 5. Integrated bio- and chemostratigraphy of the Bersek Quarry section. The lithology and ammonite data are from Fözy and Janssen (2009). The stratigraphic record of δ^{18} O and δ^{13} C and Mg/Ca variation is from this study. The separate 5-point running means are through the *Duvalia/Pseudobelus* data (dark grey line) and *Vaunagites pistilliformis/"Belemnites" pistilliformis/Hibolithes* data (light grey line).

2007a) also show relatively cool temperatures in the earliest Hauterivian and a gradual warming during the Upper Hauterivian.

Also of interest is the occurrence of a small number of lower oxygen isotope values from the Barremian part of the succession. Calculated temperatures for these data range from 40 to 44 °C. Using standard techniques, i.e. petrography and trace element geochemistry it has not been possible to identify any prominent feature consistent with diagenesis. As temperatures reaching up to 44 °C seem intuitively too high (even for subtropical latitudes), these few isotopically light data points may represent the influence of locally reduced seawater δ^{18} O possibly resulting from episodes of increased freshwater input. Ruffell and Batten (1990) describe a phase of aridity which began during the Hauterivian-middle Barremian and continued to dominate the climate of the European region until the mid-Aptian. Undoubtedly an episode of increased aridity is consistent with a seawater δ^{18} O range of -0.5 to 0.0% brought about by increased evaporation relative to precipitation in sub tropical latitudes (e.g. Zhou et al., 2008), but not necessarily with low salinity freshwater fluxes. Climatic conditions during the Hauterivian-middle Barremian were not, however, uniformly dry (Ruffell and Batten, 1990) and with potentially higher magnitude, lower frequency freshwater influxes may be envisaged.

If the difference in the shapes of belemnite rostra (Fig. 2) is reflected in the overall shape of the animal, it would be quite surprising if the taxa of different morphology inhabited the same habitats. Hence the δ^{18} O data may reflect different habitats for the different belemnite groups analysed (e.g. McArthur et al., 2007b). The data from *Pseudobelus* and *Duvalia* in general show more positive oxygen isotope values than *V. pistilliformis*, "*B.*" *pistilliformis* and *Hibolithes* (Figs. 5 and 6), and therefore possibly lived in cooler, and presumably deeper environments. The δ^{18} O difference between these groups typically ranges from 0.5 to 1.0‰ which equates to a thermal gradient of 2 to 5 °C. Although difficult to equate to precise depths, such a temperature range may translate to depth difference in the order of 50–500 m. These interpretations are borne out by palaeobiogeographical inferences. Pseudobelus is common throughout the Valanginian and Hauterivian of the Mediterranean area, but is rare in near-shore sections (e.g. Morocco; Mutterlose and Wiedenroth, 2008) whilst relatively common in deeper-water sites (e.g. Rio Argos, Spain; Janssen, 1997, 2003). Such distributions have led some authors (e.g. Mutterlose and Wiedenroth, 2008) to suggest a hemipelagic to pelagic way of life for this particular genus. There are, however, other explanations, such as migration of organisms from warmer or cooler regions which would show similar isotopic trends. Furthermore in determining palaeotemperatures, the equation of Epstein et al. (1953) was used, which is based primarily on molluscan isotope data. However, different belemnite species may require species specific temperature equations. Oxygen isotope data from other belemnites (e.g. C. gladiiformis) show a broader spread of data. Hence, these belemnites may not have been restricted to a relatively narrow habitat range, but instead may have migrated vertically within the water column possibly in search of food, warmth or for evasion from predators such as large marine reptiles. Again it cannot be excluded that the belemnites not only moved vertically within the water column but also migrated in and out of the area.

As reasonable correlations have been demonstrated between Mg/Ca and δ^{18} O in belemnites of Toarcian (McArthur et al., 2000; Bailey et al., 2003; Price, 2010) and Pliensbachian age (Rosales et al., 2004), Mg/Ca ratios might also reproduce the proposed different habitats of the belemnites. This certainly represents a test of this emerging technique. The Mg/Ca temperature proxy data do indeed show the same ecological trends, whereby *Pseudobelus* and *Duvalia* in general provides lower Mg/Ca ratios (hence cooler inferred temperatures) than *Hibolithes* (Fig. 5). A differentiation of habitats based on Mg/Ca is best seen in the lower part of the section. A breakdown of this pattern is observed, particularly in the uppermost Hauterivian–lowermost Barremian and may be related to a number of factors including the condensation, erosion and slumping noted above, as well as the applicability of using equations based on different extant organisms. However, a statistically significant correlation between Mg/Ca ratios



Fig. 6. Cross-plot of δ^{18} O (VPDB) versus δ^{13} C (VPDB) derived from belemnite samples of Bersek Quarry.

and belemnite δ^{18} O is not observed. Although a number of authors have shown that Mg/Ca ratios tend to reach higher values with increasing seawater temperature (e.g. for foraminifera, Lear et al., 2002, or for the bivalve *Mytilus trossulus*, Klein et al., 1996), other studies (e.g. Van der Putten et al., 2000) have shown considerable deviations from those expected from water temperature alone, implying that other factors, such as metabolic processes are also involved. Hence metabolic processes may have affected separate belemnite species differently and therefore species specific Mg/Catemperature equations may be required. Indeed a number of studies (e.g. McArthur et al., 2007b; Malkoč and Mutterlose, 2010) have questioned the use of Mg/Ca as a temperature proxy.

Although showing scatter, a decrease in mean values of carbon isotopes from ~1.2‰ in the Upper Valanginian to ~-0.5‰ in the Upper Hauterivian (Plesiospitidiscus ligatus/Subsaynella sayni Zones) is observed which agrees with the existing carbon isotope curves for the same interval. For example Föllmi et al. (2006) describe whole-rock carbonate δ^{13} C records from southeastern France, which although differ in absolute values, show the Upper Valanginian high and a Hauterivian low in the Subsaynella sayni Zone. Erba et al. (1999), van de Schootbrugge et al. (2000) and Föllmi et al. (2006) also show a return to more positive values in the uppermost Hauterivian followed by more variable values in the Early Barremian. The carbon isotope trends are therefore thought to reflect a global rather than regional signal. Carbon-isotope stratigraphies from Tethyan and Atlantic sections also show a minor positive excursion in the uppermost part of the Hauterivian and lowermost Barremian (e.g. Baudin, 2005; Föllmi et al., 2006; Tremolada et al., 2009), associated with the Faraoni Event. Occurring within the Pseudothurmannia ohmi Zone, the Faraoni Event, is characterised by deposition of deep-marine black shales in the Mediterranean Tethys (Baudin, 2005; Godet et al., 2006). An expression of the event close to the Hauterivian-Barremian boundary is not obvious in the δ^{13} C data from Bersek Quarry. A likely explanation is that the equivalent level is not only condensed but possibly even missing as erosion has taken place at the base of a slump (Fig. 5). Furthermore, the slumping itself may also have locally eliminated or smeared the stratigraphic details.

Superimposed on the belemnite $\delta^{13}C$ pattern may be other palaeoecological influence. For example some marine organisms (e.g. fish) with low metabolic rates or those living at low temperatures have δ^{13} C values that are precipitated close to equilibrium with ambient water, whereas fish living at higher temperatures with higher metabolic rates often possess otoliths depleted in $\delta^{13}C$ (Kalish, 1991; Sherwood and Rose, 2003; Price et al., 2009a). Lower δ^{13} C values are recorded for V. pistilliformis, "B." pistilliformis and Hibolithes when compared to *Pseudobelus* and *Duvalia* (Fig. 5). The δ^{13} C data may therefore suggest that V. pistilliformis, "B." pistilliformis and Hibolithes are organisms with higher metabolic rates possibly more active with a much greater food or calorie requirement whilst Pseudobelus and Duvalia are organisms with lower rates and possibly comparatively less active. Such an interpretation of the $\delta^{13}C$ is consistent with Rexfort and Mutterlose (2009) who suggest that slender hastate belemnites (e.g. *Hibolithes*) may have been the faster and more agile swimmers as their shape may have minimised drag. Those with conical, short, thick rostra may have been more efficient at slower swimming (Rexfort and Mutterlose, 2009). An influence of metabolic carbon upon the belemnite δ^{13} C values may also explain why the inferred warmer (surface) water dwellers have relatively more depleted carbon values, as the opposite should be expected in a normally stratified water column.

6. Conclusions

Geochemical analyses of Early Cretaceous belemnite specimens from a stratigraphically well-constrained section yielded new data for reconstructions of palaeoclimate and palaeoecology. The belemnite oxygen isotope data, if interpreted in terms of temperature, show a warming trend from 16-29 °C in the Upper Valanginian to 16-35 °C during the Hauterivian and Barremian. This trend is comparable with the number isotopic studies from western Tethys, although temperatures are warmer, consistent with the more southerly latitudinal position of the Gerecse Mountains within the Tethys Ocean. The Mg/Ca data paralleling the oxygen isotope trends confirms our temperature interpretation.

The oxygen isotope and Mg/Ca data also reveal different habitats for the morphologically different belemnite groups analysed. *Vaunagites pistilliformis*, "*B.*" *pistilliformis* and *Hibolithes* typically have more negative oxygen isotope values than *Pseudobelus* and *Duvalia* and therefore are inferred to have lived in warmer and shallower parts of the water column. Our belemnite-derived carbon isotope curve fails to record the latest Hauterivian Faraoni Event, which might be due to slumping and condensation at the equivalent part of the studied section. The observed scatter in δ^{13} C ratios may partly reflect as yet poorly understood vital effects related to different metabolic rates of morphologically different belemnite taxa.

Supplementary materials related to this article can be found online at doi:10.1016/j.palaeo.2011.02.007.

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References

- Anderson, T.F., Arthur, M.A., 1983. Stable isotopes of oxygen and carbon and their application to sedimentologic and environmental problems. In: Arthur, M.A., Anderson, T.F., Kaplan, I.R., Veizer, J., Land, L.S. (Eds.), Stable Isotopes in Sedimentary Geology. Society of Economic Paleontologists and Minerologists Short Course Notes, v. 10, pp. 1.1–1.151.
- Bailey, T.R., Rosenthal, Y., McArthur, J.M., van de Schootbrugge, B., Thirlwall, M.F., 2003. Paleoceanographic changes of the Late Pliensbachian–Early Toarcian interval: a possible link to the genesis of an Oceanic Anoxic Event. Earth and Planetary Science Letters 212, 307–320.
- Baudin, F., 2005. A Late Hauterivian short-lived anoxic event in the Mediterranean Tethys: the 'Faraoni Event'. Comptes Rendus Geoscience 337, 1532–1540.
- Bettencourt, V., Guerra, A., 1999. Carbon- and oxygen isotope composition of the cuttlebone of *Sepia officinalis*: a tool for predicting ecological information? Marine Biology 133, 651–657.
- Bulot, L.G., Ait Ouali, R., Amon, E., Baraboschkin, E.J., Canérot, J., Funk, H.-P., Guiraud, R., Hirsh, F., Masse, J.-P., Memmi, L., Mutterlose, J., Nikishin, A., Platel, J.-P., Poisson, A., Rawson, P.F., Rey, J., Sandulescu, I., 2000. Early Hauterivian (123–121 Ma). In: Dercourt, J., Gaetani, M., et al. (Eds.), Atlas Péri-Téthys. CGGM/CGMW, Paris, pp. 111–118.
- Lithostratigraphic units of Hungary. In: Császár, G. (Ed.), Cretaceous. Hungarian Geological Institute, Budapest. 163 pp.
- Csontos, L., Vörös, A., 2004. Mesozoic plate tectonic reconstruction of the Carpathian region. Palaeogeography, Palaeoclimatology, Palaeoecology 210, 1–56.
- Epstein, S., Buchsbaum, R., Lowenstam, H.A., Urey, H.C., 1953. Revised carbonate-water isotopic temperature scale. Geological Society of America Bulletin 64, 1315–1326.
- Erba, E., Channell, J.E.T., Claps, M., Jones, C.E., Larson, R.L., Opdyke, B., Premoli-Silva, I., Riva, A., Salvini, G., Torriceli, S., 1999. Integrated stratigraphy of the Cismon APTICORE (Southern Alps, Italy): a "reference section" for the Barremian–Aptian interval at low latitudes. Journal of Foraminiferal Research 29, 371–391.
- Fisher, J.K., Price, G.D., Hart, M.B., Leng, M.J., 2005. Stable isotope analysis of the Cenomanian–Turonian (Late Cretaceous) oceanic anoxic event of the Crimea. Cretaceous Research 26, 853–863.
- Fogarasi, A., 1995. Üledékképződés egy szerkezeti mozgásokkal meghatározott korakréta lejtőn a Gerecse hegységben - munkahipotézis. [Sedimentation on a submarine slope determined by tectonic movements.]. Általános Földtani Szemle 27, 15–41.
- Föllmi, K.B., Weissert, H., Bisping, M., Funk, H., 1994. Phosphogenesis, carbon-isotope stratigraphy, and platform evolution along the Lower Cretaceous northern Tethyan margin. Geological Society of America Bulletin 106, 729–746.
- Föllmi, K.B., Godet, A., Bodin, S., Linder, P., 2006. Interactions between environmental change and shallow water carbonate build up along the northern Tethyan margin and their impact on the Early Cretaceous carbon isotope record. Paleoceanography 21 (4), PA4211.
- Főzy, I., Fogarasi, A., 2002. The Lower Cretaceous biostratigraphy of the Bersek Hill (Gerecse Mts, Transdanubian Range) on the basis of the ammonites and nannofossils. Foldtani Kozlony 132, 293–324.

- Főzy, I., Janssen, N.M.M., 2009. Integrated Lower Cretaceous biostratigraphy of the Bersek Quarry, Gerecse Mountains, Transdanubian Range, Hungary, Cretaceous Research 30, 78-92.
- Főzy, I., Janssen, N.M.M., Price, G.D., Knauer, J., Pálfy, J., 2010. Integrated isotope and biostratigraphy of a Lower Cretaceous section from the Bakony Mountains (Transdanubian Range, Hungary): a new Tethyan record of the Weissert event? Cretaceous Research 31 525-545
- Fülöp, J., 1958. Die kretazischen Bildungen des Gerecse-Gebirges. Geologica Hungarica series Geologica 11 57-88
- Godet, A., Bodin, S., Föllmi, K.B., Vermeulen, J., Gardin, S., Fiet, N., Adatte, T., Berner, Z., Stüben, D., van de Schootbrugge, B., 2006. Evolution of the marine stable carbonisotope record during the early Cretaceous: a focus on the late Hauterivian and Barremian in the Tethyan realm. Earth and Planetary Science Letters 242, 254-271.
- Gröcke, D.R., Price, G.D., Robinson, S.A., Baraboshkin, E., Ruffell, A.H., Mutterlose, J., 2005. The Valanginian (Early Cretaceous) positive carbon-isotope event recorded in terrestrial plants. Earth and Planetary Science Letters 240, 495-509.
- Janssen, N.M.M., 1997. Mediterranean Neocomian belemnites, part 1: Rio Argos sequence (province of Murcia, Spain): the Berriasian-Valanginian and the Hauterivian-Barremian boundaries. Scripta Geologica 114, 1-5.
- Janssen, N.M.M., 2003. Mediterranean Neocomian belemnites, part 2: the Berriasian-Valanginian boundary in southeast Spain (Rio Argos, Cañada Lengua and Tornajo). Scripta Geologica 126, 121-183.
- Janssen, N.M.M., Főzy, I., 2004. Neocomian belemnites from the Bersek-hegy (Gerecse Mountains, Hungary), part I: Late Valanginian to earliest Barremian. Fragmenta Palaeontologica Hungarica 22, 27-49.
- Janssen, N.M.M., Főzy, I., 2005. Neocomian belemnites and ammonites from the Bersek-hegy (Gerecse Mountains, Hungary), part II: earliest Barremian-Late Barremian. Fragmenta Palaeontologica Hungarica 23, 59–86. Kalish, J.M., 1991. ¹³C and ¹⁸O isotopic disequilibria in fish otoliths: metabolic and
- kinetic effects. Marine Ecology Progress Series 75, 191-203.
- Klein, R.T., Lohmann, K.C., Thayer, C.W., 1996. Bivalve skeletons record sea-surface temperature and ¹⁸O via Mg/Ca and ¹⁸O/¹⁶O ratios. Geology 24, 415–418.
- Lear, C.H., Rosenthal, Y., Slowey, N., 2002. Benthic foraminiferal Mg/Ca-paleothermometry: a revised core-top calibration. Geochimica et Cosmochimica Acta 66, 3375-3387.
- Malkoč, M., Mutterlose, J., 2010. The Early Barremian warm pulse and the Late Barremian cooling: a high-resolution geochemical record of the Boreal realm. Palaios 25, 14-23.
- McArthur, J.M., Donovan, D.T., Thirlwall, M.F., Fouke, B.W., Mattey, D., 2000. Strontium isotope profile of the early Toarcian (Jurassic) oceanic anoxic event, the duration of ammonite biozones, and belemnite palaeotemperatures. Earth and Planetary Science Letters 179, 269-285.
- McArthur, J.M., Mutterlose, J., Price, G.D., Rawson, P.F., Ruffell, A., Thirlwall, M.F., 2004. Belemnites of Valanginian, Hauterivian and Barremian age: Sr-isotope stratigraphy, composition (87Sr/86Sr, 613C, 618O, Na, Sr, Mg,), and palaeo-oceanography. Palaeogeography, Palaeoclimatology, Palaeoecology 202, 253-272.
- McArthur, J.M., Janssen, N.M.M., Reboulet, S., Leng, M.J., Thirlwall, M.F., van de Schootbrugge, B., 2007a. Palaeotemperatures, polar ice-volume, and isotope stratigraphy (Mg/Ca, δ^{18} O, δ¹³C, 87Sr/86Sr): the Early Cretaceous (Berriasian, Valanginian, Hauterivian). Palaeogeography, Palaeoclimatology, Palaeoecology 248, 391-430.
- McArthur, J.M., Doyle, P., Leng, M.J., Reeves, K., Williams, C.T. Garcia-Sanchez, R. Howarth, R.J. 2007b. Testing palaeo-environmental proxies in Jurassic belemnites: Mg/Ca, Sr/Ca, Na/Ca, 6180 and 613C. Palaeogeography, Palaeoclimatology, Palaeoecology 252, 464-480.
- Melinte, M.C., Mutterlose, J., 2001. A Valanginian (Early Cretaceous) 'boreal nannoplankton excursion' in sections from Romania. Marine Micropaleontology 43, 1-25.
- Moriya, K., Wilson, P.A., Friedrich, O., Erbacher, J., Kawahata, H., 2007. Testing for ice sheets during the mid-Cretaceous greenhouse using glassy foraminiferal calcite from the mid-Cenomanian tropics on Demerara Rise. Geology 35, 615-618
- Mutterlose, J., Wiedenroth, K., 2008. Early Cretaceous (Valanginian-Hauterivian) belemnites from western Morocco: Stratigraphy and palaeoecology. Cretaceous Research 29, 814-829.
- Nagy, I.Z., 1967. Unterkretazische Cephalopoden aus dem Gerecse-Gebirge I. Annales Historico-Naturales Musei Nationalis Hungarici 59, 53-79.
- Nagy, I.Z., 1968. Unterkretazische Cephalopoden aus dem Gerecse-Gebirge II. Annales Historico-Naturales Musei Nationalis Hungarici 60, 41-60.
- Nagy, I.Z., 1969. Őslénytani adatok a gerecsei alsókrétából (Paleontological data from the Lower Cretaceous of the Gerecse Mountains, Hungary). Foldtani Kozlony 99, 211-214.
- Price, G.D., 1999. The evidence and implications of polar-ice during the Mesozoic. Earth Science Reviews 48, 183-210.

- Price, G.D., 2010. Carbon-isotope stratigraphy and temperature change during the Early-Middle Jurassic (Toarcian-Aalenian), Raasay, Scotland, UK. Palaeogeography, Palaeoclimatology, Palaeoecology 285, 255-263.
- Price G.D. Mutterlose I 2004 Isotopic signals from late Jurassic-early Cretaceous (Volgian-Valanginian) subArctic Belemnites, Yatria River, Western Siberia. Journal of the Geological Society of London 161, 959–968.
- Price, G.D., Nunn, E.V., 2010. Valanginian isotope variation in glendonites and belemnites from Arctic Svalbard: glacial temperatures during the Cretaceous greenhouse. Geology 38 251-254
- Price, G.D., Ruffell, A.H., Jones, C.E., Kalin, R.M., Mutterlose, J., 2000. Isotopic evidence for temperature variation during the early Cretaceous (late Ryazanian-mid-Hauterivian). Iournal of the Geological Society of London 157, 335-343.
- Price, G.D., Dashwood, B., Taylor, G.K., Kalin, R.M., Ogle, N., 2008. Carbon isotope and magneto-stratigraphy of the Cretaceous (Barremian-Aptian) Pabellón Formation, Chañarcillo Basin, Chile, Cretaceous Research 29, 183-191.
- Price, G.D., Wilkinson, D., Hart, M.B., Page, K.N., Grimes, S.T., 2009a. Isotopic analysis of co-existing late Jurassic fish otoliths and molluscs: implications for upper ocean water temperature estimates. Geology 37, 215-218.
- Price, G.D., Twitchett, R.J., Smale, C., Marks, V., 2009b. Isotopic analysis of the life history of the enigmatic squid Spirula spirula, with implications for studies of fossil cephalopods. Palaios 24, 273-279.
- Rexfort, A., Mutterlose, J., 2009. The role of biogeography and ecology on the isotope signature of cuttlefishes (Cephalopoda, Sepiidae) and the impact on belemnite studies. Palaeogeography, Palaeoclimatology, Palaeoecology 284, 153-163.
- Rosales, I., Quesada, S., Robles, S., 2004. Paleotemperature variations of Early Jurassic seawater recorded in geochemical trends of belemnites from the Basque-Cantabrian basin, Northern Spain. Palaeogeography, Palaeoclimatology, Palaeoecology 203, 253-275.
- Ruffell, A.H., Batten, D.J., 1990. The Barremian-Aptian arid phase in western Europe. Palaeogeography, Palaeoclimatology, Palaeoecology 80, 197-212.
- Shackleton, N.J., Kennett, J.P., 1975. Paleotemperature history of the Cenozoic and the initiation of Antarctic glaciation: oxygen and carbon isotope analyses in DSDP Sites 277, 279, and 281. In: Kennett, J.P., Houtz, R.E., et al. (Eds.), Initial Reports. DSDP, 29. U.S. Government Printing Office, Washington, pp. 743-755.
- Sherwood, G.D., Rose, G.A., 2003. Influence of swimming form on otolith δ^{13} C in marine fish. Marine Ecology Progress Series 258, 283-289.
- Smith, A.G., Smith, D.G., Funnell, B.M., 1994. Atlas of Mesozoic and Cenozoic Coastlines. Cambridge University Press, Cambridge. 99pp.
- Tremolada, F., Erba, E., De Bernardi, B., Cecca, F., 2009. Calcareous nannofossil fluctuations during the late Hauterivian in the Cismon core (Venetian Alps, northeastern Italy) and in selected sections of the Umbria-Marche Basin (central Italy): paleoceanographic implications of the Faraoni Level. Cretaceous Research 30, 505-514.
- Van de Schootbrugge, B., Föllmi, K.B., Bulot, L.G., Burns, S.J., 2000. Paleoceanographic changes during the Early Cretaceous (Valanginian-Hauterivian): evidence from oxygen and carbon stable isotopes. Earth and Planetary Science Letters 181, 15-31.
- Van der Putten, E., Dehairs, F., Keppens, E., Baeyens, W., 2000. High resolution distribution of trace elements in the calcite shell layer of modern Mytilus edulis: environmental and biological controls. Geochimica et Cosmochimica Acta 2000 (64), 997-1011.
- Veizer, J., 1974. Chemical diagenesis of belemnite shells and possible consequences for paleotemperature determinations. Neues Jahrbuch für Geologie und Paläontologie . Abhandlungen 147, 91–111.
- Weissert, H., 1989. C-isotope stratigraphy, a monitor of paleoenvironmental change: a case study from the early Cretaceous. Surveys in Geophysics 10, 1-61.
- Weissert, H., Lini, A., Föllmi, K., Kuhn, O., 1998. Correlation of Early Cretaceous carbon isotope stratigraphy and platform drowning events: a possible link? Palaeogeography, Palaeoclimatology, Palaeoecology 137, 189-203.
- Wierzbowski, H., 2004. Carbon and oxygen isotope composition of Oxfordian-Early Kimmeridgian belemnite rostra: palaeoenvironmental implications for Late Jurassic seas. Palaeogeography, Palaeoclimatology, Palaeoecology 203, 153-168.
- Wortmann, U.G., Weissert, H., 2000. Tying platform drowning to perturbations of the global carbon cycle with a $\delta^{13}C_{\text{Org}}$ -curve from the Valanginian of DSDP Site 416. Terra Nova 12, 289–294.
- Zhou, J., Poulsen, C.J., Pollard, D., White, T.S., 2008. Simulation of modern and middle Cretaceous marine δ^{18} O with an ocean-atmosphere general circulation model. Paleoceanography 23, PA3223.
- Ziegler, P.A., 1988. Evolution of the Arctic-North Atlantic and the Western Tethys. American Association of Petroleum Geologists Memoir, 43. 198 pp.