

## Evaluating Mg/Ca in belemnite calcite as a palaeo-proxy

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## ABSTRACT

The Mg/Ca, Sr/Ca,  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  compositions are given for well-preserved specimens of ten belemnite species/genera from three stratigraphic intervals. The data help assess the use of these proxies for palaeo-oceanography. Samples are from Dorset, UK (Pliensbachian; 5 species); Cambridgeshire, UK (Callovian; 1 species); and the Vocontian Basin, SE France (Valanginian; 4 genera). In none of these belemnite populations (at species or genera level) does Mg/Ca correlate with  $\delta^{18}\text{O}$ . Neither do values of  $\delta^{18}\text{O}$  correlate with Mg/Ca along a microsampled radial profile across a single specimen of *Cylindroteuthis puzosiana*

(Callovian). The use of Mg/Ca is therefore considered to be unreliable as a palaeo-temperature indicator for these belemnite species and genera.

*Keywords:* belemnite,  $\delta^{18}\text{O}$ , Mg/Ca, Sr/Ca, palaeo-proxies, palaeo-temperature.

## 1. Introduction

The oxygen isotopic composition ( $\delta^{18}\text{O}$ ) and Mg/Ca ratio (and later Sr/Ca) of belemnite calcite have been used to determine palaeo-temperatures and ocean salinity in Jurassic–Cretaceous time. This use is based on two assumptions: 1) that  $\delta^{18}\text{O}$  of belemnite calcite reflects calcification temperature and the isotopic composition of the ambient seawater (Urey et al., 1951; Saelen et al., 1996; Podlaha et al., 1998 and many others); and 2) the Mg/Ca, and possibly Sr/Ca, of belemnite calcite is temperature dependent (Berlin et al., 1967; Yasamanov, 1981; Bailey et al., 2003; McArthur et al., 2007a, b; Wierzbowski and Joachimski, 2009; Nunn and Price, 2010).

Some credence is given to such assumptions by the demonstration of an inverse covariance between  $\delta^{18}\text{O}$  and Sr/Ca, or Mg/Ca, or both, in some Jurassic–Cretaceous belemnites (McArthur et al., 2000, 2007a, b; Bailey et al., 2003; Rosales et al., 2004a, b). The covariance seen in Fig. 1 is for undifferentiated belemnites. By analogy with other calcitic organisms, such as foraminifera, the response of these putative palaeo-proxies in belemnites may be species-dependent, so interpreting undifferentiated belemnites, at genera or family level, may lead to misinterpretation. No correlation between  $\delta^{18}\text{O}$  and Mg/Ca was seen for Jurassic–Cretaceous belemnite species by Wierzbowski and Rogov (2011), Li et al. (2012), or Benito and Reolid (2012). Previous studies of Mg/Ca, Sr/Ca, and Na/Ca in belemnite species or genera noted intra-rostral variations and inter-species/genus differences (McArthur

et al., 2004; McArthur et al., 2007b; Wierzbowski and Joachimski, 2009; Wierzbowski and Rogov, 2011; Li et al., 2012).

In view of the above, it is worthwhile trying to understand just how well the Mg/Ca and Sr/Ca putative palaeo-proxies work. That is done here by analysis of belemnite specimens from three geological intervals and localities (Pliensbachian, Callovian, and Valanginian), comprised of 6 species, and a further 4 genera. The specimens appear well-preserved, based on petrographic examination in thick and polished section, and elemental analyses (see later). Contrary to some of our previous work (McArthur et al. 2007a), this new work suggests that the use of element to Ca ratios (El/Ca) in belemnite calcite as palaeo-proxies needs further evaluation.

## 2. Samples and analytical methods

### 2.1. Samples

Belemnite specimens were obtained from sediments of Pliensbachian and Callovian age in the UK, and from sediments of Valanginian age in SE France (Table 1; Appendices 1–3). Specimens from the UK were identified to species level. Fragmentation of those from France allowed identification of some specimens to no better than genus level, so the Valanginian belemnites are treated throughout this work at the level of genera.

Sample locations, stratigraphic levels, bed numbers, species/genus names and numbers of specimens are given in Table 1 and the Appendices. Pliensbachian belemnites were from the basal 2 metres of the Green Ammonite Beds at Seatown on the coast of Dorset, UK. The biostratigraphy and lithostratigraphy of the section is given in Lang et al. (1928) and Hesselbo and Jenkyns (1995). Specimens of the Callovian belemnite *Cylindroteuthis puzosiana* were from Bed 13 (the base) of the Peterborough Member, Oxford Clay Formation,

that is exposed in a quarry at Kings Dyke, Whittlesey, near Peterborough, UK. This 2 cm-thick bed is the uppermost layer of a condensed *Jason* Subzone. The biostratigraphy of the section is given in Callomon (1968), Duff (1975), and Hudson and Martill (1991, 1994). Valanginian specimens were from the section exposed at Vergol, in the Vocontian Basin, SE France, the stratigraphy and biozonation of which are detailed in Reboulet et al., (2006) and McArthur et al., (2007a). Specimens from Vergol are new to this paper and are not those of McArthur et al. (2007a).

## 2.2. Analytical methods

In order to approach statistical significance, data are reported only where five or more specimens of a species/genus were analysed. Prior to analysis, belemnite specimens were cut at the base of the alveolus, perpendicularly to the apical line, yielding front and back slabs (Fig. 2); the better preserved was used for analysis. Altered areas of the slab (typically the exterior and the apical line) were removed using diamond cutting tools, or dissolved away using 10% HCl for very small samples. The remainder was fragmented to sub-mm size and briefly immersed in 1.2 M HCl to remove surface dust. The best preserved fragments were then picked from a bath of ethanol under the binocular microscope, washed in ultrapure water, and dried in a clean-hood prior to analysis. Fragments that were cloudy were avoided as cloudiness indicates alteration (McArthur et al., 2007b; Rosales et al. 2004a; Benito & Reolid, 2012). Cathodoluminescence was not used to screen for alteration as the methods used proved adequate for that task; visual inspection through the microscope remains one of the best methods of assessing alteration in belemnite calcite.

Stable isotopic analysis of picked fragments was performed either in UCL, using a ThermoFinnegan Delta mass spectrometer and Gasbench preparation system, or in the NERC Isotope Geosciences Laboratory (NIGL), UK, using a VG Optima mass spectrometer. All

isotopic values are reported as permil relative to the V-PDB scale. Analytical precision, estimated within each run using an in-house standard and repeat analyses of NBS19, was better than 0.1‰ (2sd) for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ .

Elemental analysis of picked, fragmented, belemnites for Na, Mg, S, Ca, Fe, Mn, Sr and Ba, was done using a Perkin-Elmer ICP-AES at Royal Holloway University of London using 20 mg samples dissolved in 10 ml of 2% Analar<sup>®</sup>  $\text{HNO}_3$ . Reproducibility, estimated from duplicates, was better than 4% (2sd) for Ca, Mg and Sr, but more for other elements present as impurities.

One specimen of *C. puzosiana* (sample 13-49; Fig. 3a) was profiled radially for  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , and elemental composition. This species has an asymmetrical rostrum and the specimen was profiled along the longer radius of the rostrum (Fig. 3b). The isotopic profile was 15.5 mm in length and the  $\text{El}/\text{Ca}$  profiles was 12.5mm. The two profiles were correlated by matching the prominent concentric alteration bands (usually termed growth rings). This specimen, however, was not particularly well preserved. It showed many concentric rings of cloudy calcite (Fig. 3b) which are usually indicative of alteration. It was used, nevertheless, because better preserved specimens were all smaller and failed to yield sufficient sample for isotopic analysis.

For isotopic profiling of *C. puzosiana*, a New Wave Research micromill was used to micro-sample parallel to growth boundaries at intervals of 250  $\mu\text{m}$  using a longitudinal section of the front slab (Fig. 3c). Samples were measured for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  using a ThermoFinnegan Delta mass spectrometer. For elemental profiling, LA-ICPMS was used (Muller et al., 2009) on the back slab of this specimen (Fig. 3b). An ArF excimer (193 nm) laser-ablation system (RESOLUTION M-50 prototype, Resonectics LLC, USA) with a two-volume laser ablation cell (Laurin Technic, Australia) was connected to an Agilent 7500ce

quadruple ICP-MS operated at a RF power of 1250W. The spot diameter was 57  $\mu\text{m}$ , the laser repetition rate 10 Hz, and scan speed 2 mm/min. Analysis was preceded by pre-ablation cleaning using 74  $\mu\text{m}$  spot, 50 Hz repetition rate and 10 mm/min scan speed. Data reduction to elemental composition followed Longerich et al. (1996). NIST612 was used as external standard and pressed powder carbonate standard pellet USGS MACS-3 as secondary standard. Ca was used as internal standard, and a Ca concentration of 40.08% was assumed in belemnite calcite for calculation, although for element to Ca ratios (El/Ca) this value is cancelled out. Accuracy, estimated using standard MACS-3 was 1.5% - 4.5% (2sd) for Na/Ca, Mg/Ca and Mn/Ca, and 8-11% (2sd) for Zn/Ca and Sr/Ca, comparable to published accuracy of MACS-3 pellet (Jochum et al., 2012; Griffiths et al., 2013).

### 3. Results

The isotopic and elemental data of belemnite specimens are given in Figs. 4–7 and the Appendices. Concentrations of Fe and Mn are <100 ppm and <20 ppm except for the three Pliensbachian samples (D08 7/27 S3, D08 7/1 S2 and D08 120/3, see Appendix 1) which have Fe up to 239 ppm and Mn up to 47 ppm. Concentrations of Mg, Na, and Sr are similar to those in well-preserved belemnites from the literature (McArthur et al., 2000; Li et al., 2012). Radial profiles of  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$  and El/Ca across the specimen of *C. puzosiana* are shown in Fig. 8 and Fig. A in Appendices.

#### 3.1. Isotopic compositions

Within belemnites from each locality and time interval, isotopic compositions differ between species/genera. Differences of  $\delta^{13}\text{C}$  are larger than are differences in  $\delta^{18}\text{O}$  (Appendices 1–3). Specimens of *Passaloteuthis cuspidatus* and *Hastites spadaraxi* (Pliensbachian) have mean  $\delta^{13}\text{C}$  respectively of +1.38‰ and +1.24‰, somewhat higher than those of the other three Pliensbachian species (*Nannobelus acutus* +0.51‰, *Bairstowius*

*junceus* +0.69‰, *Passaloteuthis elongata* +0.60‰; Appendix 1 & Fig. 4). All five species differ little in mean  $\delta^{18}\text{O}$ , the range of means being only 0.22‰. Within the 4 genera of Valanginian belemnites, the mean  $\delta^{13}\text{C}$  ranges from -1.57‰ for *Castellanibellus* to +0.80‰ for *Duvalia*, whilst the spread of mean  $\delta^{18}\text{O}$  is only 0.37‰. Specimens of the genus *Hibolites* show the largest spread of isotopic composition among the Valanginian genera (-1.00 to -0.01‰ for  $\delta^{18}\text{O}$  and -2.15 to +1.25‰ for  $\delta^{13}\text{C}$ , Appendix 3 & Fig. 6).

There is no statistically significant correlation between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  for Pliensbachian belemnites (Fig. 4), or the Callovian species *C. puzosiana* (Fig. 5), nor for any of the Valanginian genera (Fig. 6). When lumped together, however, the 5 Valanginian genera show a weak correlation between  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  ( $r = 0.57$ ,  $n = 55$ ,  $P < 0.001$ ) after exclusion of one outlier of *Hibolites* (Fig. 6d). The significance of such correlations in lumped populations is explored later. Values of  $\delta^{13}\text{C}$  do not show statistically significant correlation with the concentrations of Mg, Sr, or Na in any species or genus presented here (data in Appendices 1-3).

### 3.2. Elemental compositions

Different species/genera tend to have different ranges and distributions of elemental composition (Figs. 4–6; Appendices 1–3). For Valanginian belemnites presented here, specimens of the genus *Hibolites* have the highest Mg/Ca ratios (9.5 to 16 mM/M), whereas specimens of the genus *Duvalia* are the lowest in Mg/Ca, with most specimens falling in a range of 7.4 to 10.6 mM/M (Fig. 6).

### 3.3. Relationship between elemental and isotopic compositions.

In none of the analyzed belemnite species/genera, does Mg/Ca correlate well with  $\delta^{18}\text{O}$  at species/genus level, nor does it do so for the lumped belemnites from each locality (Fig. 4–6).

Only the small number of *Castellanibelus* specimens appears to show a weak negative correlation between Mg/Ca and  $\delta^{18}\text{O}$  ( $r = -0.51$ ,  $n = 8$  and  $P < 0.1$ , Fig. 7), but the correlation degrades after including data for 6 more *Castellanibelus* specimens from McArthur et al. (2007a) that were from similar stratigraphic levels in the Vocontian Basin to those used here.

### 3.4 Radial profiles of El/Ca and stable isotopes in *C. puzosiana*

Along the centre-to-edge profile,  $\delta^{18}\text{O}$  ranges from +0.01 to  $-0.91\text{‰}$  (Table 2). Excluding values for the altered apical line,  $\delta^{18}\text{O}$  shows three stages (numbered 1–3 in Fig. 8); a central stage 2 of values around 0‰ is bracketed by stages with values around  $-0.8\text{‰}$ . Values of  $\delta^{13}\text{C}$  are around 2 to 2.5‰ but show irregular and short-term excursions to lower values at 5 mm and 9.5 mm and a higher single point of +3‰ at 11 mm.

Excluding the apical line (0 to 0.6 mm on Fig. 8 as altered), the radial profile of Mg/Ca shows greater variations (3 to 18 mM/M) than does Sr/Ca (0.9 to 1.6 mM/M). Both profiles show a decline by  $\sim 40\%$  from 0.6 to 3mm and remain constant thereafter to the belemnite rim. The radial trend of Mg/Ca is quite distinct in shape from that of  $\delta^{18}\text{O}$  of the same specimen. High spikes in the Mg/Ca profile (width of 10 to 100  $\mu\text{m}$ ) mostly align with localized alteration marked by cloudy calcite. The profile for Zn/Ca matches well to the profile for Mg/Ca, though Zn/Ca shows smaller variations. Ratios of Mn/Ca are mostly low ( $< 6 \mu\text{M/M}$ ), but spike in altered regions (such as the centre, growth boundaries and the belemnite exterior).

## 4. Discussion

### 4.1. El/Ca ratios

The absence of a correlation between Mg/Ca and  $\delta^{18}\text{O}$  in our belemnite species questions the assumption that Mg/Ca in belemnite calcite reflects mainly calcification temperature



(Berlin et al., 1967; Yasamanov, 1981; Bailey et al., 2003; McArthur et al., 2007a). That assumption was, in itself, based on the view that  $\delta^{18}\text{O}$  in belemnite calcite reflects the temperature and  $\delta^{18}\text{O}$  of ambient water (Urey et al. 1951 and many since) and so good correlations between Mg/Ca and  $\delta^{18}\text{O}$  meant Mg/Ca also reflects temperature of calcification.

Factors other than temperature that may affect either El/Ca, or  $\delta^{18}\text{O}$ , or both, are El/Ca of the seawater, salinity, and vital effects (i.e. growth rate, ontogeny, and species-specific fractionation). Firstly, the El/Ca of the seawater in each time interval studied here is assumed to be invariant. The durations of these intervals can be determined with reasonable accuracy. Pliensbachian samples were collected over two ammonite subzones (Appendix 1) each around 0.3 myrs in duration (Gradstein et al., 2012) and so represent a period of around 0.6 myrs at most. Callovian belemnites are from a single condensed horizon in one subzone (Appendix 2) and may represent spawning accumulations that accumulated in perhaps as little as a few tens to hundreds of years (Doyle and Macdonald, 1993). Finally, the Valanginian belemnites were collected between the mid *Tirnovella pertransiens* Zone and the lower *Neocomites peregrinus* Zone (Appendix 3), an interval of around 2.3 myrs on the timescale of Gradstein et al. (2012), or around 3.49myrs using the cyclostratigraphic approach of Martinez et al. (2013). The marine residence times of Sr, Mg, and Ca, are 2.4 myrs, 14 myrs, and 1.3 myrs, respectively (de Villiers et al., 2005; Griffith et al., 2008; Krabbenhoft et al., 2010; Tipper et al., 2010; Wimpenny et al., 2011). Given these residence times, and assuming similar values in the past, over the time intervals we consider, only changes in Ca, and so Mg/Ca and Sr/Ca, may have occurred in the case of the Valanginian specimens (Horita et al., 2002; Dickson, 2004).

Secondly, the effects of changes in salinity on  $\delta^{18}\text{O}$  cannot be reliably estimated in deep time and are considered by some to be subordinate to the effects of changes in temperature

(Price and Mutterlose, 2004; Li et al., 2012). Salinity variation may have introduced scatter into the correlations of  $\delta^{18}\text{O}$  with Mg/Ca and Sr/Ca, but it is assumed here that salinity affected  $\delta^{18}\text{O}$  less than did temperature (Li et al., 2012). Modeling of end-member mixing of river and seawater as a function of salinity and  $\delta^{18}\text{O}$  of ambient water (Fig. 9), shows that Mg/Ca and Sr/Ca in modern seawater are insensitive to salinity in the range 35 to 28 psu. It follows that changes in salinity would not much alter marine Sr/Ca and Mg/Ca ratios except at salinities too low for belemnites to flourish (Fig. 9). Furthermore, as belemnites were probably nekto-benthic in habitat (Dutton et al., 2007) the influence of salinity on their composition was probably small.

Finally, although biological fractionation of oxygen isotopes is generally small (Rexfort and Mutterlose, 2006), it may be an important control on Mg/Ca ratio in belemnites. Within belemnites from each locality used here, species tend to have distinct, albeit overlapping, distributions of Mg/Ca and Sr/Ca, but little separation in terms of  $\delta^{18}\text{O}$ . This implies little species-specific fractionation of oxygen isotopes and may indicate overlapping or shared habitats, coupled with strong species differentiation in the concentration of Mg and Sr. Radial profiles of Na, Sr, Mg, across the limited number of belemnite specimens so far profiled differ between elements, suggesting biological fractionation during trace elements incorporation into belemnite calcite (McArthur et al., 2007b; Wierzbowski and Joachimski, 2009). Differing radial elemental profiles in different species show that the degree of trace element uptake in belemnites is species-specific. Whilst the effect of temperature on elemental concentrations may be present, species effects may be as important as temperature. The reliability of Mg/Ca in belemnite calcite as a recorder of oceanic temperature is therefore questionable. Unfortunately, because belemnites are extinct, the response of their Mg/Ca ratios to seawater temperature and the controls of their biological activities cannot be tested experimentally.

#### 4.2. Mg/Ca and $\delta^{18}\text{O}$

The lack of covariance between  $\delta^{18}\text{O}$  and Mg/Ca within a species may challenge the validity of using Mg/Ca as palaeo-temperature indicator. In previous studies, the observed correlations between El/Ca and  $\delta^{18}\text{O}$  (Fig. 1) arose in undifferentiated belemnites of Pliensbachian – Toarcian age in three localities: Yorkshire in the UK, southern Germany, and northern Spain (Fig. 1; McArthur et al., 2000; Bailey et al., 2003; Rosales et al., 2004a). On the evidence presented here, those correlations may be re-interpreted as correlations arising from species differences, rather than as real correlations between  $\delta^{18}\text{O}$  and either Mg/Ca or Sr/Ca.

If belemnite species plot in species-distinct compositional fields, correlations can be induced by virtue of a multi-modal distribution of data. The simplest illustration, that of bimodal data, is illustrated in Fig. 10 using the data of Wierzbowski and Rogov (2011) who, we emphasize, did not suggest any correlations between  $\delta^{18}\text{O}$  and either Mg/Ca or Sr/Ca in their Figs. 10 and 11; rather, they specifically stated that  $\delta^{18}\text{O}$  does not correlate with Mg/Ca or Sr/Ca. The data of those authors plot in two fields, with *Hibolithes* sp. being isotopically lower, and higher in Sr and Mg, than either *Cylindroteuthis* sp. or *Lagonibelus* sp. Were the specimens not distinguished as species, a possible line of correlation might be drawn, as in Fig. 10 here. Whilst the bimodal data distribution would give rise to doubt in this instance about the wisdom of such a correlation, the differences might be overlooked were the separation of the genera less, or were an intermediate population of belemnites present that overlapped each of the two shown in Fig. 10. We suggest that this may be a reason for previously observed covariance of El/Ca with  $\delta^{18}\text{O}$  in, for example, Bailey et al. (2003) and McArthur et al. (2007a), whose interpretations based on Mg/Ca may need revision in view of the new data presented here.

Notwithstanding that, the line of correlation in Fig. 10 shows increasing El/Ca with increasingly negative  $\delta^{18}\text{O}$ , which is what would be expected from operation of a temperature effect on composition. The possibility remains, therefore, that large differences in habitat temperature between belemnite species and genera may be reflected in El/Ca, whilst biofractionation effects work to obscure such a signal within each species and genera, not least because the habitat range of a species may be small e.g. the Toarcian species *Acrocoelites (Odontobelus) vulgaris* reported by McArthur et al. (2007b).

#### 4.3. Intra-rostral profiles of belemnite *C. puzosiana*

##### 4.3.1 $\delta^{18}\text{O}$ and El/Ca profiles

The  $\delta^{18}\text{O}$  variation within the specimen of *C. puzosiana* analyzed here is 0.92‰, which is less than the 1.6‰ reported for late Cretaceous belemnites *Dimitobelus seymouriensis* (Dutton et al., 2007), or the range of 2‰ reported by Wierzbowski and Joachimski (2009) for Middle Jurassic (Bathonian) *Hibolithes*. If attributed solely to a change in temperature, the 0.92‰ shift in  $\delta^{18}\text{O}$  represents  $\sim 4^\circ\text{C}$ , using the palaeo-temperature equation of Anderson & Arthur (1983). If attributed to a change of salinity, the shift represents a change of only 2 psu, assuming a  $\Delta\delta^{18}\text{O}/\Delta\text{Salinity}$  of 0.5‰ per 1 psu, based on the modern subtropical Atlantic Ocean (Broecker, 1989).

Whether reflecting changes in salinity, or temperature, or both, the three-stage radial profile of  $\delta^{18}\text{O}$  in the *C. puzosiana* studied here is interpreted to represent three stages of life (Fig. 8). The  $\delta^{18}\text{O}$  suggests that the specimen spent the time represented by the first and third stages in water that was either warmer, or less saline, or both, than the water signature captured in stage 2. Stages 1 and 3 are thought to represent periods of shallower water than stage 2, which is interpreted to represent deeper, more offshore, environment. Such an interpretation matches a lifestyle in which inshore hatching and growth is followed by

migration offshore and an eventual return to inshore shallow waters. Assuming linear growth, each stage represents around one third of a belemnite lifetime. Migration, if not on this timescale, has been noted as a lifestyle in some cuttlefishes (Rexfort and Mutterlose, 2006), a presumed modern analogue of belemnites, and has also been invoked to by Lukeneder et al. (2010) explain the stable isotopic variations in Mesozoic cephalopods (e.g. *Cadoceras*).

The intra-rostral Mg/Ca profile shows little comparability with the profile of  $\delta^{18}\text{O}$ . In stage 1, where  $\delta^{18}\text{O}$  is around  $-0.8\%$ , Mg/Ca decreases by  $\sim 40\%$ . In stage 2,  $\delta^{18}\text{O}$  increases to around  $0\%$  but Mg/Ca remains low. In stage 3,  $\delta^{18}\text{O}$  decreases again, to around  $-0.9\%$  without noticeable change in Mg/Ca. If the Mg/Ca temperature dependence of belemnites is the same as for foraminifera ( $\sim 10\%$  per  $1^\circ\text{C}$ ), as assumed by Bailey et al. (2003), a temperature change of  $\sim 4^\circ\text{C}$  should be visible in the Mg profile. Either the change in  $\delta^{18}\text{O}$  across *C. puzosiana* represents a change in salinity, or Mg/Ca in this specimen does not reflect temperature. The alternative that Mg/Ca in *C. puzosiana* does not reflect calcification temperature is supported by the fact that Mg/Ca ratios from bulk analysis of this species do not correlate with bulk  $\delta^{18}\text{O}$  (Fig. 5). This alternative also borrows support from the proposition that a change of salinity of 2 psu would likely be associated with a change in temperature, especially if surface/deep migration was the driver of change.

#### 4.3.2 $\delta^{13}\text{C}$ profile

The  $\delta^{13}\text{C}$  profile reflects sharper fluctuations than that of  $\delta^{18}\text{O}$ , and does not correlate with  $\delta^{18}\text{O}$  profile (Fig. 8). Carbon isotopes in marine biogenic carbonates are often more difficult to interpret than oxygen isotopes. This is because firstly carbon can have multiple sources during carbon fixation. The main source of carbon for the marine calcareous skeleton is dissolved inorganic carbon (DIC), but metabolic carbon, food and fresh water can also contribute carbon (McConnaughey et al., 1997; McConnaughey and Gillikin, 2008). The

second reason is the occurrence of disequilibrium, or biological fractionation, of carbon isotopes in biogenic carbonates (McConnaughey, 1989).

For the Callovian belemnite specimen *C. puzosiana*, values of  $\delta^{13}\text{C}$  are mostly between +2.0 and +2.5 ‰. Excursions at 5.0, 9.5, and 11.0 mm depart the main trend but show no relation to alteration as evidenced by spikes in Mg/Ca, Mn/Ca, and Zn/Ca (Fig. 8). Similar variations of  $\delta^{13}\text{C}$  have been reported in the cuttlebone of a wild cuttlefish *Sepia* by Rexfort and Mutterlose, (2006), and are interpreted as the metabolically controlled biofractionation of carbon isotopes (see also (Rexfort and Mutterlose, 2006; Wierzbowski and Joachimski, 2009). Vertical migration of belemnites in the water column would change their  $\delta^{13}\text{C}$  values because increasing mineralization of organic carbon with depth drives  $\delta^{13}\text{C}$  to lower values. The trend of the  $\delta^{13}\text{C}$  profile of *C. puzosiana*, however, doesn't fit this explanation if we have correctly interpreted the temperature/depth changes implied by the  $\delta^{18}\text{O}$  profile.

#### 4.4. Comparison to modern marine calcareous organisms: e.g. foraminifera

The biological control on the uptake of trace elements from the ambient seawater during biomineralization has been documented in modern marine biogenic calcite, such as foraminifera, corals, molluscs and bivalves (Purton et al., 1999; Erez, 2003; Mitsuguchi et al., 2003; Weiner and Dove, 2003; Sinclair et al., 2005; Elliot et al., 2009). Here, foraminifera are used as an example because the Mg/Ca ratio of their tests is a proven palaeo-thermometer and the incorporation of trace elements including Mg in foraminifera has been intensively studied (Lea et al., 1999; Eggins et al., 2003; Erez, 2003; Eggins et al., 2004). In foraminiferal species *Orbulina universa*, detailed profiles of Mg/Ca indicate that temperature ranges during growth deduced from Mg/Ca exceed the maximum temperature range within the organism's habitat (Eggins et al., 2004). Factors such as biological activities may therefore in part control the Mg/Ca ratios in *O. universa* (Spero, 1988; Rink et al., 1998; Wolf-Gladrow et al., 1999;

Eggins et al., 2004). A number of foraminiferal species (e.g. *Globigerinoides sacculifer*, *Globigerinoides conglobatus*, *Orbulina universa*, *Neogloboquadrina pachyderma*, *Neogloboquadrina dutertrei* and *Globorotalia* spp.) deposit gametogenic calcite on the test's exterior at the end of their life-cycle (Bé et al., 1983; Hamilton et al., 2008), and this gametogenic calcite has a different Mg/Ca to the inner ontogenetic calcite of the test (Hathorne et al., 2003; Eggins et al., 2004; Sadekov et al., 2005). Ontogenetic calcification occurs throughout the lifespan of a species, whereas gametogenic calcification occurs over a short period of time (Bé et al., 1983; Hamilton et al., 2008). The difference in Mg/Ca between the two calcite phases may reflect calcification at different water temperature and chemistry and different calcification rates influenced by the differing biogenic precipitation regimes (Hathorne et al., 2003), or fundamentally different styles of calcification driven by cellular processes (Erez, 2003).

In comparison to foraminifera, Mg/Ca composition in belemnites is also likely to be affected by factors other than temperature and Mg/Ca in ambient seawater. The Mg/Ca ratios in belemnites are certainly species-dependent and the evidence presented here and elsewhere suggests that temperature may not be a strong control on El/Ca values.

#### 4.5. Does Mg/Ca work as a palaeo-proxy in belemnites?

The use of belemnite  $\delta^{18}\text{O}$  as a proxy for palaeo-temperature has always been compromised by uncertainty over what proportion of a change in  $\delta^{18}\text{O}$  recorded in belemnite calcite relates to change in temperature as opposed to change in salinity (e.g. Spaeth et al., 1971; Stevens and Clayton, 1971; Podlaha et al., 1998; Rosales et al., 2004a). Recently, isotopic temperatures for belemnites have been reported to be several degrees cooler than those derived from  $\text{TEX}_{86}$  (Mutterlose et al., 2010). The difference is consistent with temperature being the major control on the belemnite calcite, with  $\text{TEX}_{86}$  temperature

reflecting the surface mixed layer and belemnites recording deeper, cooler, temperatures in coastal waters (Wierzbowski, 2002; Mutterlose et al., 2010). This interpretation is also consistent with the finding of Dutton et al. (2007) that belemnite  $\delta^{18}\text{O}$  matched better the values of  $\delta^{18}\text{O}$  in benthic foraminifera compared to  $\delta^{18}\text{O}$  in pelagic foraminifera.

These studies highlight the importance of the fact that, in the belemnite species and genera presented here, no correlation is seen between Mg/Ca and  $\delta^{18}\text{O}$ . This present work suggests that unless the effects of temperature and species-specific fractionation on belemnite El/Ca ratios can be separately quantified, El/Ca ratios of belemnites may be of restricted use as palaeo-temperature indicators and need further evaluation.

## 5. Conclusions

- 1) In the 10 species/genera of Jurassic–Cretaceous belemnites studied here, Mg/Ca ratios and  $\delta^{18}\text{O}$  in bulk analysis do not correlate, either within a single belemnite species or genus, nor within a belemnite population of mixed species or genera. It is concluded that Mg/Ca ratios do not reflect calcification temperature in these belemnites.
- 2) A radial profile of  $\delta^{18}\text{O}$  across a specimen of *Cylindroteuthis puzosiana* suggests an early and late life-stages spent in shallow inshore, waters, with an intervening period spent in deeper water that was either more saline or as much as 4°C cooler.
- 3) The profiles of Mg/Ca and  $\delta^{18}\text{O}$  across the sections of the same *C. puzosiana* specimen show little comparability between the two, suggesting that intra-rostral Mg/Ca profile is unlikely to be reflecting temperature for this species.

## Acknowledgements

We thank Nathalie Grassinau for assistance with ICP-AES analysis, Dorinda Ostermann (UCL) and Hilary Sloane (NIGL) for the help with the stable isotope analyses. We are also



grateful to Finn Surlyk and two anonymous reviewers for their detailed and valuable comments, which greatly improved the final manuscript.

ACCEPTED MANUSCRIPT

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## List of Figures

**Fig. 1.** Cross-plots of El/Ca and  $\delta^{18}\text{O}$  for Pliensbachian–Toarcian belemnites from Yorkshire of the UK (data of McArthur et al. 2000), southern Germany (data from Bailey et al. 2003) and northern Spain (data from Rosales et al. 2004a). Correlation lines derived by reduced-major-axis regression.

**Fig. 2.** Preparation scheme for belemnite analysis. Front slab cut at base of alveolus. The best-preserved slab was used for chemical analysis. Figure after Wierzbowski and Joachimski (2009).

**Fig. 3.** a) Specimen of *Cylindroteuthis puzosiana* profiled for elemental and isotopic composition, showing b) the laser-ablation track across the radius of the front slab and c) the grooves cut for stable isotope sampling along the sectioned back slab.

**Fig. 4.** Cross-plots of elemental and isotopic compositions of Pliensbachian belemnite species *Passaloteuthis cuspidatus*, *Nannobelus acutus*, *Bairstowius junceus*, *Passaloteuthis elongata* and *Hastites spadixari* from Dorset, UK. The error bars are smaller than the symbols, so are not plotted here or in subsequent figures.

**Fig. 5.** Cross-plots of elemental and isotopic compositions of Callovian belemnite species *Cylindroteuthis puzosiana*, Bed 13, Oxford Clay, Cambridgeshire, UK.

**Fig. 6.** Cross-plots of elemental and isotopic data of Valanginian belemnites from Vergol, SE France. Reduced-major-axis regressions in d are  $\delta^{13}\text{C} = 4.91\delta^{18}\text{O} + 1.20$  for all genera (black solid line,  $P < 0.001$ ), and  $\delta^{13}\text{C} = 5.30\delta^{18}\text{O} + 1.62$  (red dotted line) for genus *Hibolithes* alone but excluding 1 outlier marked as ‘?’.



**Fig. 7.** Reduced-major-axis regressions for  $\delta^{18}\text{O}$  and Mg/Ca in the genus *Castellanibelus* from this study only (red line,  $n = 8$ , regression equation  $\text{Mg/Ca} = -4.73\delta^{18}\text{O} + 7.52$ ) and from both this study and those given by McArthur et al. (2007a), black solid line ( $n = 14$ , regression equation  $\text{Mg/Ca} = -5.85\delta^{18}\text{O} + 7.32$ ).

**Fig. 8.** The radial profiles of stable isotopes and El/Ca ratios from sections of *Cylindroteuthis puzosiana* specimen 13-49. The trend of Mg/Ca is fitted by eye to exclude high Mg/Ca, Mn/Ca, and Zn/Ca, which indicate localized alteration. For elemental analysis, individual analyses are too numerous to be resolved individually. The black vertical lines are drawn to divide the  $\delta^{18}\text{O}$  profile into three stages with internally consistent, but different, values. Elemental data from a radial profile of a back slab (Fig 2) of the specimen, stable isotope data from the front slab after sectioning (Fig. 2). The profiles were matched using concentric alteration bands, usually termed ‘growth rings’.

**Fig. 9.** Values of Mg/Ca and Sr/Ca modelled as a function of salinity and  $\delta^{18}\text{O}$  of ambient water (after Li et al., 2012). Marine end-members at salinity = 35 psu are  $\delta^{18}\text{O} = 0\text{‰}$ , Ca = 10.3 mmol/kg, Mg = 53.1 mmol/kg, Sr = 0.09 mmol/kg. Riverine end-members are  $\delta^{18}\text{O} = -6\text{‰}$  (after Saalen et al. 1996), Ca = 0.38 mmol/kg, Mg = 0.17 mmol/kg, Sr = 0.0006 mmol/kg. Element concentrations from Table 7-1 of Murray (2004).

**Fig. 10.** Cross-plots of elemental and isotopic compositions of three Callovian – Oxfordian belemnite species with two distinct compositional ranges. Reduced-major-axis regressions show induced (essentially two-point) correlations between  $\delta^{18}\text{O}$  and Mg/Ca (and Sr/Ca). The correlations are not present for any species, but are present in the lumped populations for which data are not distributed normally. Data are from Wierzbowski and Rogov, (2011), for belemnites from Dubki section, near Saratov, Russian Platform: it is emphasized that these authors did not claim that Mg/Ca or Sr/Ca was correlated to  $\delta^{18}\text{O}$ .

**List of Tables**

**Table 1** Belemnites analysed in this study. Numbers of specimens given in brackets followed by the number of species or, for Valanginian specimens, the number of genera (\*). *P.* is *Prodactylioceras*; *H.* is *Harpoceras*; *N.* is *Neocomites*; *T.* is *Tirnovella*; *B.* is *Busnardoites*; *O.* is *Olcostephanus*.

**Table 2.** Stable isotopic data for line of profile shown in Fig. 8, obtained from a longitudinal section of *Cylindroteuthis puzosiana* specimen 13-49 (See Fig. 3c).

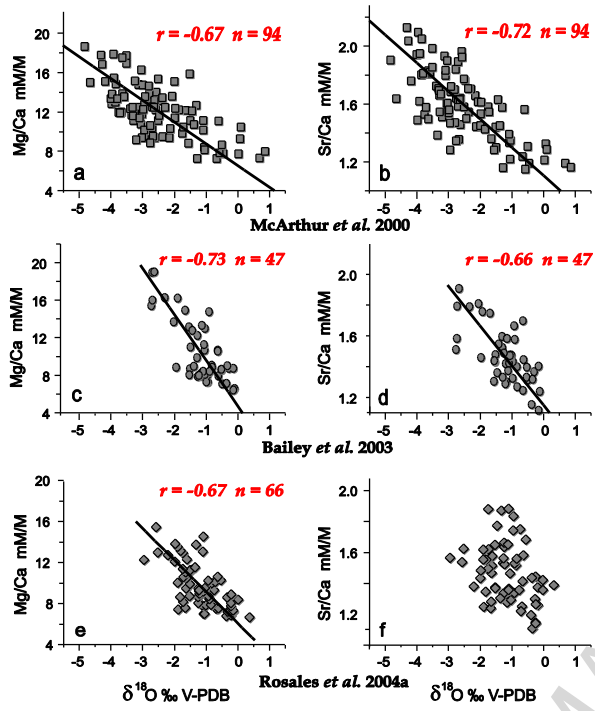
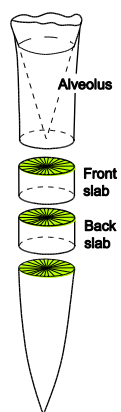
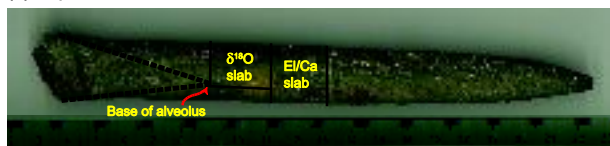


Fig. 1.



**Fig. 2.**

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(a) *C. puzosiana* 13-49

(b) Cross-section of EI/Ca slab

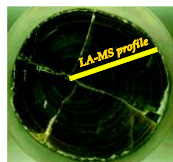
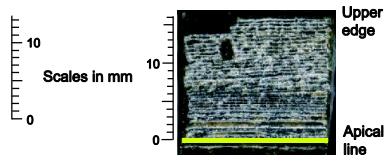
(c) Longitudinal section of  $\delta^{18}\text{O}$  slab

Fig. 3.

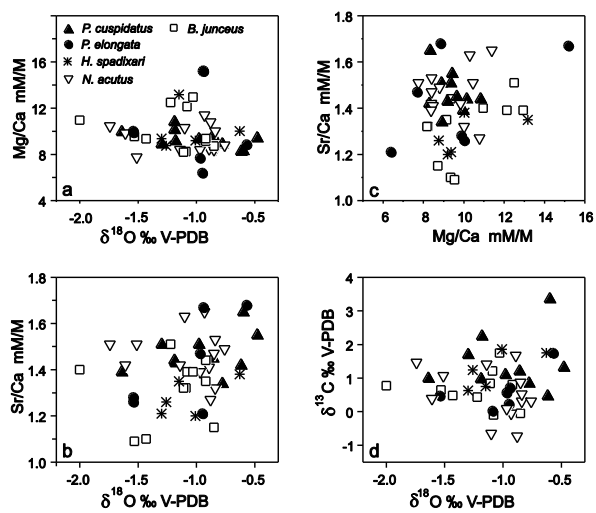


Fig. 4.

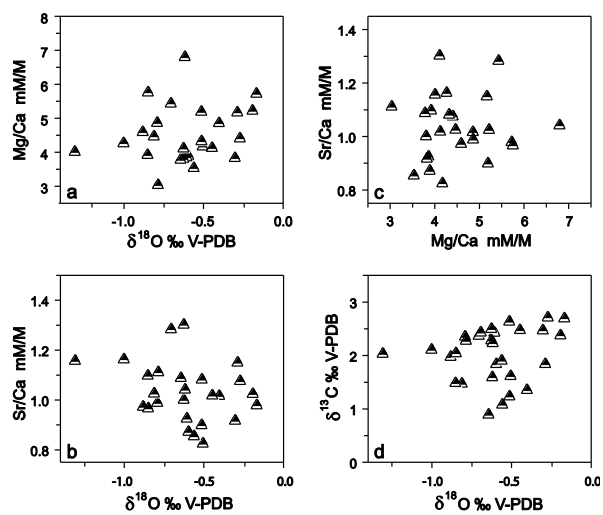


Fig. 5.

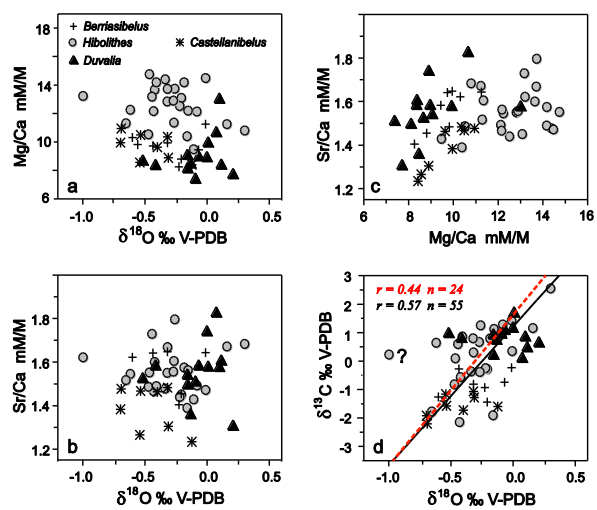


Fig. 6.



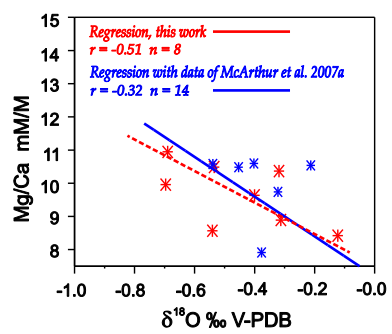


Fig. 7.

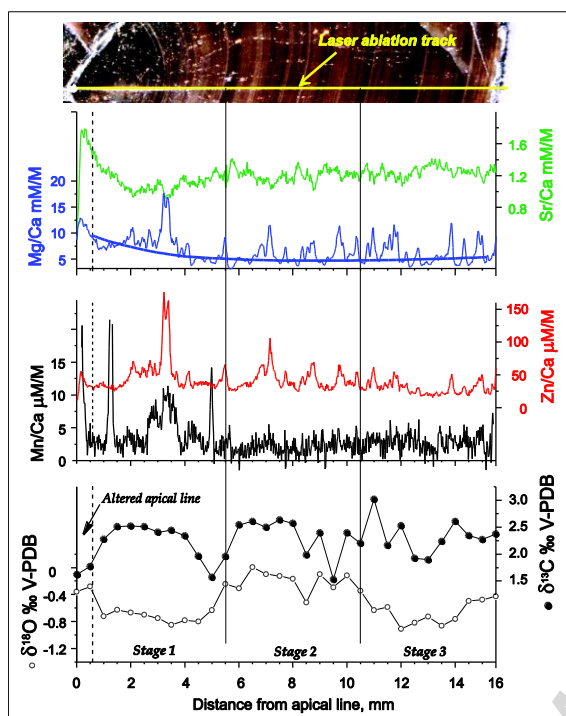


Fig. 8.

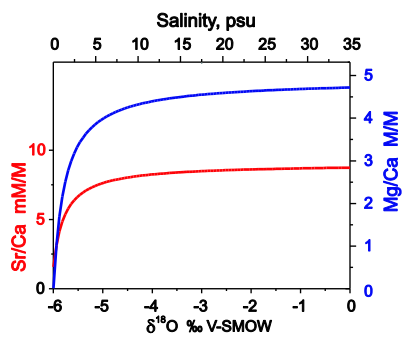


Fig. 9.

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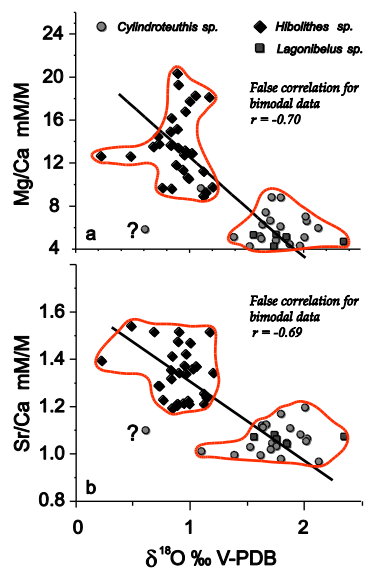


Fig. 10.

**Table 1** Belemnites analysed in this study. The numbers in brackets give numbers of specimens, followed by the number of species or genera (\*). P – *Prodactyloceras*; H - *Harpoceras*; N – *Neocomites*; T- *Tirnovella*; B - *Busnardoites*. Note: *T. pertransiens* Zone has no Subzone.

| Stage                          | Zone   | Subzone  | Species/Genera<br>*  | Formation                                      | Bed<br>No.              | Location                                |
|--------------------------------|--|--|--|--|-------------------------|---|
| <i>Pliensbachian</i><br>(57/5) | <i>P. davoei</i><br>- <i>P. ibex</i>             | <i>masseanum</i><br>-<br><i>maculatum</i>                  | <i>Passaloteuthis cuspidatus</i><br><i>Passaloteuthis elongate</i><br><i>Hastites spadixari</i><br><i>Bairdowius junceus</i><br><i>Nannobelus acutus</i> | Belemnite<br>Marls<br>- Green<br>ammonite beds | 118c,d,<br>120d-e,<br>7 | Charmouth to<br>Seatown,<br>Dorset, UK. |
| <i>Callovian</i><br>(29/1)     | <i>jason</i>                                     | <i>jason</i>   | <i>Cylindroteuthis puzosiana</i>   | Oxford Clay<br>Formation                       | 13                      | Kings Dyke,<br>Whittlesey,<br>UK.       |
| <i>Valanginian</i><br>(57/4*)  | <i>T. pertransiens</i><br>- <i>N. peregrinus</i> | <i>T. pertransiens</i><br>(Zone)<br>- <i>N. peregrinus</i> | <i>Berriasbelus</i> sp.<br><i>Castellanibelus</i> sp.<br><i>Hibolithes</i> sp.<br><i>Duvalia</i> sp.   | Inter-bedded<br>marls and<br>limestones        | 34-<br>124b             | Vergol, SE<br>France.                   |

**Table 2** Stable isotopic data for the line of profile shown in Fig. 8, obtained from a longitudinal section of *Cylindroteuthis puzosiana* specimen 13-49 (See Fig. 3c).

| Sample    | Distance (mm) | $\delta^{13}\text{C}$ | $\delta^{18}\text{O}$ |
|-----------|---------------|-----------------------|-----------------------|
| 13-49 L1  | 0.0           | 1.62                  | -0.36                 |
| 13-49 L2  | 0.5           | 1.77                  | -0.28                 |
| 13-49 L3  | 1.0           | 2.27                  | -0.72                 |
| 13-49 L4  | 1.5           | 2.51                  | -0.63                 |
| 13-49 L5  | 2.0           | 2.52                  | -0.67                 |
| 13-49 L6  | 2.5           | 2.51                  | -0.70                 |
| 13-49 L7  | 3.0           | 2.41                  | -0.75                 |
| 13-49 L8  | 3.5           | 2.44                  | -0.85                 |
| 13-49 L9  | 4.0           | 2.34                  | -0.78                 |
| 13-49 L10 | 4.5           | 1.97                  | -0.80                 |
| 13-49 L11 | 5.0           | 1.57                  | -0.63                 |
| 13-49 L12 | 5.5           | 0.00                  | 0.00                  |
| 13-49 L13 | 6.0           | 2.54                  | -0.31                 |
| 13-49 L14 | 6.5           | 2.61                  | 0.01                  |
| 13-49 L15 | 7.0           | 2.50                  | -0.10                 |
| 13-49 L16 | 7.5           | 2.64                  | -0.13                 |
| 13-49 L17 | 8.0           | 2.57                  | -0.17                 |
| 13-49 L18 | 8.5           | 1.99                  | -0.52                 |
| 13-49 L19 | 9.0           | 2.40                  | -0.10                 |
| 13-49 L20 | 9.5           | 1.53                  | -0.29                 |
| 13-49 L21 | 10.0          | 2.40                  | -0.12                 |
| 13-49 L22 | 10.5          | 2.20                  | -0.34                 |
| 13-49 L23 | 11.0          | 3.01                  | -0.63                 |
| 13-49 L24 | 11.5          | 2.16                  | -0.58                 |
| 13-49 L25 | 12.0          | 2.53                  | -0.91                 |
| 13-49 L26 | 12.5          | 1.92                  | -0.82                 |

|           |      |      |       |
|-----------|------|------|-------|
| 13-49 L27 | 13.0 | 1.90 | -0.72 |
| 13-49 L28 | 13.5 | 2.24 | -0.86 |
| 13-49 L29 | 14.0 | 2.61 | -0.76 |
| 13-49 L30 | 14.5 | 2.34 | -0.50 |
| 13-49 L31 | 15.0 | 2.27 | -0.48 |
| 13-49 L32 | 15.5 | 2.37 | -0.42 |

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**Highlights**

- In belemnite calcite, Mg/Ca does not correlate with  $\delta^{18}\text{O}$ .
- The Mg/Ca of belemnite calcite is not likely to be a valid palaeo-temperature proxy.
- Radial profiles of Mg/Ca and  $\delta^{18}\text{O}$  across a belemnite section show little comparability.
- Belemnite intro-rostral Mg/Ca is unlikely to be reflecting temperature.
- The radial profile of  $\delta^{18}\text{O}$  across the belemnite specimen suggests migrating lifestyle.

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