TITLE: Mg/Ca and Sr/Ca as Palaeothermometers: New data from Middle Jurassic Belemnites from Germany and Portugal.

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In belemnite macrofossil calcite, Mg/Ca and Sr/Ca ratios have long been proposed as a palaeotemperature proxy. However, its use has proved controversial with different studies yielding contradictory results. Oxygen isotopes (δ^{18}O) values from two sites from the Middle Jurassic of Europe show no correlation with either Mg/Ca or Sr/Ca ratios. Thus, Mg/Ca and Sr/Ca ratios are not useful palaeothermometers for Middle Jurassic belemnites from Cabo Mondego (Bajocian-Bathonian, Portugal) or the Roschbachtal section (Bathonian-Callovian, southern Germany).

Keywords: Belemnite; Cabo Mondego; δ^{18}O; Jurassic; Mg/Ca; Sr/Ca; Palaeo-proxies; Palaeotemperature; Roschbachtal

Introduction

Seawater chemistry has varied with changes in the global climate throughout geological time, making past seawater cation ratios such as Mg/Ca and Sr/Ca potential proxies for various palaeoceanographic parameters (Cohen et al., 2002). Some authors have considered both Mg/Ca and Sr/Ca ratios (e.g., Rosales et al., 2004; McArthur et al., 2007a; Wierzbowski and Rogov, 2010 and others) as potential palaeothermometers.

If this were to be the case for Middle Jurassic belemnites collected from Cabo Mondego and the Roschbachtal section, one would expect a correlation between elemental proxies with δ^{18}O values in the 1960s, some Russian authors (e.g., Berlin et al., 1967) proposed that the Mg/Ca ratios in belemnite calcite may be used as a palaeothermometer, but published data comparing Mg/Ca to δ^{18}O has thus far yielded mixed results. The use of Mg/Ca as a palaeothermometer is based on two assumptions: 1) that

$\delta^{18}O$ of belemnite calcite reflects calcification temperature and the isotopic composition of the ambient seawater (Urey et al.,1951; Podlaha et al., 1998); and 2) the Mg/Ca, and possibly Sr/Ca, of belemnite calcite thought by some researchers to be dependent on temperature (Berlin et al., 1967; McArthur et al., 2000, 2007a,b; Bailey et al., 2003; Rosales et al., 2004). This second point has some credibility as some studies are shown in several studies (see McArthur et al., 2000; Bailey et al., 2003; Rosales et al., 2004) show an inverse covariance between δ^{18}, and Sr/Ca and Mg/Ca in belemnite calcite. These studies may suggest that belemnite El/Ca ratios are a feasible palaeotemperature proxy, at least for the Early Jurassic. However, the influences of factors other than temperature on both El/Ca ratios and $\delta^{18}O$ must also be considered.

Mg/Ca and Sr/Ca are used as palaeotemperature, a proxy in other $CaCO_3$ fossil groups such as foraminifera. Some authors prefer to use Mg/Ca and Sr/Ca ratios over oxygen-isotopes as the elemental data are not as sensitive to fluctuations in salinity. Some researchers observed correlations between Mg/Ca and $\delta^{18}O$ in bulk belemnite samples and thereby proposed a temperature control on Mg/Ca (e.g., Rosales et al., 2004; McArthur et al., 2007a; Armendáriz et al.,2012). However, some studies (e.g. Wierzbowski and Joachimski, 2009, Li et al.,2013, Sørensen et al., 2015, Ullmann et al., 2015) found no such correlation between Mg/Ca and $\delta^{18}O$ in ontogenetic records from individual rostra. By analogy with other calcifying organisms, such as foraminifera, the response of these presumed palaeo-proxies in belemnites may have been species-dependent, so interpreting undifferentiated belemnites, at genus or family level, as is the case here, would inevitably lead to misinterpretation of the results. Because belemnites are extinct, their response to Mg/Ca to variations in water temperature cannot be tested experimentally. Furthermore, the skeletons of modern cephalopods are predominantly aragonitic (Wilbur, 1972) rather than calcite as in belemnites (Ullmann et al., 2015), which uptake trace and minor elements differently, and the aragonitic phragmocone of belemnites is seldom preserved (Hoffmann and Stevens, 2020).

No correlation between oxygen-isotopes and Mg/Ca was observed in Jurassic–Cretaceous belemnites by Wierzbowski and Rogov (2010), 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, often interpreted as diagenetic signals, and inter-species/genus differences (e.g., McArthur et al., 2007b, Wierzbowski and Joachimski, 2009, Wierzbowski and Rogov, 2010, Li et al., 2012). On the other hand, fossil calcite is a promising substrate for reconstructing past seawater Sr/Ca ratios, as Sr/Ca variability within a given shell is comparatively low, e.g., ~20% in modern oysters (Almeida et al., 1998), and small sample sizes (< 1 mg) are sufficient for analysis allowing for the generation of large data sets and precise average values with very little material (Ullmann et al., 2013b). A downward trend in fossil Sr/Ca ratios is observed through the Early and Middle Jurassic. The Sr flux from increased Mid Ocean Ridge activity in the Early Jurassic is thought to have outbalanced the input of riverine Sr, leading to the gradual lowing of seawater 87Sr/86Sr parallel and a substantial decrease in seawater Sr/Ca ratios (Ullmann et al., 2013a).

The most critical factors influencing Sr/Ca ratios in shell material are presented by Ullmann et al. (2013a): (I) the composition of the liquid from which they are precipitated, (II) the calcium carbonate polymorph, (III) the species-specific fractionation of the Sr/Ca ratio, (IV) metabolic controls on this fractionation factor and (V) water temperature.

Negative correlations between $\delta^{18}O$ and Sr/Ca ratios (e.g., McArthur et al.,2000; Bailey et al., 2003; Rosales et al., 2004) imply that incorporating Sr/Ca into shell carbonate may have been, at least partially, temperature-dependent. These empirical relationships contrast with the positive relationship between $\delta^{18}O$ and Sr/Ca predicted by theoretical and experimental work by Tang et al. (2008) and DePaolo (2011), but temperature-induced changes in growth rate may be a plausible explanation for negative correlations (e.g., Stoll and Schrag, 2001; Tang et al., 2008; Ullmann et al., 2013a).

Sr/Ca ratios are more challenging to interpret than Mg/Ca ratios, reflecting a combination of calcification temperature, calcification rate, carbonate chemistry, seawater Sr/Ca, and salinity, and may also be an indicator for diagenesis (Baker et al., 1982). The Sr concentration in biogenic low-magnesium calcite, such as belemnite rostra, is often higher than Sr levels in thermodynamic equilibrium from in abiogenic calcite, resulting in Sr-depletion in calcite fossils during diagenesis (Ullmann and Korte, 2015; cf. Carpenter and Lohmann, 1992; Tang et al., 2008; DePaolo, 2011) One can therefore use Sr/Ca as a diagenetic proxy in calcite shells (e.g., Bruckschen and Veizer, 1997; Korte et al., 2003; Ullmann and Korte, 2015).

Using the lower suggested limits of Sr/Ca as an alternation marker is problematic for a few reasons. Perhaps the most important concern is the primary Sr/Ca ratios present in the animals when they are still alive. This is because the rate of Sr incorporation in different taxonomic groups is related to vital effects with animals with high metabolic rates incorporating more Sr (Purton et al., 1999). These probably led belemnites to have a much higher rate of Sr incorporation than osteroids (Veizer, 1974; Korte and Hesselbo, 2011) and brachiopods (Voigt 88et al., 2003) due to belemnites having faster metabolisms and a more active lifestyle (Korte and Hesselbo, 2011).

Another issue that arises when using Sr is secular changes in seawater Sr/Ca ratios through the Phanerozoic, possibly spanning a large range between 2 and 14 mmol/mol (Ullmann and Korte, 2015). Generally, Sr/Ca ratios in low-Mg calcite are expected to be higher during predicted Calcite Sea intervals and lower in Aragonite Sea intervals because Sr is more readily incorporated in aragonite than in calcite (Ries, 2010; Ullmann et al., 2013a, b; Ullmann and Korte, 2015).

Materials

Two locations were studied in this study: Cabo Mondego and the Roschbachtal section. Ninety belemnite specimens of an undetermined species were collected from the alternating limestones and marls at Cabo Mondego (central Portugal), which forms the Cabo Mondego Formation of the upper Bajocian-Bathonian stages. The studied locality is well-dated based on ammonite biostratigraphy. The studied section covers the entire stratigraphic interval between the upper Bajocian (*garantiana Zone*) and the lower Bathonian (*zigzag Zone*; for detailed stratigraphy, see Henriques et al., 1994; Fernández-López et al., 2007).

Thirty belemnite specimens of an undetermined species were collected from the Roschbachtal section (Baden-Wurttemberg, Germany), is part of the *discus Zone* (upper Bathonian). The stratigraphy of the section is proposed by Mönnig and Dietl (2021), and a detailed belemnite geochemistry study is currently in preparation by Christoph Korte (University of Copenhagen).

Methods

To avoid altered material, sample extraction focussed on the intermediate growth increments (e.g., Ullmann and Korte, 2015). Ca. 1-2 milligrams of calcite powder were extracted using a hand-held automatic drill with a 0.5 mm steel drill. The calcite samples were subsequently split into aliquots for isotope and element analysis.

The element/Ca ratios were quantified using an Agilent 5110 VDV Inductively Coupled Optical Emission Spectrometer (ICP-OES) with Seaspray U-series glass nebuliser and double pass cyclonic spray chamber in the Wet Chemistry Laboratory in the Camborne School of Mines. Oxygen isotope ratios were measured using a Sercon 20-22Gas Source Isotope Ratio Mass Spectrometer (GS-IRMS) in continuous flow mode at the Environment and Sustainability Institute (University of Exeter). The analytical procedures used in this study were the same as those outlined in Ullmann et al. (2020), with some modifications.

An upper limit of 0.2 Mn/Ca was used as a diagenetic proxy. Mn/Ca is the most widely employed alteration marker because Mn levels in primary shell material are usually very low, while diagenesis leads to Mn enrichment (Veizer, 1974, Brand and Veizer, 1980, 198, Ullmann et al., 2014). It is imperative that highly altered samples, those with elevated Mn/Ca ratios, should be excluded. These samples exhibit lower δ^{18}O values of diagenetic origin and thus would not be representative of original calcite.

Results and Discussion

The belemnites from Cabo Mondego and the Roschbachtal section presented in this study do not show any correlation between δ^{18}O values with Mg/Ca and Sr/Ca ratios (Figure 1). Data tables for this study can be viewed in Wilkin (2021). The absence of a correlation between Mg/Ca and δ^{18} O in belemnite samples from both Cabo Mondego and the Roschbachtal section questions the assumption that Mg/Ca in belemnite calcite reflects mainly calcification temperature (e.g., Berlin et al., 1967; Bailey et al., 2003; McArthur et al., 2007a) and suggests that Mg/Ca is an unreliable palaeotemperature indicator for upper Bajocian - lower Callovian belemnites.

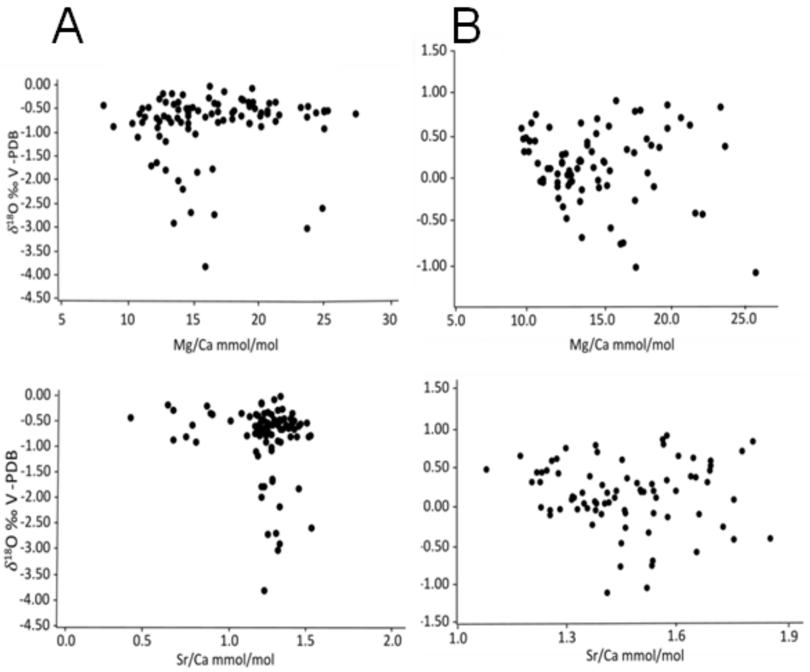

Figure 1: Cross plots of Sr/Ca and Mg/Ca versus $\delta^{18}O$ values from Cabo Mondego (A) and the Roschbachtal section (B).

The absence of the correlation of El/Ca ratios with $\delta^{18}O$ values were also found by Wierzbowski and Rogov (2010) in each of the three Callovian-Oxfordian belemnite genera from the Russian Platform. However, when the belemnite data are combined, a negative correlation can be inferred even though no such correlation is present within any of the genera. This suggests that correlations in Mg/Ca and Sr/Ca ratios with $\delta^{18}O$ values in undifferentiated belemnites represent false correlations, a view also supported by Li (2011, p.182):

> *"...species difference in the composition may be the reason for the observed correlation between El/Ca with $\delta^{18}O$, and that El/Ca ratios in belemnites are influenced by the bio-fractionation effects besides temperature and show no correlation with $\delta^{18}O$ at species level."*

The challenge in applying belemnite elemental ratios (e.g., Mg/Ca and Sr/Ca) as an independent palaeotemperature proxy is the poorly quantified temperature dependence and species-specific fractionation of these elements during belemnite calcification which is xacerbated by the lack of living descendants. Unless the effects of temperature and species-specific fractionation on belemnite El/Ca ratios can be separately quantified, El/Ca ratios of belemnites are of little use as palaeotemperature proxies.

Conclusions

(1) Previous studies of belemnite Mg/Ca and Sr/Ca as a potential palaeotemperature proxy have yielded mixed results.

(2) Mg/Ca and Sr/Ca ratios from unaltered belemnite macrofossil show no correlation with $\delta^{18}O$ from either of the studied localities presented in this study.

(3) Mg/Ca and Sr/Ca ratios are not useful palaeotemperature proxies for undetermined Middle Jurassic belemnites from the Middle Jurassic.

(4) If the belemnites in this study were from determined species, it may possible that Mg/Ca or Sr/Ca could show a correlation with $\delta^{18}O$ values within certain taxa.

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