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The effect of precipitation rate on Mg/Ca and Sr/Ca ratios in biogenic calcite as observed in a belemnite rostrum

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Abstract. Isotopic ratios and concentrations of the alkaline earth metals Mg and Sr in biogenic calcite are of great importance as proxies for environmental parameters. In particular, the Mg/Ca ratio as a temperature proxy has had considerable success. It is often hard to constrain, however, which parameter ultimately controls the concentration of these elements in calcite.

Here, multiple Mg/Ca and Sr/Ca transects through a belemnite rostrum of *Passaloteuthis bisulcata* (Blainville, 1827) are used to isolate the effect of calcite precipitation rate on incorporation of Mg and Sr into the calcite. With increasing calcite precipitation rate Mg/Ca ratios decrease and Sr/Ca ratios in the rostrum increase. In the studied specimen this effect is found to be linear for both element ratios over a precipitation rate increase of ca. 150 %. Mg/Ca ratios and Sr/Ca ratios show a linear covariation with increasing relative precipitation rate, where a 100 % increase in precipitation rate leads to a (8.1 ± 0.9) % depletion in Mg and a (5.9 ± 0.7) % enrichment in Sr. The magnitude of the precipitation rate effect on Mg is (37 ± 4) % greater than that on Sr.

Precipitation rate effects are well-defined in the rostrum of *Passaloteuthis bisulcata* but only account for a minor part of chemical heterogeneity. Biasing effects on palaeoenvironmental studies can be minimised by informed sampling, whereby the apex and apical line of the rostrum are avoided.

1 Introduction

The measurement of Mg and Sr concentrations in biogenic calcite as records of past environmental conditions and geochemical cycles has a long tradition (e.g., Odum, 1951; Turekian, 1955, Lowenstam, 1961). Palaeotemperature estimates from element concentrations in fossil calcite in particular have been intensively studied (e.g., Pilkey and Hower, 1960; Nürnberg et al., 1996; Elderfield and Ganssen, 2000; McArthur et al., 2007).

A number of empirical studies have documented positive co-variation of Mg/Ca ratios and/or Sr/Ca ratios with temperature in biogenic calcite from belemnites (Rosales et al., 2004; McArthur et al., 2007; Li et al., 2012), bivalves (Klein et al., 1996; Freitas et al., 2006; Tynan et al., in press), brachiopods (Brand et al., 2013; Butler et al., 2015), coccoliths (Stoll et al., 2001), echinoderms (Pilkey and Hower, 1960), foraminifers (Lea et al., 1999; Elderfield and Ganssen, 2000; Lear et al., 2002; de Noojer et al., 2014) and ostracods (Chivas et al., 1986; De Dekker et al., 1999). Inorganic precipitation experiments also show a significant temperature control on the incorporation of Mg and Sr into calcite (Kinsman and Holland, 1969; Katz, 1973;

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Oomori et al., 1987). While a positive co-variation of Mg/Ca ratios with ambient temperature in biogenic calcite agrees with experimental data, Sr/Ca ratios in shell calcite that are positively linked with temperature (e.g., Lea et al., 1999; Stoll et al., 2002; Ullmann et al., 2013a) contradict an expected negative correlation of these two parameters (Kinsman and Holland, 1969; Rimstidt et al., 1998).

It is evident that a multitude of parameters besides temperature can affect element concentrations in biogenic calcite, e.g., pH (Lea et al., 1999), pCO_2 (Dissard et al., 2002; Müller et al., 2014), salinity (Klein et al., 1996; Lea et al., 1999; Hönisch et al., 2013) and notably precipitation rate (e.g., Klein et al., 1996; Lorrain et al., 2005; Ullmann et al., 2015). Disentangling the effect of temperature on shell geochemistry from the effects of physiological responses triggered by temperature change, and constraining the relative contributions of these parameters on shell chemistry, is difficult in growth experiments. For micro-organisms analyses need to be done at high spatial resolution and inter-specimen offsets become a concern (e.g., de Nooijer et al., 2014). Most shell-building macro-organisms for which growth rates can be readily established (e.g, Mouchi et al., 2013; Nedoncelle et al., 2013; Pérez-Huerta et al., 2014) form growth increments that do not show consistent, significant, lateral differences in precipitation rate.

Belemnites, Mesozoic predators whose fossil calcite is of major importance for the reconstruction of palaeoenvironmental conditions during the Jurassic and Cretaceous (e.g., Podlaha et al., 1998; McArthur et al., 2000; Ullmann et al., 2014; Sørensen et al., 2015), constitute an exception to this. Their rostra are typically large (a few to tens of centimetres long and a few millimetres to centimetres in diameter) and are structured by a concentric arrangement of growth bands around the apical line, which itself traces the long axis of the fossil (Sælen, 1989; Ullmann et al., 2015). These growth bands show systematic lateral changes in thickness and can be sampled by milling, permitting high-precision analyses of element concentrations via ICP-OES or ICP-MS. In the rostra it is possible to differentiate between effects of crystal morphology, precipitation rate and other physiological or environmental controls (Ullmann et al., 2015). A significant contribution of calcite precipitation rate to Mg/Ca and Sr/Ca patterns in belemnite calcite has been noted (Ullmann et al., 2015). The observed negative correlation of Mg/Ca with precipitation rate and positive correlation of Sr/Ca with growth rate in the calcite of a rostrum of the belemnite *Passaloteuthis bisulcata* agrees with published experimental studies (Lorens, 1981; Tesoriero and Pankow, 1996; Gabitov and Watson, 2006; Tang et al., 2008; Gabitov et al., 2014) and theoretical studies (DePaolo, 2011; Gabitov et al., 2014). The magnitude of precipitation rate-induced changes of Mg/Ca and Sr/Ca ratios, however, has so far remained unquantified in belemnite calcite.

Here, a quantitative appraisal of the available data is presented and the importance of calcite precipitation rate for the interpretation of Mg/Ca and Sr/Ca ratios in biogenic calcite is discussed.

2 Materials and Methods

The studied, nearly complete rostrum of *Passoleuthis bisulcata* (Blainville 1827) was collected from the Early Toarcian (Early Jurassic) Grey Shale Member at Hawsker Bottoms, Yorkshire, UK (67 cm above the base of the *Dactylioceras tenuicostatum*

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ammonite subzone, *D. tenuicostatum* zone; Hesselbo and Jenkyns, 1995). Detailed methodology for geochemical analyses and documentation of cathodoluminescence patterns is described in Ullmann et al. (2015). In brief, the specimen was cut perpendicular to the long axis into four slabs which were glued onto glass slides, ground down to a thickness of ca. 3.5 mm and polished. Element/Ca ratios where measured on transects prepared by incremental drilling of samples through the slabs using an Optima 7000 DV ICP-OES. After grinding down the sampled slabs to ca. 0.5 mm and polishing, cathodoluminescence maps were made using a microscope equipped with a Citl Mk-3a electron source. Element/Ca ratios were screened for diagenesis using Mn/Ca ratios and only data from well-preserved samples are further considered.

3 Results

Cathodoluminescence microscopy reveals a multitude of characteristic, luminescent bands in the rostra that constitute time stamps which can be correlated through the entire rostrum (Fig. 1). Differences in the distance of these luminescent bands from the apical line in the four profiles can be used to trace the relative precipitation rate changes in belemnite rostra (Fig. 1). Due to the position of the different profiles within the rostrum (Fig. 2A), relative precipitation rate becomes greater from profile one to four and the central growth bands in profile one are progressively lost (Figs. 1, 2A, B). Profile four yields only the outer ~30 % of the growth bands present in profile one but these growth bands have thicknesses (relative precipitation rates) 2.3 to > 3 times greater than the correlative bands in profile one (Fig. 2C). Using exponential functions to express the differences in precipitation rate (Fig. 2C, Ullmann et al., 2015), Mg/Ca and Sr/Ca ratios of the four geochemical profiles can be integrated in a common ontogenetic profile (Fig. 3). These overlays show common patterns but significant offsets between the profiles. All profiles are characterised by a steady decrease of Mg/Ca ratios and Sr/Ca ratios from the innermost growth bands reaching a minimum at ~ 60 % distance from the centre of the rostrum in the reference profile one (Fig. 3). Both ratios then increase until about 75 % distance on the reference profile and towards the rim show a minor decrease with subordinate peaks and lows which are specific to Mg and Sr. In addition to this general pattern, progressively lower Mg/Ca and higher Sr/Ca ratios are observed at the margin of the rostrum with increasing profile number. Differences in element/Ca ratios with respect to the reference profile one as a function of changes in calcite precipitation rate are plotted in Figure 4. For these plots, only geochemical data from the outer 2.0 mm (profile two) to 2.6 mm (profile four) were taken into account, where differences between the profiles are thought to be dominated by precipitation rate effects (Ullmann et al., 2015). Deviations in Mg/Ca and Sr/Ca from the reference profile co-vary strongly and the resulting enrichment factors show strong co-variation with relative precipitation rate (Figs. 4A–C). Best fits for these relations are:

$$\Delta\frac{Mg}{Ca} = (0.994 \pm 0.007) - (0.081 \pm 0.009) * \Delta\, precipitation\ rate \quad (1)$$

$$\Delta\frac{Sr}{Ca} = (1.006 \pm 0.006) + (0.059 \pm 0.007) * \Delta\, precipitation\ rate \quad (2)$$

$$\Delta\frac{Mg}{Ca} = (2.37 \pm 0.04) - (1.37 \pm 0.04) * \Delta\frac{Sr}{Ca} \quad (3)$$

where Δ(Mg/Ca) and Δ(Sr/Ca) are the enrichment factors for the element/Ca ratios and $\Delta_{\text{precipitation rate}}$ is the deviation in precipitation rate from profile one (0 = 0 %; 1 = 100 %). A precipitation rate increase of 100 % thus results in a (8.1 ± 0.9) % depletion in Mg and a (5.9 ± 0.7) % enrichment in Sr.

4 Discussion

4.1 Controls on element uptake and expected precipitation rate effects

Calcite precipitation experiments have established that Sr concentration should increase and Mg concentrations decrease with increasing precipitation rate (Lorens, 1981; Tesoriero and Pankow, 1996; Gabitov and Watson, 2006; Tang et al., 2008; Gabitov et al., 2014). The same signature is expected to be imposed by decreasing temperature (Rimstidt et al., 1998), necessitating the measurement of a reliable temperature proxy alongside the element concentrations or comparing coeval growth increments. The latter approach is adopted here, which rules out that temperature can have a significant effect on the observed trends. Metabolic effects on element incorporation and/or changes in the composition of the mineralising fluid throughout ontogeny are clearly evident (Fig. 3), but are not manifested as a strong co-variation of Mg and Sr. These effects can thus be accounted for by normalising element/Ca data to element/Ca ratios of profile one, i.e., by computing element enrichment factors. Furthermore, changes in relative growth rate (within a factor of four) and likely also absolute growth rate in the rostrum are not very large, so that the observed effects are comparable throughout the studied part of the profiles. They therefore image a linear segment of a relationship, which over a wider range of precipitation rates follows a more complex, curved function (e.g., Tang et al.; DePaolo, 2011; Gabitov et al., 2014).

The observed sensitivities of Sr/Ca ratios and Mg/Ca ratios to changing precipitation rate (5.9 % increase and 8.1 % decrease per 100 % precipitation rate increase) can be compared with experimental results supported by theoretical considerations. The growth entrapment model (Watson and Liang, 1995) predicts that elements present in the surface layer of a growing crystal become more efficiently trapped the faster the crystal forms. Results of precipitation experiments at 20–25°C approximated with this model Gabitov et al. (2014) predict a Sr/Ca sensitivity observed in *P. bisulcata* for calcite growth rates of ca. 0.05 nm s^{-1} and ca. 40 nm s^{-1}, whereas measured Mg/Ca sensitivity is matched at ca. 0.3 nm s^{-1} and ca. 20 nm s^{-1}. It is conceivable that at slightly different temperatures a better match between these two elements could be obtained, because the response of Sr changes significantly with temperature (Tang et al., 2008). No equivalent experiments for Mg are available, however, so this hypothesis cannot be quantitatively explored. Nevertheless, conditions can be found in experimentally constrained relationships under which the proposed sensitivities of Mg and Sr to precipitation rate change recorded in *P. bisulcata* are met, further supporting that precipitation rate is the ultimate control of the observed signal.

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4.2 Significance of precipitation rate effects for fossil Mg/Ca and Sr/Ca data

In order to use Mg/Ca and Sr/Ca data of fossil carbonates to study aspects of palaeoenvironments, it is imperative that the dominant controls of the signal are constrained. After excluding data that are affected by crystallographic forcing near the centre of the rostrum (Ullmann et al., 2015) and samples showing clear precipitation rate effects, the residual range between the measured extreme values in the studied rostrum is still ± 25 % for Mg/Ca ratios and ± 12 % for Sr/Ca ratios (Fig. 5). Reported variability within the genus *Passaloteuthis* and all Toarcian (Early Jurassic, ca. 183–174 Ma) belemnite rostra (Bailey et al., 2003; Rosales et al., 2004; Ullmann et al., 2014) is considerably larger (Fig. 5). Some of this variability is likely related to crystallographic controls on Mg and Sr incorporation (Fig. 5, Ullmann et al., 2015). In practice, there are only a few samples affected by this factor in published data sets: Crystallographic controls leading to such Sr and Mg enrichments are most prevalent near the apical line of the rostrum (Ullmann et al., 2015), an area where sampling is avoided (if possible) because of a high probability of diagenetic overprint (e.g., Podlaha et al., 1998; McArthur et al., 2000; Ullmann and Korte, 2015). For *Passaloteuthis*, the observed range of Mg/Ca and Sr/Ca values in the genus (Ullmann et al., 2014) is reduced by a third, when the highest 5 % of the element/Ca ratios are excluded.

Significant changes of average Sr/Ca and Mg/Ca ratios have been observed for whole belemnites specimens throughout the Toarcian (McArthur et al., 2000; Bailey et al., 2003; Rosales et al., 2004). These changes are considerably larger than observed intra-specimen variability (Fig. 5) and show a large increase of both Sr/Ca and Mg/Ca ratios around the Early Jurassic Toarcian Oceanic Anoxic Event (ca. 183 Ma, McArthur et al., 2000; Bailey et al., 2003; Rosales et al., 2004). On an even longer time scale of the Early and Middle Jurassic – some 38 million years – Sr/Ca ratios in belemnite rostra averaged per ammonite biozone drift between 1.2 and 2.3 mmol mol^{-1}, probably tracing secular changes in seawater composition (Ullmann et al., 2013b).

While effects of precipitation rate on Sr/Ca and Mg/Ca ratios in belemnite rostra are significant (Fig. 4), all the above described ranges of data are considerably larger than the maximum observed effect of calcite precipitation rate in *P. bisulcata* (Fig. 5), suggesting that precipitation rate is of minor importance for controlling element/Ca ratios in *P. bisulcata*. This likely also holds for other belemnites as seen by Sr/Ca ratios in transects through multiple specimens yielding comparable results in *Bellemnellocamax mammillatus* (Sørensen et al., 2015), even though the generalisation remains to be tested rigorously. When sampling belemnite rostra for palaeoenvironmental studies, avoiding the apical zone and targeting profiles as far away from the apex as possible (i.e., profile one rather than profiles three or four) ensures the least possible bias exerted by crystallographic forcing and changing precipitation rate. Deriving information about past seawater composition then depends mostly on other potential controls on shell chemistry like temperature (e.g. Rosales et al., 2004; McArthur et al., 2007; Li et al., 2012) and the generation of large datasets which enable constraining average values precisely.

5 Conclusions

The biomineral structure of belemnite rostra provides a unique opportunity to isolate effects of calcite precipitation rate from other controlling processes during biomineralisation.

Changes in relative precipitation rate in the rostrum of the belemnite *P. bisulcata* result in a depletion of Mg (8.1 ± 0.9 % per 100 % precipitation rate increase) and enrichment of Sr (5.9 ± 0.7 % per 100 % precipitation rate increase).

While the forcing exerted by changing precipitation rate is significant and can be precisely quantified, it is of minor importance for the overall variability of Mg/Ca and Sr/Ca ratios in belemnite rostra. This is important when considering the utility of belemnite rostra for palaeoenvironmental analysis.

Sampling geochemical transects along profiles as near as possible to the protoconch of the rostrum and avoiding the apical zone helps minimising biasing effects of precipitation rate (and crystallographic forcing) on palaeoenvironmental datasets.

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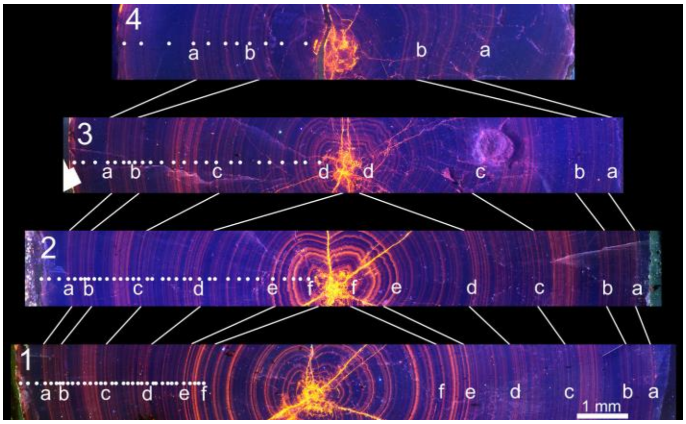

Figure 1: Cathodoluminescence pattern for sections through the rostrum adjacent to geochemical transects one to four. Letters "a" to "f" correlated between the profiles with white lines as well as white dots indicate arbitrarily chosen marker bands for illustration of differences in precipitation rate (see also Fig. 2). Note the increasing distance of marker bands from profile one to four.

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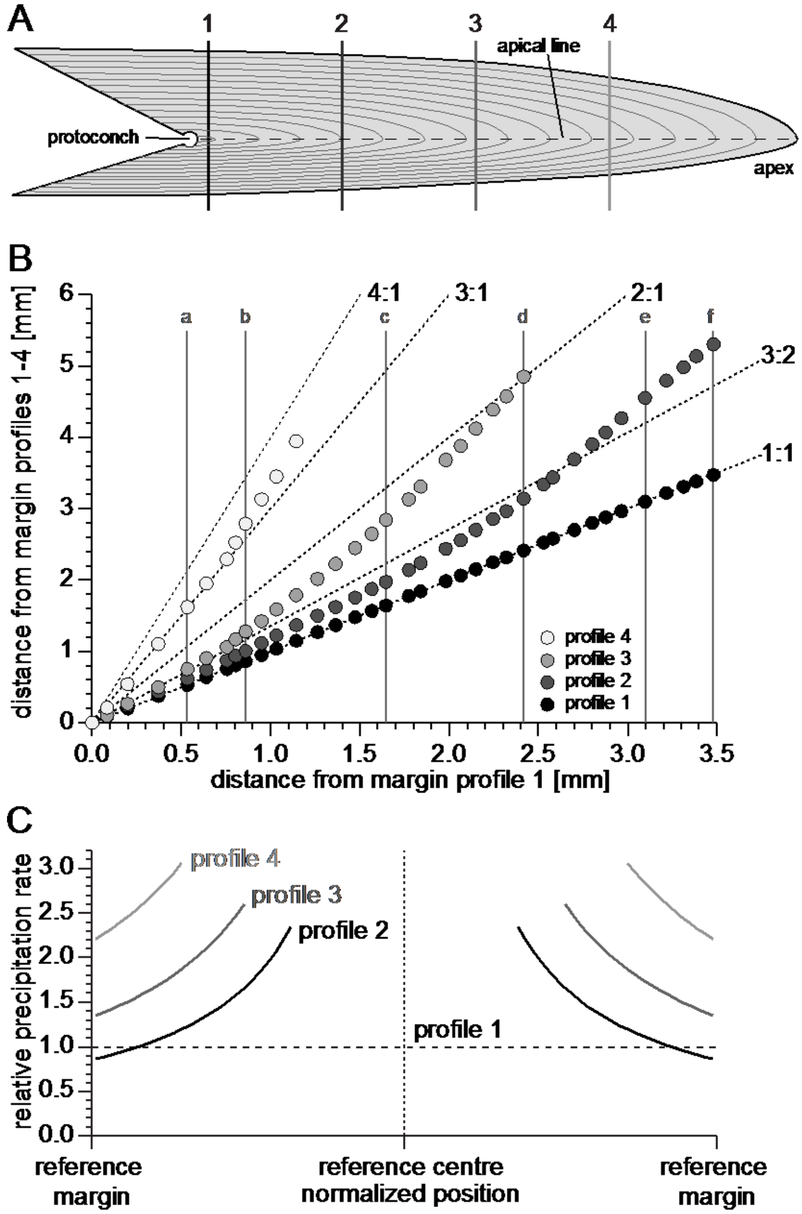

Figure 2: Studied geochemical profiles and their relative precipitation rates. A) Schematic representation of the rostrum of *P. bisulcata* with approximate positions of the transects. B) Cross plot of distance of selected luminescent bands (a–f and white dots from Fig. 1) from the margin of the rostrum in profiles one to four with respect to its position in profile one. Stippled lines indicate selected relative precipitation rates with respect to profile one. Letters and circles are positioned as in Figure 1. C) Relative precipitation rate in geochemical transects computed from exponential relationships documented in Ullmann et al. (2015).

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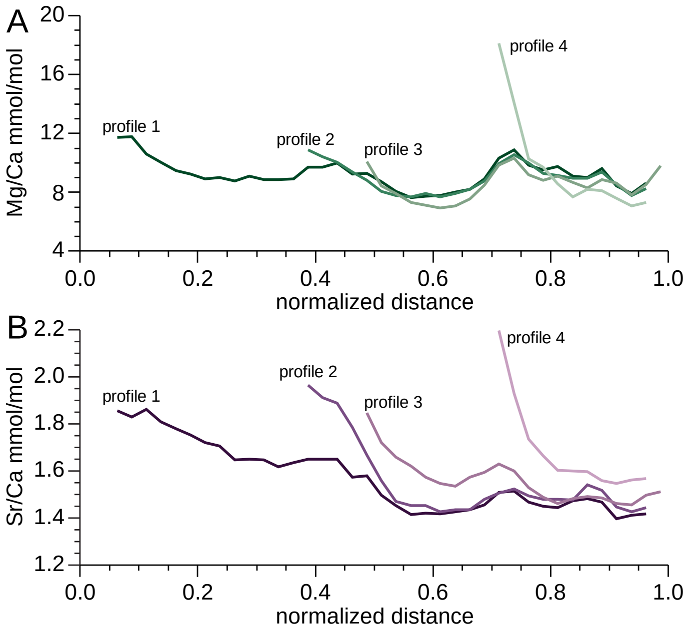

Figure 3: Aggregated geochemical data for the four profiles plotted against distance from the central apical line of the rostrum (zero) to the margin (one) with profile one as a reference. The bin size is 2.5 % of the profile length. A) Mg/Ca ratios. B) Sr/Ca ratios.

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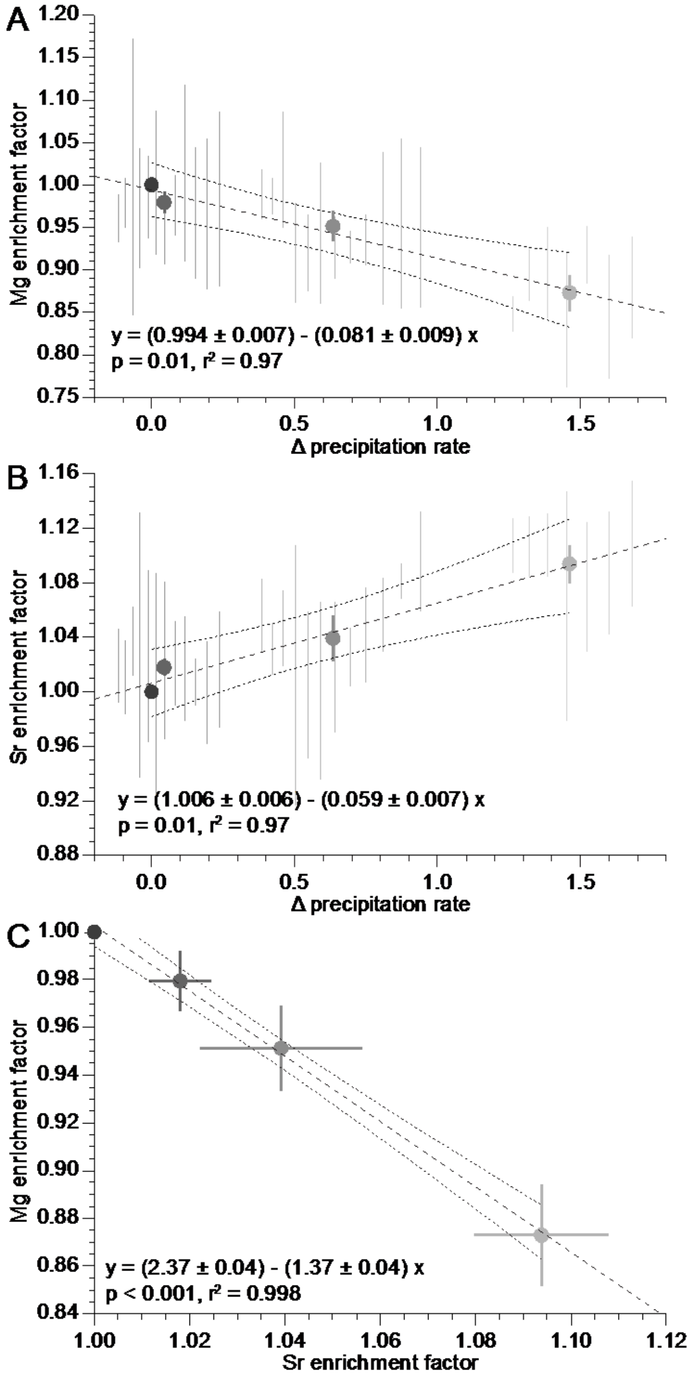

Figure 4: Changes in Mg/Ca and Sr/Ca ratios as a function of precipitation rate. A) Mg enrichment factor as a function of change in precipitation rate expressed as a relative deviation from the reference precipitation rate of profile 1. Vertical lines denote 2 standard error uncertainties for each binned interval of profiles two to four and circles show average values with two standard error uncertainty. The trend line from ordinary least square regression of the mean values is shown with 95 % uncertainty envelope. B) Sr enrichment factor as a function of calcite precipitation rate. Symbols as in A). C) Correlation of Mg depletion with Sr enrichment.

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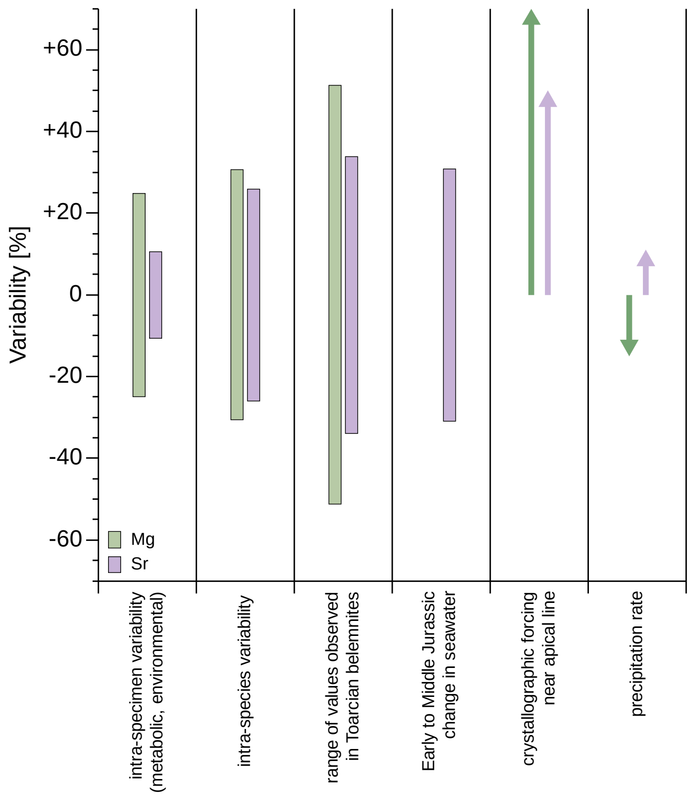

Figure 5: Variability of Mg/Ca and Sr/Ca ratios in belemnite calcite. Intra-specimen variability accounts for residual range of values in *P. bisulcata* after accounting for crystallographic forcing and precipitation rate (Ullmann et al., 2015). Intra-species variability of *Passaloteuthis* (Ullmann et al., 2014) and range of values observed in Toarcian belemnites (Bailey et al., 2003; Rosales et al., 2004; Ullmann et al., 2014) do not exclude samples potentially affected by crystallographic forcing and are thus likely overestimated. Range of reconstructed seawater Sr/Ca ratios is from Ullmann et al. (2013b). Length of arrows for crystallographic forcing and precipitation rate indicate maximum observed effect in *P. bisulcata*.