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Interactive comment on "The effect of precipitation rate on Mg/Ca and Sr/Ca ratios in biogenic calcite as observed in a belemnite rostrum" *by* Clemens Vinzenz Ullmann

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Many thanks for this critical and constructive review. I have extracted what I think are the main points of discussion from this review and provide short answers below:

1) Adoption of termini "biomineralization"; "kinetics"; "carbonate secretion"

It is true that my choice of terminology is debatable and I will certainly reconsider which terms are most suitable when revising this manuscript.

2) Comparability of inorganic with organic systems (experimental fluid vs body fluid)

I agree that processes of shell formation and composition of body fluids are much more

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complex than what can currently be modeled using inorganic precipitation experiments. It was not my intention to advocate that inorganic experiments and growth experiments of molluscs are entirely interchangable or that the former can replace the latter. However, I feel that one can count it as an encouraging sign if empirical results on biological systems and experimental results on abiogenic precipitates converge. After all, most of palaeoenvironmental geochemistry relies on the assumption that fundamental physical controls on carbonate composition hold - regardless which animal (or “non-animal”) produced it. Quite a substantial body of literature employing this underlying assumption and yielding results consistent with non-geochemical interpretations of the rock record has emerged so that one can be confident that some truth is in this assumption. I am of the opinion that one should incorporate as broad as possible a range of studies when investigating biomineralization signals whilst keeping their limited comparability in mind.

3) Multiple controls and feedbacks of shell secretion and kinetics

Prof. Immenhauser rightly points out that a multitude of environmental parameters, food availability, ontogenetic trends, stressors, sexual dimorphism, species specific effects, and many more have an effect on the chemical composition of biogenic shell materials. Many of these parameters will also have a bearing on shell secretion rate which in turn affects element incorporation, making biomineralization a very complex phenomenon. I entirely agree with Prof. Immenhauser in this point, but what I investigated in the present study is a system, in which relative shell secretion rate can be viewed upon as an isolated parameter. I did not claim that this study is able to make inferences about absolute shell secretion rates or to make a point about the environmental and biological factors that control shell secretion rate. The unique angle of the present study is to look at time slices of belemnite shell secretion. The assumption is that a growth band in a belemnite represents an ontogenetic isochron for which one particular expression of biomineralization controls is realized. The growth band, which then by definition has to represent the same amount of time, has a variable thickness along the whole of the belemnite rostrum, i.e., the rate at which it formed is variable for purely geometrical reasons, increasing from the alveolar area to the apex (Figs. 1, 2). By normalizing the chemical data of all measured profiles against data from a reference profile, all external controls on shell chemistry are then taken out of the equation and it becomes possible to isolate what the effect of this rate variability is.

4) Least squares regression doesn't solve all problems. Geochemical variability of fossil geochemistry may not represent secular global trends - heterogeneity and regional trends in oceanographic parameters have to be considered.

It is true that it is only an inference that the chemical composition of fossil materials can be used to reconstruct the chemical composition of seawater through time. This is a bit of a digression because it is not the topic of the study, but may be instructive to comment upon: I am confident that this is possible for some elements to a certain degree to reconstruct past seawater composition. The elements Mg, Sr and Ca which I look at in this study are amongst those which are thought to be uniformly distributed in the oceans due to their long residence time. Their concentrations and even their isotopic ratios vary within very narrow limits in the world oceans and this is unlikely to have been different in the past due to the particular chemical behaviour of these elements. For the above elements one can therefore neglect regional trends in fully marine environments – one reason e.g. for the success of the marine Sr isotope curve. For elements with much shorter oceanic residence times like Ce, Cr, Cd, Mn etc. it would be an entirely different story. One observation which appears to be temporally robust is that different Sr/Ca ratios in marine shells have certain relative offsets from the seawater Sr/Ca ratio they form in. Even though it is very seldom utilized, a crude chemical mapping of the composition of modern biominerals is available since 50 years (Dodd, 1967, JOURNAL OF PALEONTOLOGY). The first order observation is that Sr/Ca of average bivalve calcite is lower than the Sr/Ca ratio of the average brachiopod, which in turn (for Jurassic and Cretaceous) is lower than the Sr/Ca ratio of the average belemnite (Voigt et al, 2003, INT J EARTH SCI; Korte and Hesselbo, 2011; PALEOCEANOGRAPHY;

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Ullmann et al., 2013, GEOLOGY; Sørensen et al., 2015, PPP; Ullmann et al., 2016, GONDWANA RESEARCH). For brachiopods one finds Sr/Ca ratios decreasing from craniids to thecideids to terebratulids and rhynchonellids (Brand et al., 2003, CHEM GEOL). Within the bivalves, oysters have a lower average Sr/Ca than pectinids. This is subject to ongoing research and could be refined ad infinitum. Once the translation factor from element/Ca(fossil) to element/Ca(seawater) is known and can be reproduced through time with multiple fossil groups, the likelyhood is that the seawater element/Ca ratio thus studied can be confidently reconstructed. What I imaged in Fig. 5 is the "biomineralization noise", one has to overcome for such an approach. Due to all sorts of intra-specimen, intra-specific, and inter-specific effects a large number of analyses has to be integrated for a meaningful average. Relative shell secretion rate, however, is a small player in this game, and this is the contribution I wanted to make with this study. While one may remain critical of the idea that seawater chemistry reconstructions can be done on the basis of shell chemistry, I show that shell secretion rate is not to blame if it doesn't work, because its forcing is inconsistent with observed data variability and its magnitude is too small.

5) Is the term "quantitative" justified?

The short answer is "yes". What I present is a quantification of the effect of relative shell secretion rate on the Mg/Ca and Sr/Ca ratios found in a belemnite rostrum. I find that calcite that forms twice as fast as calcite at another point in the same growth increment will contain 8.1 +/- 0.9 % less Mg and 5.9 +/- 0.7 % more Sr than its slower-forming counterpart – regardless of the absolute Mg and Sr concentrations which are subject to more complex forcings (Figs. 3, 4). In this sense my appraisal is quantitative and reasonably precise. What I cannot quantify is which parameters led belemnites to change their shell secretion rates through their lifes.

6) The messages are "We can ignore kinetics (i.e. secretion rate)" and "belemnites are Mesozoic favourites"?

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I would say that message 1) is a first order "yes". Indeed, besides showing the utility of belemnite calcite for constraining calcite formation rate controls on element uptake, I wanted to show that this particular parameter is of minor importance for generating the chemical complexities of biogenic shell calcite. Message number 2) is up for debate. Personally, I am a "belemnite fan" and find their calcite is superior to other fossil archives for certain applications, in particular, where large amounts of calcite are necessary (non-traditional isotopes of trace elements come to mind). However, I don't want to advocate that we should neglect other fossil groups (and non-fossil records) or be uncritical about belemnite rostra. The strength of future research will lie in merging the strings of evidence coming from all available sources.

7) Selective choice of references: Missing critical voices saying everything is swamped by biology or the archive is not valid.

It was not my intention to be uncritical about the use of belemnite rostra to constrain shell secretion rate effects on element uptake and neither did I intend to cite the literature in a biased fashion. In the revised version of the manuscript I will make space for a critical assessment of what is thought about the belemnite rostrum as a geochemical archive including the articles recently published by the Bochum group. Part of the above allegation might be down to a misunderstanding about the aims of the paper as well: The dataset I present is of some value for constraining the effect of shell secretion rate on element partitioning into calcite, 1) because coeval calcite formed at various growth rates (factor of ca. 3) is available and 2) the signal of this relative secretion rate difference is significant despite overall ontogenetic changes in element/Ca ratios in the rostrum. One may consider this present dataset "a lucky find" whereas for most other fossil groups trying to constrain shell secretion rate effects would fail. I am sure that many biological systems wouldn't lend themselves to such an analysis because the shell growth geometries aren't ideal and/or the chemical variability of the system prevents any meaningful analysis. This should, however, not be taken as evidence that biomineralization processes cannot be disentangled, it simply calls for selecting the right animal group for the right question.

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