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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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Dear author, dear editor,

Thank you for providing me with the opportunity to review this paper. Dr. Ullmann reports on his statistical attempt to capture calcite secretion rates in belemnite rostra and specifically on the kinetic effects of secretion rates on Mg/Ca and Sr/Ca ratios. Dr. Ullmann is a recognized expert in this research field and has given this issue significant consideration. The main outcome of this study is that the effects of kinetics are comparably minor and can be avoided by an intelligent sampling strategy. In essence, I feel that this paper has significant merits and should be published pending what I consider significant revisions. My comments are simply suggestions to make this an even better

paper.

Below I summarize my main concerns:

I used the search option of Adobe Acrobat pro but did not find the word "biomineralization" mentioned a single time in this paper (I find metabolism once). The same accounts for "kinetics". I find this surprising. Similarly, the biomineralization by the belemnite animal is referred to as "precipitation". In my view, the manner in which organisms form their endo- or exoskeletons is referred to as "carbonate secretion". I can live with all of that as this is essentially terminology. Nevertheless, please consider.

Similar to many other metazoan biomineralizers, molluscs isolate their environment of mineral formation from the outside world. Page 2 refers to known parameters that affect Mg/Ca ratios in inorganic precipitation experiments but these are apparently placed on an identical level as those that govern the body fluids of the animal? I am very critical here!

I agree with the statement in the abstract: It is often hard to constrain which parameter ultimately controls the concentrations of a given element in biogenic calcite. Ambient environmental parameters affect the physiology and metabolism of the animal and hence there is a strong correlation between environment and metabolisms. What controls carbonate secretion rates of the belemnite rostra: Environmental parameters, food availability, ontogenetic trends, stressors and more of the like.

Moreover, there are the issues of possible stressors, sexual dimorphism and species-specific biological controls on carbonate secretion rates. In my view, but I might be wrong, the problem is that many parameters control the rates of carbonate secretion, which in turns affects – via kinetics – element incorporation. But in parallel to this, element incorporation in turn is affected by factors other than kinetics too. I understand that Dr. Ullmann is approaching this by means of least square regression approaches that are helpful but will not solve all problems. This is very briefly touched upon on page 5 and the author concludes that the observed fluctuations are such that they exceed

intra-specimen variability and hence represent secular “global” environmental patterns. I am not sure I am an advocate of the concept that the world’s oceans in the geological past did see a uniform change in their parameters? A look on the data sets provided by oceanographers reveals a very complex chemical and physical structure of the present day oceans. Plenty of heterogeneity and regional trends!

I am not sure if the author should use the label “quantitative appraisal” here? I am not convinced he can clearly separate the effects of kinetics from the bulk of parameters that govern element incorporation in these biominerals. I would agree with Dr. Ullmann, that his approach represents the perhaps best amongst all of the less-than-ideal approaches by which this difficult issue can be approached. Using sophisticated statistical tools on a non-sophisticated data set helps, that is clear, but this does not implies that the result is quantitative. Moreover, given that appraisal is often used as synonym for assessment or even opinion, the term seems somewhat contradictory.

Summing up: I applaud Dr. Ullmann in his attempt to get a better grip on the effects of kinetics on elemental ratios in belemnite ratios. In the past, many of us have assigned these proxy data to temperature alone in a rather uncritical manner, or when data were difficult to interpret, to either “biological” effects or “diagenesis”. The latter two representing popular black box interpretations. This paper represents a clear progress and the essential message brought forward is important and valid and this is why the paper should be published. I believe the paper suffers from a – in my view – uncritical application of results from inorganic precipitation experiments to biomineralization in the body of an organism. I believe the paper suffers from a selective choice of references. Yes, it is true, a number of empirical studies have documented co-variation of Mg/Ca and Sr/Ca ratios in these carbonates with what was assumed to be temperature (or in the case of recent organisms) has been measured as ambient temperature. It holds also true, however, that important papers have shown aquaria or field experiments that reveal the full complexity of these biogenic archives and kinetics was but one. What would this imply? I find these critical voices underrepresented in the present paper.

That surprises me given that the author has chosen to investigate one of the many other-than-temperature effects, here kinetics, as a topic of his paper. It seems “two souls are dwelling in his chest”? So, the messages are: (i) We can ignore kinetics and (ii) belemnites are still our favourite archive organisms for the Mesozoic?

Finally, it is certainly not my style to use a review to make an author cite my papers! Nevertheless, our recent paper in Sedimentology (Immenhauser et al. 2016) provides a wide selection of references that can be cited here and problems that should be considered. I believe that Dr. Ullmann knows this paper? Please also consider making reference to Benito et al. (2016; J. Iberian Geology, 42, 201-226 and Hoffmann et al. (2016, Sed Geol, 341, 203-215). It is perfectly fine, if you disagree with these authors, but ignoring them totally might reflect poorly on this paper.

I hope these comments are of use!

Sincerely yours,

A. Immenhauser

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