

***Interactive comment on* “Trace elements in mussel shells from the Brazos River, Texas: environmental and biological control” by Alexander A. VanPlantinga and Ethan L. Grossman**

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Review of bg-2019-323: Trace elements in mussel shells from the Brazos River, Texas: environmental and biological control by VanPlantinga and Grossman

This manuscript describes an investigation to better understand the trace element geochemistry of two freshwater mussel shells collected from the Brazos River TX in 2013. The investigators serially sampled the inner nacreous layer (INL) and outer ventral margin (VM) of a shell of specimen of *Amblema plicata* and *Cyrtonaias tampicoensis* and they analyzed the carbonate for Mg, Ca, Sr, Ba and Mn concentration. The data were placed within a temporal framework using previous oxygen isotope data (VanPlantinga

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and Grossman, 2018) and compared to other environmental data (e.g., temperature, water chemistry, water discharge rate) to better understand the origin(s) of the geochemical signatures locked in the shell. The principal outcome of the study focused on shell Mn/Ca records which correlated inversely with river discharge allowing for a reconstruction of river discharge patterns. The investigators conclude that Mn was attained primarily through the ingestion of Mn-bearing particulate organic matter.

This manuscript addresses subject matter that is of general interest to the Biogeoscience community and it identifies a novel proxy of river discharge in the geochemical record of the shell. The investigators thoughtfully consider and evaluate the relevant peer reviewed literature within the context of their study.

The manuscript is relatively well written, although I had some trouble with the PDF because the figures contained a lot of information that could not be seen easily on a paper copy.

The amount of information provided on shell geochemistry and the various correlations and comparisons made me feel overwhelmed at times. The Mg, Sr, and Ba records (as well as $\delta^{13}\text{C}$ and CL) appear ancillary at times and it is unclear if they provide meaningful supporting evidence for the major conclusions of the manuscript.

I recommend that the investigators reconsider what is really needed to support the main conclusion(s) of their study. This should help to sharpen the take home message of the study. A more highly focused revision that centers on the Mn records would be valuable to the scientific community and make a meaningful contribution to the published literature. Data that may be excluded from a revision could likely form the basis for separate manuscript(s).

Other comments, identified by line number (L), are provided below: General comment: Each time a geochemical profile is presented or discussed the investigators should identify whether it is from the inner nacreous layer or the ventral margin. Sometimes this distinction is clearly made while at other times it appears ambiguous.

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L17: The first sentence that defines the word “sclerochronology” is inaccurate. Sclerochronology is more specific than “. . . the study of the physical and chemical properties of invertebrate hard parts. . .”, it involves the temporal context in which these properties are considered.

L59: Methods: The physicochemical water sampling procedures need to be explained in greater detail, or cited properly. This extends to L99-101 where the statement is made that “. . . water samples were not filtered and acidified for analysis after months in storage.” The implications of this unusual sampling strategy should be explained in greater detail. How severely is the Mn data compromised? How are other elements affected in addition to Mn?

L74: Hydrogen isotope compositions are not discussed in the text so a description of sample/analysis procedures is not warranted. Also, anytime delta notation is used, e.g., $\delta^{18}\text{O}$, the word “value” should follow it.

L90 and L94: It appears the sampling resolution for stable isotopes (60 μg) and ICP-MS analysis (20-160 μg) differed. The implications of this should be addressed somewhere in the text.

L102: Were the CL images taken before or after the sampling of the shell for isotopic and elemental analysis? The observation of “shadows” should be explained a little better. This could be done in a better description of the CL imaging in general. What is the ultimate purpose of CL imaging? It appears the investigators wished to correlate brightness to measured Mn concentration in the shell. Was the sampling resolution for ICP-MS comparable to the width of bright and dark bands in the CL images?

L121: Oxygen isotopes. The first paragraph can be reduced if the manuscript needs to be shortened.

L146-148: Variance in a data set is independent of the scale over which the data are considered, e.g., the Mg data set (12 ppb – 20 ppm) is more variable than the Ca data

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set (19-83 ppm) regardless of whether the data are considered on a linear or log scale. Also, reference to Fig. 4 (L148) is for Me/Ca ratios and not absolute concentrations.

L155: The word “shell” should precede the word “growth”.

L162: DMg values reported in Table 3 range from 1-138 (10-3) or 0.001-0.0138, not “0.001-0.138” as stated in the text.

L163: “Mg/Ca does not show any [temporal] systematic trend in our water data. . .”

L190: Sentence starting with “Ba/Ca values. . .” is redundant given L186 . L211: Variability in shell Mn/Ca in not reported in Table 1.

L212: I think the reference should be to “Figure 3B” here and not “Figure 4B”.

L237: The final statement in the paragraph is introductory and should come earlier in the manuscript.

L238: The section entitled Cathodoluminescence is too brief. It should be expanded and integrated better in the text.

L260: Is this the only place where the carbon isotope data are discussed except for L184-185? The carbon isotope data should be integrated more fully in the text, e.g., why are there correlations between shell growth and Sr/Ca vs $\delta^{13}\text{C}$ values?

L283: Goodwin et al. (2018) is not in the reference list.

A general thought about trace elements in shell carbonate that was not discussed: Bender and Morse (1990) consider distribution coefficients to be phenomenological by nature; they depend a lot on the aqueous chemistry of the fluids in which carbonate grows and the nature of the solid phase. They use observations like those reported in Mucci and Morse (1983) who show that more Sr can substitute into calcite when more Mg resides in the crystal lattice as evidence of this. Could the possibility exist that biogenic shell aragonite shares a similar fate?

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Best of luck, Chris Romanek

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