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Biogeosciences Discussions

Interactive comment on "Chemical composition of modern and fossil Hippopotamid teeth and implications for paleoenvironmental reconstructions and enamel formation – Part 2: Alkaline earth elements as tracers of watershed hydrochemistry and provenance" *by* G. Brügmann et al.

Anonymous Referee #2

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This manuscript is the second part of a study about hippopotamid teeth as palaeoenvironmental recorders. The first part is dedicated to major and minor elements in modern and fossil samples. The second part is restricted to some alkaline elements. The scope of the manuscript is in agreement with the content of Biogeosciences.

I was not a reviewer of the first part, so I have read it.

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General comments

Quality of paleoproxies is a permanent topic, in terrestrial or aquatic environment. Recently, some papers had claimed that thanks to clumped isotopes, problems of calibration and so on were resolved.Then, at the recent Goldschmidt conference, it has been shown that clumped isotope geochemistry was not better that usual mass spectrometry. People are now aware of the “vital effect” (isotopic ratio depends on the tissue and taxa) and diagenesis. Thus, manuscripts dealing with such topics are of interest. But, because of the interest, they must be clear, with strong data and arguments. Unfortunately, it is not the case of this manuscript, despite, or because, of its length and flaws relative to the biomineralisation mechanisms.

What is missing is a control of the microstructure - histology of the enamel. A SEM control of the tissue is not a perfect guarantee of the preservation, but is a first step. Another easy control is the use of FTIR spectrometry (only some mg of samples). From such data, crystallinity index, organic matrix/mineral ratio, F... can be inferred.

On the opposite, the same chemical data are described and described again. On the other hand, a comparison with other taxa of the same sites is missing. The crystallization mechanisms of enamel are described from a purely chemical point of view, not compatible with what is known from hundreds in vivo and in vitro observations. Thus, results and interpretations are biased, when they are not over-interpretated, and because of the verbose style of the manuscript, it is confusing for a reader.

This manuscript need major changes, to be re-organized and shortened before publication.

Introduction p. 3649 - line 18... Mg/Ca are often used in Foraminifera to infer palaeosalinity and palaeotemperature, but data are often contradictory and results of numerous culturing experiments are not concordant. Several “new” calibrations are described every year. Moreover, the contents of the different layers of a single chamber differ within an individual (Rollion-Bard & Erez). As for corals, COC and fibers show

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strong differences when isotopic ratios are translated in temperature, despite they are simultaneously secreted. It is the same for brachiopods, sea urchins... Thus, there is no consensus for these elements as proxies.

p. 3651 - line 5: references are missing despite numerous papers show quantitative data about chemical alteration of fossil enamel.

Samples and methods

I am not able to know how many samples from a given site are studied. I have seen that these data are in the first paper, but why not in this one? It is only one line in the text.

p. 3653: All along the manuscript, some elements are said to be oxides, others in native form? Why? Is there any evidence of the oxide form? Morever, the use of these different forms is confusing because the units are not the same (μg g-1, or wt%).

p. 3655 - line 22... "The similar distribution...": why not a frequency histogram with statistical tests? 31 samples correspond to a good significant size.

Discussion p. 3657: references are missing (among them, see Williams CT for REE, Sandrock et al. for Malawi samples, ect).

p. 3658 - line 13: when enamel begins, cements stops. I do not understand "enamel is enclosed by cement". Is "cement" = sediment?

p. 3660: the authors repeatedly use "fluid" to describe the media in which enamel is produced. There is no fluid, but a protein gel. Moreover, the Rayleigh fractionation law is Ok for an in vitro media, or a geological one with liquid (Rayleigh fractionation: separation of each crystal as it formed = perfectly continuous fractional crystallization in a magma chamber), but it is well known by people dealing with biology and organisms that it does not apply in the biomineralogy field. The first stage of bioapatite is amorphous, not crystal (references are too abundant to be cited here).

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P. 3361 - line 3: “Ignoring the outer rims....”: why? Line 13: “The epithelial cells control the transport of Ba, Sr and MgO...” A reference for the MgO transport is needed. Why MgO and not Mg? An explanation is needed.

Interactive comment on Biogeosciences Discuss., 9, 3645, 2012.