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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.

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Discussion of the comments of referee #2

We thank referee #2 for the helpful review of our manuscript. Critical general remarks essentially are related to (1) the presentation of the biomineralisation mechanisms,

(2) missing details on the microstructure, and (3) the length and verbose style of the manuscript.

General comment #1 criticizes that the crystallization of enamel apatite is described from a purely chemical point of view ignoring "hundreds of vivo and in vitro observations". Unfortunately, the referee neither specifies these observations nor what their actual relevance would be for the purpose of this paper. Of course our discussion emphasizes the chemical aspects of enamel formation; the chemical data are the meat of our study. However, we discuss the chemical data including modern concepts of enamel formation which are based on histological and medical, in vivo and in vitro observations. Several corresponding publications are cited, for example Hubbard, M. J. (2000); Margolis et al. (2006); Pasteris et al. (2008); Simmer (2010); Smith, C. E. (1998.) All these studies indicate that enamel apatite forms by precipitation of hydroxyl apatite, probably as an amorphous phase, from a fluid media, regularly called body fluid or extracellular fluid. There is no statement describing the precipitating media as a gel, indicating that the gel-concept favored by the referee appears not to be widely considered. Without the appropriate reference we cannot discuss this idea. We would agree that Rayleigh fractionation does not perfectly describe biomineralisation processes in organisms. However, this is nowhere claimed in our manuscript. To the contrary, we continuously emphasized that as a first approximation. For example, we outlined that the compartment where apatite precipitates represents an open system; a fact we cannot model without speculating on parameters such as compositional changes of the enamel fluid with time. Thus, in order to not over-interpret our data and the crystallization model we assumed the simplest case, which nevertheless proved to be a consistent model explaining the distribution of several elements (e.g. Mg, Na, Ba, Sr, Cl).

The second major criticism asks for more data on the microstructure, for example by applying FTIR spectrometry. Such data could provide additional information on the preservation state of the specimens. This information would be important for under-

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standing changes at very small scales (<5 μm). However, the analytical tools we used can only monitor chemical changes at the scale of 50 to 1000 μm. We have no indication that small scale modifications have a significant influence on the element distribution across the enamel. We find similar element distributions in fresh modern and partially altered fossil specimens although the fossil samples have probably experienced recrystallization processes at small scale. Additional data on the histology of enamel, therefore, would neither be able to support nor to challenge our conclusions on the element distribution in enamel.

Finally, regarding the length of our manuscript we will shorten and streamline the text by avoiding long-winding descriptions. However, we cannot see the need for reorganization. The referee provides no specific advice on which parts should be reorganized in the manuscript; certain paragraphs, chapters or the whole text? The aim of our study is to reconstruct paleoenvironmental change using chemical proxies. The logical organization of the discussion is set by this aim, as we discuss the major processes effecting the distribution of the elements in enamel (alteration, enamel formation, nutrition) before discussing habitat characteristics on spatial and temporal scales.

Specific comments

Comment to line 18 page 3649: There might be no overall consensus on the significance of chemical proxies, in particular if one looks in such a generalizing way at the subject like the referee does. Thus, we are not sure what the message of the referee is. Every year more and more organisms are studied and of course different calibration curves will be the result given the different metabolic processes. Culturing experiments will only approximate natural conditions. If one appreciates the complex interplay of environmental and biological processes in different organism one would never expect such a universal consensus on the significance of chemical proxies.

Comment to line 5, page 3651: Key references regarding the chemical alteration of teeth are given at the end of the paragraph (lines 12-13).

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Comment to page 3653: In the geochemical community, it is common use to express major components in minerals as oxides, as they can be regarded to form compounds with oxygen. For example in apatite the cations MgO or CaO are coupled with the anions of PO43+ or CO32-. Trace element concentrations are conventionally given in elemental form. Both, μg g-1 and wt.% are concentration units and are used for convenience to avoid unhandy large numbers. However, we inconsistently used MgO or Mg in order to describe Mg concentrations in fluids. In this case, the use of MgO is not warranted, because in fluids Mg is certainly not transported as MgO. We will correct this throughout the manuscript, for example on page 3361, line 3.

Comment to line 22, page 3655: Because we are supposed to shorten the manuscript, we would like to avoid an additional figure which would have to be explained with additional text. We have given statistical values outlining the significant difference.

Comment to page 3657: We cannot trace the papers of Williams CT. Sandrock et al. have published several papers on the taphonomy of hominid sites near Lake Malawi. We will add Sandrock et al. (1999) who discussed alteration effects in bones.

Comment to line 13, page 3658: We used "cement" as an anatomical term describing the outer apatite rim of the tooth. We will clarify this.

Comment to page 3660: see general comment #1 above.

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