Biogeosciences Discuss., 8, C2736–C2742, 2011
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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: 1. major and minor element variation" *by* G. Brügmann et al.

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Received and published: 30 August 2011

Review of Brügmann et al. - Chemical composition of modern and fossil hippopotamid teeth and implications for paleoenvironemental reconstructions and enamel formation 1. major and minor elements

General comments: Brügmann and co-authors present a significant, large and new data set on the spatial distribution of major and trace elements in tooth enamel apatite of hippopotamids using in situ analytical techniques such as EMPA and LA-ICPMS. It is one of the most detailed and throrough high resolution studies of this kind. From the element data the authors draw important conclusions concerning enamel biomineralization, diet and diagenetic processes. They propose fractionation models commonly used in magmatic petrology to describe equilibrium and fractional crystallisation to explain enamel mineralization processes and the measured trace element distribution patterns, which works quite well and is an elegant approach. Hence their study is an important contribution to enhance the understanding of major and minor element incorporation during in vivo enamel formation as well as its modification during postmotem alteration processes. Furthermore, their study nicely reveals, which elements and element ratios may be useful to learn about lifetime environmental differences and which are controlled by tissue formation processes and may thus indicate preservation of original chemical compositions. Therefore this manuscript is an important and valuable contribution to the field of enamel biogeochemistry which has implications for many palaeoenviromental, palaeoecological and archaeological studies using enamel as a chemical proxy archive. Therefore I recommend the paper for publication in Biogeosciences with only several minor corrections, e.g. the readability of some figures can be still improved.

I have only one critical point and some problems with the use of MgO/CaO and MgO/Na2O ratios to reconstruct the salinity changes of ambient water although this is an interesting approach. You say (P5219, L9), that MgO and SrO concentrations are much higher in enamel of hippopotamid teeth from Kikorongo than in specimens from Lake Albert. If you want to use such elements to reconstruct ambient water salinity you are assuming that these elements are predominantly incorporated from the ambient/drinking water. However, Sr (and Mg?) are usually ingested predominatly from the diet and as hippopotamus is a grazer that feeds on C4 grasses on land at night the Sr and Mg incorporated in the enamel may come from the food and thus may reflect soil and ultimately bedrock Sr and Mg concentration differences and not lake water salinities as suggested. The latter would only be true if you can argue from a concentration

BGD

8, C2736–C2742, 2011

Interactive Comment

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and mass balance point, that most of the ingested Sr, respectively, Mg comes indeed predominantly from the lake water because the concentration of these elements is so high in saline waters that the dietary input is relatively small. This point needs to be addressed and supported by data and/or further discussion. I do not know how much water hippopotamuses as semiaquatic animals incorporate but something about the dietary intake should be known. From element concentrations of grass and lake waters one might be able to make a rough, back of the envelope calculation to see which intake controls the body fluid pool. This may help to strenghten (or weaken) the relation of enamel element concentrations to lake water salinity. Your new MgO/Na2O proxy to infer the Lake Albert hydrologic history suggests no significant evapriation between 7 and 1.5 Ma, which is, as you say, in contradiction to the oxygen isotope results, which indicate a continous evaproation in this time interval. This already indicates some unambiguity of the element proxy which needs explanation.

Specific comments: The order of authors of the references in the text is not consistent and there is no systematic order. Usually it should be in chronological order, rarely in alphabetical. Check with the journal guideline and adjust throughout the text accordingly.

Do you have any information about the diet of the zoo rhinoceros to explain the different Na/Ca, Cl and Mg/Na than its modern african counterparts? If not from this individual, may be you can check with the zoo in Frankfurt for information how they feed their rhinos. Is it by the way an animal that was raised in the zoo or may it be a wild capture? Probably not but may be worth checking, if it is an old museum specimen as in this case it might have formed its enamel before it was brought to the zoo. Might be in any case interesting to learn about the rhino diet to see how this may affect element concentrations and ratios.

What is the porespace volume in modern enamel? How can the enamel contain up to 24wt.% FeO? Is there a replacement of apatite by FeO occuring?

Technical corrections: P 5201, L 13: you can add Koch, 2007 here P 5201, L 15: dentin P 5202, L 4: remove s of elements P 5202, L 13: the reference Tütken et al., 2008 is not appropriate in this context, remove P 5202, L 20: you should add here Longinelli, 1984 as well as Cerling et al., 1997 concerning C3 and C4 and you may also add here Tütken et al., 2006 as well as Tütken and Venneman, 2009 P 5202, L 23: you may add aside Sr and Pb also Nd and the reference Tütken et al., in press P 5202, L 29: You may refer here also to the Bone Diagenesis special issue in Palaeo3 that is in press. P 5203, L 5: remove fossil in front of diagenesis P 5203, L 14: and instead of und P 5203, L 26: lacustrine with c P 5204, L 1: sample with s? P 5204, L 6: Can you give a number here how small in km2 is the average/range of hippopotamid home range size (I think territory is more a politcal term) P 5204, L 14: Please be more specific and say which molars you analyzed, M1, M2 or M3? Always the same molars? Is there any information about the molar eruption sequence? E.g. in humans the first molar starts already mineralizing its enamal at birth, hence can be partly influenced by suckling. P 5206, L 13: specimens with s P 5208, L 22: do you mean indeed <0.07 or >0.07 instead (as you speak of higher ratios for both MgO/P2O5 here a larger sign would make more sense) P 5209, L 20: here you should be more specific, not just stating very low but give the maximum concentrations of the respective element oxides $<$Xwt.% or range x-y wt.% alternatively give the detection limits for the respective oxides. P 5212, L 26: systematic P 5213, L 1: I would erase primeval as this is not a common term for animals P 5215, L 4: Mg is an element that is mobile during diagenesis. Therefore it may well be possible that concentration differences between fossil dentin and cement specimens reflect effects of alteration and not necessarily of habitat. This would only be true if you are sure that original compositions are still preserved. Can you? P 5216, L 13: You say enamel at the EDJ is the least altered to sample, which is plauible and reasonable, however, you also mention U-shaped trace element profiles and in this case the enamel in the central part of the thickness would be the appropriate area to sample to retrieve pristine chemical compositions. P 5216, L 22/23: Why Total with capital T? P 5216, L 26-28: You say that the carbonate content decreases from the EDJ

BGD

8, C2736–C2742, 2011

Interactive Comment

outwards and may compensate for the increase of the total element concentration in the same direction. Can you give numbers to justify this statement mass-balance-wise? How much in wt.% does the CO_3 content decrease? P 5217, L 3: better explain instead of rationalize P 5217, L 18: controlling mechanisms P 5218, L 14: unlikely instead of hard to exist P 5218, L 22-25: I like this argument and the Na and Cl distribution in enamel should hence be a good indicator of significant enamel alteration. Are there any indications of deviations from the concentration trends, e.g. at the outer enamel rim or in clearly altered enamel areas? P 5219, L 1: instead which demarcate sample origins may be better "which potentially enable to distinguish sample provenance from different sites." P 5219, L 22: continous instead continual P 5219, L 24: plants (plural) P 5219, L 24: somewhere between 4 and 2 Ma P 5220, L 2: White Nile enamel this is not correct enamel specimens from the White Nile P 5220, L 11: dito. Is the Mg concentration of White Nile river water higher than for the Blue and Upper Nile? P 5220, L 18: bedrock instead of country rock P 5220, L 19: Nile River with R P 5221, L 15: porcupines (plural) P 5221, L 29: occurs instead of organized P 5222, L 1: animals (plural) P 5222, L 23: undergoes P 5222, L 26: Mg and Na P 5223, L 7: fan shaped P 5223, L 18-19: are there any data on the enamel fluid composition measured that support this reasonable statement? P 5223, L 25: DAp/Fl to be consistent with the other text P 5223, L 26: consist without s P 5223, L 27-29: What do you mean by recrystallisation? Dissolution and reprecipitation? Why is this necessary to explain the observed element concentration patterns of Na, Mg and Cl, this is not perfectly clear to me. I suggest that you add a sentence explaining the reasoning. Furthermore, is this conclusion of partial dissolution of enamel supported by data from the literature? Does it mean that some of the 14% enamel formed during the secreation phase is dissolved and again precipitated in the maturation phase? If so how much of the preexisting enamel is affected? P 5224, L 10 and 14: DAp/Fl to be consistent with the other text P 5224, L 9, 12: use consistently hydroxyapatite (ones you use hydroxyl apatite) P 5224, L 26: remove point after bracket P 5225, L 15: I would change the order to Na_2O and Cl to be consistent with the order in the bracket afterwards. P 5226, L 13: spatial

BGD
8, C2736–C2742, 2011

instead of areal P 5226, L 19: teeth instead of tooth P 5226, L 22: concentrations (plural) P 5226, L 25: erase worldwide as this is redundant P 5227, L 5: been instead of being P 5227, L 9: structures (plural) P 5227, L 17: may be better despite instead of notwithstanding? P 5227, L 28: compositions (plural) P 5228, L 11: waters (plural) P 5228, L 12: been affected instead of suffered (people suffer)

References: The Journal Palaeo3 is not correctly abbreviated throughout the reference list. It must be Palaeogeogr. Palaeoclimat. Palaeoecol. P 5231, L 20: Quaternary with Q P 5232, L 15: Mitt. Geol.-Paläont. Inst. Univ. Hamburg P 5232, L 16: Annu. Rev. Earth Planet. Sci. should be the right abbreviation? P 5232, L 27: Reviews in Mineralogy and Geochemistry P 5232, L 30: large hyphen between page numbers P 5233, L 31: Échanges Géologiques check also spelling in P 5234, L 18-19 and make it consistent.

References that can be added: Cerling, T.E., Harris, J.M., MacFadden, B.J., Leakey, M.G., Quade, J., Eisenmann, V. and Ehleringer, J.R.: Global vegetation change through the Miocene–Pliocene boundary. Nature, 389, 153–158, 1997. Koch, P.L. 2007. Isotopic study of the biology of modern and fossil vertebrates. – In: Michener, R. & Lajtha, K., eds., Stable isotopes in Ecology and Envrionmental Science: 99–154, 2nd edition, Oxford (Blackwell). Longinelli, A.: Oxygen isotopes in mammal bone phosphate: a new tool for palaeoclimatological and palaeoenvironmental research? Geochim. et Cosmochim. Ac., 48, 385–390, 1984. Tütken, T., Vennemann, T.W, Janz, H. and Heizmann, H.E.P.: Palaeoenvironment and palaeoclimate of the Middle Miocene lake in the Steinheim basin, SW Germany, a reconstruction from C, O, and Sr isotopes of fossil remains. Palaeogeogr. Palaeoclimatol. Palaeoecol., 241, 457–491, 2006 Tütken, T. and Vennemann, T.W.: Stable isotope ecology of Miocene mammals of Sandelzhausen, Germany. Paläontologische Zeitschrift, 83, 207–226, 2009. Tütken, T., Vennemann, T.W. and Pfretzschner, H.-U.: Nd and Sr isotope compositions in modern and fossil bones – proxies for vertebrate provenance and taphonomy. Geochim. Cosmochim. Ac. doi: 10.1016/j.gca.2011.07.024, 2011. Tütken, T. and Vennemann,

T.W.: Fossil bones and teeth: Preservation or alteration of biogenic compositions? Palaeogeogr. Palaeoclimatol. Palaeoecol. doi:10.1016/j.palaeo.2011.06.020, 2011.

Tables: Tables 1-3: Generally you should distinguish/clarifiy better modern and fossil specimens in the data tables by adding (e.g., material) an additional line stating modern and fossil for each tooth Tables 1-3: It would be good if you add the standard deviation (SD) in brackets after the average values as you did in Table 4 Table 1: How did you quantify the water content? Table 2: <0.04 in the line SiO2 (2x) Table 6: CFluid with F, F: coefficient apatite/fluid

Figures: Fig. 1: point instead of comma as decimal separator: 3.5 cm. May be better put in all Fotos a 1 cm scale bar? Fig. 2: You should enlarge Fig. 2 for better visibility as the legend and text in the figures are hard to read. In the caption dentine without e (2x) Fig. 3: Here you should not duplicate the legend 8 times. Why not put the three legend symbols once at the bottom of the figure in a horizontal row? This avoids redundant text and makes the figure less busy. In the same regard I would only state once Modern and Fossil on top of each 4 diagrams. If you work with colours why not lable the modern and fossil symbols and the word modern and fossil differently and accordingly? Fig. 4: again, format this figure larger as some text becomes difficult to read. Also it becomes not clear from the caption and legend which are modern and fossil specimens Fig. 5: Triangular diagram of chemical ... hippopotamid with small h. I would just state ones Enamel and Dentin & Cement on the top of each group of three triangles. Further I would put only ones the legend with the three symbols but in larger font size outside the triangles. This makes the figure less busy and enhances readability. Fig. 6: Again the diagram is to busy with the redundant repetition of the legent each time. Just state Modern, respectively Fossil Hippopotamus Dentin & Cement once for each set of diagrams as well as only the legend in larger sizes one time for each set. Fig. 7: same as for Fig. 5 and 6 Fig. 8: White Nile in legend of B

Interactive comment on Biogeosciences Discuss., 8, 5197, 2011.

BGD

8, C2736–C2742, 2011

Interactive Comment