

Interactive comment on “Boron isotope fractionation during brucite deposition from artificial seawater” by J. Xiao et al.

Anonymous Referee #2

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General comments:

With major interest, I reviewed the manuscript entitled “Boron isotope fractionation during brucite deposition from artificial seawater” by Xiao et al. This original work describes experimental exercises of incorporation of boron species (borate ions and acid borate) and isotopes into brucite ($\text{Mg}(\text{OH})_2$) depositions for various pH conditions. From results of B concentrations, B-isotopes and deduced KD both in brucite depositions and in seawater, 3 models of incorporation are described. Such lab experiments appear well done and exhibited results give new highlights on isotopic fractionation level of boron in marine environment. However I would like address to editor the fact that subject described in this manuscript concerns geochemical experiments which are still far from main subject areas covered by *Climate of the Past* and more particularly

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the scientific topics (website):

development and validation of new proxies, improvements of the precision and accuracy of proxy data; At my knowledge boron isotopes in brucite are not used in paleo-applications and this work I reviewed here clearly doesn't develop a new proxy of pH. The authors mainly justify their study by the fact that brucite can be found in some biogenic carbonates (corals) and in this case could affect the paleo-pH technique based on B-isotopes which is today more and more applied on tropical or more recently on cold sea corals. However and for example through chapter 3.2, partition coefficients KD are compared to oxides or clay minerals (page 897, line 1-2) but never with corals. If you consider corals like Porites (B# 50 ppm of Boron) commonly used in paleo-pH applications, seawater boron concentration (4.5 ppm), and the concentration of boron in the initial artificial seawater used here (45.9 ppm), finally the level of B concentration in brucite depositions described here can be divided by 10. In this case the expected B content would range between 22 and 95 ppm (excluding the aberrant value of 185.9 ppm obtained at pH 9.5). Such range of B concentrations is the same order of magnitude of the common B contents measured in tropical or cold sea corals (40-110 ppm). So as the pH conditions studied here (high pH necessary for brucite precipitation) are clearly higher than pH of 8.1 (ambient seawater value), we think unrealistic the probability to have a significant contribution of brucite in aragonite corals. Only one study (Nothdruff et al., 2005, the second reference cited here is an abstract) qualitatively claimed the presence of brucite microbialite in living scleractinian coral colonies but in this 2005-paper no weight quantification of this presence was made. In addition, various B-isotopes studies in progress (and focused on biogenic corals in order to apply the $\delta^{11}\text{B}$ -pH technique) are tending to show that when $\delta^{11}\text{B}$ values are low, the level of Mg concentrations increases in coral skeletons. Such observations argue against the influence of production of brucite favoring the incorporation of boric acid $\text{B}(\text{OH})_3$ and consequently higher $\delta^{11}\text{B}$ values. And finally the authors admitted themselves that “brucite in older corals was lack due to being dissolved in seawater, where it is undersaturated” (Page 904, Lines 3-4). This sentence reinforces my opinion that this

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study doesn't give us new major highlights concerning B-isotopes in corals as seawater pH proxy and will have a very limited impact for further paleo-pH applications. So I'm convinced that this exploratory study has to be introduced differently and be re-submitted to a scientific journal more dedicated to geochemical processes (Chemical Geology, Marine Geology, etc. . .).

However if the editor finally considers this manuscript acceptable for publication in *Earth and Planetary Science Letters*, moderate revisions has to be made before acceptance.

Detail of these corrections was listed as follows:

Page 888, Line 23: please clear reference Marshall & McCulloch (2002), paper uniquely on Sr/Ca !

Page 889, Line 11: Pokrovsky & Shott (2002) and Pokrovsky & al. (2005): No B-isotope data were discussed in these two papers, again please verify each reference and clear here such references!

Page 889, Line 28: please correct reference "Hemming & Hanson (2005)" to "Hemming et al. (2005)"

Last paragraph of the page 889, Lines 24-29: the authors previously made the hypothesis of potential presence of brucite mainly for corals. Please replace bio-carbonates by corals in this paragraph and the following ones and revise all the text and the reference list here by restricting their number and their works focused on corals. So delete here Sanyal, Hönisch, Palmer, Pearson et al. references dedicated to forams and add the most recent applications on corals:

For example: HEMMING and HANSON, 1992; PELEJERO et al., 2005; LIU et al., 2009; WEI et al., 2009 DOUVILLE et al., 2010;

Hemming N. G. and Hanson G. N. (1992) Boron isotopic composition and concentration in modern marine carbonates. *Geochimica et Cosmochimica Acta* 56, 537-543.

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Liu Y., Liu W., Peng Z., Xiao Y., Wei G., Sun W., He J., Liu G., and Chou C.-L. (2009) Instability of seawater pH in the South China Sea during the mid-late Holocene: Evidence from boron isotopic composition of corals. *Geochimica et Cosmochimica Acta* 73, 1264–1272.

Pelejero C., Calco E., McCulloch M. T., Marshall J. F., Gagan M. K., Lough J. M., and Opdyke B. N. (2005) Preindustrial to Modern interdecadal variability in Coral Reef pH. *Science* 309, 2204-2207.

Wei G., McCulloch M. T., Mortimer G., Deng W., and Xie L. (2009) Evidence for ocean acidification in the Great Barrier Reef of Australia. *Geochimica et Cosmochimica Acta* 73, 2332-2346.

Douville E., Paterne M., Cabioch G., Louvat P., Gaillardet J., Juillet-Leclerc A., and Ayliffe L. K. (2010) Abrupt sea surface pH change at the end of the Younger Dryas in the central sub-equatorial Pacific inferred from boron isotope abundance in corals (Porites). *Biogeosciences* 7, 2445–2459.

Page 892, Lines 1 & 2: for every given value, please delete 0: ex: 9.5 and not 9.50.

Page 892, Line 5: precision of 0.01 for pH measurements is very low and strongly unrealistic (drift and salinity effect) excepted if the authors used spectrophotometric method. In order to confirm this level of precision, the authors are invited to describe the equipment used for pH monitoring.

Page 894, Lines 9 & 14: for each equation, replace symbol \rightarrow by \leftarrow

Page 894, Line 20: please cite Foster's value for seawater: 39.6 +/- 0.2 ‰ (FOSTER et al., 2010)

Foster G. L., Pogge von Strandmann P. A. E., and Rae J. W. B. (2010) The boron and magnesium isotopic composition of seawater. *Geochemistry Geophysics Geosystems* 11(8), Q08015, doi:10.1029/2010GC003201.

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Page 895, Line 24: Palmer et al. (1987) and not Palmer (1987), please modify it!

Page 896, Line 9: Replace studies by study!

Page 896, Line 16: "Fuente" or "de la Fuente"? Please verify!

Page 897, Lines 1-4: The author refers to oxides or clay minerals but not carbonates. . . Please could they really compare KD and B concentration values found here with published values in corals?

Page 898, line 12: delete "s" to carbonate

Page 901, line 23: delete "." before d11Bisw3 and add a space after!

Page 903, line 12: Correct the reference "Hemming et al., 1992" by "Hemming and Hanson, 1992"

Page 911, Table 2: please correct the first line alignment and limit the length of each number. 3 significant characters are sufficient!

Page 913, Figure 1 and the following figures: please systematically indicate the alpha value used (for example Figure 1b for the isotopic fractionation curves), if possible describe their choice of the values used in the text and give references (for example 0.9804, Hönisch et al. 2007, or 0.975 Klosschko et al., 2006, etc. . .)

Pages 919-920, Figures 7-8: 1) the authors would more describe their Figures in captions by identifying for example each peak, for example borate peak as described in the text; 2) In order to easier compare diffractogram changes for brucite (Fig 7b to 7g), each diffractogram needs to have the same size and scales 3). In caption of the Figure 8, please change Fig. "6b" by "7b".

All references of the end list are cited in the text but the authors have to rigorously check if each citing is adapted or not to their text. The credibility of their work depends on this.

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