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

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Dear reviewer, Thank you for your letter and constructive comments concerning our manuscript entitled “Boron isotope fractionation during brucite deposition from artificial seawater”. We have studied your comments carefully and have made big modifications, including grammar, figures, abstract, introduction, and part 5 of our manuscript. We really hope these will meet with your approval. We answer your questions or comments in details in the following texts.

Detailed answer to review: 1. Page 888, Line 23: please clear reference Marshall & McCulloch (2002), paper uniquely on Sr/Ca! Reply: We verified this reference and deleted it in our paper. 2. 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! Reply: We have rewritten the introduction of our manuscript, and this paragraph was deleted.

of seawater pH in the South China Sea during the mid-late Holocene: Evidence from boron isotopic composition of corals, Geochem. Cosmochim. Acta., 73, 1264-1272, 2009. Pelejero, C., Calvo, E., McCulloh, M. T., Marshall, J. F., Gagan, M. K., Lough, J. M., and Opdyke, B. N.: Preindustrial to Modern interdecadal variability in Coral Reef pH, Science, 309, 2204-2207, 2005. Wei, G. J., McCulloch, M. T., Mortimer, G., Deng, W. F., and Xie, L. H.: Evidence for ocean acidification in the Great Barrier Reef of Australia, Geochim. Cosmochim. Acta., 73, 2332-2346, 2009. Douville, E., Paterne, M., Cabioch, G., Louvat, P., Gaillardet, J., Juillet-Leclerc, A., and Ayliffe, L.: 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, 1959-1993, 2010. 4. Page 892, Lines 1 & 2: for every given value, please delete 0: ex: 9.5 and not 9.50. Reply: The decimal digit of pH is kept for one digit. The sentence of “Solutions of NaOH were slowly added to each beaker to achieve the following range of pH values: 9.50, 10.00, 10.50, 11.00, 11.50, 12.00, 12.50, and 13.00.” has been corrected to “Solutions of NaOH were slowly added to each beaker to achieve the following range of pH values: 9.5, 10.0, 10.5, 11.0, 11.5, 12.0, 12.5, and 13.0.” 5. 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. Reply: the pH meter used in our experiment is TP 310 type, made in Beijing Time Power Co. LTD. The precision of it is ±0.02pH, and the instrument resolution of it is 0.01pH. The sentence of “The pH fluctuations were measured by a pH meter with a precision of 0.01.” is revised to “The pH fluctuations were measured by a pH meter with a precision of 0.02.”. 6. Page 894, Lines 9 & 14: for each equation, replace symbol → by ←. Symbol “→” was replaced by “←”. The equation 1 and 2 have been revised to $B(OH)_3 + H_2O \leftrightarrow B(OH)_{3+} + 10B(OH)_{4-}$, respectively. 7. Page 894, Line 20: please cite Foster’s value for seawater: $39.6 \pm 0.2 \permil$ (FOSTER et al., 2010). Reply: We have read this reference and cited it in our paper (Foster, G. L., Pogge von Strandmann, P. A. E.,...).
Åd11Bisw3 calculated using pKa 7.0, 8.0 and 9.0 (Åd4/3=0.975) are 16.08‰, 5.57‰ and -4.74‰ respectively for pH 8, and 18.44‰, 18.21‰ and 15.89‰ respectively for pH 10."

Page 903, line 12: Correct the reference "Hemming et al., 1992" by "Hemming and Hanson, 1992" Reply: the reference "Hemming et al., 1992" has been correct 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!

Reply: the table has been corrected and only 3 significant characters have been kept.

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, Hönsisch et al., 2007, or 0.975 Klochko et al., 2006, etc...)

Reply: Fraction of the major dissolved boron species B(OH)3 and B(OH)4– in seawater was calculated using pKb=8.597 (Dickson, 1990), and the isotopic fractionation curves were calculated using α4-3=0.974 (Klochko et al., 2006). Here we just want to show the major dissolved boron species B(OH)3 and B(OH)4–, and the isotope of them. The adopted α4-3 may be different (0.952-0.984), whatever the α4-3 is, but the shape of the curve is the same. So we chose the α4-3=0.974, the accepted value at present (Klochko et al., 2006). We draw the Figure 1 again, using the Åd11Bseawater= +39.61±0.04 ‰. The new Figure 1 was shown as follows:

Fig. 1. Fraction (a) of the major dissolved boron species B(OH)3 (green curve) and B(OH)4– (red curve) in seawater, using pKb=8.597 (Dickson, 1990) and stable boron isotope fractionation (b) between them as a function of pH, using α4-3=0.974 (Klochko et al., 2006). At low pH (pH<7), virtually all of the boron in seawater is in the B(OH)3 species; conversely, at high pH (pH>10), virtually all of the boron is in the B(OH)4-species (Fig. 1a). Only the B(OH)4– incorporated into the marine bio-carbonates is one of the essential hypotheses for using boron isotopic composition in marine bio-carbonate to reconstruct the paleo-environment (Hemming and Hanson, 1992).

Page 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”. Reply: We have added more information in the Figures captions. In order to easier compare diffractogram changes for brucite, Figure 7 and 8 was drawn again, and the Y-axes were labeled consistently. In caption of “Figure 8”, the Fig. “6b” was corrected to “7c”. The new Figures are shown as follows:

Fig. 7. X-Ray diffractogram of brucite deposited from artificial seawater at different pH values. (a) XRD of brucite standard, (b) XRD of brucite from boron-free artificial seawater at pH 10.0, (c-h) XRD of brucite in our experiments. The brucite peak in our samples is clear compared with brucite standard (Fig. 7a).

Fig. 8. X-Ray diffractogram of brucite deposited from B-containing artificial seawater at pH 9.5. It is a magnified figure of Fig. 7c. Compared with Fig. 7b, the brucite peak in Fig. 8 is clear, with apparent peaks of pinnoite (Mg(BO2)2â ˘A´c3H2O) and szaibelyite (MgBO2(OH)). Judged from quantity and intensity of these peaks, pinnoite content should be higher than that of szaibelyite. As pH increases, the borate peak gradually weakens (Fig. 7c-h). When pH is 12.5 (Fig. 7h), its peak is very close to that of Mg(OH)2 standard (Fig. 7a), though the characteristic pinnoite peak is still observed. 19. 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. Reply: We have checked all the references carefully, and each citing is adapted to our text. 20. The topics of our paper and its further applications for better using of Åd11B and Mg/Ca in corals to reconstruct paleo-marine environment. Reply: In recent years, topics such as the reconstruction of ancient seawater pH using the isotopic composition of boron in corals (or foram), the calculation of the past pCO2, and the influence of these two factors on changes in the ancient climate, have become important issues for the international boron isotope geochemistry community, which is called Åd11B-pH proxy. One of the essential hypothesis of this proxy is that only the B(OH)4– is incorporated into corals or foram. A series of inorganic calcite precipitation
experiments had shown that B(OH)4- is the dominant species incorporated into calcite. However, more and more researches have shown that both B(OH)4- and B(OH)3 incorporated into carbonates. For example, from inorganic carbonates deposition, Xiao et al. (2008) found that both B(OH)4- and B(OH)3 incorporated into carbonates. Klochko et al. (2009) found that both trigonal and tetrahedral coordinated boron existed in biogenic and hydrothermal carbonates. Rollion-Bard et al. (2011) also found that both boron coordination species, but in different proportions depending on the coral microstructure, i.e. centres of calcification versus fibres. They suggested that careful sampling is necessary before performing boron isotopic measurements in deep-sea corals (Rollion-Bard et al., 2011). Inorganic calcite precipitation experiment has been carried out by Xiao et al. (2006a), indicating that the δ11B of inorganic calcium carbonate did not in parallel with the calculated curve of B(OH)4-, but deviated increasingly from the parallel trend as pH increased. When pH was increased to a certain value, the isotopic fractionation factor of boron between precipitation and solution was greater than 1. Xiao et al. (2006a) reasoned that the presence of Mg2+ or other microelements was the main reasons of this observation and concluded that B(OH)3 may incorporate preferentially into brucite. If this is true, the isotopic compositions of boron in corals can be affected by the existence of brucite in corals and the preferential incorporation of B(OH)3 into brucite. If brucite did exist in corals and the brucite-bearing corals were used in 17Ad11B-pH proxy, the measured 17Ad11B of corals and the calculated pH will be higher than the normal value. So the pH equation calculated by the 17Ad11B of corals or form should be rewrite and the 17Ad11B-pH proxy will become more complex. Rollion-Bard et al. (2011) suggested that careful sampling is necessary before performing boron isotopic measurements in deep-sea corals. Researches have shown that brucite did exist in corals (Smith and Delong, 1978; Nothdurft et al., 2005). So if the mechanisms of boron incorporated into brucite is as we expected, (B(OH)3 is incorporated into brucite preferentially), the existence of brucite in corals will bring negative influences to 17Ad11B-pH proxy. Although some adsorption researches have been done on brucite, the influence of brucite on boron isotopic fractionation during adsorption is not researched, so that the mechanism of boron incorporated into brucite is unclear. So experiments on the incorporation of boron during the deposition of brucite from magnesium-free artificial seawater at various pH values were carried out. The incorporation species of boron into brucite, the boron isotope fractionation during deposition of brucite were determined. Our results did confirm that B(OH)3 is incorporated into brucite preferentially, which is entirely different from that into marine bio-carbonates. We think our result will shed some light on the application of 17Ad11B-pH proxy. In addition, the incorporation of Mg into coral skeleton was controlled by varying factors. Fallon et al. (1999) suggested that variations in Mg data in Porites could be a result, not of temperature changes, but of possible micro-scale heterogeneities. Mitsuguchi et al. (2003) reported an Mg/Ca offset and believed to be a result of a biological/metabolic effect. Weinbauer et al. (2000) studied the potential use of Mg as an environmental indicator in the coral Corallium rubrum, founding that overall Mg incorporation was controlled by temperature. But that the physiology within the coral colony may account for differing amounts of Mg among skeletal structures. Recent study (Nothdurft et al., 2005) showed that brucite exists in a wide range of common reef-building coral in Great Barrier Reef and Florida. Elevated Mg concentrations in modern scleractinians may promote the formation of high-Mg calcite cements, as observed in Holocene corals from Heron Reef (Nothdurft et al., 2005), and then causing the deviation from the normal SST-Mg/Ca curves. Sample of brucite-bearing corals could be responsible for anomalies Mg/Ca vs. SST plots in corals (Nothdurft et al., 2005). Thus, it must be cautious to using coral, especially brucite-bearing corals to reconstruct SST. If the variation of Mg/Ca can not be defined exactly, the Mg/Ca-SST proxy would become more complex. So the existence of brucite in corals can bring negative influence on Mg/Ca-SST proxy and 17Ad11B-pH proxy. How to judge the variation of 17Ad11B and Mg/Ca in corals is caused by brucite is important for 17Ad11B-pH proxy and Mg/Ca-SST proxy. Our previous research (Xiao et al., 2006a) showed that when brucite coprecipitate with calcite, 17Ad11B and Mg/Ca of inorganic calcite have good positive relationship, with
correlation coefficients of 0.98 (Fig. 9a). In addition, Mg/Ca was independent of SST, but increased with seawater pH (Fig. 9b), indicating the high Mg/Ca ratio and $\delta^{11}B$ were due to the increasing brucite deposition as seawater pH increases. These observations provide a new method for differentiating the existence of brucite in corals. The weak negative relationship between $\delta^{11}B$ and Mg/Ca in corals in Sanya Bay (Fig. 9b), indicating there is no brucite existing in corals in this area. Thus, the relationship between $\delta^{11}B$ and Mg/Ca in corals can be used to judge the existence of brucite in corals, which should provide a reliable method for better using of $\delta^{11}B$ and Mg/Ca in corals to reconstruct paleo-marine environment. The foramin or other shells was also used to reconstruct the paleo-environment. Because this is the first time of boron isotope in brucite was reported, whether brucite also exists in form or other shells is still unknown. Since the component of corals, foram and shells is almost the same, and the brucite can exist in corals, we have reason to believe that it may also exist in foram or shells. This is the next step of our researches. As far as our paper was concerned, we think it can provide theoretical basis for better using of $\delta^{11}B$ and Mg/Ca in corals to reconstruct paleo-marine environment and will have an affect on them. We believe that our research should belong to the environment change, and $\delta^{11}B$ with Climate of the Past topics. So we submitted it to Climate of the Past firstly. I really hope that these modification can meet with your approval. Thank you very much. Thank you very much. Yours Sincerely, Jun Xiao 5/20/2011

Please also note the supplement to this comment:
http://www.clim-past-discuss.net/7/C587/2011/cpd-7-C587-2011-supplement.zip

Interactive comment on Clim. Past Discuss., 7, 887, 2011.
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