

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 theses 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:

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We have rewritten the introduction of our manuscript, and this paragraph was deleted. 3. Page 889, Line 28: please correct reference “Hemming & Hanson (1995)” to “Hemming et al. (1995)” 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. 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. Reply: This is a good suggestion. Bio-carbonates have been replaced by corals in this paragraph and the following ones. Sanyal, Hönisch, Palmer, Pearson et al. references dedicated to forams have been deleted and the most recent applications on corals have been added. The new cited references are listed as follows: Hemming, N. G. and Hanson, G. N.: Boron isotopic composition and concentration in modern marine carbonates, *Geochim. Cosmochim. Acta.*, 56, 537-543, 1992. Liu, Y., Liu, W. G., Peng, Z. C., Xiao, Y. K., Wei, G. J., Sun, W. D., He, J. F., Liu, G. J., and Chou, C. L.: Instability

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of seawater pH in the South China Sea during the mid-late Holocene: Evidence from boron isotopic composition of corals, *Geochim. Cosmochim. Acta.*, 73, 1264-1272, 2009. Pelejero, C., Calvo, E., McCulloch, 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 $\pm 0.02\text{pH}$, 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 \rightarrow by \leftrightarrow Reply: Symbol " \rightarrow " was replaced by " \leftrightarrow ". The equation 1 and 2 have been revised to $\text{B(OH)}_3 + \text{H}_2\text{O} \leftrightarrow \text{B(OH)}_4^- + \text{H}^+$ and $10\text{B(OH)}_3 + 11\text{B(OH)}_4^- \leftrightarrow 11\text{B(OH)}_3 + 10\text{B(OH)}_4^-$, respectively.

7. Page 894, Line 20: please cite Foster's value for seawater: $39.6 \pm 0.2 \text{‰}$ (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.,

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and Rae, J. W. B.: Boron and magnesium isotopic composition of seawater, *Geochem. Geophys. Geos.*, 11, Q08015, doi:10.1029/2010GC003201, 2010.). The $\delta^{11}\text{B}$ of seawater has been revised to $+39.61 \pm 0.04 \text{‰}$. Page 895, Line 24: Palmer et al. (1987) and not Palmer (1987), please modify it! Reply: Palmer (1987) has been modified to Palmer et al. (1987).

9. Page 896, Line 9: Replace studies by study! Reply: "studies" has been corrected to "study". The sentence of "In the studies of Xu and Ye (1997), the point of zero charge (PZC) of brucite is close to 11.9, which approximates to the inflexion point (pH 12) in our experiment." is revised to "In the study of Xu and Ye (1997), the point of zero charge (PZC) of brucite is close to 11.9, which approximates to the inflexion point (pH 12) in our experiment".

10. Page 896, Line 16: "Fuente" or "de la Fuente"? Please verify!" Reply: We checked the reference and verified "Fuente" to "de la Fuente".

11. 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? Reply: Boron concentrations show a variation from 49 to 58 ppm in the recent corals, and from 39 to 52 ppm in ancient corals (Gaillardet and Allègre, 1995), from 51.4 to 79.7 ppm (Vengosh et al., 1991), from 39 to 60 ppm (Liu et al., 2009), and from 50.2 to 117.5 ppm (Xiao et al., 2006b). So the boron concentration in corals varies from 39 to 117.5 ppm. If 4.5 ppm of the seawater boron concentration is used, the K_d between coral and seawater varies from 8.7 to 26.1. In our experiments, 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 and the K_d is the same order of magnitude of the common B contents measured in corals (39-117.5 ppm). We have added this compare in our rectified paper.

12. Page 898, line 12: delete "s" to carbonate. Reply: the "carbonates" has been corrected to "carbonate".

13. Page 901, line 23: delete "." before $\delta^{11}\text{B}$ and add a space after! Reply: the "." before $\delta^{11}\text{B}$ has been deleted and a space has been added after $\delta^{11}\text{B}$. This sentence has been corrected to "For example, the

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$\delta^{11}\text{B}$ calculated using pK_a 7.0, 8.0 and 9.0 ($\alpha_{4/3}=0.975$) are 16.08‰, 5.57‰ and -4.74‰ respectively for pH 8, and 18.44‰, 18.21‰ and 15.89‰ respectively for pH 10.” 14. 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”. 15. 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. 16. 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...) Reply : Fraction of the major dissolved boron species $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ in seawater was calculated using $\text{pK}_b=8.597$ (Dickson, 1990), and the isotopic fractionation curves were calculated using $\alpha_{4/3}=0.974$ (Klochko et al., 2006). Here we just want to show the major dissolved boron species $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$, and the isotope of them. The adopted $\alpha_{4/3}$ may be different (0.952-0.984), whatever the $\alpha_{4/3}$ is, but the shape of the curve is the same. So we chose the $\alpha_{4/3}=0.974$, the accepted value at present (Klochko et al., 2006). We draw the Figure 1 again, using the $\delta^{11}\text{B}_{\text{seawater}} = +39.61 \pm 0.04$ ‰. The new Figure 1 was shown as follows:

Fig. 1. Fraction (a) of the major dissolved boron species $\text{B}(\text{OH})_3$ (green curve) and $\text{B}(\text{OH})_4^-$ (red curve) in seawater, using $\text{pK}_b=8.597$ (Dickson, 1990) and stable boron isotope fractionation (b) between them as a function of pH, using $\alpha_{4/3}=0.974$ (Klochko et al., 2006). At low pH ($\text{pH}<7$), virtually all of the boron in seawater is in the $\text{B}(\text{OH})_3$ species; conversely, at high pH ($\text{pH}>10$), virtually all of the boron is in the $\text{B}(\text{OH})_4^-$ species (Fig. 1a). Only the $\text{B}(\text{OH})_4^-$ 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). 17. 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

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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 ($\text{Mg}(\text{BO}_2)_2 \cdot 3\text{H}_2\text{O}$) and szaibelyite ($\text{MgBO}_2(\text{OH})$). 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 $\text{Mg}(\text{OH})_2$ 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 $\delta^{11}\text{B}$ 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 pCO_2 , 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 $\delta^{11}\text{B}$ -pH proxy. One of the essential hypothesis of this proxy is that only the $\text{B}(\text{OH})_4^-$ is incorporated into corals or foram. A series of inorganic calcite precipitation

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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 $\delta^{11}B$ 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 Mg^{2+} 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 $\delta^{11}B$ -pH proxy, the measured $\delta^{11}B$ of corals and the calculated pH will be higher than the normal value. So the pH equation calculated by the $\delta^{11}B$ of corals or form should be rewrite and the $\delta^{11}B$ -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 $\delta^{11}B$ -pH proxy. Although some adsorption researches have been done on brucite, the influence of brucite on boron

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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 $\delta^{11}B$ -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 *Coralium 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 $\delta^{11}B$ -pH proxy. How to judge the variation of $\delta^{11}B$ and Mg/Ca in corals is caused by brucite is important for $\delta^{11}B$ -pH proxy and Mg/Ca-SST proxy. Our previous research (Xiao et al., 2006a) showed that when brucite coprecipitate with calcite, $\delta^{11}B$ and Mg/Ca of inorganic calcite have good positive relationship, with

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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 $\delta^{11}\text{B}$ 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 $\delta^{11}\text{B}$ 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 $\delta^{11}\text{B}$ 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 $\delta^{11}\text{B}$ and Mg/Ca in corals to reconstruct paleo-marine environment. The foram 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 foram 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 us researches. As far as our paper was concerned, we think it can provide theoretical basis for better using of $\delta^{11}\text{B}$ 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 $\delta^{11}\text{B}$ with Climate of the Past topics. So we submitted it to Climate of the Past firstly. I really hope that theses 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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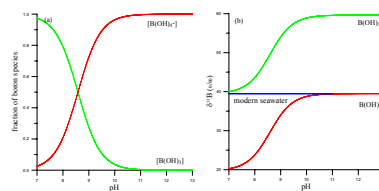


Fig. 1. Fraction (a) of the major dissolved boron species B(OH)_3 (green curve) and B(OH)_4^- (red curve) in seawater, using $pK_a=8.597$ (Dickson, 1990) and stable boron isotope fractionation (b) between them as a function of pH, using $\alpha_{\text{B}}=0.974$ (Kishchko et al., 2006). At low pH (pH<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)_3 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).

Fig. 1.

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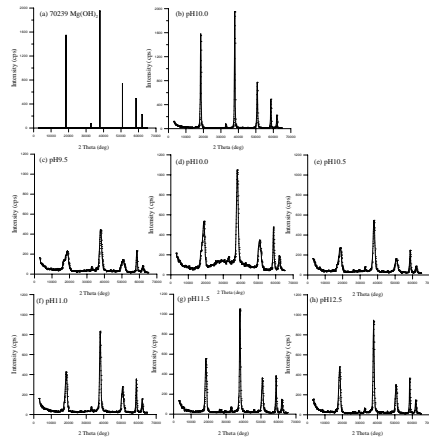


Fig. 7. X-Ray diffractogram of brucite deposited from artificial seawater at different pH values. (a) XRD of brucite standard, (b) XRD of brucite from boron-free artificial seawater at pH 10.0, (c-h) XRD of brucite in our experiments. The brucite peak in our samples is clear compared with brucite standard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

Fig. 2.

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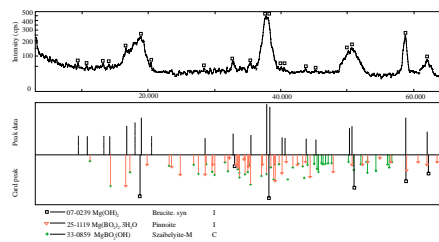


Fig. 8. X-Ray diffractogram of brucite deposited from B-containing artificial seawater at pH 9.5. It is a magnified figure of Fig. 7c. Compared with Fig. 7b, the brucite peak in Fig. 8 is clear, with apparent peaks of pinnoite ($Mg(BO_3)_2 \cdot 3H_2O$) and szabolyite ($MgBO_3(OH)$). Judged from quantity and intensity of these peaks, pinnoite content should be higher than that of szabolyite. 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.

Fig. 3.

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