

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

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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  $p\text{CO}_2$ , 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 experiments had shown that  $\text{B}(\text{OH})_4^-$  is the dominant species incorporated into calcite. However, more and more researches have shown that both  $\text{B}(\text{OH})_4^-$  and  $\text{B}(\text{OH})_3$  incorporated into carbonates. For example, from inorganic carbonates deposition, Xiao et al. (2008) found that both  $\text{B}(\text{OH})_4^-$  and  $\text{B}(\text{OH})_3$  incorporated into

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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  $\delta^{11}\text{B}$  of inorganic calcium carbonate did not in parallel with the calculated curve of  $\text{B}(\text{OH})_4^-$ , 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  $\text{Mg}^{2+}$  or other microelements was the main reasons of this observation and concluded that  $\text{B}(\text{OH})_3$  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  $\text{B}(\text{OH})_3$  into brucite. If brucite did exist in corals and the brucite-bearing corals were used in  $\delta^{11}\text{B}$ -pH proxy, the measured  $\delta^{11}\text{B}$  of corals and the calculated pH will be higher than the normal value. So the pH equation calculated by the  $\delta^{11}\text{B}$  of corals or form should be rewrite and the  $\delta^{11}\text{B}$ -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, ( $\text{B}(\text{OH})_3$  is incorporated into brucite preferentially), the existence of brucite in corals will bring negative influences to  $\delta^{11}\text{B}$ -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

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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 *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  $\delta^{11}B$ -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 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. Thus, the relationship between  $\delta^{11}B$  and Mg/Ca

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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.

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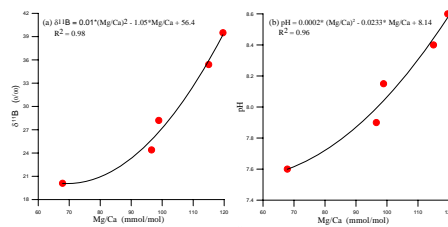
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Fig. 9 Relationship (a) between Mg/Ca and  $\delta^{11}\text{B}$  in inorganic calcite, and (b) between Mg/Ca and seawater pH (Xiao et al., 2006a). The Mg/Ca was positive with  $\delta^{11}\text{B}$  in inorganic calcite and increased with seawater pH, which provide a new method for differentiating the existence of brucite in corals.

Fig. 1.

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