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Interactive comment on "A novel paleo-bleaching proxy using boron isotopes and high-resolution laser ablation to reconstruct coral bleaching events" *by* G. Dishon et al.

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Anonymous Referee #2

This is an interesting study that investigates the potential of using boron isotopes to detect coral bleaching events. Further the authors examined past published coral 11B records to see if such events were obvious in the paleo-record. This may be an important contribution to a big problem. The rationale for pursuing such a study is obvious and the authors are on track in this regard.

Major issues:

1. **However, before this study should be considered for publication, the authors need to connect the dots mechanistically between decreasing 11B values and bleaching events. In other words, the authors do not link how bleaching events could actually lower coral 11B values. Correlation does not equal causation. Convince the readers by developing a mechanistic relationship between these two variables. The lack of a mechanistic model is a major weakness of the current manuscript.**

The mechanism by which d11B is related to pH was previously established by others (e.g. (Hemming and Hanson, 1992)) and here only shortly outlined: "*Skeletal d11B values are used for paleo pH reconstruction as they correlate with surrounding ambient waters' pH levels. This correlation is based on the assumptions (1) that internal pH (i.e. where calcification takes place) is correlated with ambient pH, and (2) that in seawater only one B species, namely the isotopically lighter borate, is reacting with the aragonitic surface of corals rather than the isotopically heavier boric acid. The B species distribution and the d11B of the B species are pH dependent. If borate represents the only source of B in the skeletons of corals, than its d11B is equal to the d11B of the coral. Therefore, the d11B of corals is utilized as a proxy of ocean pH levels at the time of calcification."* (Section 1.2).

In this paper, we use this previously established pH proxy, but suggest that physiological changes in coral-zooxanthellae symbiosis result in pH changes inside the coral (photosynthesis elevates the pH of the environment where calcification occurs). These internal pH changes are unrelated to ambient (bulk) sea water pH and can be recorded as $d^{11}B$ changes measured by high resolution LA-MC-ICP-MS. Coral bleaching is an extreme case of physiological change, where photosynthesis abruptly ceased and therefore hypothesized to leave a pronounced footprint on $d^{11}B$ records. Overall, this simple, straight-forward approach is illustrated in the attached diagram (Figure 1).

2. **Additionally, 11B values are largely controlled by pHsw (as the authors**

note) but they are also influenced by seawater temperature and salinity. This needs to be addressed in the introduction. Hence, calculations of paleo pH based on 11B records need to estimate both salinity and seawater temperature. This also needs to be carefully considered. Outside of the experiment described here, how can the authors be sure that decreases in 11B coral values are solely related to bleaching effects rather than changes in seawater temperature, pH, or salinity?

Previous studies have shown no significant effect of food supply and light intensity (in a range between 200-1210 uE) on $d^{11}B$ and no effect, or less than 1 permil **increase**, in $d^{11}B$ as a result of temperature elevation (22-28 C deg) and depth (1-8 m) manipulations (Dissard et al., 2012; Hönisch et al., 2004; Reynaud et al., 2004)). The effect of all of these parameters on $d^{11}B$ remains within the "normal" (i.e. non-bleached) vital effect, much smaller than the boron-bleaching signature of $<$-1.5 permil.

Since our proposed proxy relies on the $d^{11}B$-pHsw relationship, it is indeed not trivial to tell whether a low $d^{11}B$ is indicative of low pH or coral bleaching. Here we suggest that coral bleaching can be traced by examining the relative $d^{11}B$ change from background values together with relevant climate proxies, to get to the most likely answer. It's important to stress here that interpreting a $d^{11}B$ drop of more than 1.5 permil as an ocean water pH decrease would yield a drop of more than 0.2 pH units (comparable to a glacial-interglacial change!), which we conclude, in most cases is not realistic. Nevertheless, such pH drops or those of an even greater magnitude occur virtually instantaneous when keeping a coral in the dark or bleached state (i.e. no photosynthesis (Al-Horani, 2005; Venn et al., 2011). We also refer to Rink et al. (1998), showing a pH change of more than 0.8 units in the ambient environment of a planktonic foraminifer, depending on whether the light (i.e. symbiont photosynthesis) was on or off.

Following the advice of Reviewer #2, we added a section in the introduction discussing the effects of factors other than pH on $d^{11}B$.

BGD

12, C4799–C4805, 2015

3. **The literature review on the controls on 11B in corals is not fully developed. Other proxies are also used to construct pCO2 of the atmosphere beyond 11B and ice core air bubbles (e.g., paleosols and plant proxies). This needs to be addressed more comprehensively.**

Among the methods commonly used to evaluate pHsw/pCO2 atm, those that are most relevant for the time frame (0-150,000 yr) and habitat (marine) of our topic are the ice trapped air bubbles and Boron marine carbonate analyzes. We also added a brief summary of other techniques with a reference to a recent review paper (Wang et al., 2014) into section 1.2.

4. **Please report the error associated with the measurements in the methods section. Currently they are only reported in the figure captions. What is the standard to sample ratio?**

The error associated with $d^{11}B$ measurements was less than 0.30 ppt (SE), smaller than the size of symbols on the plot. We now added the error report also to the methods section. The sample to standard ratio of 11B/10B signal was 1.017 on average**.**

5. **The authors "cleaned" the organics using NaClO, but that would only remove organics at the surface. How do the organics in the carbonate matrix affect the 11B measurements? Are the authors completely confident that they are only measuring boron from carbonate and not organics within the carbonate matrix? How deep does the laser penetrate the surface of the coral?**

Before NaClO cleaning, corals were sliced to thin (5̃mm) cross sections and then cleaned. After cleaning, Laser was used to ablate the coral skeleton on chosen spots along growth axis. We estimate the depth of the laser crater to be ~20um. Although we cannot exclude the possibility that all organics were completely removed to this depth, we argue that if not all organics were removed, the situation would be comparable for the whole transect.

6. **What about diagenesis? Could diagenesis be partly responsible for the 11B changes in the paleo-record? How can the authors rule this out?**

Diagenesis may pose a challenge when measuring ancient corals. As for the ancient bleaching events suggested by us, (Liu et al., 2009) reported no diagenesis contamination in their record (checked by X-ray diffraction analysis and SEM examination). Douville et al. (2010) didn't report any diagenesis checks and Gaillardet and Allegre (1995) even stated that their findings might be the outcome of diagenesis processes. In the scope of this manuscript we treat Douville (2010) and Gaillardet and Allegre (1995) as pH dependant records. Nevertheless, following the reviewer's important comment, we added a "disclaimer" as for possilbe diagenetic effects in the suspected bleaching event 11.5 Kyr BP.

For future studies, a careful examination of diagenetic alteration and/or the use of laser ablation techniques for recognition and specific sampling of unaltered material (suggested by Hathorne et al., 2011) is recommended.

Minor issues:

7. **The pictures alongside of Figure 1 are too small to see.**

Pictures on Fig. 1 are only to get a rough feeling of corals' color and cannot be any larger. We added a new figure (Fig. S1) in the supporting information file.

8. **Line 20, page 8134- better to say kinetic effects apparently do not interfere with isotopic equilibrium during calcification.**

Corrected

9. **The word correlation (see line 6, page 8135) is used too often in this manuscript. I suggest using relationship instead.**

We changed most of the "correlations" to other phrases such as association/ relation/ link. . .

10. **Do not use lighter or heavier. Use lower or higher 11B values. See the Sharp textbook for the many reasons why.**

Corrected

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