Biogeosciences Discuss., 9, C2062–C2067, 2012
www.biogeosciences-discuss.net/9/C2062/2012/

Biogeosciences Discussions

Interactive comment on "Light and temperature effect on δ^{11}B and B/Ca ratios of the zooxanthellate coral *Acropora* sp.: results from culturing experiments" *by* D. Dissard et al.

Anonymous Referee #1

Received and published: 21 June 2012

Dissard et al. cultured Acropora sp. under 3 different temperatures and two different light conditions, to study the effects of temperature and light on the boron isotope (d11B) and B/Ca proxies. They observe increasing d11B and B/Ca at higher temperatures, which they interpret as a temperature effect on both proxies, and observe relatively lower d11B and B/Ca at 400 μE compared to 200 μE. This data set is interesting but the data presentation and evaluation shows several shortcomings.

First, in order to gauge the reproducibility of the geochemical analyses, it would need to be stated whether replicate analyses were splits of homogenized coral samples or true replicates of separate coral nubbins. Table 3 provides average data of replicates and 1

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

standard deviation of those averages. Those uncertainties are often much larger than the stated external uncertainty of d11B measurements (0.25‰, and given the low data density, they should be given as 2 sd, or better the actual data of individual replicates should be provided. Once that is done, I suspect it will become clear that the supposed temperature effect on d11B is not significant. However, even if there was a true difference in d11B between the different temperature treatments, the authors should consider the temperature-dependent changes in the pKB value, which decreases from 8.63 at 22°C to 8.56 at 28°C. They reflect on this briefly in Section 4.2.1 but only to generally compare the apparent pH offset between the site of calcification and seawater-pH. Because that pH-offset is essentially constant between the different treatments (0.36, 0.40, 0.39 and 0.33, 0.36, 0.35 at 200 and 400 μE, respectively), those values seem incompatible with a significant temperature effect as suggested by the authors. In addition, a more rigorous evaluation of temperature effects on aqueous boron fractionation should be performed. For instance. Zeebe (GCA, 2005) and Hönisch et al. (EPSL, 2008) provide guidelines for how this could be done. The actual data could then be evaluated within the framework of those theoretical considerations.

Similar problems exist for the B/Ca data: The individual data should be provided in Table 3 and the 1sd uncertainties appear too small: In section 2.4.2 the analytical uncertainty for B/Ca analyses has been reported as 3% at 2sigma. Translating that to the data shown in Table 3, the uncertainty of each sample should be at least 14 μmol/mol, and that does not yet include any difference between replicates. Comparing this to Figure 5 then suggests that the difference between 400 and 200 μE in B/Ca is not significant. Given that only 3 conditions were analyzed, all replicate data should be shown similar to d11B data (see above). The discussion of the B/Ca data also shows shortcomings: The introduction presents the basis for this proxy as proposed by Hemming & Hanson (GCA, 1992, not Vengosh et al. 1991!). Based on prior studies of B/Ca in marine carbonates, it is clear that borate ion is important for B/Ca, and either carbonate ion or bicarbonate ion. While it should be noted that the control on B/Ca in benthic foraminifers is Delta carbonate ion (i.e. the difference between actual carbon-

BGD

9, C2062–C2067, 2012

Interactive Comment

ate ion and carbonate ion at saturation in seawater, and not simply carbonate ion as erroneously presented on page 5973 (line 24)), the authors forgot again to consider changes in borate ion under different temperature conditions. This is difficult to assess at this point because the carbonate chemistry analyses shown in Table 1 cannot reflect the carbonate chemistry under the respective culture conditions but must have been done at a constant temperature. Because pH decreases with temperature, it is not possible that alkalinity and pH were both constant at 2536 μmol/kg and 8.02 for all temperature conditions. Because alkalinity was determined constant and alkalinity is independent of temperature, pH thus must have differed between the actual culture conditions. A simple estimate using given alkalinity and assuming DIC=2200 μmol/kg, gives a pH of 8.11 at 22°C and 8.02 at 28°C. This difference needs to be considered for all estimates of borate, carbonate and bicarbonate ion, to which the authors should compare their data. It is also obviously not correct that the measurements were performed "in the culture tanks". Alkalinity and pH samples may have been taken from the culture tanks but measurement must have been done at a different temperature in a vessel outside of the tank. Alkalinity titration in the tank is simply not possible.

In general, nowhere in the manuscript is any mention of cleaning the coral material before preparation for analysis. Biogenic carbonates, and in particular cultured corals, are loaded with organic matter, which itself can contain significant amounts of boron. Was really no oxidative cleaning protocol applied to remove that organic matter? This is hard to believe but if correct, would jeopardize all analyses. This information needs to be provided to gauge the data quality.

More specific comments:

Introduction: There is no experimental indication that "significant concentrations of boric acid" are incorporated in biogenic carbonates. This is later on better described but NMR analyses can only distinguish between trigonal and tetrahedral coordination in the carbonate but cannot determine which species was adsorbed in the first place. This has been obvious since Sen et al. (American Mineralogist, 1994) performed phase

BGD

9, C2062–C2067, 2012

transformations from aragonite to calcite and observed coordination changes of B in CaCO3 without concomitant changes in d11B.

Section 2.1: A seawater renewal rate of 5 times per day may actually not be that high. I am surprised the temperature should not have varied over a light/dark cycle, and in particular between the two different light treatments. If the temperature was controlled in the external tanks rather than the illuminated culture tanks, as appears to be indicated in Section 2.2, then those temperature conditions may not actually apply to what the corals in their tanks have experienced. This could have significant consequences for the geochemical data and their interpretation and needs to be assessed.

The statistical tests presented in section 3.2 and 3.3. should be performed with individual data measured on the replicates, not their averages.

It should also be acknowledged that the B concentrations measured by Hönisch et al. (2004) were done by isotope dilution and not by MC-ICP-MS. Those measurements are not comparable in precision to ICP-MS analyses and should be considered very carefully. In particular the estimated decrease in B/Ca with pH seems questionable.

Section 4.1: This section describes the data and then "interprets" them as, e.g., a temperature effect (e.g., line 22-25). Simple data description is not an interpretation, which would include assessments of why patterns change as they do. This entire section could be shortened significantly as it does not find anything new but is only used to confirm that changes in physiological parameters are consistent with earlier studies.

Section 4.2.1: It should be noted that Venn et al. (2011) did not perform any temperature experiments, so all the authors refer to in this comparison is the overall offset in pH compared to the site of calcification. The explanation of daily (i.e. day/night) cycles in pH variations at the site of calcification and their effect on the integrated geochemical signals should be expanded.

BGD

9, C2062–C2067, 2012

Section 4.2.2: The presentation of carbonate chemistry at the site of calcification in this section is confusing and seems to suffer from chicken-and-egg problems: Of the three mechanisms described herein, 1 and 3 are essentially the same, as they argue for CO2 uptake by photosynthesis/dinoflagellates. This effect thus should result in higher pH at the site of calcification, higher CO3=, and thus improved conditions for calcification. If the proton and CO2 concentration were high at the site of calcification, CO3= and pH would have to be low and calcification would not be favored. This interpretation thus cannot explain the observed data. This problem is extended in Section 4.2.3, where the authors argue once around the observed pH values and once around the calcification data, but they cannot bring the two observations in line. Here again it would be interesting to see the true d11B data spread of individual analyses, to see if the offset is truly significant. I would also be curious if all geochemical data were measured in the same analytical session, or if an analytical bias could be involved. I am also having a hard time putting much faith into the statistical significance of the temperature difference between 22 and 28°C. Given that only 3 conditions were analyzed and no explanation can be given why this effect should be different between 22-25°C and 25-28°C, it would be better to consider the entire temperature range rather than only the difference between 22 and 25°C. In summary, I am not convinced that this temperature effect is in fact non-linear. A decrease in aqueous fractionation would be consistent with thermodynamic theory but only if the temperature effect were consistent, not non-linear. Again, the actual pH seen by the corals in the tanks needs to be taken into account to evaluate the observed differences.

Page 5989/line 20ff: If the enzyme system worked at a constant rate above a certain threshold value, that would not explain higher calcification rates, as observed in this study. The argument is therefore flawed.

Section 4.3.1: Considering true analytical uncertainties, the B/Ca data obtained under the two different light conditions are essentially the same.

Section 4.3.2/line 14: the light conditions would not have varied between the culture

BGD

9, C2062–C2067, 2012

Interactive Comment

conditions, or were the experiments done outside? As described above, the pH and temperature dependent changes in borate concentration need to be taken into account for the correct evaluation of borate to carbonate species variations. The comment on the debate on temperature effects on B/Ca in planktic foraminifers needs to be either expanded or deleted. Also, references should be provided. Culture experiments with planktic foraminifers have already been performed (Allen et al., 2011, EPSL) and did not reveal a temperature effect on B/Ca.

Section 4.3.3: Here again the effect of variable culture water pH and temperature on B/Ca need to be removed before comparison with other data is possible.

Section 4.3.4: The presentation of the recovery data omits important data. In Figure 4 the authors must have assumed that corals record pH at the site of calcification after Klochko and thus placed their data onto the d11B of borate curve. However, there is some inconsistency in this exercise because following that line of argument, all 5 data should fall on the solid line, and not some on the solid and some on the dashed line. A crossplot of this pH estimate with the B/Ca data (using data provided in Table 3) shows that there is no significant correlation between the two parameters. This is an interesting piece of information, as it either reflects on the assumption that pH (or some related carbonate parameter) is the unifying parameter between both proxies, or on the data quality. Again, individual analyses data should be provided for all data collected in this study. There is some agreement between B/Ca and d11B in that the data are overall lower compared to phase 2 data but the crossplot does not show much consistent behavior beyond this.

In summary, the data set is interesting but shortcomings in the culture procedures, cleaning, data presentation and evaluation need to be addressed. The data evaluation should be much more rigorous and include thermodynamic considerations in addition to the simple comparisons with environmental parameters.

Interactive comment on Biogeosciences Discuss., 9, 5969, 2012.