Biogeosciences Discussions

Biogeosciences Discuss., referee comment RC1
https://doi.org/10.5194/bg-2021-21-RC1, 2021

Comment on bg-2021-21

Anonymous Referee #1

Referee comment on "Growth rate rather than temperature affects the B/Ca ratio in the calcareous red alga *Lithothamnion corallioides*" by Giulia Piazza et al., Biogeosciences Discuss., https://doi.org/10.5194/bg-2021-21-RC1, 2021

Review for Biogeosciences

Piazza et al., : Growth rate rather than temperature affects the B/Ca ratio in the calcareous red alga Lithothamnion corallioides

The authors present B/Ca Mg/Ca, Li/Ca and Sr/Ca data measured by LAICPMS in the currently understudied *Lithothamnion corallioides* species of coralline algae. The motivation for the paper is good and I agree, detangling growth rate effects from paleo-proxy capabilities in these elements is important. The geochemical data collected from CA samples in the Med and Atlantic are indeed unique (understudied species) and a useful contribution to the field. They would be well placed in the journal Biogeosciences. However, I am sorry to say that I do not find the findings in this manuscript to support the results and I cannot recommend the manuscript for publication in its current form without revision of the discussion.

I give a list of suggestions for the manuscript to improve readability, however my major concerns regarding the work are:

The authors say in the abstract "We produced the first data on temperature proxies (Mg, Li and Sr/Ca)" but it would be really nice to see more made of these important data. If these results are to be used to establish temperature dependency (or not) on B/Ca, the temperature dependency of Mg Li and Sr must first be convincingly made first. Many papers are cited here that show the correlation between these variables on seasonal cycles, but it has not been established that temperature is the main driver of the incorporation over seasonal growth rate. The use of Li/Ca in particular as a "temperature proxy" requires more consideration. The Darrenougue paper cited does indeed shows that Li/Ca is high in the warm summer months, but it is not clear that this is driven by temperature. Li has a very low partition coefficient, so as growth rates increase during summer kinetics and growth entrapment models would suggest that Li/Ca go up. This

growth rate dependency may mask the Li/Ca temperature effect which some have argued is a negative slope in carbonates and should be ratioed to Mg for reliable temperatures (Anagnostou et al., 2019; Stewart et al., 2020 EPSL; Marriott et al., 2004 EPSL and Chem Geol.). It would be interesting to see where these Li/Mg data fall on calibration lines of Anagnostou et al., 2019 and Stewart et al., 2020 (EPSL). Do they agree with the linear fit of Anagnostou for cultured CCA or the speculative exponential relationship found across all high-Mg calcites suggested in Stewart et al., 2020? The Li/Mg results here (I am estimating as raw Li/Ca ratios were not provided in a table) seem perhaps a little high compared to Anagnostou culture data, but this could be due to analytical offsets that can occur during laser ablation analysis compared to solution chemistry. Do the short or long cells measured offer a better temperature reconstruction? It would be great to see the authors bring this into the discussion and would add to the interpretation of these elemental ratios as being temperature dependent thus permitting their use to unpack competing effects on B/Ca.

Of particular concern, the main finding that growth rate is driving B/Ca is based on a correlation of just 4 data points (figure 9), three of which have very similar growth rates. The lack of variety of environmental conditions and growth rates means that, despite the presentation of p values, the significance of this relationship is highly questionable. I cannot see that the authors are in a position to establish the outright controls on B/Ca with the data collected. The 4 samples presented here, 3 of which are in the Med, simply do not cover a wide enough array of hydrographic conditions to pick these effects apart.

Given the uncertainty on driving factors of all of these elements, not just B, I would recommend the authors take a more explorative approach to their results rather than categorically stating which are temperature dependent. It would be useful to see all elemental data plotted as a time series to see if there are trends along the growth axis and the cyclical nature of each elemental ratio with season. This could be compared to the CA image to show the matching cycles to light and dark banding. It would be great to see these annual banded timeseries matched to gridded SST records for each site (e.g. ERSST https://www.ncdc.noaa.gov/data-access/marineocean-data/extended-reconstructed-sea-surface-temperature-ersst-v5 or HADISST https://www.metoffice.gov.uk/hadobs/hadisst/data/download.html). This would really help to convince the reader about the temperature control on each element.

In short, I would very much like to see these important data published, but with a more measured approach to the discussion.

Minor points

Line 16: “from shallow to deep waters” seems misleading. None of these are truly deep waters. Perhaps “from across the photic zone depths” would be better.

Line 22: “This evidence suggests”

Line 32: pK_B is pressure, temperature, and salinity dependent therefore the value of 8.6 is only applicable to surface waters (c.f. the value in deep waters is 8.8). Be clear that this is not a constant and that this refers to “typical surface seawater conditions”

Line 35: The Klochko value for the fractionation factor is more commonly given in the 1.0272 format.

Line 35: “Seawater isotopic composition δ11Bsw is 39.61‰ (Foster et al., 2010) and varies with the isotopic composition of B(OH)3 and B(OH)4-, both enriched in δ11B with increasing pH (Dickson, 1990).” This sentence is poorly worded. Seawater δ11B does not vary with the isotopic composition of boric acid and borate. Rather the δ11B of seawater is fixed and the 11/10 ratios of boric acid and borate have to change to maintain the fractionation factor as their abundances change with changing seawater pH.

Line 50: It is worth stating that these B/Ca vs CO32- relationships are only empirically derived observations.

Line 52: Paragraph starting “Warming and acidification…” should be the opening of the introduction leading to a statement about proxies for the carbonate system are therefore much needed. The discussion of δ11B and B/Ca (currently starting at line 25) will then follow better.

Line 55: Unclear what is meant by “longevity by indeterminate growth,”. As outlined in the next sentence many specimens have annual growth bands therefore we can determine their growth axis and age.

Line 78: “culture experiment”

Line 80: Suggested rewording: “The factors which influence the B incorporation in CA are therefore still debated.”

Line 88: I think Hetzinger et al., 2011 should be Hetzinger et al., 2009. The 2011 paper is about Ba rather than Mg Li or Sr

Table 1 and 2 could be combined, that way the reader can see how the collection depth compares to the Temperature data. Also strange to have table 2 A and B – all of these columns could be combined into one table. Please consider if all columns are necessary. For example, Lat and Long could be moved into the caption of Fig1. If you have Temp max and min, do you need to spell out the range? Do you even need the range when you have the st. dev? Is standard dev not a better measure of the variability at each site than the range and demonstrates the point about the Atlantic being more variable on its own? It is also strange to present this info in a table and then take up words spelling it all out again in the main text (section 3.1 can be very much shortened).

It would be nice to see all trace metal data tabulated somewhere too.

Table 2 caption. It is not clear what is meant by data "elaboration". Please consider wording here.

Line: 118: "Particularly,…" should read "In particular,…"

Line 121: Suggest rewording "Once its inclusion under the genus *Phymatolithon* was excluded, the Morlaix sample…"

Line 133: Suggest "Element/Ca ratios were calculated for these isotopes,"

Line 133: What about these elemental ratios was "in agreement with Yu et al., (2005) and Darrenougue et al., (2014)"? Presumably Yu and Darrenougue didn't measure these same samples, but did they measure the same standards? Was it the methods that are similar? It is not clear what is mean here.

Fig 2: Please label long and short cells on panel b

Line 140: this method section requires more information. What is the measurement accuracy and precision? NIST 612 was used as an "external standard" (does this mean a bracketing standard?), but were any other reference materials used to demonstrate measurement accuracy (e.g. JCp-1 coral powder pressed as a pellet)? Bracketing with NIST glass for carbonate laser ablation is far from ideal in terms of matrix matching, but others have demonstrated that it can give reasonable results (Fietzke et al., 2010).

Line 150: Suggest: "Carbonate system parameters for each site have also been estimated"

Line 160: suggest: "Growth rates were estimated under light microscope by measuring…"

Section 2.5. Suggest simpler subtitle "Statistical analysis"

Line 178: Lower amplitude seasonal temperature change. The word "excursion" implies an aberration from the norm, this doesn't fit when describing an annual cycle.

Line 179: "site" rather than "one"

Line 189: The pH gradient described here doesn't really exist as described. pH estimates at the Mediterranean sites are all similarly high ~8.13 and less variable than the Atlantic site (~8.06). Similarly for DIC, as this is largely dictating the pH

Fig 3: p values of 2.2e-6 could just be written as $p<0.01$ as the extra decimal places after the 99% offer little additional information to the reader. Also no need to repeat these R and p values in the main text if they are in the figure. Title of "spearman correlation" should be removed as figure titles are redundant with a caption and this info is already in the caption. It this all data or one CA sample? It would be interesting to see how points vary by location. Perhaps colour code the points or use symbols for each site (this could be applied throughout to all figures, including the map, for consistency). Change Y and X of regression lines to Mg/Ca and Li/Ca

Section 3.2 more repetition of mean values that are shown in Figure 4. Consider making the Results section more concise throughout using the information presented in the figures and tables rather than repeating.

Line 216: "areas" rather than "spots" and "within light growth bands" rather than "positioning on"

Box plot figures would make more sense if the sites were ordered Aeg, Elba, Pontian, and then Morlaix so that the Med sites are next to each other and the Atlantic site. Given the similarity of the Med sites hydrographic data effectively two environments are being compared: the Med and the Atlantic.

Line 231: see mainpoint above. It is important to establish which direction Mg, Li, and Sr are expected to change as temperature changes. It remains unclear to what extent these

elements themselves are driven by growth rate and to what extent they are driven by temperature. A full discussion of their partition coefficients to establish their respective response to growth rate is required before temperature effects can be established and used to unpack the effects on B/Ca.

Line 237: "shows" rather than "evidenced"

Line 251: Showed an analogous trend to what? Please be clear here

Section 3.4 these extension rate results should be included in the combined table 1 and 2. It is noteworthy that the growth rate at Pontian was lower despite its similarities in other environmental conditions with the other Med sites.

Line 277 This begs the question how often did light and dark band match Mg/Ca patterns. A figure would be useful to show this matching to convince the reader that there is indeed a Mg/Ca pattern that fits the colour banding.

Figure 9: As with all figures, please identify the sites by colour or data point.

Line 280: consider wording here. Mg/Ca ratios do not go "negative". Suggest high and low

Line 287 to 295: It is not surprising that the ranges in B/Ca measured here using a laser (capable of picking up more heterogeneity within samples) are wider than the bulk carbonate analyses measure by solution ICPMS performed by Anagnostou and Donald. Sure, it might be environmental, but the analytical difference must be acknowledged.

Line 299: I think this statement is rather unsupported. It has been established that Mg data covary with Li and Sr, not that Li and Sr are temperature dependent. This could be growth rate particularly given the statement on line 307 about temperature covarying with irradiance.. Also, again, the use of "deep water" is misplaced.

Line 319: This is also little consensus on the B/Ca effect in biogenic carbonates. New coral culture data by Gagnon et al., 2021 ESPL (see supplement) show that B/Ca increases with carbonate ion when DIC is held constant, and decreases with carbonate ion when pH is constant. This paper also shows a strong negative DIC effect on B/Ca (unlike the inorganic experiments of Uchikawa) however this may be strongly related to scleractinian biocalcification mechanisms and the rate of replenishment of the calcifying fluid with seawater.

Line 321: check the DIC value. I think this should read 2.32 rather than 8.23. Also this value extremely similar to all of the other Med sites and is therefore unlikely to be driving B/Ca. Indeed the lowest DIC site (Morlaix) also has a high B/Ca (>700). This is acknowledged later on, but the statement about DIC causing the high B/Ca at Elba is completely unsupported by the results at the other sites.

Line 333: "suggested" rather than "proved"

Line 343: Similar to my point about the questionable significance of a correlation between just 4 data points, the relationship between B/Ca and ΔT could be considered absent or strongly positively covarying if Elba is considered anomalous. There are just not enough data to say either way. It is also not entirely clear why the magnitude of the seasonal cycle (ΔT) should be correlated to B/Ca and temperature itself not? This needs further explanation.

Line 350: here a "poor correlation with temperature" is mention but it is a poor correlation with the magnitude of the seasonal temperature change that is plotted in fig9. Please change wording here.

Line 354: This ending to the discussion unfairly represents the empirical calibration work that has gone into calibrating the δ11B proxy in CA (e.g. Anagnostou et al., 2019). The controls on B/Ca in corals and foraminifera are also less well known compared to the strong seawater pH control on the δ11B of these carbonates and therefore the use of δ11B should not be discouraged for reconstructing past seawater pH

Line 363: There is no mention of Mg/Ca relationship in with deltaT in the main text, so it is strange to see this in the conclusions. It is again unclear why correlation to seasonal temperature range is important particularly when average Mg/Ca appears to correlate poorly with average temperature at these sites.