

Biogeosciences Discuss., referee comment RC2
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Comment on bg-2021-21

Anonymous Referee #2

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-RC2>, 2021

The present study shows new analytical results of trace element/Ca ratios of calcifying algae living in the Mediterranean Sea measured by using LA-ICPMS. The results are new and worth being published, but there are many logical leap in the manuscript. Thus I recommend the authors thoroughly revise the manuscript. Also, I had a great difficulty reading the manuscript, thus English needs to be thoroughly revised, too.

Major points:

The authors use samples collected from different time intervals (1990–2017), but does not discuss how global warming changed water temperature and how much this consideration influence their discussion.

Similarly, they discuss relationship between B/Ca and pH/DIC, but correction due to anthropogenic CO₂ invasion (ocean acidification) is not considered.

There is no explanation about analytical precision of LA-ICPMS used in this study. I wonder how reliable and reproducible their analysis is?

There is no figure on Mg/Ca variation and its comparison to dark/light growth bands for each sample, which likely aids readers to understand the discussion. For example, the authors argue that the Aegadian sample records 10 years of growth, but the reader can not see this.

The authors argue that Li/Ca and Sr/Ca of CA are temperature proxy, because there is linear relationships between Li/Ca and Mg/Ca as well as between Sr/Ca and Mg/Ca, but I don't agree this. There is no figure supporting a significant correlation between Mg/Ca and temperature. The relationship between Mg/Ca and temperature is a key of the discussions of this manuscript. A box plot in Fig. 4 shows no significant differences among sites (N = 4). Also, there could be a pseudo-correlation between Li/Ca and Sr/Ca with temperature, because many environmental factors vary in the same phasing (e.g., irradiance, temperature, growth rate).

Minor points:

"p" of pK_b and pCO₂ should be italic.

Line 32: What is "normal pH conditions"?

Line 35–36: The notion that "Seawater isotopic composition $\delta^{11}\text{B}_{\text{sw}}$ is 39.61‰ (Foster et al., 2010) and varies with the isotopic composition of B(OH)₃ and B(OH)₄⁻ depend on timescales concerned.

Line 41: The expression that TA and DIC "are closely related to the $\delta^{11}\text{B}$ of the borate" is wired. Yes, DIC and TA is related to pH, and pH can be indirectly estimated from $\delta^{11}\text{B}$ of some kind of calcium carbonate.

The notion that "the boron-to-calcium ratio (B/Ca) is informative about past seawater CO₂ concentrations (Yu and Elderfield, 2007; Yu et al., 2007; Rae et al., 2011)" is only true to foraminifera. As for reef building corals, B/Ca is related to other carbonate parameters (see Holcomb et al., 2016).

Holcomb, M., DeCarlo, T. M., Gaetani, G. A., & McCulloch, M. (2016). Factors affecting B/Ca ratios in synthetic aragonite. *Chemical Geology*, 437, 67–76.
<https://doi.org/10.1016/j.chemgeo.2016.05.007>

Line 58: What is "indeterminate growth". Please be more quantitative. Also, "no ontogenetic trend" of what?

Lines 70–73: I could not understand this line "Achieving the best reliability of geochemical proxies for climate reconstructions is indeed crucial, which drives a growing interest on multiple approaches, by considering multi-proxies for a single environmental factor (D'Olivo et al., 2018; Zinke et al., 2019; Cuny- Guirrec et al., 2019), as well as the influence of multi-factors on a single proxy (Kaczmarek et al., 2016; Donald et al., 2017)."

Line 76: "positive correlations" between what?

Line 77 "B" should be "B/Ca" or "[B]"?

Line 79 "Foslie 1898" should be (*Foslie*)?

Line 78: Is "sea surface temperature (SST)" relevant to this study? Temperature is better here.

Line 83 About "calcifying species". Mg/Ca is a paleo-thermometer with regard to calcifying organisms that have calcite crystal form such as foraminifera and CA. Sr/Ca, not Mg/Ca, is paleo-thermometer in coral skeleton.

Line 82–87: I wonder why the authors don't mention Li/Mg temperature proxy (especially for coral) here, because which is commonly used.

K. Cuny-Guirriec, E. Douville, S. Reynaud, et al., Coral Li/ Mg thermometry: Caveats and constraints, *Chemical Geology*, Volume 523, 30 September 2019, Pages 162-178

Lines 92–95: Please revise these sentences: "In this paper, we measure by LA-ICP-MS for the first time the temperature proxies (Mg/Ca, Sr/Ca, Li/Ca) and B/Ca in the non-geniculated CA Lithothamnion corallioides (P. Crouan & H. Crouan) P. Crouan & H. Crouan 1867 collected from different geographic settings and depths across the Mediterranean Sea and in the Atlantic Ocean."

Line 97: Remove "Here, "

Line 100: Please revise these sentences: "In this paper, we test the B/Ca ratio versus the temperature proxies and the growth rates in order to evaluate their effects on B incorporation, which, indeed, could distort the B signal used for paleoclimate reconstructions."

Line 116–122: Please revise these sentences: "Morphological identification was based on Adey & McKibbin (1970), Irvine & Chamberlain (1994), and other information about maerl species distribution provided by Carro et al. (2014) and Melbourne et al. (2017). The samples selection started from a much wider collection than the one eventually selected for the chemical analyses. Particularly, the Atlantic sample (Morlaix) was used as voucher specimen for the subsequent identification of the Mediterranean samples, since *Phymatolithon* spp. and *L. corallioides* are the major components in the Atlantic maerl (Hall-Spencer et al. 2010; Carro et al., 2014). Hence, once excluded the belonging to the genus *Phymatolithon*, the Morlaix sample identified as *L. corallioides* was used as a reference for the most reliable identification of the other Mediterranean samples."

Line 124: How large "algal branches" were? I guess less than 5 mm from Fig. 2.

Line 125 What is "treated samples"? Does this mean that the samples were maintained for 24h in a resin under the vacuum (drying)?

Line 132: Should be "according to", instead of "in agreement with"?

Line 130 (Section 2.3) I wonder the authors did pre-ablation of CA sample surface? The usage of distilled water instead of MQ water is enough to remove surface contamination? Especially, boron is easily contaminated from the environment.

Lines 144–149: Please revise these sentences: "In the absence of in-situ environmental data, the seawater temperature data have been extracted by at least 11 years of monthly reanalysis spanning 1980-2017 from ORAS5 (Ocean ReAnalysis System 5), at 0.25-degree horizontal resolution (Zuo et al., 2019). The nearest sea point of the three-dimensional numerical grid was considered for each sample location. Details of the time interval considered for each sampling site are shown in Table 2. Minimum, maximum and mean values, as reported in Table 2, refer to the temperature at sampling depth and have been measured on the entire time interval for which the data have been extracted"

Lines 150–158: Please revise these sentences: Carbon data in each sampling site have also been extracted. They were not available in the same time interval of temperature data. Nevertheless, the seasonal variations occurring in the extracted period have allowed the characterization of the sampling sites. Monthly mean seawater pH has been derived by the CMEMS (E.U. Copernicus Marine Service Information) global biogeochemical hindcast spanning 1993-2018, at 0.25-degree horizontal resolution. Monthly means of DIC in 2019 and 2020 have been extracted by CMEMS biogeochemical analysis and forecasts for the Mediterranean Sea, at 0.042-degree horizontal resolution (Salon et al., 2019; Bolzon et al., 2020). In the Atlantic site, monthly means of DIC were derived from CMEMS IBI biogeochemical forecasts, at 0.028-degree horizontal resolution covering the years 2019-2020. Minimum, maximum and mean values of DIC, as reported in Table 2, refer to sampling depth and have been measured on the entire time interval of extraction."

Also, I have a great concern here. Surface seawater DIC is changing over time due to CO₂ invasion from the atmosphere. Thus, the authors need to correct this influence when comparing pH and DIC among sampling sites (Lines 189–192).

Line 191 and Table 2: An more common unit of DIC is $\mu\text{mol/kg}$, not mol/m^3 .

Line 160–161: I wonder why they made estimation of linear growth rate in this manner, because this can be done by using image software such as Image J using Fig. 2b. Is it due to the fact that CA has many "faint bands" and variation of Mg/Ca is more reliable to see summer/winter seasonality?

Line 179: Please explain what " ΔT " stands for in the main text, not in the Table caption.

Lines 181–189: Does the second decimal place in water temperature have any meaning?

Line 208 The word "widest oscillation" sounds wired. Please rephrase it.

Lines 216–217: It's a circular argument, because the authors use variation of Mg/Ca to distinguish light and dark bands.

Lines 233–234: Is there any statistics showing no correlation between B/Ca and temperature?

Line 271–272: Positively correlated, but insignificant, right? (Probably due to a small sample number: $N = 4$)

Lines 288–295: I could not understand this lines. How important the B/Ca range comparison between cultured and naturally obtained (wild) CAs is? There is no mention about correlation between B/Ca and pH/pCO₂/DIC, etc.

Line 297: What does "the preservation state of mineral structures" influence trace element/Ca ratio of CA? Does this mean that they can be altered in a live-caught specimen?

Lines 299–301: I'm not convinced by this argument, because there is no figure supporting a significant correlation between Mg/Ca and temperature. A box plot in Fig. 4 shows no significant differences among sites. Based on a correlation of Mg/Ca with temperature (not shown), the authors argue that "For the first time, we confirmed here the reliability of the temperature proxies Li/Ca and Sr/Ca on a deep-water Mediterranean CA"? I wonder how reliable these proxies as thermometer are. Similarly, there is no evidence that "The results of the statistical analyses on Mg/Ca evidenced a strong relationship with the seawater temperatures extracted from ORAS5 (Table 2), as expected."

Lines 311–313: There could be a pseudo-correlation between Li/Ca and Sr/Ca with temperature, because many environmental factors vary in the same phasing (e.g., irradiance, temperature, growth rate). Classically, Mg/Ca of reef-building corals had been regarded as temperature proxy (now we know it is not). See, for example: Inoue M., Suzuki A., Nohara M., Hibino K. and Kawahata H. (2007) Empirical assessment of coral Sr/Ca and Mg/Ca ratios as climate proxies using colonies grown at different temperatures.

Geoph. Res. Lett. 34, L1261. <https://doi.org/10.1029/2007GL029628>.
B/Ca is also well co-related with Mg/Ca (Fig. 6), but not regarded as temperature proxy, according to the authors.

Line 321: 8.32!?

Line 326: pH and DIC "results"? The authors did not analyze seawater but just extracted data from the database.

Line 351: The title of this paper is based on the fact that there is "a closer relationship with growth rate rather than temperature" even though there is no statistical significance?

Line 356: Does the authors would like to mention possibility of local modification of boron isotopic composition of seawater?