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Discussions

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Interactive comment on "δ^{11}B as monitor of calcification site pH in marine calcifying organisms" *by* Jill N. Sutton et al.

Anonymous Referee #1

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This paper presents the boron isotopic composition of 6 different marine calcifying organisms (both aragonite and calcite), and suggests that divergent 11B values of each species result from different pH values in their calcifying fluid, as these organisms can physiologically regulate the composition of their calcifying fluid. Generally, the results are robust and interesting, but do not offer any new or significant explanation and insights into the current knowledge of 11B of marine carbonates.

My biggest concern for the manuscript is the pH calculation for calcite 11B, for instance the coralline algae, urchin and oyster. The assumption of the 11B-pH calculation is based on that only borate ion enters into the mineral lattice. But as confirmed by recent theoretical calculation (ab initio), and NMR and X-ray spectromicroscopy experiments (Balan et al., 2016, GCA; Branson et al., 2015, EPSL; Mavromatis et al.,

2016, GCA;Noireaux et al., 2015, EPSL), trigonal B also incorporates into the lattice (especially for calcite) to substitute CO_3^{2-} in a large proportion. Therefore, the derived pH from calcite 11B is questionable and may bias the interpretation of the data. I think the authors should mention this in their ms to open the mind of readers that there are other possibilities to interpret marine carbonate 11B.

Moreover, numerous literature works have confirmed that 11B-derived pH reflect the pH of calcifying fluid (or extracellular body fluid) instead of ambient seawater (Allison et al., 2014; Georgiou et al. 2015, PNAS; Trotter et al., 2011, EPSL; McCulloch et al., 2012, 2017; GCA; Heinemann et al., 2012, G3), though most of these results are for aragonitic calcifiers. It's therefore not surprising that boron isotope compositions in different calcifying organisms or even different species are different, since the ability of calcifying organisms to regulate their calcifying fluid pH may vary among taxa. Furthermore, although the calcification mechanism for each calcifier remains largely unknown, a brief introduction of current understanding would be helpful for the readers to understand the relationship between 11B and calcifying fluid pH, and between the internal pH and seawater pH.

Specifically,

Lines 42-43, some of the references cited here are not related to boron isotopes, e.g. Saenger et al., 2013; Zinke et al., 2014.

Lines 46-47 "11B composition of borate in seawater (11BSW; Pagani et al.,2005) " 11Bsw is commonly used to indicate boron isotope composition of seawater other than that of borate. Please modify.

Line 59, "The 11B of modern seawater is 39.61 ± 0.04 ‰ (Foster et al., 2010)", 2SD should be used when reporting a replicated and certified value, so the value should be 39.61± 0.20 ‰ (Foster et al., 2010).

Lines 164-168: The setup of culturing experiment should be illustrated in details in the

Methods and Materials Section, as well as the method to identify and separate the new growth part of each skeleton or shell for isotope measurement.

Lines 168-171 This is a replicate of Section 2.3, and not an important part for the Introduction, so please remove.

Line 279 Is the analytical precision shown here 2SD or SD? Lines 285-286 Please remove this section.

Lines 333-334 "polymorph mineralogy was not found to influence boron isotope fractionation (Noireaux et al. 2015)." This seems to be in contrary to the conclusion of Noireaux et al. 2015 who claim that "Our results indicate that the main controlling factors of 11B are the solution pH and the mineralogy of the precipitated carbonate mineral".

Lines 336-337 "if shell mineralogy was the primary driver of the observed interspecific variation in $\delta11B_{CaCO3}$ compositions – a trend that is not observed". As suggested by Noireaux et al. 2015, both solution pH and mineralogy are important factors controlling 11B in carbonates, differences in calcifying fluid pH may also obscure "this mineralogical trend", especially the underlying calcification mechanisms of each calcifier remain largely unknown. So, I don't think mineralogical influences can be easily excluded.

Lines 368-370 With such high proportion of trigonal B incorporation, the classic 11B-pH equation cannot be used to calculate the pH, as 11Bcarb = 11Bborate is the basic assumption for the calculation.

Line 426 but also mineralogy dependent

Lines 427-432 The premise of using the equation mentioned in the paper to calculate pH by carbonate 11B is that borate ion is the only species that enters into the lattice (for example in aragonite). As suggested by both theoretical calculation and NMR experiment, both boric acid and borate ion exist in the lattice of calcite. Therefore, for those calcite organisms, this 11B-pH equation may not be applicable, and the calculated pH

C3

value may not reliably reflect the pH of calcifying fluid.