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Biogeosciences Discussions

Interactive comment on "A universal carbonate ion effect on stable oxygen isotope ratios in unicellular planktonic calcifying organisms" *by* P. Ziveri et al.

Anonymous Referee #2

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This study shows that the carbonate ion effect on stable isotope fractionation in the carbonate produced by coccolithophorids is similar to that previous observed for planktonic foraminiferal tests. The effect on the oxygen isotopes of calcite cysts produced by dinoflagelates is, however, rather different. This is an important observation and potentially of great use to the paleoclimate reconstruction community. To be able use one single underlying mechanism to explain the carbonate ion effects in planktonic foraminifera, coccolithophorids and dinoflagelate cysts the authors propose that different relative amounts of bicarbonate are pumped into a confined calcifying space. Different relative amounts of species with different isotopic values, not completely equilibrate results in different overall isotopic values for the carbonate precipitated. Whereas such

an isotopic mass balance model is able to explain the observed differences no independent evidence is provided for it's validity. Mathematically looked upon it is also clear that with 3 degrees of freedom it will always be possible to mimic 2 target parameters. To my opinion the provided data is interesting enough to warrant publication. The modeling section, however, still needs an independent target parameter to be convincing. It seems relatively easy to include the carbon isotopes. The carbon isotope data for the carbonates is available from the oxygen isotope analyses. With the d13C of the DIC analyzed (or possibly this has been analyzed already?) such an approach should be rather straightforward. Ideally this could be taken even one step further, but that would probably be beyond the scope of the present manuscript: difference in DIC pumping would affect pH of the calcification space as well. It would be interesting to see whether the B-isotopes are in line with the inferred mechanism. For this manuscript I propose to include the carbon isotopes and add an paragraph in which future work on B-isotopes is advocated.

Minor comments:

Throughout the manuscript: be careful with using "vital effect", this does not refer to all secondary effects influencing proxy relationships, but rather those effects that are related to the impact of the live processes of the organisms involved. This is why it is called "vital", i.e. a live. This should be corrected throughout the manuscript.

P. 7576 Line 5: Add "field studies and" after "relationships derived from" Line 8-9: Delete: "and possibly for developing new biomarkers". Line 13: "suggesting" is not entirely true as this an empirical relationship that is here presented as well. Line 21: In fact the fractionation involved is a-biotic, not biological. Fractionation factors used later in the ms come from a-biotic experiments.

P.7577 Line 11-14: Rephrase this section as dinoflagelate cysts will not be significant for carbonate fluxes. (I guess the authors did not imply this, but it reads a bit awkward) Line 18: is the Stoll and Ziveri 2004 paper truly the first paper showing a link

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between carbonate chemistry and paleoclimate? Please add other refs. Line 18-19: Delete “Among other biomarkers associated to calcite” Sentence would start with “The oxygen. . ..” Line 19: change “sediments” into “fossils” Line 28: change “shallower” into “more gentle”

P.7578 Line 7: add “cyst producing” between “calcareous” and “dinoflagellate” Line 8: change “monitor” in “determine” Line 9: change “In addition” in “Based on” Line 12-14: Rephrase sentence “The applicability etc..” into “This models is subsequently applied to explain. . ..

P.7579 Line 1-4: Please add how much the relative shift is for [HCO3-] and [CO32-], which is more relevant for the subsequent discussion. An 8% shift in DIC seems quite large compared to the overall only 15% change needed to create the experimental range (Line 15, same page). Line 15: CO2 should probably be between square brackets as you refer to its concentration and not DIC

P.7580 Line 2: Is “Stoll et al. 2001” the first paper describing photometrical analyses of DIC?

P.7581 Line 9-10: Delete “equipped with. . ..device).” One Kiel device is enough. Line 19: The regression line is given as “-0.0048±0.02”. This would imply that the relative uncertainty of the regression is rather large (20 times larger than the slope). The uncertainty interval plotted in Fig 1 is also much lower. At line 21 it is even worse “-0.0243±1.74). If these uncertainty intervals are correct (which I suspect they are not) we basically would know nothing. Line 25: delete “anomalously” as it is difficult to call something abnormal when you have only two other slopes to compare to. Line 26: Why would this suggest a “strong biological control” ? That is rather subjective as it depends on the mechanism advocated.

P.7582 Line 2: please add the paper showing the fractionation in the organic precipitates. Line 14: add “and temperature” after “vesicle” Line 14-15: The sentence starting with “We assume” could better start with “Because of the limited size of the vesicles it

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seems reasonable to . . .." Or something similar. Line 16: delete "establishment of the" Line 17: replace [CO32-] by DIC (all carbonate species will be changed to CO32- depending on proton pumping) Line 20: Calcium is supposed to start calcifying as soon as [CO32-]v equals [CO32-]sat, i.e. omega=1. This needs some extra explaining as seawater is already several times oversaturated and its is the inhibition by Mg2+ and PO4 that prevents random calcite precipitation. I guess you mean that after a certain threshold is reached an equilibrium concentration needs to be maintained?

P.7583 Line 4: add "partly" after "will" Line 13: "(f x [CO32-]ext)" should this not rather be the ratio between the carbonate and bicarbonate ion concentrations? Or is this implicit part of f? Please explain. Line 20: add "and to a lesser extend" between "and" and "salinity" Line 21: please explain what cell you are referring here to? Foraminiferal, coccolithoforid?

P. 7584 Line 9: better formulate this the other way around: This slope would require f=0.53 using the proposed model. The shallower slope of . . . and . . . requires a f factor value of 0.24.

From Line 14 onward it becomes somewhat difficult to understand the line of reasoning. As I think I understand now it implies that application of the same model to the dinoflagellate species studied requires an unrealistic value of f=1, which can only be achieved by the dinoflagelate species having less saline water in its calcifying space. This makes no sense to me. What would be the underlying mechanism for this. It would require strong pumping against osmotic pressures and lowering pH also makes it more difficult to calcify as Ca2+ goes down. The simpelest, most straightforward solution would be that the dinoflagellate is showing a different response because it is actually calcifying fundamentally different. I propose to keep the line of reasoning the same as it is for forams and cocco's and add that dinoflagellates behave differently.

P.7585 Line 15: See general comment on using the term "vital". Line 19-End: delete, this is not adding anything to the discussion, but distracts from the main message.

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Figure 2 should be omitted. Everything in this figure is already discussed in the text.

Interactive comment on Biogeosciences Discuss., 8, 7575, 2011.