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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.

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Anonymous Referee #2

We would like to thank referee #2 for the detailed review. We address each comment separately below.

REFEREE #2: The isotopic mass balance model: Mathematically looked upon it is also clear that with 3 degrees of freedom it will always be possible to mimic 2 target parameters.

ANSWER: We have actually 1 degree of freedom, the factor f. The 2 oxygen isotope

fractionation factors (α) are derived from independent measurements by Beck et al. (2005). Also, we have not only 2 target parameters. With 1 degree of freedom (f) we describe the entire function δ18O for the full range of [CO32-]. Hence, with 1 degree of freedom it is possible to mimic all data points for a given species.

REFEREE #2: 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.

ANSWER: The description of the pH at the calcification space requires the kinetics and regulation of the Ca2+ and DIC transporters involved in the pH and Ca2+ homeostasis of the cells. The transporters involved in Ca2+ and DIC transport are mostly unknown let alone their kinetics and regulation. Thus, pH homeostasis is indeed beyond the scope of the present manuscript.

REFEREE #2: For this manuscript I propose to include the carbon isotopes and add an paragraph in which future work on B-isotopes is advocated.

ANSWER: The model approach is based on the assumption that the time required to establish chemical equilibrium is very short compared to the time required to establish isotopic equilibrium. The latter is fulfilled for the oxygen isotopes, but not for the carbon and B-isotopes. As described in the ms, the chemical equilibrium in the carbon dioxide system is obtained after several seconds (approx. 15 s at seawater pH = 8.2 and 25°C, (Zeebe et al., 1999), which is negligible compared with the 1.4 h (calculated using data in Langer et al., 2006) required for the formation of one coccolith. The time to establish δ18O equilibrium, on the other hand, is one order of magnitude higher than the time required for coccolith formation (see table 3.3.9 of (Zeebe and Wolf-Gladrow, 2001)). The time to establish carbon isotopic equilibrium is 17.5 s (Zeebe et al., 1999). Hence, there is only a small difference in the time to establish chemical and isotopic equilibrium for 12C and 13C. The same is true for the boric acid-borate system (95 μs vs. 125 μs, (Zeebe et al., 2001)). Consequently, the model approach presented in this manuscript

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cannot be applied to δ13C and B-isotopes.

Minor comments:

REFEREE #2: 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.

ANSWER: This will be carefully checked and correct when appropriate throughout the manuscript.

REFEREE #2: P. 7576 Line 5: Add “field studies and” after “relationships derived from”

ANSWER: We will do so.

REFEREE #2: Line 8-9: Delete: “and possibly for developing new biomarkers”.

ANSWER: We will do so.

REFEREE #2: Line 13: “suggesting” is not entirely true as this an empirical relationship that is here presented as well.

ANSWER: We have now changed the sentence: “A similar result has previously been reported for planktonic foraminifera, supporting the idea that the [CO32$-$] effect on δ18O is universal for unicellular calcifying planktonic organisms.”

REFEREE #2: Line 21: In fact the fractionation involved is a-biotic, not biological. Fractionation factors used later in the ms come from a-biotic experiments.

ANSWER: The cellular control can facilitate calcite precipitation, but cannot alter the thermodynamic properties of the different phases. The α values characterize the isotopic fractionation between different phases or compounds of the system at thermodynamic equilibrium and are therefore thermodynamic properties defined by T and S. Thus, the α values derived from abiotic experiments can be applied to both abiotic and

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biological calcification.

REFEREE #2: 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)

ANSWER: The sentence at page 7577 Lines 11-14

“Another group of organisms that contributes to pelagic carbonate production is a mono- phyletic lineage of peridiniphycidean dinoflagellates that live in the upper water column where light is available for photosynthesis. During their life cycle they produce cysts that are characterized by the incorporation of calcite in at least one layer of the cyst wall.”

doesn’t not imply that calcareous dinocysts are important contributor to the global CaCO3 export production. The sentence is just stating that calcareous dinocysts are planktonic calcifying organisms contributing to the carbonate production.

REFEREE #2: Line 18: is the Stoll and Ziveri 2004 paper truly the first paper showing a link between carbonate chemistry and paleoclimate? Please add other refs.

ANSWER: We will add the following refs.:

J. Erez, B. Luz, 1983, Experimental paleotemperature equation for planktonic foraminifera, GCA, 47, 6, 1025-1031

M.E. Katz, B.S. Cramer, A. Franzese, B. Hönisch, K. G. Miller, Y. Rosenthal, J. D. Wright, 2010, Traditional and emerging geochemical proxies in foraminifera. The Journal of Foraminiferal Research, 40; 2; 165-192

REFEREE #2: Line 18-19: Delete “Among other biomarkers associated to calcite” Sentence would start with “The oxygen. . ..”

ANSWER: We will do so.

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REFEREE #2: Line 19: change “sediments” into “fossils”

ANSWER: We will change “carbonate sediments” into “carbonate fossils”.

REFEREE #2: Line 28: change “shallower” into “more gentle”

ANSWER: We will do so.

REFEREE #2: 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. . ..

ANSWER: We will follow the above suggestions.

REFEREE #2: P. 7579 Line 15: CO2 should probably be between square brackets as you refer to its concentration and not DIC

ANSWER: Yes.

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

ANSWER: This is the first paper describing exactly the method we used.

REFEREE #2: P.7581, Line 9-10: Delete “equipped with. . ..device).” One Kiel device is enough.

ANSWER: We will do so.

REFEREE #2: P.7581 Line 19: The regression line is given as “-0.0048$\pm$0.02”. This would imply that the relative uncertainty of the regression is rather large (20 times larger than the slope). The uncertainty interval plotted in Fig 1 is also much lower. At line 21 it is even worse “- 0.0243$\pm$1.74). If these uncertainty intervals are correct (which I suspect they are not) we basically would know nothing.

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ANSWER: The regression line is now given as -0.0048 for C. leptoporus and -0.0243 for T. heimii. The 1σ confidence bounds are shown in Figure 1. The uncertainties were not correct.

REFEREE #2: P.7581 Line 25: delete “anomalously” as it is difficult to call something abnormal when you have only two other slopes to compare to.

ANSWER: We will do so.

RREFEREE #2: P.7581 Line 26: Why would this suggest a “strong biological control” ? That is rather subjective as it depends on the mechanism advocated.

ANSWER: We state that there is a strong biological control in d18O since T. heimii shows the largest dissimilarity in δ18O/[CO32$-$] slope between biological and inorganic precipitates

REFEREE 2: P.7582 Line 2: please add the paper showing the fractionation in the organic precipitates.

ANSWER: The term "...biological and ... precipitate“ on P7582 Line 2 is probably misleading, since " biological“ implies "organic precipitates“. We are focusing more on the process. We will replace biological with biogenic.

REFEREE 2: P.7582 Line 14: add “and temperature” after “vesicle”

ANSWER: The statement on isotopic composition of CO32- does not depend on temperature, the sentence is true for all temperatures. Therefore we would like to keep it as is.

REFEREE 2: P.7582 Line 14-15: The sentence starting with “We assume” could better start with “Because of the limited size of the vesicles it seems reasonable to ....” Or something similar.

ANSWER: Our assumption on the carbon species transported into the vesicle does not depend on the size of the vesicle. According to the suggestion of the referee we have

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improved the wording:

“Since at alkaline pH values CO32- is the major carbon source for CaCO3 it is seems reasonable to ... “

REFEREE 2: P.7582 Line 16: delete “establishment of the”

ANSWER: We will do so.

REFEREE 2: P.7582 Line 17: replace [CO32-] by DIC (all carbonate species will be changed to CO32- depending on proton pumping)

ANSWER: This is true that all carbonate species will be changed to CO32-, but HCO3- and CO32- have a different isotopic signature. The mechanism is based on the assumption that two different C pools with different isotopic composition contribute to the CO32- in the vesicle: external CO32- contributing the equilibrium isotopic composition of CO32, whereas the CO32- in the vesicle which is formed via HCO3- conversion to CO32- contributes the equilibrium isotopic composition of HCO3-. Therefore, writing [CO32-] is correct.

P.7582 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.

ANSWER: The suggested mechanism is not based on endocytosis of seawater. Probably, there is a strong fractionation against Mg2+ and PO4 during the intracellular transport of Ca2+ and CO32-. Since the transport mechanism is unknown, we have not taken into account the impact of Mg2+ and PO4 on calcite precipitation.

REFEREE 2: P.7583 Line 4: add “partly” after “will”

ANSWER: The time required to establish chemical equilibrium is very short compared to the time required to establish isotopic equilibrium (see reply to general comments).

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Hence, for oxygen isotopes we can assume a complete disequilibrium state. Hence, the CO32- “will” carry the isotopic fingerprint ... “partly” is not strong enough.

REFEREE 2: 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.

ANSWER: We introduced the factor f to characterize the source of CO32- in the calcifying vesicle. The concentration of CO32- in the vesicle is defined by the saturation product with respect to calcite ([CO32-]sat), i. e. it is constant for a given T, S. Our model is based on the assumption that two different C pools with different isotopic composition contribute to [CO32-]sat in the vesicle: One source of [CO32-]sat is a direct transport of CO32- from the external medium into the vesicle. The other source is the conversion of HCO3- to CO32-. The assumption is that the CO32- in the vesicle that originates from the external medium is proportional to the concentration of CO32- in the environment : f$\times$[CO32-]ext. Then, the contribution from bicarbonate conversion is given by [CO32-]sat - f$\times$[CO32-]ext. The value of the proportionality constant f depends on the transport pathways for the substrate Ca2+ and CO32- from the environment to the site of calcite precipitation, which is not known. For endocytosis as the substrate uptake mechanism we have f = 1 (full accessibility of external CO32-). In case that no CO32- is taken up by the cell, we have to assume f = 0 (no accessibility of the external CO32). The reality is probably somewhere in between 0 < f < 1.

REFEREE 2: Line 20: add “and to a lesser extend” between “and” and “salinity”

ANSWER: We will do so.

REFEREE 2: Line 21: please explain what cell you are referring here to? Foraminiferal, coccolithoforid?

ANSWER: This statement applies to both foraminiferal and coccolithofore cells. We will keep the general term cell.

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REFEREE 2: 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.

ANSWER: We will do so.

REFEREE 2: Line 14 ... : ... application of the same model to the dinoflagellate species studied requires an unrealistic value of f = 1 ....

ANSWER: As explained in P.7583, Line 13 a value of f = 1 means full accessibility of external CO32-, which is not necessarily unrealistic, and would be the case if CO32- is taken up via endocytosis.

REFEREE 2:... dinoflagelate species having less saline water in its calcifying space .... would require strong pumping against osmotic pressures ...

REFEREE 2: ANSWER: This is not necessarily the case, since part of the osmotic pressure of cellular compartments is sustained due to the presence of organic molecules.

REFEREE 2: ... lowering pH also makes it more difficult to calcify as Ca2+ goes down.

ANSWER: Due to pH homeostasis (see reply to general comments) the pH will be kept constant during calcite precipitation.

REFEREE 2: ... the dinoflagellate is showing a different response because it is actually calcifying fundamentally different.

ANSWER: We are copying here the same response provided to referee T. Toyofuku and now added to the main text.

“A similar vesicle-based calcification mechanism has been proposed for the common calcareous dinoflagellate Thoracosphaera heimii (Inouye and Pienaar, 1983)). Although planktonic foraminifera are thought to calcify in an extracellular space (Bentov et al., 2009), mechanism is indeed remarkably similar to the one of coccolithophores and

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T. heimii. The extracellular calcification space of foraminifera is isolated from the seawater by a so called pseudopodial network, so that, in effect, also foraminifera calcify in a space which is isolated by means of plasmamembrane not only from the seawater, but also from the cytoplasm. This common basic feature of the calcification of the three phylogenetically distinct groups of calcifiers, coccolithophores, foraminifera, and dinoflagellates, can partly account for the fact that it is possible to formulate one single model explaining the dependency of d18O on carbonate chemistry as will be discussed in the following."

REFEREE 2: P.7585 Line 15: See general comment on using the term "vital".

ANSWER: Fine.

REFEREE 2: Line 19-End: delete, this is not adding anything to the discussion, but distracts from the main message.

ANSWER: This can be removed.

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

ANSWER: Figure 2 provides a sketch of the proposed mechanism discussed in the text where the δ18O calcite composition of the precipitate simply reflects the isotopic composition of CO32$-$ in the vesicle.

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