Biogeosciences Discuss.,
https://doi.org/10.5194/bg-2019-461-RC2, 2020

Biogeosciences
Discussions
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Interactive comment on "Oxygen isotope composition of waters recorded in carbonates in strong clumped and oxygen isotopic disequilibrium" *by* Caroline Thaler et al.

Stefano Bernasconi (Referee)

stefano.bernasconi@erdw.ethz.ch

Received and published: 15 January 2020

This paper proposes that the deviation from equilibrium for clumped isotopes and oxygen isotopes is closely related by a constant relationship, and that due to this relationship the isotopic composition of the delta 18O value of paleowaters can be reconstructed even from carbonates precipitated out of equilibrium. This is an interesting concept, but it to be reinforced by using additional calibration curves for clumped and oxygen isotopes (see details below) before the conclusions can be considered robust. In particular the Bonifacie et al.2017 curve is not calculated with the "Brand" parameters whereas the data presented here are, thus there is the possibility of an offset

(see comment below) thus alternatives have to be considered. Similarly, there are other curves for calcite-water oxygen isotope fractionation that are probably closer to equilibrium (see below) and these alternatives should also be tested to evaluate the robustness of the conclusions. In addition, there are also other datasets available in the literature on dolomite that can be used to support the conclusions of this paper, and these should be included as well.

As the paper is not very long, it would be better to incorporate the supplementary information into the main manuscript, this would make the paper more easily readable as all the important information is in one document.

Detailed comments:

Line 29: The delta 18O of carbonate not "the delta 18O composition of carbonate"

Line 32 Abundance not abundancy

Line 36-37 these two papers report disequilibruium but these are extreme cases, and not so common,. In particular other occurrences of Methane seep carbonates have been shown to precipitate in equilibrium (see Zhang et al. EPSL 512, 207-213).

Line 38 change to "in some biogenic carbonates" Disequilibrium is found in corals and possibly in brachiopods, but other widespread carbonates do not show disequilibrium (foraminifera, Peral et al. 2019 for example are in equilibrium). As the sentence is formulated here it seems to indicate that disequilibrium is dominant in biogenic carbonates, which is not the case. This may suggest that the clumped isotope thermometer is seldom useful. Please correct.

Line 121 change to "...measured ratios of the sample CO2"

Line 128 "Equilibrium Scale " not "Equilibrated Scale"

Line 150 and supplementary information: The Bonifacie et al. 2017 is not calculated with the Brand parameters, thus it should not be used to calculate temperatures of samples whose D47 is calculated using the Brand parameters, as there could be an offset. For example the Kele et al. 2015 calibration before recalculation was indistinguishable from the Bonifacie et al. 2017 common calibration (it was also part of it). However, upon recalculation by Bernasconi et al. 2018; Geochem. Geophys. Geosys.), the intercept has changed by -38 ppm, thus the authors should be careful in establishing "equilibrium" with an equation that is not based on the Brand parameters. The temperature difference calculated with the recalculated Kele et al.2015 instead of the Bonifacie et al. 2017 is up to 25 degrees lower for the samples with high disequilibrium. The samples produced with the carbonic anhydrase with the Bernasconi et al. 2018 calibration give yield temperatures of 35 to 40°C about 5°C closer to equilibrium than using the Bonifacie et al. 2017 calibration. Does this change the interpretation of the trends? This should be taken in consideration and discussed. Many of the calibrations used in the Bonifacie calibration were indeed recalculated by Petersen et al. 2019; G3) and the values of some of the datasets changed significantly. It is difficult to evaluate what difference it would make to the Bonifacie curve, but this should be checked.

Due to these uncertainties, the inferences on difference to equilibrium could be biased and the calculated water compositions as well. I suggest that the temperatures should be recalculated using for example the recalculated Kele et al. 2015 and see how the interpretations may change.

The same discussion is valid also for the Kim and O'Neil calibration, does that really represent equilibrium? More and more evidence is that it is not (see discussion in Daeron et al. 2019). How would the interpretations in this paper change if another oxygen isotope calibration would be used ot calculate the oxygen isotope temperature? For example the Daeron et al. 2019 or O'Neil et al. (1969)? This point should be tested and possible implications discussed also in the discussion section.

Even if this is given in detail in Thaler et al. 2017, it would be useful for this paper to put a figure with the reaction pathway for ureolysis. It would be useful to have a formula which shows where the oxygen in the carbonate molecule comes from.

Line 201: its better to talk about depleted in 18O rather than enriched in 16O which is the more abundant isotope

Lines 211 -2015 Schmid 2011 (ETH dissertation, https://doi.org/10.3929/ethz-a-006551449) also reported some analyses of carbonates produced by ureolytic bacteria in strong disequilibrium, and data from carbonates produced by direct hydroxylation at high pH showed the effect of hydroxylation on the clumped isotopes of carbonates. The high D47 of the carbonates formed from directly hydroxylated CO2 can also be due to the direct inheritance of the isotopic composition of the CO2 as at high pH the equilibration time with water is very long, longer than the precipitation rate of carbonate.

Lines 268 The Kim & O'Neil calibration is based on samples precipitated to temperatures between 10 and 40 thus not the best one for higher temperatures. Simply the fact that is the most used does not mean that it it's the best one to use.

Lines 285ff It is not true that the Tang and Staudigel data are the only published data reporting, water, delta 18O Water and delta 18 calcite. The authors should include the Kele et al. (2015) data with the recalculated D47 in Bernasconi et al. 2018 in their analysis as they also have all the necessary data 18 o carb 18O water and clumped isotopes to test the validity of their hypothesis. Additional datasets that would be interesting to test would be the Dolomite data of Bonifacie et al. 2017 (op. cit) and the dolomite data of Müller et al. 2019 (Chem. Geol., 525, 1-17) I think this would make the message of this paper much more robust.

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