Biogeosciences Discuss.,
https://doi.org/10.5194/bg-2019-158-SC6, 2019

Biogeosciences Discussions
Open Access
EGU

Interactive comment on "Validation of carbon isotope fractionation in algal lipids as a PCO_2 proxy using a natural CO_2 seep (Shikine Island, Japan)" *by* Caitlyn R. Witkowski et al.

Cailtyn Witkowski

caitlyn.witkowski@bristol.ac.uk

Received and published: 16 August 2019

Response to RC4 comments

The authors of the manuscript use natural CO2 seeps in the vicinity of Shikine Island(Japan) to investigate the relationship between different concentrations of aqueouspCO2 and carbon isotope fractionation in three organic compounds extracted from surface marine sediments, diatoms, plankton tow, and microalgae. It is a novel approach that utilizes a unique natural setting. The subject of the manuscript fits well within the scope of the journal, and the results of this project would certainly be of significant interest to paleoceanographers and paleoclimatologists who use carbon isotopic

Printer-friendly version

Discussion paper

composition of biomarkers as a proxy for pCO2. The manuscript, however, contains several major and minor issues that need to be addressed before the manuscript is considered for publication.

We thank the reviewer for the comments and recommendation for publication. Below we will respond to each of the comments, which will improve the manuscript.

MAJOR ISSUES

FIRST, the choice of organic compounds (biomarkers). The authors need to provide a clear rationale as to why loliolide, phytol and cholesterol were chosen for this work. None of these compounds can uniquely be linked with a source (i.e. they can come from a variety of sources including marine and terrestrial), so it is not clear how applicable their work (assuming these compounds are targeted) would be to paleo studies. In fact, the problem with significant underestimation of reconstructed pCO2 (see the next issue below) might be due to a poor control of what those compounds actually represent in terms of the source in this study.

We chose these organic compounds because they are representative of a wide range of producers, the concept being to offer a complementary approach to species-specific compounds (i.e. alkenones) that are temporarily and spatially limited. By exploring a larger groups of producers in open ocean settings, we may be able to extend the PCO2 record derived from epsilon p, as has been done for the Cretaceous (Bice et al., 2006; Sinninghe Damsté et al., 2008; Naafs et al., 2016) and for the Phanerozoic (Witkowski et al., 2018), both reconstructed from phytol's diagenetic product phytane. Although the sources of these compounds may be both terrestrial and/or marine, when viewed in an open marine setting will almost entirely be from phytoplankton (and in the case of cholesterol, also the zooplankton that consume and retain the isotopic composition of these same phytoplankton). Here, we are on the coast of a small island in open ocean and

Printer-friendly version

Discussion paper

have scanned our chromatogram for characteristic terrestrial biomarkers to test whether the contributors of these compounds also include terrestrial inputs from the island. The lack of triterpenoids and long-chain alcohols typical of higher plants suggests that our source signal is overwhelmingly marine.

SECOND, underestimation of reconstructed pCO2 Figure 5 and the accompanying discussion show that the reconstructed pCO2 are significantly lower than the measured values at both the Mid and High pCO2 sites by almost a factor of two. The possible reason(s) for this are not really addressed and mainly limited to "some site limitation". This issue requires a more detailed discussion particularly with regard to possible influences of different OM sources and the validity of the assumptions used for calculating the epsilon values for each compound (Section 4.2).

In section 4.3, we reconstruct PCO2 and describe why these reconstructed values are lower than the measured high PCO2 sites, primarily focused on the novelty of using such a site and the further research required. We have discounted different OM sources due to the lack of terrestrial biomarkers.

However, we agree with the referee and will expand on several sections to further consider the criticisms of epsilon p. First, we will expand the end of 4.2 to include why epsilon f (maximum fractionation) is not fully expressed at the high CO2 site, such as species' affinity for carbon concentration mechanisms which utilize 13C-enriched bicarbonate, as well as the recent studies that show different Rubisco types may yield lower epsilon f than previously assumed (Thomas et al., 2018). Second, we will expand the end of section 4.3 to raise the possibility of changing b value (factors influencing fractionation other than CO2) which has been shown to vary (Zhang et al., 2019).

MINOR ISSUES p. 1, line 16, "general algal compounds": What does this mean? Are these compounds sources only by algae?

As per our response in major issues 1, general algal compounds contrast to

species-specific algal biomarkers, i.e. alkenones. General algal biomarkers refer to compounds that are derived from a multitude of species, presumably overwhelmingly from phytoplankton sources based on our analyses. We will clarify this in the text.

p. 2, line 1, "current proxies leave much to be desired, often with large uncertainties and conflicting values": Could the authors elaborate on this, i.e. what specific issues with the current proxies do the authors have in mind and how this work would reduce these limitations?

We will elaborate on this. Although there has been much progress in development of PCO2 proxies, there are few proxies which can span timescales over 100 Ma. The few that can span longer periods are terrestrial biomarkers, which tend to have larger uncertainties, e.g. paleosols. Epsilon p has its problems, particularly at lower PCO2 but tends to have smaller uncertainties and so if this could be applied to longer timescales, it would offer a marine record (less influenced by local carbon cycling) and could help constrain the estimates for these older records.

p. 3, line 25, "SPM": What does SPM stand for?

Another reviewer also pointed this out. We have now defined this as suspended particulate matter the first time this is mentioned.

p. 6, line 14, "lighter d13C values": a d13C value cannot be 'lighter' or 'heavier'. It is a number. Use 'lower' or 'higher' instead.

We will change this to higher (13C enrichment) or lower (13C depletion) throughout the manuscript.

p. 6, lines 18-19, 29-30, "the primarily diatom-limited compound loliolide": It is an very common compound derived from many sources, including macrophytic algae and terrestrial plants, so linking it specifically with diatoms is somewhat risky. Furthero-

more, this compound is know to be a degradation product of fucoxanthin and other carotenoids, whick are also difficult to link to a particular source during paleoreconstructions.

We will add a small section to further describe the sources and, as per Major Issues 1, describe why we chose these specific compounds.

Regarding the source of loliolide, it is established that it is a product primarily from fucoxanthin. Repeta (1988) explores possible carotenoid sources of loliolide in modern sediments and demonstrate the fucoxanthin contributes to loliolide but are unable to demonstrate a parallel conversion of diadinoxanthin and other carotenoid epoxides to loliolide. Fucoxanthin is found in diatoms, as well as brown seaweeds, and is not common in terrestrial plants. The vast majority of fucoxanthin in the world is derived from diatoms, which make up a vastly larger mass of producers than brown seaweeds and generally contain more than four times as much fucoxanthin as brown seaweeds.

We will add a sentence to further describe the different possible sources of loliolide. However, given that all the theoretical sources are carotenoids, these should have the same biosynthetic pathways to be produced and thus should not affect the isotopic composition of the degradation product loliolide.

p. 9, lines17-18, "allochthonous input of sediment": Need to provide more detail here. Is it just about sediment or about are organic matter/biomarker sources with different epsilon values that would make reconstructing pCO2 more complex?

We will add more detail here to describe what we mean by allochthonous input, here referring to the deposit of sediment that contain our organic compounds that has originated at a distance (e.g. the control) into our elevated PCO2 sites. Sediment mixed between the high PCO2 site and the control site would likewise mix the epsilon p signal derived from these sediments.

FIGURES Figure1: The figure is confusing, i.e. it is difficult to know where this island is. It needs to be shown in a broader context, e.g. with a map of Japan at least. Geographic maps also typically have lines of latitude and longitude (shown as grid) along the X- and Y-axes. Also, the direction of the geographic North should be indicated.

We will revise this map to include an insert of the larger region (i.e. Japan) with the location of the island. We will also include latitude and longitude lines on the x- and y-axis, as well as geographic North.

Figure 2: Is it a GC-FID trace or GC-MS (TIC or SI mode, if so which m/z?)? Why not to give the names of the compounds next to the peaks rather than list them in the caption?

This is an GC-FID trace, which we will label. We will put the compounds next to the peaks rather than in the caption.

Figure 3: A), B), and C) are not shown on the plots. These need to be labelled. What are the error bars associated with the d13C values shown on the plots? Also, instead of 'Control', 'Mid', and 'High' show the actual pCO2 values.

We will add labels for A, B, and C. The error bars are 0.5‰ as described in the text. These were difficult to see in the figure, as they all overlap with one another. We will add these in for the referee. We will add the actual PCO2 values.

Figure 4: Here and in text (p. 8, lines 18-20), explain how the errors associated with the epsilon(p) values were calculated?

We thank the referee for pointing this out (especially as this was quite time-consuming, and we did not explain it!). We will add a section on how the uncertainties are calculated for both epsilon p and PCO2, which show one standard deviation (68 percent) uncertainty in based on Monte Carlo simulations, culminating the uncertainty in every equation parameter outlined in this manuscript.

Interactive comment on Biogeosciences Discuss., https://doi.org/10.5194/bg-2019-158, 2019.

Printer-friendly version

Discussion paper