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Biogeosciences Discussions

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

Anonymous Referee #3

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The authors of the manuscript use natural CO2 seeps in the vicinity of Shikine Island (Japan) to investigate the relationship between different concentrations of aqueous pCO2 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 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.

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.

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).

MINOR ISSUES

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

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?

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

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

p. 6, lines 18-19, 29-30, “the primarily diatom-limited compound loliolide”: It is a 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 paleorecon-structions.

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?

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.

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?

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.

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

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