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Biogeosciences Discussions

Interactive comment on "Ecology and biogeochemistry of contrasting trophic environments in the South East Pacific by carbon isotope ratios on lipid biomarkers" *by* I. Tolosa et al.

Anonymous Referee #2

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This paper describes the distribution and stable carbon isotopic compositions of phytoplanktonic biomarkers in the South East Pacific. Compounds with reasonably constrained origins are discussed with respect to data published in other papers submitted in this special theme whilst the stable carbon isotope data are discussed with respect to fractionation relative to CO2 and the impact of CO2 concentrations and nutrients. The paper presents a nice and extensive data set and most of the results agree more or less with previous observations (however, see also following comments). However, after reading it I was left with the feeling that there were not many new insights gained

by these data. This is sort of exemplified in the conclusion section where some general conclusions are drawn which could have been made regardless of the data. For example, the statement “It has become clear that the natural variability in carbon isotope fractionation among algal taxa, is a consequence of multiple factors” is highly unspecific and not new (I do not think you will find anyone claiming otherwise). More important are which factors ? Which are important and which not ? How did they impact fractionation ?. The conclusion section should be much more specific in what the study has achieved. Nevertheless, I do think this study is of value and worth publishing providing some comments below are addressed.

Major comments. One of my major concerns has to do with the calculation of Ep. This calculation has a number of uncertainties (e.g. are the compounds really that specific for these groups of organisms) but two major ones are obvious for this paper: the 13C of CO2 was not determined but estimated and the estimated difference between the 13C of the compound and that of the biomass. Concerning the first point it is a great pity that a study seemingly designed to look at the isotopic composition of biomarkers simply did not measure the 13C of DIC. A discussion on potential errors in the estimates of 13C CO2 and thus Ep would be very useful to constrain the impact of this omission. A more important concern is the estimated difference between the 13C-content of the compound and the biomass. The authors have only two compounds for which this estimate is somewhat constrained in the literature, i.e. alkenones (though the estimates vary from 3.8 to 5.8 per mill depending on each study; see Riebesell et al., 2000) and the C17 n-alkane (though this was determined for only 1 cultured mesophilic cyanobacteria). Interestingly, the authors take the 4.2 per mill offset determined for the alkenones also as being the offset for the other eukaryotic compounds (p. 4661; line 10). This is in contrast to a number of other studies which show that isotopic compositions of phytol and sterols vary widely compared to biomass depending on species (-2 to +8 per mill; Schouten et al.,1998, Geochim. Cosmochim,. Acta ; Riebesell et al., 2000, GCA; summarized in Hayes J.M., 2001, Rev. Mineral. Geochem.) and also ignores the fact that phytol and sterols are isoprenoid compounds with different

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biosynthetic pathways than straight chain compounds. In addition, the authors do also not take into account that the isotopic difference between compound and biomass is not always constant (see eg Riebesell, 2000; discussion in Hayes, 2001). Hence, there is a great uncertainty associated with the calculation of Ep and I wonder how valid this calculations really are in discriminating Ep between the various phytoplankton taxa. At minimum the authors should acknowledge these uncertainties and discuss the potential range in errors in their Ep calculations. Alternatively, and perhaps preferably, the authors should restrict themselves to calculating Ep based on compounds which would make comparisons of Ep relative to each other more difficult and potential differences in growth rates between algal taxa. However, they can still correlate Ep to nutrients and CO2 concentrations to investigate factors influencing isotopic fractionation. The isotopic composition of some biomarkers is already mentioned a few times in 3.1 and 3.2 while the real discussion takes place in 3.3. I would not discuss the isotopes yet in 3.1 and 3.2. Furthermore, the discussion on the impact of nutrients and CO2 concentrations on Ep in 3.3. switches quite a lot and is not fully addressed. For example, on p. 4670, l. 9-16., the correlation for Si is given but not for the other nutrients as it is only stated that they are “lower”. How much lower ? Still significant ? Perhaps the authors could give the results in a Pearson correlation matrix and indicate which correlations are reasonably significant (eg van Breugel et al., 2006, Am. J. Sci). Even more importantly for p.4673 l6-12 where they discuss correlations but do not give any values about the degree of correlation. Significant ? Is it the same correlation as Bidigare et al, 1997 and Benthien et al. ? This would give much more value to this discussion. Finally, one factor which is not discussed is light limitation which, in cultures, has shown to give different fractionation patterns than with nutrient-limited cultures. This discrepancy has to some extent been resolved by Cessar et al. (2006, Geochim. Cosmochim. Acta) and some discussion on this with respect to this data would be useful. Finally, regarding the discussion on the origin of biomarker lipids there is often reference to data published in separate accompanying papers. Presumably these will become available for inspection once they are published but for the reader it would be

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quite helpful if these data were presented in the figures in some form or another. Eg. P. 4665, l. 12.

Minor comments. Title: A bit of an odd title and awkwardly phrased. I presume you are not looking at the ecology of an environment but of phytoplankton ?. Furthermore, I prefer the phrasing “stable carbon isotopic compounds of lipid biomarkers” p. 4654, l. 2: remove different p. 4656. L. 14-16. I do not think your study evaluates sources of organic matter but rather sources of biomarker lipids as outlined later. I suggest to rephrase the last paragraph. p. 4660. L. 14. Note that TMS is actually not a very good derivitization agent for isotopic analysis though likely in this study it will not have a great impact (Shinebarger et al., 2002, Anal. Chem. p. 6244). p. 4660, l. 20; Besides abundance, the isotopic data of sterols are notoriously difficult to obtain due to co-elutions of other sterols. Perhaps it would be useful to provide some comments on this or a chromatogram in the supplementary material showing how the sterols are seperated. p. 4663, l. 9: C25 HBI are excellent biomarkers for diatoms (Volkman et al., 1994; Org. Geochem.; publications by the Plymouth group) and I wonder why the authors did not report their isotopic compositions and estimated Ep. This would make a nice comparison with the “diatomsterol” data. p. 4664, l. 6. Linear alcohols p. 4664, l. 10: I am unfamiliar with the idea that monounsaturated C20 and C22 fatty acids are markers for herbivorous zooplankton. Are there more examples of this besides the Lee et al. reference ? p. 4665, l. 15. The same, I am unfamiliar with this ratio, please provide a reference. Cholesterol is also abundantly present in algae (eg Volkman et al., 1986; Org. Geochem.). p. 4555, l. 22-24. Interesting conclusion. Does this mean that the isotope values of lipids perhaps also represent a “living” and “fossil” component and thus not always match in situ conditions ? p. 4668, l. 21: As far as I know the UK37 is not a growth index. p. 4667, l. 19: I do not think you want to distinguish between different CO2 fixation pathways as you are only looking at compounds produced via Rubisco. I presume you mean CO2 indirectly via bicarbonate or via diffusion.

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Tables 4-5. A large number values are reported in too many significant numbers here (e.g. 15.76 ng l for concentration or 1.61 d for growth rate). Please decrease this to a sensible number.

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