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Biogeosciences Discussions

Interactive comment on "Whole water column distribution and carbon isotopic composition of bulk particulate organic carbon, cholesterol and brassicasterol from the Cape Basin to the northern Weddell Gyre in the Southern Ocean" *by* A.-J. Cavagna et al.

Anonymous Referee #2

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The authors investigate the concentrations and carbon isotopic composition of bulk particulate organic carbon, and two sterols (cholesterol and brassicasterol) in the whole water column from the Cape Basin to the northern Weddell Gyre in the Southern Ocean. The manuscript is suitable for publication in Biogeosciences because there is a great need to understand the factors that determine C isotopic signatures of autotrophic and heterotrophic organisms, as well as their changes through the water column. The potential use of the carbon isotope ratios of marine biomarkers as recorders of CO2

levels has also been reconsidered, and, although previous works already proved the relationship between surface CO2 concentrations and δ13C of lipid biomarkers from the surface waters, here they show that this relationship might also be valid in deeper waters. It is regrettably that a study designed to look at the isotopic composition of biomarkers simply did not calculate the photosynthetic carbon fractionation between the inorganic carbon source and that of organic carbon synthesized by autotrophic organisms (epsilon p). Potentially clearer relationships between epsilon (p) and CO2 concentrations, as well as other environmental conditions, e.g. nutrients, could provide more insights on the factors that affect the carbon isotopic fractionation in the study area. Although the discussion and conclusions are not exciting because mostly based on hypothesis, the study contributes to a better understanding on the fate of organic material exported to the deep Southern Ocean.

According to the scientific and technical aspects, the work might be acceptable for publication in this journal, after a significant revision.

Some other criticisms and comments are given below:

Tables 2 and 1 could be merged into one Table, to facilitate the comparison of δ13C values for POC (suspended particles) to those of sterols.

Pag. 1673, l-25. The water volumes sampled with the large volume filtration systems should be specified.

Table 1. The number of replicates used to calculate the standard error on δ13C measurements (SD =$\pm$ 0.10 ‰ is missing.

Pag. 1675, line 5-6. It is unfortunate that the authors did not use a surrogate standard to account for losses, such as, 5a-androsterol, to take into account the losses? Was the data corrected for these underestimations?

Pag. 1677, line 15 states that uncertainty of δ13C was calculated by propagating standard deviations from triplicate measurements and correction for derivatization. What

was the s.d for the derivatization?

I have some concerns on the compound specific isotope analysis: The accuracy of the δ13C measurements are impacted by signal size or linearity of the GC-IRMS (Sherwood-Lollar, B., et al., (2007). Analytical Chemistry 79, 3469-3475). Were these parameters taken into account for the whole range of concentrations, noting that in deep waters the concentration levels were very low and could be the reason of the enrichment of δ13C cholesterol with depth?. Was the signal size for the sterols higher than 0.5V? Besides abundance, the isotopic data of sterols might be difficult to obtain due to co-elutions of other sterols. Was the chromatographic column (DB-5, 30mx 0.32 x0.25um) good enough to resolve the target sterols from their saturated counterparts (cholestanol and C28Δ22)? It would be useful to provide some comments on this or a chromatogram in the supplementary material showing how the sterols are separated.

Equation (1) seems to be incorrect since the tri-methylsilyl group (TMS from the BSTFA) contains 3 carbon atoms. Therefore the corrected formula should subtract 3 x the 13C of BSTFA, and n should be the number of carbon atoms of the sterol without derivatization, and not the number of replicates!!!!

Fig. 2. I consider that this figure is not necessary for the content of the paper. Otherwise, as this figure is compiled of 2 graphs, I would recommend adding letters to the different graphs included in each figure to be referred with the text. I recommend starting from left to the right (A for the left figure and B for the right).

Pag 1678, line 1, What are the detection limits for brassicasterol? They should be specified in Tables 2 and 3.

Fig. 3. Since you do not discuss the data based on the water masses distribution, I would recommend for clarity, to plot the parameters vs. depth rather than density or better show two y-scales.

Pag 1680, l 22: Looking at Table 3, large particles in surface waters have not slightly

larger brassicasterol/cholesterol ratios than underlying waters, but just station 5!!!

Pag. 1681, l 27: "At S4 within the upper 100m δ13C LP$-$POC and δ13C SP$-$brassicasterol decreased with depth". Due to the plot with density and not depth, it is difficult to see this statement from Fig. 4. As I said before, I recommend changing the density y-axis for the depth-axis.

4.1. Section: Variation of brassicasterol and cholesterol content with depth. The outcomes of this section are not novel, and the data presented are for the most part sound.

I suggest presenting Fig. 5B separated from Fig. 5A, since Fig. 5B is discussed under another section. Also the Fig 6B (zoom of panel A) could be removed and Fig 6B integrated together with Fig. 5 A.

4.2. section: The authors stated that the $\Delta\delta$13C values of -7 per mill obtained below 500m is in accordance with previous laboratory experiments. However, they cite Bidigare et al., 1997, which only provides values for alkenones and not sterols. As the estimated differences between the δ13C content of the biomarker and the biomass vary from -2 to 8.5‰ for different cultures of phytoplankton taxa (Shouten et al., 1998, Riebesell et al., 200, GCA, 64:4179 and summarized in Hayes, 2001 (Hayes, J.M., 2001. Mineralogical Society of America., Washington, pp. 225-277), it is recommended that the authors integrate this data variability in their discussion and not just take the value of -7.

p. 1684, l 21: The authors hypothesized that the stable value offset of -7 per mill below 500m indicates that brassicasterol is biosynthesized in the surface water and not below. However, this hypothesis is a bit flaw since the components that integrate the bulk POC degraded at different rates, and the offset between δ13C primary photosynthate and δ13C eukaryotic biomarkers does not necessarily reflect the offset between δ13C POC and δ13C biomarkers in the waters below the euphotic layer. In other words, the assumption that the δ13C of POC is assumed to be that of the phytoplankton. might still be valid in the euphotic layer but it can become less reliable in the deep layers,

where phytoplankton is not necessarily the major component of the POC.

Pag. 1684, line 24-28, If the Suess effect should be responsible for the enrichment of δ13C cholesterol with depth, the same enrichment will apply to the δ13C of brassicasterol and δ13C POC.

Another factor that affects the carbon isotopic fractionation of the algae is the change in irradiance and this should also be discussed in section 4.2.

Page1685, l 15-20, If the enriched cholesterol in the deeper waters comes from a previous bloom from the surface waters, enrichment for brassicasterol should also be observed. Moreover, higher concentrations of POC and sterols will likely be present in the deeper waters.

4.2.3. The hypothesis of the sea-ice algae related effect could be confirmed by the identification of specific sea-ice diatom biomarkers in the same samples, e.g. the IP25 (Belt et al., 2007, Org. Geochem., 38:16).

Pag 1688, l 1-5. The hypothesis on the high pressure on cholesterol biosynthesis occurring below the surface water seems very unlikely because kinetic isotope effects should have a minor contribution compared to the factors that affect the natural variability in carbon isotope fractionation among algal taxa: growth rate, T, dissolved CO2, cell geometry, irradiance, etc.

Why are the slopes shown in Table 5 differing from those exhibited in Figure 7? If they are the same, I recommend integrating the information of Table 5 into the Figure 7 and removing Table 5.

Interactive comment on Biogeosciences Discuss., 9, 1667, 2012.