

# ***Interactive comment on “Highly branched isoprenoids for Southern Ocean semi-quantitative sea ice reconstructions: a pilot study from the Western Antarctic Peninsula” by Maria-Elena Vorrath et al.***

**Anonymous Referee #1**

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The last decade has seen the rise of diatom-specific biomarkers, HBIs, to reconstruct past changes in sea ice. Although the HBI proxy has been studied for its production, seasonal and spatial distribution, export, mineralization and preservation in the peri-Arctic Ocean (Belt, 2018 and references cited therein) much less is known about its Antarctic counterpart. There, very few studies intended to validate the HBIs as a sea ice proxy (Massé et al., 2011; Belt et al., 2016; Smik et al., 2016). Nonetheless, HBIs were applied in several cores to reconstruct sea ice conditions off East Antarctica (Denis et al., 2010; Barbara et al., 2013; Campagne et al., 2015) and the Antarctic

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Peninsula (Collins et al., 2013; Etourneau et al., 2013; Barbara et al., 2016), generally in complement to diatom records. The present study represents therefore a timely effort to better understand and validate the HBI proxy. Mimicking the approach done in the northern hemisphere, the present study goes a step beyond previous publication by comparing HBIs to other organic compounds and by providing a semi-quantitative calibration of HBIs vs Antarctic sea ice concentration. However, I have few concerns about the region where the study has been conducted and the subsequent calibration robustness, along with minor concerns, detailed below. Main concerns 1. As stated by the authors, the western Antarctic Peninsula has experienced drastic environmental changes over the past decades with a strong warming and a strong reduction of sea ice cover. It is also known to present a very complex oceanography due to the interaction between a westerly flow entering Bransfield Strait from the South and an easterly flow entering by the North. The Drake Passage, where half of the surface samples were retrieved from, is also swept by the strong ACC that transports settling particles to the East and winnows surface sediments. As an example, the influence of the AAP-sourced iron to Southern Ocean surface waters is evident until  $0^{\circ}$  (de Jong et al., 2012) and even diatoms are transported away from their production zone (Crosta et al., 1997). One may question the behavior of organic compounds in these settings. I reckon that authors may have a limited access to sediment material, but the WAP and Drake Passage are not the best regions to calibrate such a tool due to fast changing conditions and strong lateral transport. 2. Fast changing conditions are the hypothesis put forward by the authors to explain the unexpected correlation of PIPSO to winter sea ice, while the IP25 (and probably its IPSO counterpart) is known to be produced in spring (Brown et al., 2011). Here lies the main problem to me. Can we state that the PIPSO preserved in surface sediment relate to past spring sea ice cover and that the correlation to modern winter sea ice cover is because of the close resemblance of past spring sea ice cover to modern winter sea ice cover (page 12, lines 10-19)? Another explanation is that the relationships between PIPSO and spring sea ice and PIPSO and winter sea ice are exactly the same, as shown by figure 5, but that the correlation is

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lower for spring sea ice due to a much lower gradient (0-20%) compared to winter sea ice (0-60%) and a greater spread. Additionally, it is worth noting that the relationships between PIPSO and spring/winter sea ice concentration (Fig 5C-D) is evaluated with a simple linear regression while the biplots show an inverse Z with low PIPSO values at low WSIC, a vertical increase (at ~30% for WSIC) and high “quenched” PIPSO values at high sea ice concentration. The spread around the regression line appears very large. 3. Methodological information is lacking. How were stored the freeze-dried samples? In a freezer as recommended? What about potential sulfurization of the HBIs observed in some OSuthern Ocean sediments? What is the detection limit of the GCMS for organic compounds? I think that there is not a single paper on HBIs that discuss analytical reproducibility to account for analytical errors during extraction and measurement on the GCMS. The concentration value itself is calculated via the integration of the MS peak at the organic compound retention time, which is performed via a software. However, from my own knowledge, each sample needs to be visually check for a robust integration, i.e. how the baseline is drawn. Different slopes, double peaks, tailing, etc... may induce an error and I always wondered how large can be the error if the baseline is moved a bit. As the PIPSO is a ratio of MS-sourced values, there even might be a propagation of the errors. Can they be quantified? I am also surprised that there is no coherent concentrations between studies and laboratories whereby publications co-signed by Belt present values below 1  $\mu\text{g/g}$  sediment of IPSO (Belt et al., 2016) while publications co-signed by Massé present values between few to tens of  $\mu\text{g/g}$  sediment for the same regions (references in Belt et al., 2016). As it cannot be related to the nature of the sediment itself (same areas), it might be related to laboratory protocols and analytical differences mentioned above. Although this is beyond the scope of the present paper to deal with general questions, I believe that additional information related to the evaluation of the laboratory protocol used and analytical errors is needed. 4. No information is given on the export and preservation (or potential different degradation) of the organic compounds analyzed here nor on the impact of lateral transport on their distribution. As HBIs and others organic compounds

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are produced by different organisms and may be exported at different rates, they may suffer from different degradation rates and variable winnowing, thus altering the PIPSO calculation and the calibration. In conclusion, although the present study is extremely important I believe it fails on its main goal and that it is not possible here to provide a semi-quantitative calibration for sea ice.

Minor concerns 1. Page 2 lines 5: I do not see how relevant are the listed references, especially Anderson et al. 2009. For impact of sea ice meltwater on intermediate and bottom water formation I would check Shin et al., 2003, Rintoul 2007; for heat and gas see Morisson et al. 2015, Holland 2014. 2. Page 2 lines 6: Total Antarctic sea ice increase. 3. Page 2 lines 14-16: Diatom and biogenic silica dissolution mainly occur in the photic zone, not in the sediment (Ragueneau et al., 2000). 4. Page 4. Oceanographic settings are a bit weak. I would recommend to better detail the current. For example, the TBW seems shallower than the TWW, Sangra et al., 2011). What about deeper currents (CDW) than can also winnow particles. What about SST and sea ice cover? Maybe few words on productivity? 5. Page 7, line 1. I would not say that *Eucampia antarctica* is an open ocean diatom, especially when dealing with its variety *recta*. Previous works showed that it is mainly affiliated to cold waters and to melting ice (Leventer et al., 2002). So which variety is used here? 6. Page 7, lines 5-8. As far as I know, SMMR is available between 1978 and 1987. Since then, sea ice images are based on SSMI, though several sensors were used over the years, or AMSRE since 2002. 7. Page 8, lines 12-14. Can the presence of PIPSO in central and eastern Bransfield Strait be due to lateral transport? 8. Page 8, lines 20-24. What organisms produce the brassicasterols? How B are exported? It is worth noting that winnowing, due to strong ACC in Drake Passage, can strongly bias surface sediment concentration (focusing, winnowing, etc...). For these samples, what can be the impact of lateral transport? 9. Page 9, lines 3-6. d13C was not measured on Triene, Brassicasterol and Dinosterols? Not enough carbon or not necessary? I think that B and D d13C would have been interesting to check whether these compounds were synthesized by sea-ice welling or phytoplankton organisms. Especially as B and D have high concentrations in



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Bransfield Strait, similar to IPSO, and we do not know whether this is an autochthonous production, and during which season, or an allochthonous production transported by the westerly currents. 10. Page 10, line 14. I am not sure that sea ice persists until summer in WAP and BS. At least, low winter sea ice concentrations argue against that. Figure 2 also argues against this. As mentioned above this can be solved by improving the oceanographic settings. 11. Page 10, lines 16-19. This sentence is not totally true. High values of PIPSO are observed at  $\sim 60^{\circ}\text{W}$  in the westernmost BS, where there is no winter sea ice. It should be discussed. 12. Page 11, line 5. Please note that sea ice edge is generally at the 15% threshold. Here 5% means no sea ice. 13. Page 11, lines 24-26. A WSIC of 23% is very low, indicating a very marginal zone. So maybe sensible not to find IPSO but high concentrations of HBI trienes (Figure 3). 14. Page 13, lines 5-8. The interpretation of the biplots is too simplistic. The “good” positive correlations are based on linear regressions that link two patches of samples. There is no gradient. We can imagine intermediate samples out of the linear model. Additionally, there are no t-test for the significance of the correlation. 15. Page 17, references. Check spelling of references. The two first ones mention Science (80- ).

Comments on figures Figure 2. Add sea ice limits on box B? Caption mentions that the mean WSI and SSI extents were calculated between 1980 and 2010, while it is written 1980 to 2015 in the methods section. Figure 3. There are several ways to present HBIS, ng/g of sediment, normalized to total HBIs, normalized to TOC as in the present study. Are results similar if other options are chosen? Figure 4. I wonder whether that wouldn't be more visual to have colored dots for organic compounds superimposed on WSI concentration fields. Or at least, I would recommend not to interrupt the dash lines for sea ice isocontours. Figure 5. Revise caption whereby plots A-B present spring sea ice concentrations while C-D present winter sea ice concentrations.

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