

### **Response to reviewer 1 (our replies are in bold)**

Ashley et al. present an assessment on the usefulness of  $\delta^{13}\text{C}$  of fatty acids to assess paleoproductivity in an Antarctic coastal setting. The manuscript is well-written, the data appropriate and extensive, and the research question interesting and relevant. The rationale for this work is fully explained, the introduction is clear and the methodology is sound. The main results and discussion section is generally clear, but not enough attention and focus is given to linking the data to productivity. At present, it almost looks like productivity was chosen because the trends could not be explained by anything else. I am sure this is not the case, but it needs to be made clearer for the reader as well.

**There are numerous processes affecting carbon isotopes in organic matter, so interpreting the algal  $\delta^{13}\text{C}$  signal in marine sediments is never going to be an easy task. We therefore feel it is best practise to explore all these possible factors, in the context of the Antarctic polynya environment, before we can conclude, parsimoniously, that productivity is the most likely driver. Various previous studies have shown that productivity is an important driver of  $\delta^{13}\text{C}$  of organic matter in similar high productivity environments (e.g. the Ross Sea) and this was a starting point for the work. However, we wanted to consider a range of potential drivers. In our final submission, we will therefore add some text at the start of the discussion to explain this.**

There are a few criticisms I have which ought to be addressed before this manuscript is ready for publication.

1. The manuscript is focusing on one specific site, and while the observed links to productivity are observed here, the site is very particular and in no way is this ready to be extrapolated at all to any other sites in Antarctica or any other settings. Hence, the title is a little presumptuous, while at the same time the phrasing as a question makes it vague. The phrasing of "fatty acid carbon isotopes" won't be valued by some in the isotope community as it can sound a little bit colloquial. I would suggest changing to "d $^{13}\text{C}$  of fatty acids trace paleoproductivity off the coast of Adelie Land, Antarctica" or something along these lines.

**We agree with the reviewer that our approach may not be applicable as a productivity proxy in many other sites in Antarctica. However, the principal could be applied to other highly productive polynya environments on the Antarctic margins. We agree the title may therefore be slightly misleading so we will change it to: 'Exploring the use of compound-specific carbon isotopes as a palaeoproductivity proxy off the coast of Adélie Land, East Antarctica.'**

2. The manuscript gives a lot of space for trying to pin down a single, or majority, producer, for fatty acids such as C<sub>18</sub>. I think this is impossible as so many organisms produce C<sub>18</sub> FA, and thus this discussion can be shortened and focused.

**Understanding the source(s) of the organic compounds is key to interpreting the signals recorded by  $\delta^{13}\text{C}$ . We do acknowledge in the manuscript that the C<sub>18</sub> fatty acid is likely to be produced by various different organisms and is unlikely to have a single producer. But even if the source cannot be pinned down to a specific species, understanding the predominant type of producer can make difference to the interpretation of the signal, for example a phytoplankton producer versus a higher trophic level source. However, there is evidence in the literature that the predominant producer of the C<sub>18</sub>, within the context of an Antarctic polynya, can be narrowed down to a particular species i.e. *Phaeocystis antarctica*. Therefore, we feel it is important to include a discussion around what the predominant producer(s) are and the limitations of this. However, we are happy to reconsider our phrasing and condense this section.**

3. The changes observed in d13C are very small and some comments on how significant changes of 1‰ really are would be useful.

**The fatty acid  $\delta^{13}\text{C}$  data is discussed in the manuscript in comparison with other environmental  $\delta^{13}\text{C}$  signals to help understand the importance of the ~5‰ range in fatty acid  $\delta^{13}\text{C}$ . For example, we discuss previous studies which show the range of DIC  $\delta^{13}\text{C}$  in different water masses around Antarctica to be ~1.5‰ (lines 336 – 341) and the change in phytoplankton  $\delta^{13}\text{C}_{\text{org}}$  due to anthropogenic CO<sub>2</sub> estimated to be up to 3.3‰ (lines 411 – 416). More importantly we discuss previous studies from the Ross Sea polynya, where sedimentary sterol  $\delta^{13}\text{C}$  has been shown to vary spatially by 5.6‰, from an area of high productivity within the polynya to an area low productivity further offshore. These changes follow a spatial variation in surface water CO<sub>2</sub> of <150 ppm to >400 ppm (lines 467-477). While our changes in fatty acid  $\delta^{13}\text{C}$  are not able to give a quantitative estimate of surface water CO<sub>2</sub> changes, the range in values is very consistent with the spatial variation observed in the Ross Sea sedimentary sterols suggesting they may reflect similar changes in CO<sub>2</sub> drawdown.**

Since our fatty acid  $\delta^{13}\text{C}$  has a relatively high signal to noise ratio, we tend to limit our discussion to only large shifts in the data, greater than 1‰.

Furthermore, we have calculated our error on  $\delta^{13}\text{C}$  measurements as 0.26‰, based on duplicate analyses, suggesting that a shift of 1‰ is significant as an environmental signal.

4. I can see a number of analytical issues that should be addressed. First of all, there is no explanation on how the correction for the methyl-group 13C values was carried out. This needs to be explained, or, if the C used for methylation has not been analysed for 13C and is not available anymore, and it is thus impossible to make this correction, it needs to be clearly acknowledged that values are not absolute.

**We thank the reviewer for pointing out that this was missing from our methods section. The  $\delta^{13}\text{C}$  was corrected for the extra C added during derivatization and in our final submission we will include some additional text in the methods about how this was done.**

The second issue is that the standard used (C19) is not the best for FAME as it is an n-alkane, and was only added post-extraction, hence analysis is semi-quantitative at best which needs to be made clearer.

**We chose to use an n-alkane standard since these were not present in the FAME fraction and would therefore not risk co-eluting with any compounds within the sample. In our final submission we will make it clear that this was added post extraction and that our estimates of fatty acid concentration are therefore only semi-quantitative. This does not affect our  $\delta^{13}\text{C}$  measurements as these were corrected using an external Indiana F8 standard.**

5. Throughout the manuscript, often words such as “extremely”, “very high”, etc. are used – I would recommend a thorough edit removing these descriptions and replacing them with actual values that allow the reader to put them into context.

Line 68: Give a number instead of “extremely high” – how high?

Line 70: “highly productive” as above

**These comments refer to general descriptions of the polynya environments. However, in our final submission, we will add reference to Arrigo et al. (2015) which quantifies the annual net primary**

**production of the Dumont D'Urville polynya as 30.3 g C m<sup>-2</sup> a<sup>-1</sup> and the Mertz polynya as 39.9 g C m<sup>-2</sup> a<sup>-1</sup>.**

Line 94: See comment 4 on internal standard – when was it added?  
Does it really allow quantification at this point?

**As above, in our final submission we will make it clear that this was added post extraction and that our estimates of fatty acid concentration are therefore only semi-quantitative.**

Line 97: Are these values corrected for Me? Are these errors subsequently appropriately propagated? What is the significance of a change of just above 3 x SD (0.26 vs 1 ‰)?

**The  $\delta^{13}\text{C}$  errors are based on the duplicate measurements which we believe is a conservative approach to estimating error.**

**We refer to our response to point 3 above in which we discuss the significance of a change of 1‰.**

Line 102: Which internal standards?

**To measure the HBI concentrations, we added 7 hexyl nonadecane (m/z 266) as an internal standard during the first extraction steps, following the Belt et al (2007) and Massé et al. (2011) protocols. We will include these details in the methods for our final submission.**

Line 194: Saying that a marine source is “entirely possible” sounds strange – do you want to say likely?

**Yes, in our final submission we will change this to likely.**

Lines 213-214: There are more novel studies on FA, Wakeham and also Hilary Close

**It is not clear which specific papers the reviewer is referring to here, or whether they are more relevant/add much to the discussion compared to the references already cited.**

Line 291: What do you mean by weaker coherence?

**What we mean is that there is less similarity between the C24 fatty acid and HBI triene concentration, compared with the C18 and HBI triene. In our final submission we will change the wording to make this clearer.**

Lines 547-549:

We know that there are many algae that make these FA so this is not likely to be resolved. At the same time, the non-distinctive nature of these molecules will make it difficult to apply this proxy to other settings where there are likely other producers. The whole paragraph is not particularly relevant and I would shorten and/or delete or move up so the work does not finish on a weak statement.

**We thank the reviewer for this helpful suggestion. In our final submission we will condense the last paragraph and move it up, and instead end with second paragraph so as not to finish the paper on the limitations of the proxy.**