CP-2021-134 Reviewer 1

The reviewer comments are in black text; our replies are in blue italicised text.

This paper describes a detailed investigation of an ancient deposit of snow petrel oil in Antarctica and how it relates to changes in climate and sea ice conditions during the late Pleistocene. It is a unique record and the authors used a number of analytical methods and proxies to infer changes in petrel diet and a paleoclimate record dating from ~22,000 to 28,000 yrs ago. The multiple methods they used served as a cross-check on the results of each analysis, providing strong evidence to back their conclusions, such as the Cu signature for krill in the diet. The paper is also well written and presented, so I do not have many comments for revising this paper for publication.

We thank the reviewer for their positive comments.

The method for calibrating their radiocarbon ages needs more explanation. The papers they refer to for their delta-R value of 880 +/- 150 yrs are based on penguin dates, and to my knowledge similar corrections based on dates from modern, pre-bomb snow petrels have not been completed. Using penguin corrections may be okay since the diet of the petrel is somewhat similar, but another analysis of radiocarbon corrections based on two additional modern, pre-bomb penguin dates can be found in Emslie (2001, Antarctic Science). This study indicates that a delta-R of 700 +/- 50 yr is more accurate for the Antarctic Peninsula and perhaps the Weddell Sea as well. I'm not sure how much this would change their age ranges for the petrel oil, but it should at least be considered. In addition, the diet of penguins from which corrections are based is not that similar to the diet of snow petrels. Penguin prey are larger size—larger krill, larger silverfish, etc., and we know from other studies that isotope values in krill will change with ontogenetic stage, or size of the krill, and oceanographic conditions (see Polito et al. 2019, doi:10.1002/lom3.10314). This is likely true for squid and silverfish as well and, since snow petrels are feeding on much smaller prev than penguins, it could affect the stable isotope values in the petrels by up to 2.4‰ (or more than the change seen in their samples) as well as their delta-R value.

We agree with the reviewer that there are challenges in the calibration of the radiocarbon ages. The reviewer highlights 2 related concerns: (1) the value of delta-R (ΔR) we chose to use; (2) the use of penguin data in generating that ΔR , and the potential for isotopic differences between penguin prey and snow petrel prey.

In response to (1), the comment to our manuscript by Tim Heaton et al. (cp-2021-134-CC1supplement) also notes a recommendation to use the ΔR given for Hope Bay in the MARINE20 Reservoir Age database (ΔR 670 \pm 50 ¹⁴C years), which draws on the penguin bone data from Hope Bay presented in Björck et al. (1991), and which was applied by Sterken et al. (2012) with a minor error in the calculation. We will apply the recommended ΔR value in our revised manuscript, editing Table 1 and the subsequent figures accordingly (see our reply to Heaton et al.). This change does not lead to significant shifts in our chronology given other uncertainties in the calibration process, as detailed in our reply to Heaton et al.

In response to (2), we acknowledge it is likely that additional calibration uncertainties are introduced by using ΔR values obtained from penguins, for the reasons and published works noted by Reviewer 1. Different ¹⁴C signals have been reported in modern shells, seaweeds and selected predator tissues (Gordon and Harkness, 1992). A range of ¹⁴C ages was also reported in three samples of post-bomb snow petrel stomach oils (550-800 ¹⁴C yr)(Hiller et al., 1995). Further research is warranted to better understand and quantify uncertainties introduced by using penguin bone ΔR : until this is resolved we will apply the recommended values from the MARINE20 database (Heaton et al., 2020).

One weakness of this study, as discussed by the authors, is determining if baseline polynya carbon and nitrogen values changed over time (and very likely did), which in turn would influence the stable isotope values independent of dietary change. One way to test this is by using compound-specific stable isotope analysis so that source and trophic amino acids can be analyzed to determine if a true dietary shift occurred, or if changes in baseline productivity occurred, or both. I am not familiar enough with the stomach oils of petrels to know if the proper amino acids can be extracted and analyzed in this manner, but the authors do not mention this either way. Perhaps their use of multiple proxies helps resolve this issue and if so that should be stated. Their measurements of Cu certainly help show the likely change of krill in the petrel diet over time.

We agree with the reviewer that this is a challenge for our interpretation of the stable isotope data. We presented compound-specific δ^{13} C measurements from fatty acids as one approach to try to disentangle different contributions to the bulk δ^{13} C signal, but as both we and the reviewer note, we did not find a clear signal of the baseline changes. We agree that targeting amino acids could provide a solution to this problem (e.g. Johnson et al., 2019; McMahon et al., 2015). We plan to undertake further work in this direction, but it is beyond the scope of this paper.

Another set of data that might help would be from ice cores. In Fig. 6 they present some of the WAIS ice core data, but has DMS been analyzed from these cores? DMS can be a proxy for sea ice extent (e.g., Goto-Azuma et al. 2019, Nature Communications). This would be another independent data set that could help strengthen their results for presence of polynyas and open water, or extensive sea ice in the past.

The oxidation products of dimethyl sulphide (DMS) found in ice cores are methanesulphonate (MSA, exclusively from DMS) and sulphate ($SO_4^{2^-}$, multiple origins). We note that not all phytoplankton are strong sources of DMS (Kaufmann et al., 2010).

Reduced marine biogenic sulphate fluxes at EDML (and other ice core sites) during the last glacial were proposed by Goto-Azuma et al. (2019) to reflect reduced DMS emissions overall, since leads and polynyas might be expected to contribute DMS emissions as observed today. We agree with the reviewer that this would be useful information to include in Fig. 6., acknowledging that the age model uncertainties on the stomach-oil deposits and temporal smoothing on the ice core data limit our ability to link our millennial-scale changes between the two records. A preliminary comparison with the data of Goto-Azuma et al. (2019) is shown below, noting that the nssSO₄²⁻ record is relatively low resolution and that Kaufmann et al. (2010) caution against over-interpretation of millennial-scale changes in this record. In broad terms, however, our stomach-oil deposit lies during an interval of broadly low residual nssSO₄²⁻ indicating a time of low DMS emissions when the ssNa+ record also indicates more extensive winter sea ice.

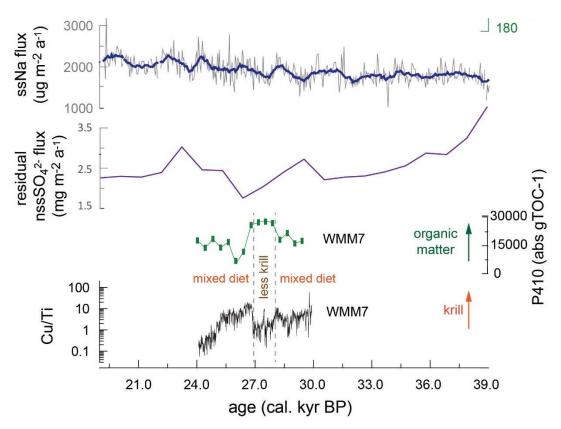


Figure 1. A selection of data from Fig.6 in the original manuscript, adding the residual $nssSO_4^{2-}$ flux calculated by Goto-Azuma et al. (2019) at the EPICA Dronning Maud Land ice core, which records aerosol changes in the Weddell Sea. The age model here is adjusted from our original submission, using the Holocene "no ice" ΔR proposed in the Comment by Heaton et al. (cp-2021-134-CC1-supplement).

Line 545: wouldn't enhanced upwelling increase (enrich) the carbon isotope values?

We are guided here by the observed upwelling of $CO_{2(aq)}$ rich waters from the Circumpolar Deep Water to the surface ocean, which is characterised today (and during the last glacial stage) by lower $\delta^{13}C$ than at the surface (Bostock et al., 2004). Our proposal was that a greater influence of low $\delta^{13}C$ CDW could have reduced the $\delta^{13}C$ of the krill via its prey: this can be clarified in a revised version of the manuscript:

"Alternatively, declining $\delta^{13}C_{14:0}$ could reflect enhanced upwelling of $CO_{2(aq)}$ rich <u>but low $\delta^{13}C$ </u> circumpolar deep water (e.g. Bostock et al., 2004) during the season of krill production."

Section 4.3 is a bit long, with some repetition from previous sections so I suggest cutting this down a bit.

We will review section 4.3 to identify repetition and delete as needed during the generation of a revised version of the manuscript.

Figures and tables are all necessary for the paper and are well presented.

We thank the reviewer for this positive comment.

References cited in the authors replies:

Björck, S., Hjort, C., Ingólfsson, O., and Skog, G.: Radiocarbon dates from the Antarctic Peninsula – problems and potential, in: Radiocarbon Dating: Recent Applications and Future Potential, edited by: Lowe, J. J., Quaternary Research Association, Cambridge, 55-65, 1991.

Bostock, H. C., Opdyke, B. N., Gagan, M. K., and Fifield, L. K.: Carbon isotope evidence for changes in Antarctic Intermediate Water circulation and ocean ventilation in the southwest Pacific during the last deglaciation, Paleoceanography, 19, 10.1029/2004PA001047, 2004.

Gordon, J. E., and Harkness, D. D.: Magnitude and geographic variation of the radiocarbon content in Antarctic marine life: Implications for reservoir corrections in radiocarbon dating, Quaternary Science Reviews, 11, 697-708, <u>https://doi.org/10.1016/0277-3791(92)90078-M</u>, 1992.

Goto-Azuma, K., Hirabayashi, M., Motoyama, H., Miyake, T., Kuramoto, T., Uemura, R., Igarashi, M., Iizuka, Y., Sakurai, T., Horikawa, S., Suzuki, K., Suzuki, T., Fujita, K., Kondo, Y., Hattori, S., and Fujii, Y.: Reduced marine phytoplankton sulphur emissions in the Southern Ocean during the past seven glacials, Nature Communications, 10, 3247, 10.1038/s41467-019-11128-6, 2019.

Hiller, A., Hermichen, W.-D., and Wand, U.: Radiocarbon-dated subfossil stomach oil deposits from petrel nesting sites: novel paleoenvironmental records from continental Antarctica, Radiocarbon, 37, 171-180, 1995.

Johnson, J. J., Olin, J. A., and Polito, M. J.: A multi-biomarker approach supports the use of compound-specific stable isotope analysis of amino acids to quantify basal carbon source use in a salt marsh consumer, Rapid Commun Mass Spectrom, 33, 1781-1791, 10.1002/rcm.8538, 2019.

Kaufmann, P., Fundel, F., Fischer, H., Bigler, M., Ruth, U., Udisti, R., Hansson, M., de Angelis, M., Barbante, C., Wolff, E. W., Hutterli, M., and Wagenbach, D.: Ammonium and non-sea salt sulfate in the EPICA ice cores as indicator of biological activity in the Southern Ocean, Quaternary Science Reviews, 29, 313-323, https://doi.org/10.1016/j.quascirev.2009.11.009, 2010.

McMahon, K. W., Polito, M. J., Abel, S., McCarthy, M. D., and Thorrold, S. R.: Carbon and nitrogen isotope fractionation of amino acids in an avian marine predator, the gentoo penguin (Pygoscelis papua), Ecol Evol, 5, 1278-1290, 10.1002/ece3.1437, 2015.

Sterken, M., Roberts, S. J., Hodgson, D. A., Vyverman, W., Balbo, A. L., Sabbe, K., Moreton, S. G., and Verleyen, E.: Holocene glacial and climate history of Prince Gustav Channel, northeastern Antarctic Peninsula, Quaternary Science Reviews, 31, 93-111, <u>https://doi.org/10.1016/j.quascirev.2011.10.017</u>, 2012.