CP-2021-134 Reviewer 2

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

The manuscript by McClymont and co-authors presents an innovative multi-proxy study in one sequence of stomach oil deposits from Dronning Maud Land, Antarctica, over the ~29-22 ka BP period. Their geochemical and isotopic data suggest changes in the diet of snow petrels, which they relate to changes in summer sea-ice conditions affecting the birds' foraging areas. If the Antartic winter sea-ice edge during the Last Glacial Maximum is relatively well known (Gersonde et al., 2005; Allen et al., 2011; Benz et al., 2016; Lhardy et al., 2021), it is not the case for the summer sea-ice edge. Previous studies (Gersonde et al., 2005; Lhardy et al., 2021) suggested that a tongue of summer sea-ice cover covered the Weddell Sea until 15°E, probably as a result of a stronger transport of sea ice by the Weddell Gyre (Ghadi et al., 2020). However, it is unclear whether this tongue is made of compacted sea ice or not. Here, the sole presence of the stomach-oil deposits argues for spring/summer open waters at foraging distance from the nesting area. This indicates that the tongue did not reach 15°E at very high latitudes (near coastal) or that summer polynyas existed within the sea ice over the 29-22 ka BP period. The present study provides important insight into an almost unknown parameter and is therefore of prime importance.

The manuscript is very well written, well-structured and well-illustrated. The data (XRF corescanner, FA concentrations and isotopes) are promising and give much more information than the commonly used bulk d15N.

We thank the reviewer for their positive comments.

I however have several concerns with over-interpretation of the data and overall reaching of the manuscript that I would like to be addressed-discussed. I hope that my comments are sensible and will prove useful.

Major concerns

As a non-specialist in fatty acids (FA) I found the proof of concept, summarized in Table 3, a bit weak and vague. A better case for modern FA production and preservation must be done as it is the backbone of this paleo-study. Even though if the main interpretations are drawn from Cu/Ti (XRF data) and chlorins (pigment data) (figure 6). For example, the low C18:1 and C16:1 concentrations in the WMM7 deposits, as compared to modern values, is thought to reflect a "dietary intake" (lines 378-387) different than today. The subsequent paragraph (lines 389-402) try to define the whole spectrum of the FA concentrations in snow petrel preys, but somehow fails to explains the low concentrations of C18:1 and C16:1 in WMM7. Indeed, it is mentioned that krill and fish have high C18:x. Nothing is said about C16:1. There are also other parts where I was a bit lost with FA. Overall, and maybe because there might be little modern data, the reader is left with a lot of uncertainties and with the feeling that the use of FA is stomach oil deposits is very tentative.

The use of FA in stomach-oil deposits is indeed very tentative, and in our manuscript (and in our previous work by Berg et al., 2019) we highlight that there are several potential controls over FA distribution including dietary sources and post-depositional alteration (Section 4.1). Table 3 was intended to highlight our guide for interpreting the stomach-oil deposits, since as the Reviewer also notes for lines 389-402, there is a range of literature examining FA distributions in a range of snow petrel prey but few studies are from our region or assess all snow petrel prey in a systematic way, generating uncertainties as we here (and in Berg et al., 2019) discuss. We were careful not to over-interpret the data given these uncertainties,

and Table 3 was an attempt to tease out the main signals we use for interpretation here, hence the note in the caption "The prey biochemistry information is used as a framework to interpret the chemical signatures".

Our suggestion that a dietary intake drives the FA signals was outlined in lines 378-387 as a result of the similarities of our FA distributions to some modern snow petrel stomach oils and prey, and Holocene stomach-oil deposits. We are actively pursuing a better characterisation of snow petrel stomach oil FA in modern birds and in latest Holocene deposits, to better understand the relative influence of diet and post-depositional alteration. To address the reviewer concerns about the tentative nature of the work, we could end this paragraph with the following addition (underlined) to the existing sentence:

"<u>Acknowledging these uncertainties in the role played by location, prey FA signals, and post-</u> <u>depositional alteration, we here suggest that the fatty acid signatures in WMM7 primarily signal a</u> dietary intake, rather than variable preservation."

The reviewer expresses concern that we do not discuss C16:1 nor C18:1 (lines 389-402). The previous paragraph noted the possible influences over C18:1. We note here that our text in lines 389-402 refers to C16:0 not C16:1. In this paragraph, we explore the range of key FA recorded in snow petrel prey and our stomach-oil deposit (using Table 3 to summarise the complexities of this section). We note (line 397-398) that C16:0 has a mixed signal from multiple sources. As a result, we did not use this FA alone to infer dietary changes since it could reflect different contributions from krill, fish and squid (in the later sections we note where we think e.g. krill could have been contributing, line 419-420). We can clarify the sentence here with the following addition (underlined):

"The C16:0 thus has a mixed origin from krill, fish and squid in contrast to C14:0 (krill) and C18:x (fish), and thus cannot be used in isolation as an indicator of diet."

The WMM7 deposits is structurally composed of three units, which is confirmed by cluster analysis performed on XRF core-scanner data, especially Cu/Ti, Br/Ti and S/Ti. Authors attribute these units to different foraging and diets, which they try to support with organic data (FA and pigments). I however disagree with the description-interpretation of many records. Indeed, when looking at figure 4, it is clear that the cluster analysis conducted on organics is only driven by variations in pigments (P410 and P435 define units O3-O1). All other records show either no temporal differences (FA %) or high variability throughout the sequence with no relation to the units (C/N, FA ratios). The same is true for figure 5 in which all records appear very noisy. The authors nonetheless mention that many of these records bear differences between the three units (lines 415-433; lines 455-457) and their descriptions of the records do not fit what is observable. Probably because they based their descriptions on the cluster analyses, which are driven by specific records (not all of them). However, a simple ANOVA would show that the values in unit II and are not statistically different than the values in units III and I for FA%, FA ratios, FA d13C and C/N.

We guided our discussion of the data by the outputs of the cluster analysis using the brokenstick model, which by its nature identifies clusters of similar samples and the point at which those clusters are no longer statistically significant. We want to reiterate here that we do not exclusively use the clusters (and the lithological units) to interpret our data. Our discussion is structured by cluster, since they are the large-scale features of the deposit, but we continue to describe and discuss the evolution of the data through time including <u>within</u> units e.g. in lines 417-418 when we note that the FA likely show decreasing contributions of krill through time within Unit I.

We have performed a Kruskal-Wallis test on the organic indicators, to test the null hypothesis that samples taken from Units I, II and III were taken from populations with the same median. The Kruskal-Wallis test is advised rather than a one-way ANOVA test because the samples sizes were unequal between Units (Hammer et al., 2001). The

Kruskal-Wallis test gave a p-value of 2.116⁻²⁶ and a statement that "there is a significant difference between sample medians", confirming the result of our cluster analysis. Given the reviewers concern that our analysis might be biased by the presence of the pigment data, we also ran the same statistical test on the fatty acid % alone: this showed a smaller but still significant difference between sample medians (p=1.313⁻¹⁵). Thus, although the variations in fatty acid composition are harder to visualise on our graphics, they are still recording changes through the deposit which can be differentiated when examined collectively.

For example, author state lines 415-417 "Between 28.8-26.8 ka (~Unit III) elevated Cu/Ti and C14:0 contributions (low C16:0/C14:0 and C18:0/C14:0) identified krill as an important component of snow petrel diet, but likely decreasing through time". However, C16:0/C14:0 and C18:0/C14:0 ratios appear identical, both in term of absolute values and point-to-point variability, in between the three units. Similarly, there is such a high variability in the FA d13C data (Fig 5c) that it is difficult to see any correspondence between records (lines 455-457) and any trend (lines 418-420), defined herein on 2-3 points. Although being a clear improvement over bulk d15N, I think that authors ought to be more cautious in (over)interpreting their FA% and FA d13C data.

The text the reviewer cites here shows our exploration of the data <u>within</u> the Units, but we did not use the FA data to define those units. We agree that the FA and C/N data do not strictly follow the 3 unit structure, and so we describe their trends through time within each unit in the Discussion, or note where there is support between proxies e.g. low Cu/Ti in Unit II has some support from declining C16:0/C14:0 in terms of a reduced krill input (Fig. 4).

We disagree with the reviewer that the C16:0/C14:0 and C18:0/C14:0 ratios are the same in Unit III: both are declining moving upwards through Unit III (supporting our note that krill contributions were decreasing through time), but C16:0/C14:0 is ~1.75 and C18:0/C14:0 is ~0.3. We note that we should expect to see some differences between these two ratios, since we are comparing C14:0 ("krill") to C18:0 ("fish") or C16:0 ("mixed" source as noted above).

We agree with the reviewer that there is high variability in FA δ^{43} C which makes correspondence with other records difficult to assess. Although we tried to focus on shorterterm oscillations in our text, we can insert the following text (underlined) to the start of our FA results description (line 326 in the submitted manuscript):

"<u>No long-term trends in fatty acid d¹³C are observed through WMM7:</u> several short-term oscillations are observed instead (Fig. 5c)."

Authors may consider using SIZER software (Chaudhuri and Marron, 1999) to check whether transitions between units in relevant records are significant.

We have noted above that both the broken-stick model used in our cluster analysis (and our subsequent Kruskal-Wallis tests of unit differences) confirm that there are significant differences between Units/clusters. Whilst SiZer may allow an independent assessment of trends through time, we are concerned that for many of the records the low number of data points (\leq 15) would make this analysis difficult, meaning that only the XRF data are likely to be compatible, but relying on XRF data is expressed as a concern in the next reviewer comment.

In conclusion, only pigments and XRF ratios, including Cu/Ti, appear to vary according to the deposit units. Other records are too noisy to be robustly interpreted. I however do not think that this alters the main interpretations about the snow petrel diets and foraging habits. However, one may question the utility of the FA data in the present study, especially as

additional tests on individual records would be necessary to ascertain that values are significantly different in each unit.

We agree that the strongest signals come from the XRF and the pigments, with supplementary information provided by the other proxies. Indeed, we focus our attention on these records for our climate summary (Fig. 6), because they show that snow petrel diet changed through time, which we seek to understand.

The authors state several times that "Our results challenge hypotheses that the development of extensive, thick, multi-year sea-ice close to the continent was a key driver of positive sea ice-climate feedbacks during glacial stages". If I understood well, the rationale behind this statement is that polynyas within LGM summer sea ice would have allowed strong outgassing of CO2 to the atmosphere. This would have reduced the impact of Antarctic sea ice onto the carbon partitioning between the ocean and the atmosphere. Authors mainly refer to two old publications, Stephens and Keeling (2001) and Morales-Magueda and Rahmstorf (2002), to support this statement. However, it is worthnoting that there is no seaice seasonality in S&K2001 who prescribed a fixed sea-ice cover, probably the LGM winter sea ice defined by CLIMAP (1976, 1981). So obviously, any polynya in such a high sea-ice cover (maximum winter sea-ice extent) would led to CO2 outgassing. There is similarly no seasonality in MM&R2002, but their representation of winter sea-ice cover was closer to geological evidences (Burckle et al., 1982; Crosta et al., 1998). Because of the presence of leads within the winter sea ice, the direct impact of sea ice on atmospheric CO2 (ice capping reducing CO2 outgassing) was reduced compared to S&K2001. Here, the new data from WMM7 deposits suggest the presence of SUMMER polynyas off Droning Maud Land when LGM sea ice has already retreated from its winter mean extent of 35-40 million of km2 to its summer mean extent of 10 million of km2, thus exposing a large surface of open ocean in which CO2 outgassing can take place. For this reason, I doubt that removing few thousands of km2 of sea ice, if polynyas were present, would have changed anything to the CO2 balance. At least, through the ice capping process. More recent hypotheses on the control of Antarctic sea ice on CO2 involve less vertical mixing either by subsurface stratification (Sigman et aL, 2021) and/or deep stratification (Galbraith and Delavergne, 2018; Marzocchi et al., 2019). Polynyas could potentially have enhanced deep stratification if sea-ice formation was sustained during the summer season and that salt were advected to the seafloor without promoting vertical mixing (brines hypothesis in Bouttes et al., Bouttes et al., 2011). Which is not proved. Additionally, one may question how sea-ice formation in such polynyas compares quantitatively to the ~30 million of km2 of sea ice formed seasonally to reach back the winter extent.

In conclusion, I would tame the term "challenge" and the overall reaching of the manuscript on this aspect. It is far beyond the science presented therein.

We thank the reviewer for the exploration of the complexities of the glacial sea-ice environment and its feedbacks, including nuances of the models which we cited. We propose to update our citations and text accordingly for the final paragraph of the discussion (where we outlined the impact of polynyas on the previous suggestions of the sea-ice cap mechanism, lines 577-587):

"Polynyas may also have affected the strength of the sea ice/climate feedbacks during MIS 2: introducing only 2-8% open waters into the LGM sea-ice pack (compared to 10-20% for winter today) reduces the Southern Ocean contribution to the LGM CO₂ draw-down from ~80% to 15-50% via enhanced ocean-atmosphere CO₂ transfer (Morales Maqueda and Rahmstorf, 2002). In contrast, increasing brine formation during sea-ice formation transfers dense water and carbon to the deep ocean (Bouttes et al., 2011), and could have been enhanced by polynya formation (Paillard and Parennin, 2004). Brine formation over the continental shelves or at the ice-sheet margin, has been

proposed as would have been conducive to formation of dense glacial AABW and the associated deep-ocean storage of CO₂ (Paillard and Parrenin, 2004; Adkins, 2013; Adkins et al., 2002). It is currently difficult to evaluate the relationship between the proposed variability in polynya positions and the millennial-scale oscillations in atmospheric CO₂ (Fig. 6), in part because it is unclear whether the variations in surface ocean productivity observed in the stomach-oil deposits are related to changes in the efficiency of the biological pump and CO₂ drawdown (e.g for Unit II with high chlorin inputs). Furthermore, the relative impact of polynyas compared to other Southern Ocean carbon cycle processes is unclear, given that a combination of brine formation related to sea ice growth, changes in deep ocean stratification, and iron fertilisation of subantarctic waters is invoked to account for the observed CO₂ drawdown (e.g. Bouttes et al., 2011; Marzocchi and Jansen, 2019; Sigman et al., 2021). The relative impact of the polynyas between winter and summer seasons during the last glacial stage is also uncertain, since the large changes in sea-ice extent (Fig. 1) will likely also have affected the air-sea gas exchange on seasonal timescales. Our age model uncertainties also limit confident correlation between WMM7 and the ice core CO₂ record, so that further testing is required to explore whether polynya development along the DML coastline impacted contributed to observed changes in atmospheric CO₂."

In the conclusions, where the reviewer is concerned about the use of the term "challenge", we can alternatively state:

"These results challenge existing hypotheses add to a growing body of evidence which shows that seasonal changes in sea-ice extent and the presence of polynyas emphasise multi-year sea ice as a key were likely important drivers of sea ice-climate feedbacks including drawdown of CO₂ during glacial stages,"

Minor comments

Throughout the text: Harmonize sea ice (when a noun) and sea-ice (when an adjective). I found "sea ice" and "sea-ice" along with "sea-ice cover" and "sea ice cover".

We will thoroughly check.

Lines 88-89: I may have misunderstood the sentence, but crustaceans are invertebrate (not vertebrate)

This is a typo; we will correct it.

Line 117: Please give more evidence for the absence of hiatuses.

We can add to this sentence (addition underlined):

"No hiatuses were visible in the stratigraphy, <u>which would be indicated by breaks in the structure or</u> <u>visible sediment which would be deposited and concentrated during an interval when stomach oils</u> were not being deposited. The linear age model (Fig. 2) also indicates continuous accumulation".

Lines 139-141: A greater deltaR during the LGM, as evidenced for the SO open ocean (Siani et al., 2013; Gottschalk et al., 2020), would make the age of the sequence younger by few hundreds of years. But I doubt that this has any implication on the interpretations as it would still be dated from around the LGM.

We have addressed this concern in response to the comment by Tim Heaton and co-authors (cp-2021-134-CC1-supplement). A higher delta-R does make the overall deposit age younger, but does not change the relative sequence of events described here.

Line 227: I think that PAST as a fixed number of degrees of freedom, which might not be sufficient to deal with the autocorrelation of the series (Bretherton et al., 1999). However, this may not be very important here given the high score on PC1.

We have been unable to isolate the details of the PAST3 approach to addressing autocorrelation, but as the reviewer suggests this may not be problematic given the high score on PC1.

Line 253: Does the fact that there is no trend in Fe/Ti and Si/Ti mean that Fe and Si are mainly of minerogenic origin. The very high absolute values in Fe cps and the high score on PC1 argue for that. Are Fe/Ti and Si/Ti useful?

In this deposit the absence of a trend in Fe/Ti and Si/Ti suggests a mainly minerogenic origin since Ti is a minerogenic indicator. To ensure that this message is clear we can add text (underlined) to our original statement

"There were no clear down-core trends in Fe/Ti and Si/Ti (Fig. 3a,b) <u>indicating a dominant</u> minerogenic source for Fe and Si".

We think that it is still useful to show this data, because Fe has been found in krill (Palmer Locarnini and Presley, 1995) and Si could be an indicator of diatom abundance, even though in this particular instance their source can be shown as mainly minerogenic.

Lines 424-434: I do not agree that unit II shows increasing C16:0/C14:0 and C18:0/C14:0 values. Similarly, I do not agree that unit II shows a decrease in d15Nbulk. I did not get what are the "prey with a phytopkankton-dominated diet" if not the krill. But low Cu/Ti values argue for a lower krill preying.

We are describing a trend within Unit II i.e. the increase in the two FA ratios from low values at the base of Unit II to higher values at 26.0 ka (both ratios have a peak within Unit II at this point) (Fig. 4.). The early part of Unit II also sees $\delta^{15}N$ decreasing from ~12 ‰ at the base of Unit II to a minimum at ~26.5 ka. Since the reviewer notes concern in an earlier comment about how the FA data is described, we can clarify this sentence by shifting the FA data to the end:

"Low Cu/Ti and increasing C16:0/C14:0 and C18:0/C14:0 indicate a prolonged (~1100 yr) interval where krill was not a major component of snow petrel diet (Figs 3,4) supported by increasing C16:0/C14:0 and C18:0/C14:0 in the early part of Unit II."

With reference to the "phytoplankton-dominated diet" in the prey: this means that the direct prey of the snow petrels are dominated by a phytoplankton diet, which is then reflected in the prey tissues, but this does not need to be krill given other herbivores and omnivores in the Antarctic ecosystem.

Lines 455-457: Not very evident from Fig 5c. Concomitant peaks and lows.

Our text indicated that from 24.2-23.5 ka (the uppermost 3 peaks in the FA d13C data), the FA d13C "fluctuate in parallel". This is visible in Fig. 5c: all FA are low at the first data point, increase to the next data point, then all decrease again for the uppermost point. However, we recognise that the magnitudes of change in each indicator are not the same, and can use the term "concomitant".

Lines 526-529 & 549-550: How could there be polynyas over the shelf when the ice sheet covered it all (figure 12 in Hillenbrand et al., 2014?

This specific point is addressed in lines 563-570 and in our delineation of ice-sheet extent in Fig. 1. Two scenarios are proposed for ice sheet extent during the LGM by Hillenbrand et al. (2014), whereby the ice may have been close to the modern (allowing access to the continental shelf) or at the continental shelf edge. We note that our data may in fact suggest the more restricted scenario of Hillenbrand et al. (2014) is feasible (lines 565-567).

Lines 566: Mackintosh et al., 2014, deals with east Antarctica from 30°E to 140°E, not the Weddell Sea sector.

This citation should be Hillenbrand et al. (2014) and will be corrected in a revised manuscript.

Figures and tables

Fig 3: As the XRF data are presented on a log scale, the variations do not appear very important and it is sometimes difficult to see differences between the three units. And even for Cu/Ti, differences appear very small on a log scale.

We agree that the presentation of element ratios on a log scale sometimes makes it difficult to see differences between the units since it smooths some of the variability (we showed a comparison in our Figure E1). We did this to focus our attention on the longer-term trends, but can present the data without the log scale in the main body of the manuscript in a revised Figure 3:



Fig. 4: It is clear that the O clusters are here driven only by the pigment records. The FA and FA ratio records do not follow the deposit units (I, II and III) nor the organic clusters (O1, O2 and O3), and are, as such, not discriminatory for the cluster zones and subsequent interpretations.

We addressed this concern above.

Fig. C1: the orange square at ~26.2 ka BP does not fit with the peak in Cu/Ti observed at that time. This is the only one that is offset from the raw and smoothed curves. It shows a low bin when raw and smoothed values are as high as in units III and I. Weird.

This is a function of the plotting format: the orange square (the re-sampled data) spans more of the data than the size of the symbol implies e.g. the data point of concern here includes both the peak in the un-smoothed Cu/Ti but also the troughs before and afterwards. The squares actually represent continuous sampling through the sequence, without gaps, but our plotting software shows them as separated and centred on the mid-point of the re-sampled part of the sequence. We can replot this graphic with the heights of the square boxes increased to ensure that they form a continuous sequence if this would improve the message in Fig. C1:



Comparison of original Cu/Ti smoothing display (left) shown in Fig. C1 and the result of extending the boxes to span the smoothing window (right). As the re-sampling was undertaken by depth, the height of the bars varies through time. Note that the revised graphic is also plotted on the "Holocene no ice" radiocarbon calibration suggested by Heaton et al. (cp-2021-134-CC1-supplement).

Table 2: PCA is driven by only one element, Fe. This might be because raw data have been used and that Fe cps are much higher than any other element cps. The use of log data or,

even better, normalized data would probably reduce the overwhelming statistical importance of Fe. Other elements may appear significant too.

Our initial exploration of the data by PCA (as shown in the manuscript) sought to identify which components accounted for the overall geochemical variations in the sequence, so we did not normalise them, and used the variance-covariance approach recommended by Hammer et al. (2001).

When we run the same analysis on the normalised XRF data (i.e. all elements expressed as X/Ti) we still get the same dominance in PC1 by Fe, then Cu and then Ca (see Table below). PC2 is also dominated by Cu (negative loading) then Ca (positive loading). PC1 on the normalised data accounts for 84% of the variance and PC2 accounts for 12%.

Principal component loadings			PC loadings of		
(no corrections)	PC 1	PC 2	element / Ti data	PC 1	PC 2
Si	0.003	0.001	Si	0.001	0.004
Р	0.001	-0.002	Р	0.002	-0.004
S	0.004	-0.009	S	0.008	-0.019
Cl	0.013	-0.034	Cl	0.024	-0.010
K	0.028	-0.051	Κ	0.034	-0.072
Са	0.162	-0.165	Са	0.1747	-0.275
Ti	0.026	-0.019	Ti	-	-
Cr	0.004	-0.003	Cr	0.006	-0.010
Mn	0.010	-0.006	Mn	0.010	-0.010
Fe	0.961	-0.181	Fe	0.960	-0.130
Cu	0.217	0.962	Cu	0.207	0.925
Zn	0.008	-0.005	Zn	0.014	-0.021
Br	0.019	-0.008	Br	0.053	-0.134
Rb	0.002	-0.004	Rb	-0.000	-0.000
Sr	0.041	-0.091	Sr	0.053	-0.130
Zr	0.009	-0.005	Zr	0.010	-0.020

Table 2 from the main manuscript, showing principal component loadings of the original XRF data (left), and the results when all element data are normalised to Ti (right).

References cited in extra

Bouttes, 2011, GRL, 38, L02705

Burckle, 1982, Nature, 299, 435-437

Bretherton, 1999, Journal of Climate, 12, 1990-2009

Chaudhuri, 1999, J. Am. Stat. Assoc., 94, 807-823

Crosta, 1998, Paleoceanography, 13(3), 284-297

Galbraith and Delavergne, 2018, Climate Dyn, https://doi.org/10.1007/s00382-018-4157-8

Ghadi, 2020, Marine Micropal, 160, 101894

Lhardy, 2021, Climate of the Past, 17, 1139-1159

Marzocchi, 2019, Nature Geoscience, 12, 1001-1005

Sigman, 2021, Quat Sc Rev, 254, 106732

References cited in the reply by the authors:

Hammer, Ø., Harper, D. A. T., and Ryan, P. D.: PAST: Paleontological Statistics Software Package for Education and Data Analysis, Palaeontologia Electronica, 4, 9pp., 2001. Palmer Locarnini, S. J., and Presley, B. J.: Trace element concentrations in Antarctic krill, Euphausia superba, Polar Biology, 15, 283-288, 10.1007/BF00239849, 1995.