



## RESEARCH ARTICLE

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### Key Points:

- Modern stomach oil and feces of snow petrels are used to validate paleo-proxies for environmental reconstructions in East Antarctica
- Biomarkers and isotopic composition of fossil stomach oil deposits of snow petrels reflect past composition in diet
- Changes in the composition of the paleo-ecological diet reflect variations of environmental conditions in the coastal Southern Ocean

### Supporting Information:

Supporting Information may be found in the online version of this article.

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# Reconstructing the Paleo-Ecological Diet of Snow Petrels (*Pagodroma nivea*) From Modern Samples and Fossil Deposits: Implications for Southern Ocean Paleoenvironmental Reconstructions

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**Abstract** Snow petrels (*Pagodroma nivea*), which are endemic to the Antarctic region, produce proventricular stomach oil from ingested food for feeding purposes but also spit the oil in the immediate surrounds of the nests, where it forms encrustations over time (Antarctic mumiyo). These deposits provide a unique opportunity to understand the paleo-ecological diet of snow petrels and because the seabirds forage in the ocean, they potentially provide an archive of past marine environmental conditions in the Southern Ocean. For validating methods for reconstructions we use compositional data obtained on modern stomach oils and DNA data from fecal samples of snow petrels. We find that the distribution of carboxylic acid compounds in modern stomach oils and in the fossil deposits are consistent with variable contributions of fish and krill, which are the main constituents of modern snow petrel diet, and allows inference of past changes in snow petrel diet from the fossil record. Analyses of mumiyo deposits from six regions in East Antarctica reveal systematic differences in the isotopic composition of organic matter ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) and carboxylic acid patterns. This may suggest regional and/or temporal variability in the composition of snow petrels diet, likely differing in response to the prevailing environmental conditions in the foraging range of the birds, such as sea-ice variability, polynya activity and primary productivity. Our study provides confidence for using these approaches for broader scale paleo-studies in the future and for an assessment of the temporal changes and regional variability in snow petrel diet.

**Plain Language Summary** To better understand interactions of biological and physical processes in Antarctic marine ecosystems, we investigate fossil deposits of stomach oil of snow petrels for their use as a geological archive for past environmental changes. The deposits form over time in the surroundings of the nesting cavities of snow petrels, which produce stomach oil from ingested food but also spit it at nest robbers. In fresh oil the lipid and isotopic composition can be traced back to the composition of snow petrel food, such as variable proportions of fish and krill. From comparing the lipid and  $\delta^{13}\text{C}$ -isotopic composition of modern oil to fossil deposits we suggest it is possible to identify changes in the diet of snow petrels in the fossil record. Since the composition of the diet is closely linked to the prevailing environmental conditions in the marine foraging region of the birds, such as summer sea ice extent, this information can be used for paleoenvironmental reconstructions. Our study of deposits from widely separated regions in Antarctica shows that there are spatial and temporal differences in the composition of stomach oil deposits, likely related to the prevailing environmental conditions. This finding underpins the application of our approach.

## 1. Introduction

Sea ice is a profound and variable feature of the Southern Ocean and the Antarctic coastal marine ecosystem. On a geological time scale, there have been large changes in the sea ice environment, and these can affect global carbon cycling and the presence of latent heat polynyas (e.g., Guo et al., 2019; Ohshima et al., 2013; Smith et al., 2010). Its seasonal distribution south of the southern boundary of the Antarctic Circumpolar Current

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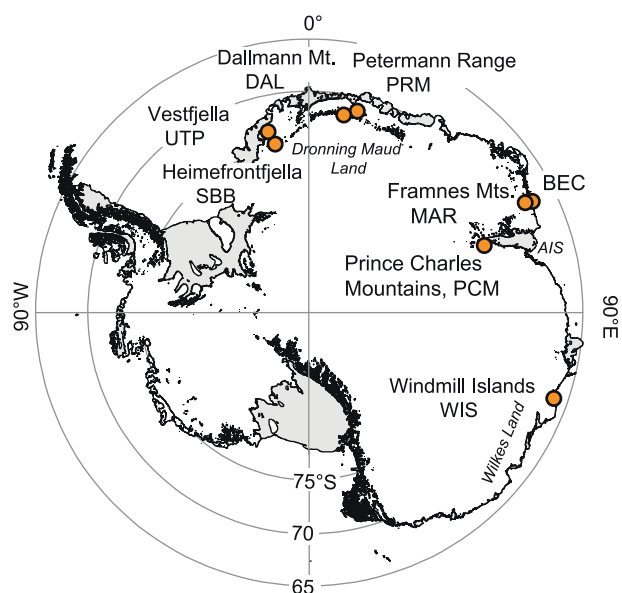
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(ACC) also controls access to foraging grounds and breeding success of Antarctic seabirds (e.g., Barbraud & Weimerskirch, 2001; Emmerson et al., 2015). A common seabird breeding and feeding in the Antarctic and surrounding oceans is the snow petrel (*Pagodroma nivea*). Foraging of snow petrels is closely linked to the occurrence of pack ice, particularly the pack ice edge, in the coastal zone of the Southern Ocean (Ainley et al., 1984, 1993). During the breeding season from early December to early March, snow petrels stay in relative proximity to the coast, while undertaking foraging trips to provision the chicks at their ice-free, land-based nesting sites (Delord et al., 2016). Similar to other fulmarine petrels, snow petrels produce proventricular stomach oil for chick-feeding. As a defense snow petrels spit the oil at nest robbers (mainly skuas) and it accumulates in the surroundings and entrances of the nest cavities over time. These deposits (also termed “Antarctic mumiyo”) can reach several decimeters in thickness, contain consistent stratigraphies and can be well-dated by radiocarbon analysis (e.g., Berg, Melles, et al., 2019; Hiller et al., 1995; McClymont et al., 2022; Wand & Hermichen, 2005). While the regional distribution and age of the deposits provides information on past distribution of snow petrel breeding sites (e.g., Berg, White, et al., 2019; Thor & Low, 2011; Verkulich & Hiller, 1994), the isotopic and lipid composition of the stomach oil deposits reflect changes in (paleo) diet, which in turn is expected to relate to summer sea-ice variability in coastal regions (Ainley et al., 2006; McClymont et al., 2022).

The link between the composition of the diet of seabirds, and environmental conditions in the foraging habitat lies in the ecology of a species and the species' interactions with biotic and abiotic factors characterizing the specific foraging habitat (e.g., Ainley et al., 1984; Connan et al., 2007). Although the food composition of seabirds reflects the general availability of prey, foraging strategies can be species-specific even for species with overlapping foraging areas (Ainley et al., 1984; Delord et al., 2016; Dehnhard et al., 2019, 2021). Information on the foraging habitat and diet can be obtained not only from direct observations at sea (e.g., Ainley et al., 1984, 1993), but also from analyzing the composition of diet from chick-provisioning birds on land and indirectly from the position of the birds within the oceanic food web. Stable isotope analysis ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) of feathers showed that the diet of snow petrels contains higher proportions of fish and foraging is more confined to the shelf and shelf break compared to other fulmarine petrels breeding at the same sites (Delord et al., 2016; Rau et al., 1992). Hence, our expectation is that snow petrels are likely to feed closer to their colonies than other fulmarine species and could therefore be more responsive to changes in the coastal sea ice environment.

For procellariiform seabirds, such as snow petrels, blue petrels (*Halobaena caerulea*) or Antarctic prions (*Pachyptila desolata*), stomach oils are used in biological studies to infer the composition of diet by comparing the patterns of lipid distribution in prey organisms and stomach oils (e.g., Connan et al., 2007; Watts & Warham, 1976). The trophic position within a food web can be assessed from isotopic data obtained from body tissue, blood or feathers of birds and prey organisms (e.g., Rau et al., 1992), as well as from prey DNA from faecal samples, which has been successfully used for Adélie penguins (Jarman et al., 2013; McInnes et al., 2015) and Black-browed albatross (McInnes et al., 2017). These proxies are used to define trophic niches, but may also reflect regional oceanic features (e.g., Cherel & Carrouée, 2022; Quillfeldt et al., 2005).

The aim of this study is to use modern observations on the composition of snow petrel diet for validating paleo-reconstructions derived from fossil stomach oil deposits. This will allow improved confidence in the method for broader scale (paleo)studies in the future and for an assessment of the temporal changes and regional variability in snow petrel diet in response to environmental changes from the fossil record. We investigate the lipid composition (carboxylic acid and alkanols) and the isotopic composition ( $\delta^{13}\text{C}$ ) of total lipids in fresh stomach oil and DNA in modern fecal samples to provide a reference for the evaluation of the fossil samples with respect to (a) effects of fossilization on the original lipid composition, (b) the representation of the dietary composition in the lipid and isotopic data of the fossil material and (c) possible environmental interpretations of dietary changes in the paleo record. Regurgitated, fresh stomach oil may experience alteration due to degradation (physical and microbial) after being deposited, which may reduce the information that can be derived for paleo studies. To capture a variety of possible compositions and ages, we study stomach oil deposits from six regions across East Antarctica. The deposits comprise material from occupied nesting sites, which was likely deposited recently, as well as older material that was dated to the Holocene and to the last glacial by radiocarbon analysis. The wide spatial distribution of investigated sites presented here offers first insights into the regional variability in snow petrel diet in the paleo-record.



**Figure 1.** Sample locations of modern samples and stomach oil deposits. BEC = Béchervaise Island, Mac. Robertson Land; AIS = Amery Ice Shelf.

## 2. Materials and Methods

### 2.1. Samples

We distinguish four types of samples, which are (a) fresh stomach oil, (b) modern fecal samples, (c) surface scrapes of stomach oil deposited recently at snow petrel nesting cavities, and (d) nesting cavity mumiyo deposits. These materials comprise the modern and fossil compositional endmembers needed to track dietary information in the fossil record. Fresh stomach oil was collected from breeding petrels on Béchervaise Island (BEC, Kista Islands in Mac. Robertson Land), at Masson Range (MAR, Framnes Mountains in Mac. Robertson Land), and in the Windmill Islands (WIS, Wilkes Land) (Figure 1, Table 1). The stomach oil was wiped off the ground with pre-heated aluminum foil directly after regurgitation. The samples were kept frozen in sealed glass jars until analysis.

Snow petrel fecal samples were collected in the 2012/2013 austral summer at BEC and at WIS (Table 1). Fresh fecal samples were collected at the nesting cavities from the non-uric acid portion of the feces and stored in 80% ethanol. The samples were stored at  $-20^{\circ}\text{C}$  until analysis. DNA amplification and sequencing of samples, high-throughput amplicon sequencing, sequence data processing and statistical analysis were carried out as described by McInnes et al. (2015). Surface scrapes were taken from stomach oil thinly encrusting the surroundings of recently occupied nests. The uppermost 1–3 mm were scraped off with a scalpel to remove only the most recent layers. Samples were collected at WIS, BEC, MAR and UTP (Utpostane, Vestfjella; Fromm et al., 2019) (Table 1).

Mumiyo deposits of several centimeters to decimeter in thickness were collected and subsequently cut in the lab with a band saw to produce smooth profiles perpendicular to the internal layering for detailed stratigraphic sampling. We used sub-samples of 1–5 mm in thickness, which were taken from specific depths within the profiles. Some of the deposits were subject of previous investigation, but all lipid and isotope data presented here were analyzed for this study. Age determination was done by radiocarbon ( $^{14}\text{C}$ ) analysis (see SI for method description and results). The deposits DallSW1830 from DAL and PRM4, PRM6 and PRM10 from Petermann Range (PRM, Wohlthat Massif in Dronning Maud Land) were previously described in Berg, Melles, et al. (2019). The focus of the previous study was on the stratigraphy and the inorganic composition of the deposits. Only few samples were analyzed for their lipid composition, and provided a first idea of possible dietary signals in the fossil record.  $^{14}\text{C}$ -analyses showed that the deposit DallSW1830 consists of a Holocene and a pre-Holocene section, while the deposits from PRM date to older than c. 20 ka (Berg, Melles, et al., 2019). From UTP (Vestfjella), four individual deposits were investigated, which are of late Holocene age (see Table S1 in Supporting Information S1 for  $^{14}\text{C}$  ages obtained for this study). Stomach oil deposits collected at Scharffenbergbotnen (SBB, Heimefrontfjella; Fromm et al., 2020), located 150 km inland from UTP, comprise material from two Holocene deposits. Stomach oil deposits from MAR in the Framnes Mountains comprise four deposits of mid-to late Holocene age (see Table S1 in Supporting Information S1 for  $^{14}\text{C}$  ages obtained for this study). The deposit from southern Prince Charles Mountains (PCM, located inland of the Amery Ice Shelf) was dated to the mid-to late Holocene (Berg, White, et al., 2019), and here we obtain compositional data for that deposit. It differs from the other deposits in being less waxy and containing high proportions of feathers and guano.

### 2.2. Lipid Analysis

In order to characterize and compare the carboxylic acid and *n*-alkanol distribution in the fresh stomach oils, surface scrapes and sub-samples of fossil stomach oil deposits total lipids were extracted from all three sample types by ultrasonication in dichloromethane (DCM)-methanol (MeOH) (9:1, v/v) three times to obtain the total lipid extract (TLE). The TLE was separated from insoluble residue by decanting. Residues, abundant in surface scrapes and mumiyo deposits were dried at room temperature and recovered quantitatively for analyses of stable isotopes and elemental analysis (see next section).

TLE was further transesterified using MeOH:HCl (37%) 95:5, at  $80^{\circ}\text{C}$  over night. Free lipids (including the compounds of interest) were then partitioned into hexane by phase separation with water (MilliQ). The result-

**Table 1**  
*Sampling Sites for Fresh Stomach Oil, Modern Feces, Surface Scrapes and Fossil Stomach Oil (Mumiyo) Deposits*

Site	Region	Latitude/Longitude	Minimum age occupation	Sample ID	Sample type	Date of collection
Utpostane (UTP)	Vestfjella, DML	73°53.392'S/15°41.343'W	3 ka	UTP-FM02	Surface scrape	13.12.18
				UTP-FM03	Surface scrape	13.12.18
				UTP-MD-03 (1)	Fossil deposit	13.12.18
				UTP-MD-06 (1)	Fossil deposit	13.12.18
Scharffenberg-botnen (SBB)	Heimefront-fjella, DML	74°34.998'S/11°13.002'W	>37 ka <sup>a</sup>	SBXI/1g (3)	Fossil deposit	13.01.98
				Mumiyo2/4 (3)	Fossil deposit	03.02.20
Dallmann Mts. (DAL)	Wohlthat Massif, DML	71°46.000'S/10°11.000'E	18 ka <sup>b</sup>	DallSW1830 (8)	Fossil deposit	26.12.95
PetermannRange (PRM)	Wohlthat Massif, DML	71°22.000'S/12°35.000'E	>56 ka <sup>b</sup>	PRM4 (6)	Fossil deposit	21.01.96
				PRM6 (3)	Fossil deposit	21.01.96
				PRM10 (2)	Fossil deposit	23.01.96
BéchervaiseIsland (BEC)	Kista Islands, Mac. Robertson Land	67°35.372'E/62°49.612'S	-	3 samples	Fresh stomach oil	11.12.18
				17 samples	Modern feces	02.02–09.02.2013
				7 samples	Surface scrape	11.12.18
Masson Range (MAR)	Framnes Mts., Mac. Robertson Land	67°46.944'S/62°48.016'E	7 ka	2 samples	Fresh stomach oil	14.02.20
				MAW-FM-14	Surface scrape	14.02.20
				MAW-FM-06	Surface scrape	15.12.19
				MAW-FM-07	Surface scrape	15.12.19
				MAW-FM-15	Surface scrape	14.02.20
				MAW-MD-02 (3)	Fossil deposit	26.11.18
				MAW-MD-03 (2)	Fossil deposit	26.11.18
				MAW-MD-05 (2)	Fossil deposit	26.11.18
MAW-MD-06 (3)	Fossil deposit	26.11.18				
Prince Charles Mts. (PCM)	Prince Charles Mts.	73°13.800'S/68°12.000'E	3 ka <sup>c</sup>	M2Greenall (3)	Fossil deposit	16.01.03
Windmill Islands (WIS)	Wilkes Land	66°16.824'S/110°31.992'E	2.5 ka	6 samples	Fresh stomach oil	11.02.1
				10 samples	Modern feces	02.01. and 19.01–25.01.2013
				WM-FM01	Surface scrape	07.02.19

**Table 1**  
Continued

Site	Region	Latitude/Longitude	Minimum age occupation	Sample ID	Sample type	Date of collection
				WM-FM02	Surface scrape	11.02.19
				WM-FM04	Surface scrape	11.02.19

*Note.* For the fossil deposits the number of sub-samples is given. Snow petrel occupation ages are derived from radiocarbon dated stomach oil deposits in each region (Figure 1). We report the respective oldest ages, which represent a minimum age of snow petrel occupation for each site, DML = Dronning Maud Land; ka = thousand years. Radiocarbon ages obtained for this study are given in Tables S1 and S2 in Supporting Information S1.

<sup>a</sup>Thor and Low (2011). <sup>b</sup>Berg, Melles, et al. (2019). <sup>c</sup>Berg, White, et al. (2019).

ing fraction was separated into polarity fractions using open column chromatography with silica gel for flash chromatography (high-purity grade, 60 Å, 230–400 mesh particle size, 40–63 µm). Carboxylic acids were eluted as methyl esters in Hexane/Ethylacetate (95:5, v/v), alkanols and α-ω-dicarboxylic acids in Hexane/Ethylacetate (85:15, v/v). Quantification and identification of compounds was done by capillary gas chromatography with GC-FID (Flame ionization detector, Agilent 7890B, Agilent Technologies, USA), equipped with a 50 m DB5 MS column (0.2 mm i.d. and 0.33 µm film thickness; Agilent Technologies, USA) with external authentic standards (FAME-mix C8-C24 (CRM18918), BAME-mix (47080-U), dodecanedioic acid (D1009), sebaic acid (283,258) all Sigma Aldrich). *n*-Alkanols were analyzed as trimethylsilyl ester (TMS) derivatives.

The position of double-bonds in unsaturated carboxylic acid compounds was identified by DMDS adduction and GC-MS analysis. Carboxylic acids were separated into saturated and un-saturated compounds by open column chromatography (SiO<sub>2</sub> coated with AgNO<sub>3</sub>). Identification was achieved by GC-MS (single quadrupole mass spectrometer HP 5989 coupled with a HP 5890 gas chromatograph, both Hewlett Packard). The position of double bonds in mono-unsaturated compound could not be determined for all homologs due to low concentrations/insufficient sensitivity of the MS. Identification was done for selected samples of the fresh stomach oils. For the remainder of the samples homologs were identified by comparing retention times.

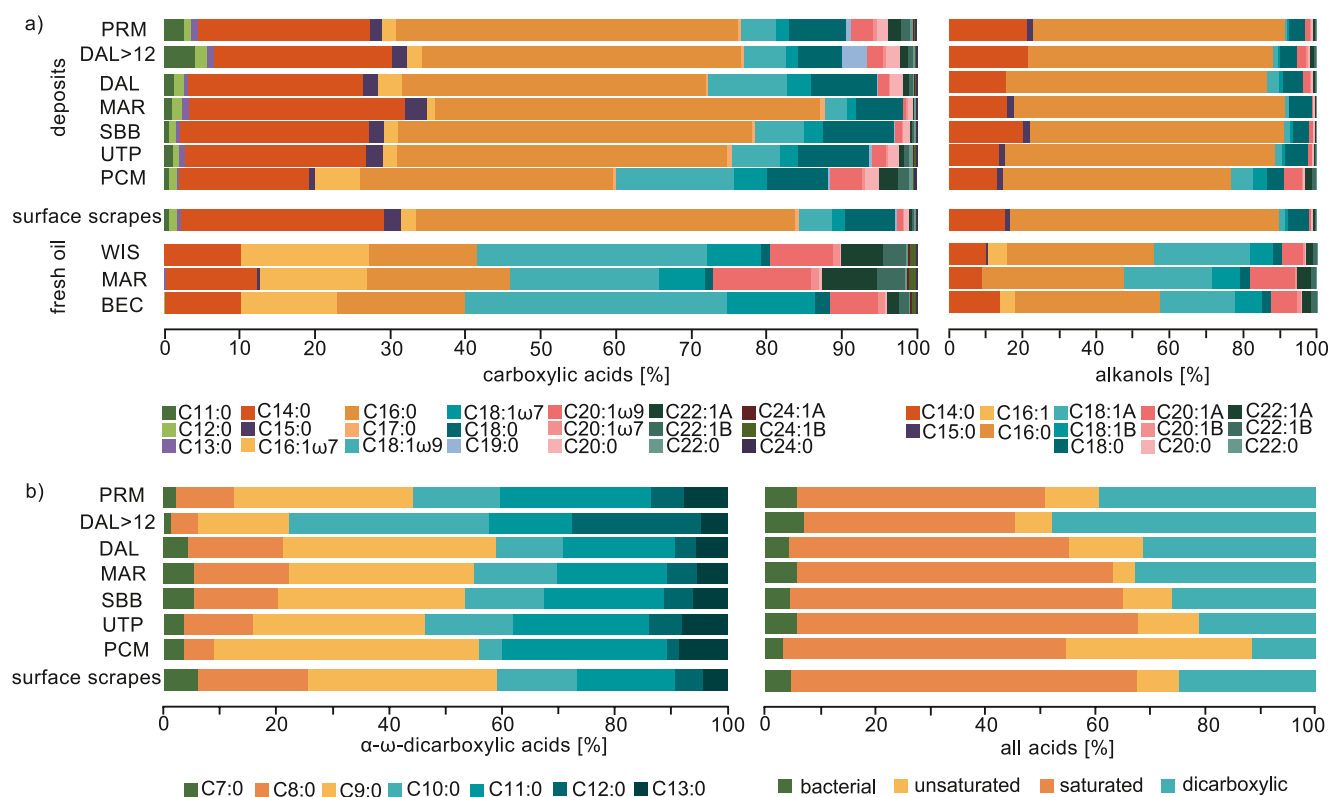
### 2.3. Stable Isotopes and Elemental Analysis

In order to obtain additional proxies for dietary and environmental reconstruction the δ<sup>13</sup>C and δ<sup>15</sup>N as well as total carbon (TC) and nitrogen (N) were analyzed. A first dataset was acquired from the TLE (δ<sup>13</sup>C<sub>TLE</sub>) of fresh stomach oils, surface scrapes and stomach oil deposits. The second dataset was obtained from analyzing the non-lipid residual material, which contains a variety of insoluble organic remains (δ<sup>13</sup>C<sub>RES</sub>, δ<sup>15</sup>N<sub>RES</sub>).

Samples were transferred into tin capsules and measured using an EuroVector EA 3000 elemental analyzer (Hekatech, Wegberg, Germany) coupled via a Conflow III Interface to a Delta V Advantage isotope ratio mass spectrometer (IRMS both from Thermo Fisher Scientific, Bremen, Germany) at the Institute of Agronomy and Nutritional Sciences, Soil Biogeochemistry, Martin Luther-University Halle-Wittenberg. The oxidation reactor was filled with tungsten dioxide and aluminum trioxide and cobalt (II, III) oxide (silvered) and heated at 1,020°C. Nitrous oxides were subsequently further reduced to N<sub>2</sub> by a reduction reactor filled with copper wires and heated at 650°C. Water was removed by a magnesium perchlorate trap. Helium (purity 99.9997%) was used as carrier gas at 100 mL min<sup>-1</sup>. The results were calibrated using standard materials with known TC, N, δ<sup>13</sup>C, and δ<sup>15</sup>N values (IAEA N2, IAEA CH6, IAEA NO3, IAEA CH7, IAEA 305A, and USGS 41). The precision of the stable isotope analyses as determined by replication measurements of standards was 0.3 and 0.2‰ for δ<sup>13</sup>C and δ<sup>15</sup>N, respectively. All results are reported in the common δ-notation.

### 2.4. Statistical Analysis

Principal component analysis (PCA) was used to identify autocorrelations within the data sets. It was performed with the program past 4.04 (Hammer et al., 2001). To obtain information on the correlation of lipid compounds independently of their relative proportions in each sample, values were standardized to zero-mean and unit variance prior to PCA analysis.



**Figure 2.** (a) Mean distribution of carboxylic acids and *n*-alkanols in stomach oil deposits, surface scrapes and fresh stomach oil samples. For some compounds the position of the double-bond could not be identified, those isomers are indicated by A and B (b) Mean distribution of  $\alpha$ - $\omega$ -dicarboxylic acids in stomach oil deposits and relative proportions of bacterial, saturated, unsaturated and  $\alpha$ - $\omega$ -dicarboxylic acids.

### 3. Results

#### 3.1. Lipid Composition

The 11 samples of fresh stomach oil contain even-numbered *n*-carboxylic acids from C14:0 to C24:0 (Figure 2, Table S4 in Supporting Information S1). Odd-numbered homologs are either abundant in minor proportions (<0.5%) or absent. The most abundant carboxylic acids are C18:1 $\omega$ 9 (29.7  $\pm$  6.5%), C16:0 (15.9  $\pm$  3.4%), C16:1 $\omega$ 7 (15.4  $\pm$  2.7%), and C14:0 (10.5  $\pm$  2.3%). Mono-unsaturated carboxylic acids dominate over saturated carboxylic acids (70.6  $\pm$  5.7% and 28.2  $\pm$  5.7%, respectively). While the proportions of the saturated homologs are rather similar across regions, the mono-unsaturated compounds (i.e., having one double-bond) C16:1 $\omega$ 7, C18:1 $\omega$ 9, C18:1 $\omega$ 7, and C20:1 $\omega$ 9 show distinct differences in relative distributions between samples from Windmill Islands (WIS), Masson Range (MAR) and Béchervaise Island (BEC).

*n*-Alkanols of fresh stomach oil comprise chain lengths ranging from C14:0 to C22:0. Similar to the carboxylic acids, odd numbered homologs are absent, except for C15:0, which is abundant in some stomach oil samples from WIS in concentrations of 0.6  $\pm$  0.6%. The most abundant homologs in the alkanol fraction are C16:0 (39.7  $\pm$  2.2%), C18:1 (24.0  $\pm$  3.2%), and C14:0 (11.2  $\pm$  2.4%). While mono-unsaturated carboxylic acids dominate in the acid fraction, saturated and mono-unsaturated alkanols are abundant in almost equal amounts (53.5  $\pm$  2.5% and 46.1  $\pm$  2.5%, respectively).

A total of 56 samples of surface scrapes and mumiyo were analyzed for their lipid composition. Surface scrapes and stomach oil deposits contain *n*-carboxylic acids ranging from C11:0 to C24:0 (Figure 2). The most abundant *n*-carboxylic acids are C16:0, C14:0, C18:0, and 18:1 $\omega$ 9. The proportion of mono-unsaturated homologs is highly variable between samples, ranging from 0% to 66.8%. All stomach oil deposits contain  $\alpha$ - $\omega$ -dicarboxylic acids of chain lengths from C7 to C13, with the homologs C9:0 and C11:0 being the most abundant ones (Figure 2). The proportion of  $\alpha$ - $\omega$ -dicarboxylic acids is higher than the proportion of mono-unsaturated carboxylic acids in all stomach oil deposits, except for the deposit from PCM, which contains relatively high proportions of



mono-unsaturated compounds (Figure 2). Carboxylic acids of bacterial origin (methyl-carboxylic acids and the odd *n*-carboxylic acids homologs C11:0 to C19:0) are abundant in all samples, accounting for  $3.8 \pm 1.3\%$  of carboxylic acids. In the *n*-alkanol fraction the most abundant homologs are C16:0 and C14:0. Mono-unsaturated compounds are only of minor abundance in surface scrapes and fossil stomach oil deposits, respectively (Figure 2).

### 3.2. DNA in Modern Snow Petrel Fecal Samples

The results of the DNA analysis were averaged for samples from each site ( $n = 10$  for WIS and  $n = 17$  for BEC). For both sites the most important group identified in the fecal samples are bony fish (Actinopterygii), comprising 37.5% and 47.3% of the averaged DNA proportions, respectively. The second most abundant group is krill (Euphausiidae) with 14.9% for WIS and 20.2% for BEC (Figure 2). Fish were present in 59% and 70% of the samples, and krill in 71% and 70% of the samples at BEC and WIS respectively. Other abundant groups are Calanoid copepods (Calanoida), salps (Salpidae), and jellies (Anthomedusae, Scyphozoa, and Siphonophora). The most evident difference between the two sites is the abundance of Amphipod DNA in diet of snow petrels from BEC (9.5%), which was not detected in the samples from WIS.

### 3.3. $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ Isotopic Composition and TC and N Content

In the fresh stomach oil samples  $\delta^{13}\text{C}_{\text{TLE}}$  values range from  $-30.4$  to  $-34.6\text{‰}$  (Table S3 in Supporting Information S1). The values are lowest in BEC samples ( $-33.9 \pm 0.8\text{‰}$ , mean  $\pm$  stdev.,  $n = 3$ ), highest in MAR samples ( $-31.4 \pm 0.1\text{‰}$ ,  $n = 2$ ) and intermediate and more variable in WIS samples ( $-32.7 \pm 1.1\text{‰}$ ,  $n = 6$ ). Residual material, hence, not soluble during extraction with organic solvents, could not be recovered for isotopic analyses from the fresh stomach oil. For the surface scrapes and stomach oil deposits  $\delta^{13}\text{C}_{\text{TLE}}$  values range from  $-27.8$  to  $-31.6\text{‰}$  and  $\delta^{13}\text{C}_{\text{RES}}$  from  $-24.7$  to  $-30.1\text{‰}$  (Figure 4). Samples from MAR, PRM, and DAL ( $> 12$  ka), have slightly higher  $\delta^{13}\text{C}_{\text{TLE}}$  values ( $> -29.0\text{‰}$ ) than the remainder of studied deposits. In most of the samples the  $\delta^{13}\text{C}_{\text{TLE}}$  values are lower than the corresponding  $\delta^{13}\text{C}_{\text{RES}}$  values, with off-sets ranging from 0.2 to  $-4.7\text{‰}$  ( $\Delta\delta^{13}\text{C}$ , Figure 4c).

$\delta^{15}\text{N}_{\text{RES}}$  values range from 6.1 to 11.7‰ (Figure 4b). The samples from PRM and the stratigraphically older samples from the deposit from DAL ( $> 12$  ka) have consistently higher values ( $> 10\text{‰}$ ) than most of the Holocene deposits from all regions. Surface scrapes from BEC have lowest values ( $< 7\text{‰}$ ) in this dataset. The carbon to nitrogen ratio (C/N) in the residual ranges from 1.2 to 12.6 and does not show a regional trend. Instead, high C/N ratios correspond to a low  $\Delta\delta^{13}\text{C}$  (Figure 4d).

## 4. Discussion

While the use of mumiyo samples has indicated major changes in snow petrel diet over tens of thousands of years at isolated sites (Ainley et al., 2006; McClymont et al., 2022), previous studies were unable to validate the approach, and there remained uncertainty regarding the potential and likely degradation of samples when exposed to the weather, over thousands of years. Here we address that limitation by comparing recent and ancient samples to explore degradation processes, and to understand the consequences of these on inferring past changes in diet. Our results indicate that even though stomach oil undergoes some degradation through time, this is likely to occur relatively soon after deposition. By attaining detailed knowledge about the modern diet and feeding ecology of snow petrels, this information can assist in developing robust proxies for paleoenvironmental and palaeoecological reconstructions based on their fossil stomach oil deposits. We propose that our results provide the validation needed for using ancient deposits for dietary reconstructions based on alkyl lipid distributions, and inferring past changes in marine conditions. Below we describe (a) the validation of the approach of using fossil stomach oil deposits as marine paleoenvironmental archives, and (b) describe initial results of the application of this approach to paleo studies around a large part of the Antarctic coastline.

### 4.1. Composition of Fossil Stomach Oil Deposits

Lipid, elemental and isotope composition of fresh stomach oils may be altered after regurgitation, which leads to loss of information in fossil deposits compared to the fresh stomach oils. Based on the compositional data of fresh stomach oil samples, we investigate systematic effects of degradation and weathering on the lipid and isotopic composition of the fossil deposits in order to assess the validity of these deposits with regard to paleodietary and paleoenvironmental reconstructions.

#### 4.1.1. Effects of Degradation on the Lipid Composition

The surface scrapes and fossil stomach oil deposits contain much lower proportions of unsaturated compounds than the fresh stomach oil (Figure 2), which indicates a conversion of unsaturated compounds after regurgitation. The process could be microbially mediated, as bacterial markers (e.g., C15:0) are abundant in the surface scrapes and stomach oil deposits and absent in the fresh, modern stomach oils samples. Other processes that lead to the alteration of carboxylic acids and conversion of unsaturated to saturated compounds may be autoxidation and polymerization of triacyl glycerols (TAG) and free carboxylic acids (e.g., Paradiso et al., 2018), that may occur upon exposure of the stomach oil to subaerial conditions.

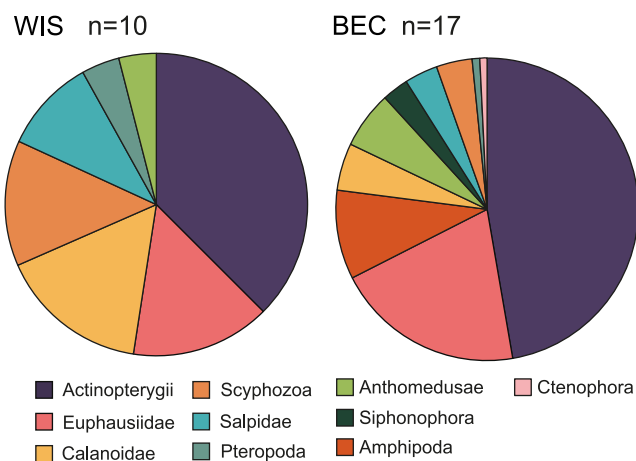
Short chain  $\alpha$ - $\omega$ -dicarboxylic acids that occur in the surface scrapes and fossil stomach oil deposits in high concentrations were not found in fresh stomach oils, indicating a post-depositional formation of these compounds. A likely source of the short-chain  $\alpha$ - $\omega$ -dicarboxylic acids are unsaturated carboxylic acids that can be converted into  $\alpha$ - $\omega$ -dicarboxylic acids via enzymatic pathways (Yeon & Park, 2018) and by photo-oxidation (Marchand & Rontani, 2001). Support for such an origin in stomach oil deposits comes from the chain lengths distribution of  $\alpha$ - $\omega$ -dicarboxylic acids, which are high in C9:0, C11:0, and C13:0 compounds, corresponding to unsaturated carboxylic acids having double bonds at positions  $\alpha$ 9,  $\alpha$ 11 or  $\alpha$ 13 (C16:1 $\omega$ 7, C18:1 $\omega$ 9, C18:1 $\omega$ 7, C20:1 $\omega$ 9, C20:5 $\omega$ 3, C22:6 $\omega$ 3, C22:1 $\omega$ 11, C22:1 $\omega$ 9). Other  $\alpha$ - $\omega$ -dicarboxylic acid homologs (C8:0, C10:0) have been found to be alternative products that form during the photo-oxidation of unsaturated carboxylic acids (Marchand & Rontani, 2001).

The alteration of carboxylic acid patterns in stomach oil deposits may be a function of the age of the deposits or their level of exposure to the elements. However, the proportion of bacterial compounds and  $\alpha$ - $\omega$ -dicarboxylic acids is very similar in surface scrapes and stomach oil deposits of all ages (Figure 2b), indicating that degradation likely happens relatively soon after deposition. It is possible that regurgitated fresh stomach oil is protected from rapid/complete degradation by formation of a protective coating (drying of carboxylic acids) and successive burial under younger stomach oil which may reduce ongoing exposure to oxygen, UV radiation and water, hence reducing the rate of conversion of carboxylic acids and organic matter resulting in degradation in terrestrial environments.

In the stomach oil deposits differential degradation may lead to a shift in alkyl lipid distribution over time. In sedimentary systems, short chain carboxylic acids are preferentially degraded, resulting in a relative enrichment of longer chain homologs (Caradec et al., 2004). Additionally, alkanols may show a relative enrichment over carboxylic acids in the course of persistent diagenesis: In fresh stomach oils the initial proportion of saturated to unsaturated carboxylic acids is higher in TAG than in wax esters (WE) (Connan et al., 2007). A conversion of unsaturated compounds will result in a relative enrichment of alkanols over time. In our dataset, the surface scrapes and Holocene samples show slightly higher proportions of shorter carboxylic acids (C14:0 and C16:0) relative to longer chain homologs (C20 and C22) and lower proportions of alkanols relative to carboxylic acids than the pre-Holocene samples, which may indicate a higher degree of decomposition of the older deposits. However, the modern stomach oil samples show a wide compositional range as well and the difference between Holocene and pre-Holocene deposits could as well reflect a shift in food composition and hence be an original signal.

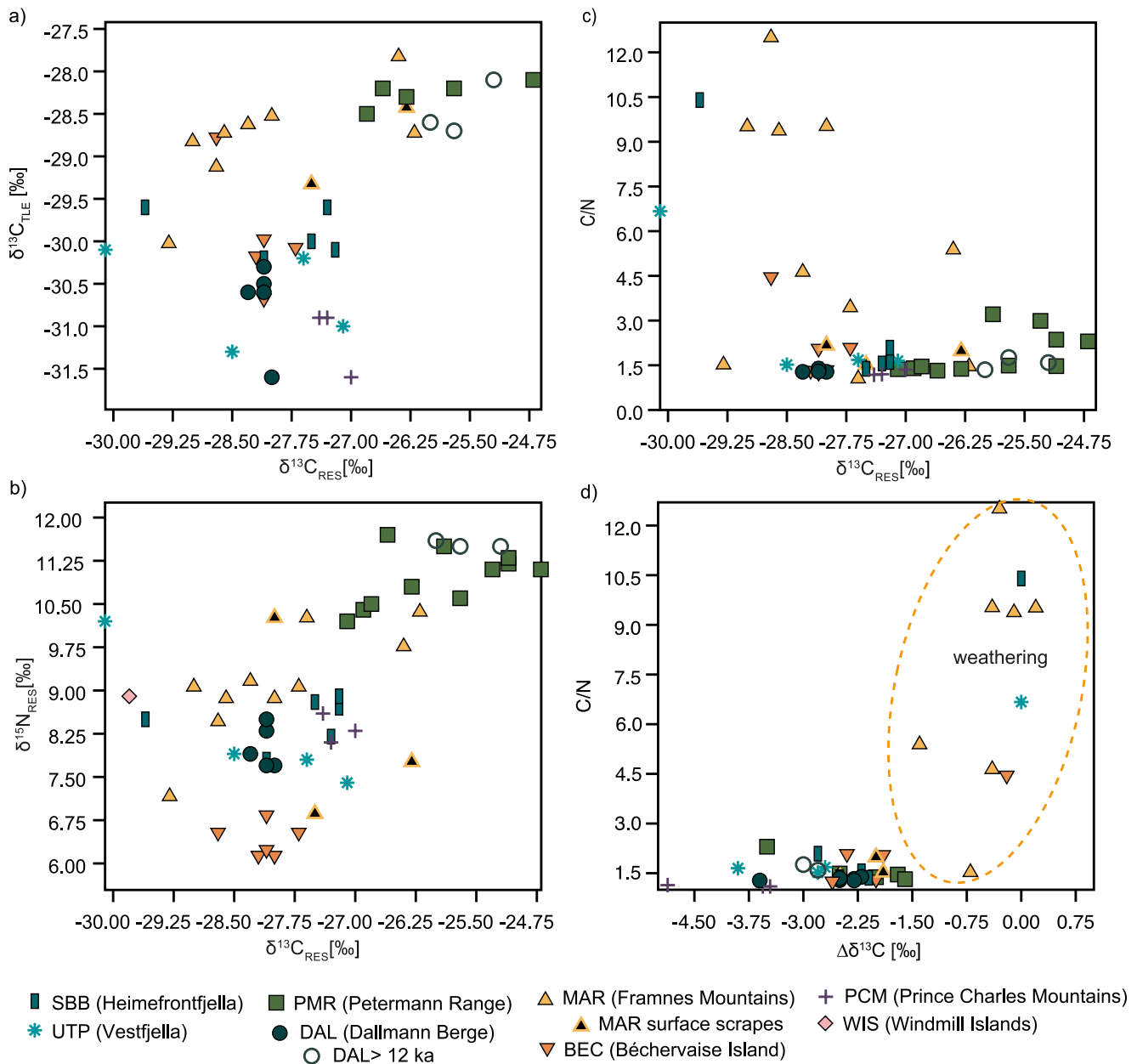
#### 4.1.2. Effects of Degradation on the Stable Isotope Composition

For the paleoenvironmental interpretation of  $\delta^{13}\text{C}$  isotope ratios the choice of the analyzed material is relevant, since  $\delta^{13}\text{C}$  values are not only controlled by environmental variables, such as POC  $\delta^{13}\text{C}$  values in the ocean, but are highly variable, depending on the type of organic material used for analysis. Lipids are generally more depleted (lower  $\delta^{13}\text{C}$  values) than for example, blood, feathers or muscle tissues, within one specimen (e.g., Chérel et al., 2011; Hodum & Hobson, 2000). For environmental studies, it is therefore important to use well-defined fractions of organic matter to allow for a comparison between samples/records/sites. In our study, we separated the lipid from the non-lipid fraction to receive two relatively well-defined fractions of organic matter. The depletion of lipids relative to other organic components is also reflected in our dataset, showing lower  $\delta^{13}\text{C}_{\text{TLE}}$  than  $\delta^{13}\text{C}_{\text{RES}}$  in most of the samples (Figure 3). While the lipids in TLE originate from stomach oil, the organic carbon in the residual material in stomach oil



**Figure 3.** Distribution of prey groups in fecal samples of snow petrels from Windmill Islands (WIS) and Béchervaise Island (BEC) identified from DNA analysis.





**Figure 4.** Stable isotope values and C/N ratios of stomach oil deposits and surface scrapes. (a)  $\delta^{13}\text{C}_{\text{TLE}}$  vs.  $\delta^{13}\text{C}_{\text{RES}}$ . In most samples  $\delta^{13}\text{C}_{\text{TLE}}$  values are lower than those of the residual organic matter of the corresponding sample, which is typical for lipids. (b)  $\delta^{15}\text{N}_{\text{RES}}$  vs.  $\delta^{13}\text{C}_{\text{RES}}$  (c)  $\text{C/N}_{\text{RES}}$  vs.  $\delta^{13}\text{C}_{\text{RES}}$  (d)  $\text{C/N}_{\text{RES}}$  versus  $\Delta\delta^{13}\text{C}$  illustrating that samples with high C/N ratios of the non-lipid residual are characterized by a small off-set between  $\delta^{13}\text{C}_{\text{TLE}}$  and  $\delta^{13}\text{C}_{\text{RES}}$ .  $\delta^{13}\text{C}$  values of such samples are likely not valid for paleoenvironmental interpretations due to alteration.

deposits originates from guano and may also contain feathers and remnants of bones of snow petrels and prey organisms (Berg, Melles, et al., 2019). The C/N ratios of bulk material roughly reflect the proportion of stomach oil to guano-derived organics (Berg, Melles, et al., 2019; McClymont et al., 2022). In contrast, the C/N ratio of residual material ( $\text{C/N}_{\text{RES}}$ ), which we analyzed for this study, allows for a characterization of the non-lipid organic component in the deposits.  $\text{C/N}_{\text{RES}}$  values between 1.2 and 2.5 in most samples support previous assumptions that urates ( $\text{C/N} = 1.1$ ) from guano are main constituents of the non-lipid organic fraction in stomach oil deposits (Berg, Melles, et al., 2019). However, some  $\text{C/N}_{\text{RES}}$  values are higher (>3), indicating a high carbon/low nitrogen component in the residue of these deposits (Figure 4c). These samples at the same time show smaller offsets between  $\delta^{13}\text{C}_{\text{TLE}}$  and  $\delta^{13}\text{C}_{\text{RES}}$  ( $\Delta\delta^{13}\text{C} < 1.5\text{‰}$ ) than samples with  $\text{C/N}_{\text{RES}} < 3$  (Figure 4). This observation could be explained by the presence of diagenetic products of lipid degradation in  $\text{C}_{\text{RES}}$ -fraction of the deposits,

such as insoluble “adipocere” and polymers that formed from carboxylic acids, resulting in  $\delta^{13}\text{C}_{\text{RES}}$  values reflecting a mixed signal of lipids and non-lipids. Since the off-set between the two carbon fractions in stomach oil deposits has a similar magnitude as the range expected to occur from variations in environmental parameters, a paleoenvironmental interpretation of  $\delta^{13}\text{C}_{\text{RES}}$  should be restricted to samples that do not contain a mixed composition. From our dataset, we suggest that such samples can be identified by  $\Delta\delta^{13}\text{C}$  values of  $>-2\text{‰}$  and  $C/N_{\text{RES}} < 2$ . Interestingly, this kind of stomach oil alteration is not a feature of the older deposits from PRM and DAL. Instead, the Holocene deposits, particularly those from MAR, are affected. This suggests that the formation of insoluble carboxylic acids is a type of weathering that could be a function of the physical surroundings of the individual nesting sites, such as exposure to solar irradiation and moisture, rather than of the age of the deposit.

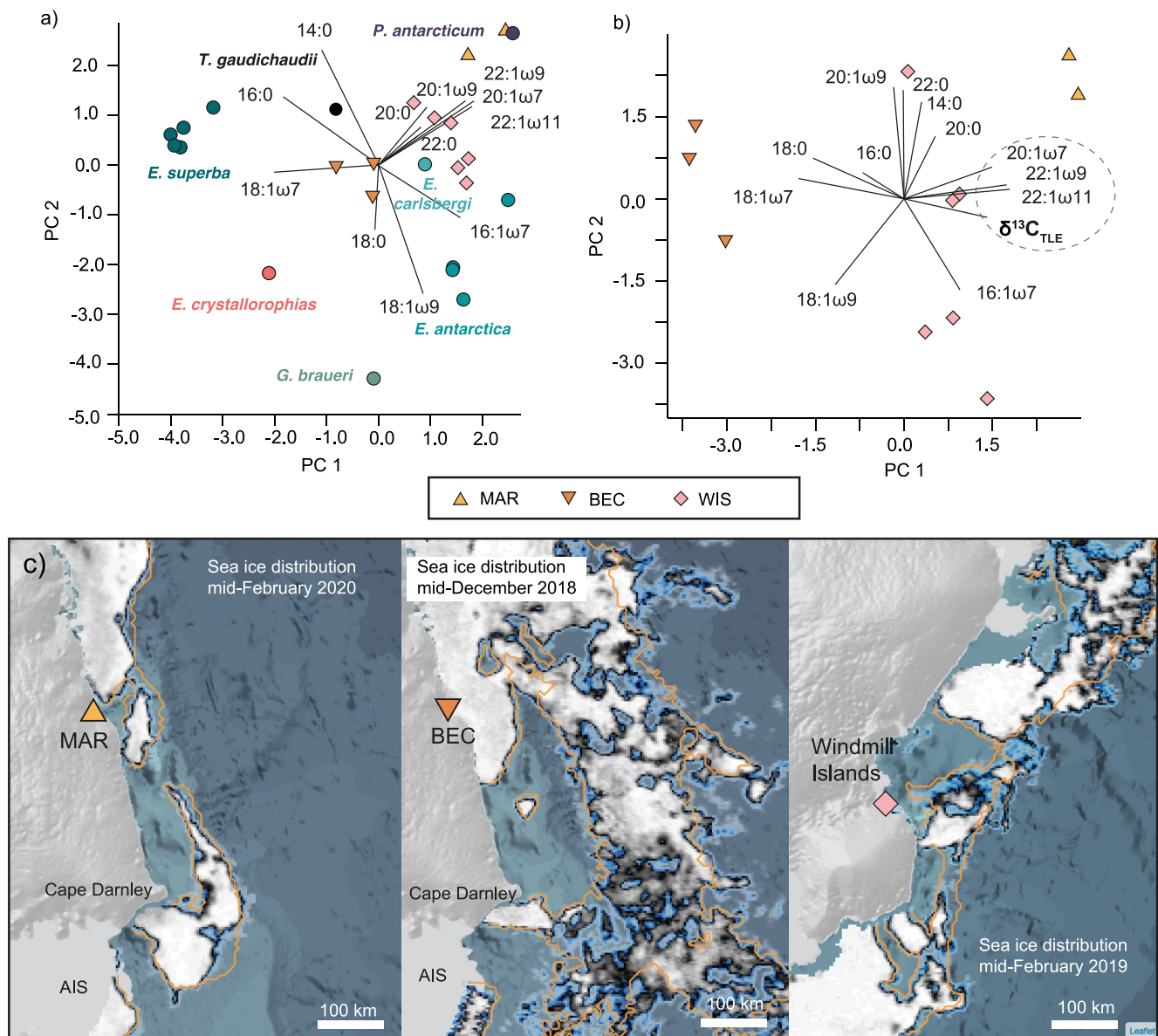
## 4.2. Modern Diet of Snow Petrels and Dietary Information in the Fossil Record

Snow petrels are widely known to feed on fish, krill and other crustaceans and squid in variable proportions (e.g., Ainley et al., 1992; Ferretti et al., 2001; Fijn et al., 2012; Ridoux & Offredo, 1989). Regional variability of snow petrel diet is evident from different fish species being caught by the snow petrels in different regions. For example, *Electrona antarctica*, a myctophid fish, is found in their diet around South Orkney Islands (Ainley et al., 1993; Ferretti et al., 2001; Fijn et al., 2012) and *Pleuragamma antarcticum*, a notothenioid fish, dominates their diet in the Ross Sea region (Ainley et al., 1984). This variability in their diet in different regions likely reflects the close link between snow petrel foraging and the occurrence of pack ice (e.g., Stroeve et al., 2016; Sauser et al., 2018) rather than necessarily being driven by the availability of specific prey species (e.g., Ainley et al., 1984, 1992) although further studies are needed to resolve this. We interpret therefore that the dietary composition, at least to some extent, reflects the foraging area of snow petrels and is therefore a likely indicator for past changes of/in the foraging region with regard to the prevailing sea ice conditions (McClymont et al., 2022).

### 4.2.1. Modern Diet of Snow Petrels-Evidence From Stomach Oil Lipids and Fecal DNA

The prey DNA data from modern snow petrel fecal samples from WIS and BEC showed that bony fish and krill were the most abundant prey groups, which is broadly consistent with previous studies (e.g., Ainley et al., 1992; Ferretti et al., 2001; Fijn et al., 2012; Ridoux & Offredo, 1989). In contrast to other studies (Ainley et al., 1984; Ferretti et al., 2001; Ridoux & Offredo, 1989.), squid were not detected in the fecal samples investigated in this study, which may indicate a limitation of the DNA analysis as they were also missing from the Adelie penguin diet presented in Jarman et al. (2013). For these modern samples, there is little difference in the snow petrel diet between WIS and BEC, apart from the large presence of amphipods at BEC but not at WIS. The difference could be due to a slightly different time of the breeding season for sampling which may reflect a different shelf-pelagic foraging location. A general geographical difference in diet is also possible as demonstrated for the Adélie penguins at WIS and BEC in the same years (McInnes et al., 2015), but cannot be clearly deduced from the limited data set presented here. The prey DNA data reveals some complexity of the dietary composition, likely also including prey items from secondary ingestion. This complexity is however, unlikely to be preserved in the fossil record, but the results of the main prey items provides a basis for the evaluation of the fossil samples.

In stomach oils of procellariiformes seabirds, the lipid composition of prey is retained and allows for reconstructing the composition of diet of the respective birds (e.g., Connan et al., 2005, 2007). Prey species are distinct in their lipid compositions, reflecting individual strategies of energy storage and feeding ecology. *E. antarctica*, for example, is rich in WE, while Antarctic krill *E. superba* contains high proportions of TAG (e.g., Cho et al., 1999; Lea et al., 2002; Phleger et al., 2002). Among the carboxylic acids, mono-unsaturated and poly-unsaturated compounds are highly specific (e.g., Connan et al., 2007). In order to test if the main groups of prey can be identified in the fresh stomach oil samples from BEC, MAR and WIS, we performed a PCA, based on the carboxylic acid data of fresh stomach oil samples from this study and literature data of typical prey species (Figure 5). We selected the four fish species *E. antarctica*, *Electrona carlsbergi*, *Gymnoscopelus braueri*, and *P. antarcticum*, the two krill species *E. superba*, and *E. crystallophias*, and the amphipod *T. gaudichaudii*, which have been identified in snow petrel diet (e.g., Ainley et al., 1984; Fijn et al., 2012). Squid was not considered here since this group is likely not identifiable from carboxylic acid patterns. Carboxylic acids in squid mostly originate from the content of the digestive gland, hence reflecting the diet and not the animal itself (Phillips et al., 2002). Further,



**Figure 5.** (a) Biplot of PCA based on carboxylic acid distribution in stomach oil samples and species that are representative for potential prey species of snow petrels. *E. superba* (Liu et al., 2019; Phleger et al., 2002; Yang et al., 2016), *E. crystallorophias* (Yang et al., 2016), *T. gaudichaudii* (Phleger et al., 1998), *E. antarctica* (Lea et al., 2002; Phleger et al., 1997), (e) *carlsbergi* (Lea et al., 2002), *P. antarcticum* (Mayzaud et al., 2011), *G. braueri* (Phleger et al., 1999) (b) Biplot of PCA based on carboxylic acid distribution and  $\delta^{13}C_{TLE}$  in stomach oil samples only. (c) Sea ice distribution on the date of stomach oil sampling (white = 100% sea ice) and mean sea ice distribution for the respective month (orange line). Maps from Meereisportal.de.

for the modern snow petrel populations at BEC and WIS squid was not reported as an important contributor to diet in summer (although note possible alternate explanation for this above).

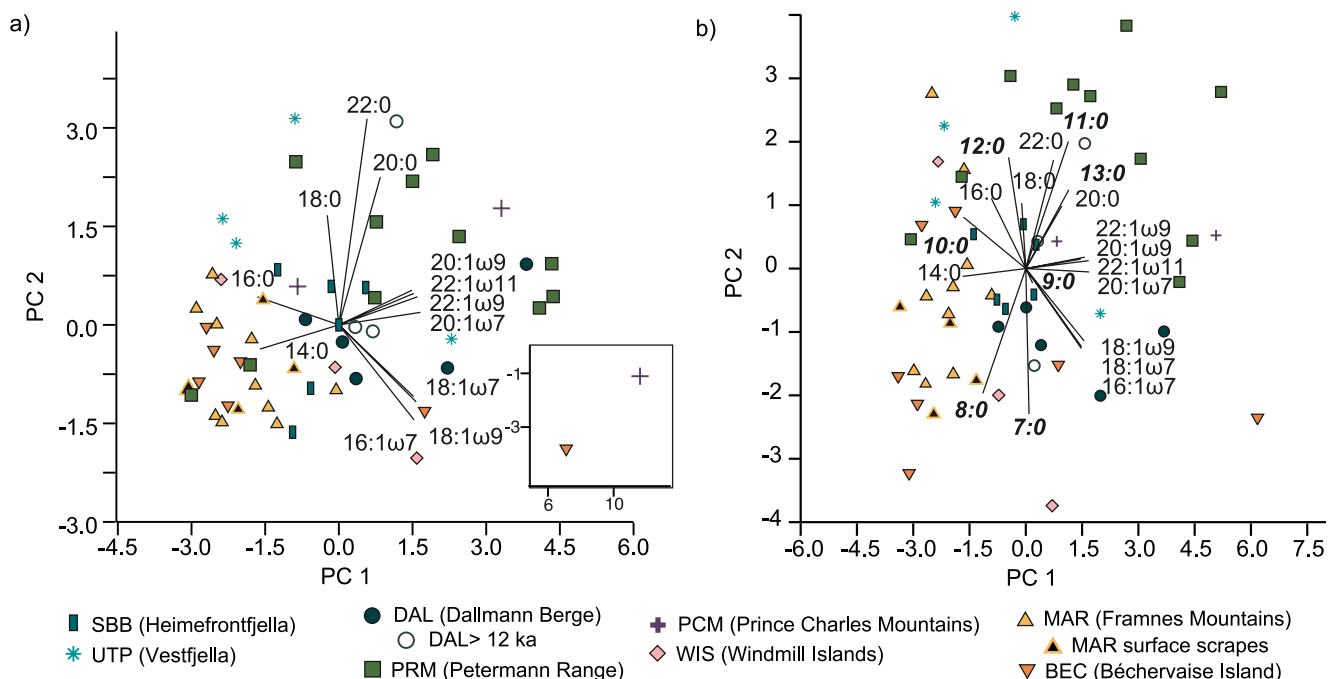
The PCA of carboxylic acid distribution in stomach oil and prey species shows that PC1 (explaining 40.7% of the variance) is characterized by high positive loadings on 16:1ω7, 18:1ω9 and C20:1 and C22:1 isomers and negative loadings on C18:1ω7, C16:0, and C14:0 (Figure 5). It clearly separates krill (*E. superba* and *E. crystallorophias*) and *T. gaudichaudii* from fish. Krill and *T. gaudichaudii* have high negative scores on PC1 and correlate to C18:1ω7, C16:0, and C14:0. Fish species *E. antarctica*, *E. carlsbergi* and *P. antarcticum* have positive scores on PC1 and correlate to 16:1ω7, 18:1ω9, C20:1 (ω9 and ω7), and C22:1 (ω11 and ω9) (Figure 5). The exception among the considered fish species is *G. braueri*, which cannot be assigned to either fish- or krill-type distribution patterns of carboxylic acids (Figure 5). The ratio of the two isomers 18:1ω9 and 18:1ω7 is used as a trophic indicator, for instance in krill (Yang et al., 2016) since 18:1ω7 is more abundant relative to 18:1ω9 in herbivorous than in carnivorous

species (Dalsgaard et al., 2003). This finding is consistent with our data evaluation, showing a separation of species from higher trophic levels (fish) from species with lower trophic level (krill) based on the C18:1 distribution. Correlation of carboxylic acids C20:1 ( $\omega$ 9 and  $\omega$ 7), C22:1 ( $\omega$ 11 and  $\omega$ 9), C20:0, and C22:0 to fish species in PC1 is consistent with low concentrations in krill and higher concentrations in fish, making these compounds an indicator to distinguish fish-from krill-rich diet in snow petrel stomach oils. PC2 (22.9% of variance) has positive loadings for C16:0 and C14:0 and C20:1 ( $\omega$ 9 and  $\omega$ 7), C22:1 ( $\omega$ 11 and  $\omega$ 9), C20:0 and C22:0 and negative loadings on C18:0, C18:1 $\omega$ 9, C16:1 $\omega$ 7, and C18:1 $\omega$ 7 (Figure 5). Among the fish species, it separates *P. antarcticum* (positive scores for PC2) from *E. antarctica* (negative scores of PC2), among the krill species it separates *E. superba* from *E. crystallorophias* (Figure 5). The common feature of species that have positive scores on PC2 is that they are rich in TAG, while the species that have negative scores on PC2 use dominantly WE (Lea et al., 2002; Liu et al., 2019; Mayzaud et al., 2011; Phleger et al., 1997, 1998, 1999, 2002; Yang et al., 2016). Since the alkanols were not included in this analysis, the discriminability likely arises from the differences in carboxylic acid patterns in WE and TAG, as found in studies on stomach oils of procellariiform seabirds (Connan et al., 2005, 2007).

The carboxylic acid distribution in the snow petrel stomach oils analyzed in this study can be explained by mixing of the endmembers as given by the main prey species, allowing for some inferences on the prey composition. The stomach oils from BEC reflect a mixed diet, likely containing higher proportions of krill (negative scores on PC1) compared to the other two investigated sites (Figure 5). The two stomach oil samples from MAR are very similar to the *P. antarcticum* carboxylic acid patterns, indicating a high proportion of *P. antarcticum* (high positive scores on PC1 and PC2). The samples from WIS reflect a diet dominated by fish with variable proportions of *P. antarcticum*, *E. antarctica*, and *E. carlsbergi*. The six samples can be divided in two groups. One group contains high proportions of *P. antarcticum*, the other group could either contain equal contributions from *P. antarcticum* and *E. antarctica* or consist of mainly *E. carlsbergi*. None of the stomach oil samples indicates consumption of *G. braueri* (Figure 5). For the stomach oils, samples with higher carboxylic acid to alkanol ratios have higher scores on PC2, which supports the interpretation of PC2 as reflecting an initially either WE- or TAG-rich lipid composition.

#### 4.2.2. Dietary Information From Surface Scrapes and Fossil Deposits (Mumiyo)

In order to investigate if the carboxylic acids in the surface scrapes and fossil deposits retain some information of the original composition of snow petrel diet, we performed a PCA, including the same carboxylic acid compounds as used for the modern samples (Figure 6a). In the fossil sample set the pattern of co-varying carboxylic acid



**Figure 6.** Principal component analysis (PCA) of carboxylic acid compounds (a) and carboxylic acids and  $\alpha$ - $\omega$ -dicarboxylic acids (in italic) (b) in mumiyo deposits. Data points are color-coded by regions, which are mostly represented by samples from more than one deposit.

compounds is broadly similar to the distribution found in modern samples. The short-chain homologs C14:0 and C16:0, indicative for krill species in the modern dataset, are grouped, as well as the C20:0 and C22:0 (saturated and monounsaturated) homologs, indicative for fish (predominantly *P. antarcticum*). This suggests that the main groups of prey are also reflected in the carboxylic acid patterns of fossil stomach oil deposits. A difference to the modern data is the correlation of C18:1 $\omega$ 7, C18:1 $\omega$ 9, and C16:1 $\omega$ 7, which were assigned as being indicative for *E. superba* (C18:1 $\omega$ 7) and *E. antarctica* (C18:1 $\omega$ 9 and C16:1 $\omega$ 7). The correlation of all three compounds in the fossil stomach oil may indicate a common uptake of *E. superba* and *E. antarctica* (either separately or as secondary ingestion) due to the regional overlap of their occurrence in more pelagic, sea ice marginal areas, hence reflecting the species assemblage in the foraging area rather than providing detailed information of dietary composition on species level.

Since un-saturated compounds may be subject of preferential degradation in the fossil record, we investigate if the distribution of  $\alpha$ - $\omega$ -dicarboxylic acids may add some dietary information as well. We performed a second PCA including carboxylic acid compounds (C14 to C22) and the  $\alpha$ - $\omega$ -dicarboxylic acids C7 to C13 (Figure 6b). The C11 and C13  $\alpha$ - $\omega$ -dicarboxylic acids correlate with C20:0 and C22:0 carboxylic acids, in accordance with a hypothesized origin from cleavage of C20:1 and C22:1 carboxylic acids. The positive loadings of C11 and C13 on PC1 (explaining 46.8% of the variance), which separates fish from krill-rich diet, suggests that both compounds could be indicative for fish-rich diet. In PC2 (explaining 17.7% of the variance) the shorter homologs (C7 to C9) are separated from the longer homologs (C10 to C13). The position of C9 in the biplot PC1 versus PC2 reflects its relatively low specificity, when considering the original compounds (e.g., C16:1 $\omega$ 7, C18:1 $\omega$ 9, C20:5 $\omega$ 3, C22:6 $\omega$ 3, C22:1 $\omega$ 11). Short homologs are possibly forming from polyunsaturated carboxylic acids, but cannot be proven based on our data.

The dietary composition as reflected by the distribution of carboxylic acids in the stomach oil deposits indicates regional characteristics. The deposits from PRM are characterized by C20:0 and C22:0 (saturated and un-saturated) homologs (higher up-take of *P. antarcticum*), while samples from BEC and MAR are associated with C14:0 and C16:0 (higher up-take of krill species). These patterns likely reflect regional foraging strategies of snow petrels in response to region-specific controls on the availability of prey organisms (e.g., presence/absence of polynyas, shelf width, sea ice). Reconstructions of paleo-diet will therefore allow inferences about how snow petrels adapt to environmental changes, since extensive sea-ice years can have a negative impact on breeding success and adult survival of snow petrels (Barbraud et al., 2000; Olivier et al., 2005).

### 4.3. Linking the Composition of Diet to Environmental Conditions in the Foraging Region

In order to use the lipid- and isotopic composition of stomach oil deposits for reconstructing past environmental conditions, the connection between dietary information and actual environmental conditions needs to be established. In the following we will discuss possible links between snow petrel diet and environmental variables, such as marine productivity, foraging region and sea ice. Further, we will discuss to what extent the modern observations can be transferred to the fossil record, taking into account the degradation and weathering of the stomach oil after deposition.

#### 4.3.1. Possible Environmental Controls on Snow Petrel Diet

The carboxylic acid patterns in the fresh stomach oils indicate different composition of snow petrel food between the samples. Although, we cannot determine whether there is a general difference in feeding strategies of birds from the three sites, due to the limited number of individuals or years studied, these differences can be used to discuss possible environmental controls on the snow petrel diet.

The colonies in MAR and BEC are c. 25 km apart, which is a very short distance given the foraging range of c. 750 km for snow petrels (Delord et al., 2016) as well as other fulmarine Antarctic breeding species (Dehnhard et al., 2019, 2021) and thereby comparable conditions for access to a common foraging area can be assumed for the two sites. The carboxylic acid patterns suggest that the birds sampled from MAR were probably feeding in the waters over the shelf and inner slope, consistent with a diet rich in *P. antarcticum*, that is common in high Antarctic shelf waters (La Mesa et al., 2010), while the sampled birds from BEC consumed higher proportions of *E. superba* and *E. antarctica*, that live in water depths of >1,000 m (Duhamel et al., 2000), indicating a foraging area in waters over the outer slope and in pelagic waters. The fresh stomach oil samples from BEC and MAR were taken in consecutive years (18/19 and 19/20, respectively) and at different times of the season (mid-December



and mid-February, respectively) and therefore may reflect interannual and seasonal variation in food composition, rather than site-specific behavior. In particular, there can be a considerable difference in the sea-ice conditions and the extent of the fast ice along this coastline at these two times within a breeding season (Emmerson & Southwell, 2008; Emmerson et al., 2011).

Sea ice coverage and sea-ice extent are important controls on the accessibility to feeding areas and the availability of prey for Adélie penguins (Emmerson & Southwell, 2008; Emmerson et al., 2015), and potentially also for snow petrels even though they are not constrained to walking across the fast ice like Adélie penguins. The shelf directly off MAR and to the east was largely ice-free by the time of sampling MAR in mid-February 2020 (Figure 5c). Under such conditions birds may preferably catch fish on the shelf, which allows for shorter flying distances during foraging trips (higher proportion of *P. antarcticum*). The sampling of BEC was earlier in the season (mid-December) and there was no direct access to open water off BEC due to the presence of sea ice, particularly fast ice (Figure 5c). Sea ice distribution at that time suggests foraging in a sea ice marginal environment, across the shelf break and open ocean as also suggested from prey species composition derived from the carboxylic acids (*E. superba* and *E. antarctica*; Figure 5b). We think that it is likely that the different food composition reflects the prevailing sea-ice conditions at the time of the foraging trip, and the consequence that has on where they forage in relation to the coastline and features such as the shelf break. Apart from primarily environmental factors (such as accessibility of specific foraging regions depending on sea ice), snow petrels are selective in the uptake of prey species, as chicks are fed by a more fish-rich diet than what is eaten by adult birds (Delord et al., 2016; Hodum & Hobson, 2000; Ridoux & Offredo, 1989). In fact, the two stomach oil samples from MAR that indicate high proportions of fish from carboxylic acid distribution, were from chicks. Samples from the Windmill Islands are from mid-February 2019, similar to the sampling at MAR. Sea ice at the date of sampling was patchy with open water, surrounded by sea ice of variable density (from <10% sea ice to areas with 100% coverage) on the shelf and across the shelf break and fully open waters off-shore (Figure 5). Carboxylic acid distribution in the stomach oil from WIS indicates a mixed diet of *P. antarcticum* and *E. antarctica*, which likely reflects that some petrels were feeding preferably on the shelf (higher proportions of *P. antarcticum*), while others were foraging in the sea ice marginal areas and in deeper waters, further off the coast (higher proportions of *E. antarctica*). Understanding the spatial- and temporal variability in snow petrel diet from geographically separated colonies as well as those near each other is an important next step to resolve the controls on their foraging locations and success, taking account of the presence of sea ice in their foraging range on their diet.

In addition to the composition of fecal samples and the lipid distribution in stomach oil, the isotope composition can be indicative of prey composition and habitat characteristics (Cherel et al., 2011). Trophic level is well reflected in  $\delta^{15}\text{N}$  isotopic values (e.g., Cherel et al., 2011; Quillfeldt et al., 2005). However, this proxy cannot be used for the fresh stomach oil samples, due to a lack of nitrogen in the TLE but faeces may be used for this purpose. The  $\delta^{13}\text{C}$  value of primary producers is essentially conservative through the trophic level and is applied to infer foraging regions (e.g., Hodum & Hobson, 2000; Quillfeldt et al., 2005). In our dataset the correlation of  $\delta^{13}\text{C}_{\text{TLE}}$  of stomach oil with C20:1 $\omega$ 7, C22:1 $\omega$ 11, and C22:1 $\omega$ 9 carboxylic acids may indicate that  $\delta^{13}\text{C}$  reflects a specific food composition here (Figure 5b). The samples with high  $\delta^{13}\text{C}$  have been assigned as having high contributions of *P. antarcticum* (indicating foraging over the shelf and inner slope), while a mixed, more pelagic food composition of *E. superba* and *E. antarctica* is associated with lower  $\delta^{13}\text{C}$  values (Figure 5b). This interpretation is consistent with isotope studies that show distinct  $\delta^{13}\text{C}$  values for krill and fish (Emslie & Patterson, 2007; Hodum & Hobson, 2000) and with oceanographic observations that show higher  $\delta^{13}\text{C}$  values of particulate organic matter (POM) closer to the coast than off shore (Zhang et al., 2014).

#### 4.3.2. Implications for Paleoenvironmental Reconstructions From Stomach Oil Deposits

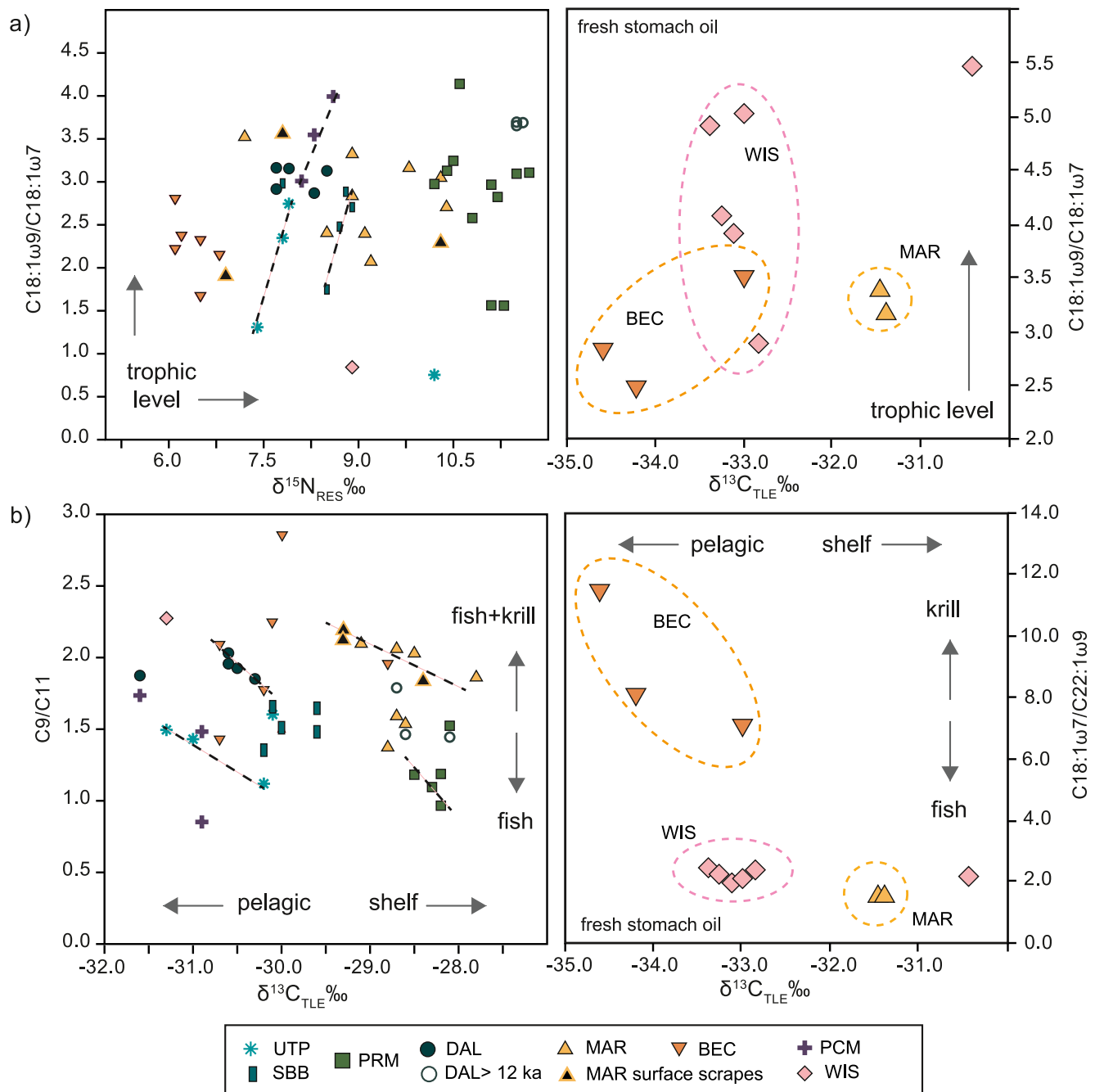
After regurgitation the stomach oil undergoes some alteration by oxidation and bacterial activity. In the following we will discuss how past changes in the marine habitat of the snow petrels can be derived from mumiyo deposits, despite of a certain loss of information on the composition of diet compared to fresh stomach oils. This will be achieved by taking a paleoecological perspective of the dietary information obtained from the lipid and isotopic composition that will allow the link between dietary and environmental information.

$\delta^{15}\text{N}$  of body tissue reflects the trophic position of organisms within a food web, expressed in an enrichment of c. 3.2‰ per trophic level (Sweeting et al., 2007). For the stomach oil deposits higher  $\delta^{15}\text{N}_{\text{RES}}$  values may reflect a diet composed of prey organisms of higher trophic level as compared to samples with lower values, hence

higher contribution of fish (e.g., *P. antarcticum*, 9.6–10.7‰) versus krill (e.g., *E. superba*, 4.0–5.2‰) (Hodum & Hobson, 2000). However, in addition to changes in diet, the  $\delta^{15}\text{N}$  value also reflects the baseline  $\delta^{15}\text{N}$  value within the food web (as represented by phytoplankton), being controlled by oceanic environmental conditions.  $\delta^{15}\text{N}$  values in phytoplankton, namely diatoms, correspond to the degree of nutrient supply and utilization in the photic zone in response to ocean circulation, upwelling or iron availability (e.g., Crosta & Shemesh, 2002; Horn et al., 2011). The  $\delta^{15}\text{N}$  values in stomach oil deposits are well within the range of modern biological samples, likely indicating that diagenetic overprinting does not have a strong effect (Mizutani et al., 1985). Therefore,  $\delta^{15}\text{N}$  values likely reflect a mixed signal of trophic position of snow petrel paleodiet and nutrient supply and utilization in the photic zone of the foraging region of the birds. In order to separate the trophic and oceanic signal in the stomach oil deposits, we combine the isotopic data with the lipid data (Figure 6a). Comparably to  $\delta^{15}\text{N}$ , the ratio of C18:1 $\omega$ 9/C18:1 $\omega$ 7 can be employed as a measure of the proportion of higher/lower trophic level organisms to snow petrel diet (Dalsgaard et al., 2003; Schmidt et al., 2006). The data obtained from all stomach oil deposits does not show a correlation of the two indicators for trophic position (Figure 7a). The deposits are distinct in the range of  $\delta^{15}\text{N}$  values, depending on the region and depositional age (Holocene vs. pre-Holocene), while the range of C18:1 $\omega$ 9/C18:1 $\omega$ 7 overlaps for all regions/deposits. However, a clear trend of higher  $\delta^{15}\text{N}$  values with higher C18:1 $\omega$ 9/C18:1 $\omega$ 7 ratios (trophic level of food) is given on regional scale for the deposits from UTP, SBB and PCM, respectively. The variation of the C18:1 $\omega$ 9/C18:1 $\omega$ 7 ratio goes along with a range of 0.4–0.5‰ in  $\delta^{15}\text{N}$ , reflecting relatively small changes in the composition of diet with respect to the trophic level of prey organisms. This finding is in accordance with the generally fish-dominated diet of snow petrels, without differentiating different fish species. In modern snow petrels the range is larger (c. 2‰ between chicks and adults, Hodum & Hobson, 2000).

In the fossil record, differences between foraging trips or short-term inter-annual variability are likely levelled-out, because the fossil record represents an integrated temporal signal. The variability between regions we find in the  $\delta^{15}\text{N}$  data of the stomach oil deposits therefore likely reflects differences in initial  $\delta^{15}\text{N}$  values of POM in connection with regional oceanographic conditions of the specific foraging regions (Schmidt et al., 2006). For paleo-reconstructions, the stomach oil deposits can likely provide information on shifts in baseline  $\delta^{15}\text{N}$  values through time for a specific region. For the two sites in Mac. Robertson Land, BEC and MAR,  $\delta^{15}\text{N}$  values differ by c. 3‰, which cannot be explained by different dietary composition alone. Since the surface scrapes from BEC reflect the present-day signal, while the samples from MAR comprise a mid-to late Holocene record, the differences in  $\delta^{15}\text{N}$  may reflect changes in marine productivity over time, probably connected to changes in the activity of the Cape Darnley polynya. Further evidence that the deposits record shifts in oceanic baseline  $\delta^{15}\text{N}$  values comes from the pre-Holocene stomach oil deposits from Dronning Maud Land (PRM and DAL > 12ka), that have higher  $\delta^{15}\text{N}_{\text{RES}}$  values compared to most Holocene samples (Figure 6c). Although the lipid distribution assigned relatively high proportions of fish (likely *P. antarcticum*) to snow petrel diet during that time, a full trophic control of the  $\delta^{15}\text{N}$  signal is unlikely, since the C18:1 $\omega$ 9/C18:1 $\omega$ 7 ratio in these samples spans a similar range as the Holocene samples. Instead, the off-set of c. 3.5‰ between the Holocene and pre-Holocene sections in DAL is of the same magnitude as the shifts found in  $\delta^{15}\text{N}_{\text{diatom}}$  in sediment records from the Atlantic sector of Southern Ocean (Crosta & Shemesh, 2002; Horn et al., 2011). This suggests that large-scale changes in ocean circulation and ocean-atmosphere  $\text{CO}_2$  exchange on glacial-interglacial timescales are preserved in stomach oil deposits.

The feeding ecology of snow petrels is linked to the distribution of sea ice (specifically pack ice and the pack ice edge) in the foraging range, making the stomach oil deposits possible archives for sea ice reconstructions (Ainley et al., 1984, 2006; McClymont et al., 2022). In modern stomach oil the composition of snow petrel prey can be distinguished into a more outer slope/pelagic assemblage, consisting of krill and fish (*E. superba* and *E. antarctica*), and a more shelf-based assemblage, characterized by the fish *P. antarcticum*, based on a combination of the carboxylic acid distribution and  $\delta^{13}\text{C}_{\text{TLE}}$  values. For the fossil record carboxylic acid ratios combining saturated and un-saturated compounds are not suitable to compare different deposits with respect to the original dietary information, due to the variable preservation quality of un-saturated compounds. To test, if the observation on modern stomach oil is resembled in the fossil record, we therefore compare the variation in  $\delta^{13}\text{C}_{\text{TLE}}$  to the ratio of C9/C11  $\alpha$ - $\omega$ -dicarboxylic acids (Figure 7b). The C9- and C11  $\alpha$ - $\omega$ -dicarboxylic acids are likely products of the un-saturated compounds that reflect the pelagic versus shelf prey assemblage in modern stomach oils (see Section 4.2). Clear trends exist within regions (e.g., for DAL, UTP, PRM, and MAR), supporting the environmental interpretation of the data. The shifts in the foraging region from predominantly shelf to predominantly pelagic areas likely reflect past sea ice coverage across the continental shelf and coastal ocean. Modern



**Figure 7.** Stable isotopes and selected lipids from stomach oil deposits/surface scrapes and fresh stomach oil samples. Interpretation of environmental variables is indicated (a) Ratio of C18:1ω9/C18:1ω7 versus δ<sup>15</sup>N<sub>RES</sub> (stomach oil deposits and surface scrapes) and versus δ<sup>13</sup>C<sub>TLE</sub> (fresh stomach oil) (b) Ratio of C9 and C11 α-ω-dicarboxylic acids (stomach oil deposits and surface scrapes) and C18:1ω9/C18:1ω7 (fresh stomach oil) versus δ<sup>13</sup>C<sub>TLE</sub>.

observations on snow petrels and Adélie penguins (*Pygoscelis adeliae*) have shown that the breeding success and adult survival of the birds are closely linked to the type, extent, and location of sea ice in their foraging range (Barbraud et al., 2000; Emmerson & Southwell, 2008; Emmerson et al., 2015). Prolonged fast ice or extensive consolidated pack ice during spring and summer or high sea ice coverage on the shelf will likely result in snow petrels moving further out on the ocean during their foraging trips. Such shifts in foraging region in response to the prevailing sea ice conditions is likely reflected in the composition of the stomach oil deposits. In order to test this hypothesis, more studies are needed that combine evidence from stomach oil deposits and from marine sediment cores (e.g., diatom-based sea ice reconstructions) from the foraging region of the birds (Ainley et al., 2006).

From the data shown here some preliminary conclusion on the regional differences in the paleo-diet of snow petrels can be drawn. The overall  $\delta^{13}\text{C}_{\text{TLE}}$  values in the stomach oil deposits cover a range from  $-27.7$  to  $-31.7\text{‰}$  but show more confined ranges on regional scale (Figure 7b). The  $\delta^{13}\text{C}$  isotopic signature in the deposits likely does not only reflect the composition of diet, but also the regional oceanic base line of the predominant foraging region, as has been suggested by Ainley et al. (2006), who reported concurrent shifts in  $\delta^{13}\text{C}_{\text{TLE}}$  of mumiyo deposits and  $\delta^{13}\text{C}$  of organic carbon in Holocene marine sediments. For the deposit that were assigned to the last glacial, lower  $\delta^{13}\text{C}$  values and higher contribution of fish relative to the Holocene, suggest that the snow petrels where predominantly feeding in a shelf and inner slope environment, likely in coastal polynyas, that provided an open water environment within the extensive sea ice during the last glacial maximum (as also shown by McClymont et al., 2022). For the Holocene, the diet likely contained higher proportions of krill, which is consistent with an increase of the foraging range to more pelagic regions in response to the absence of prolonged fast ice during summer.

The relatively large shift in  $\delta^{13}\text{C}$  values between the glacial and interglacial samples likely reflect large-scale changes in ocean circulation (Crosta & Shemesh, 2002; Horn et al., 2011). For the sites BEC and MAW the paleo-data indicates that the diet of birds at BEC probably preferred more pelagic feeding locations than the birds at MAW (Figure 7). Similarly, the mumiyo samples from UTP and SBB indicate slightly different foraging ranges of the birds from either site. These preliminary findings probably indicate that snow petrel populations from different, albeit spatially close-by breeding sites may not necessary visit the same foraging locations. However, given the limited amount of data it will be a goal of future studies to further investigate regional patterns of snow petrel foraging.

## 5. Conclusions

For reconstructing past changes in marine environmental conditions from fossil stomach oil deposits it is crucial to consider the present-day feeding ecology of snow petrels. The use of modern samples (fresh stomach oils and fecal samples) allows for a characterization of the modern dietary composition and provides the necessary reference for paleo-reconstructions. The DNA data from modern fecal samples reveal a highly complex dietary composition, representing a wide range of ingested prey groups and likely including items of secondary ingestion. In contrast, the carboxylic acid distribution in fresh stomach oils likely best represent prey species rich in TAG and WE, generally having a high calorific contribution to snow petrel diet and therefore being important for the diet of the birds. In our sample set of fresh stomach oil the carboxylic acid distribution can be best explained by changing relative contributions of myctophid and notothenioid fish and krill. Based on the carboxylic acid patterns and concurring  $\delta^{13}\text{C}$  values of total lipids in fresh stomach oil we suggest that these two parameters reflect relative contributions of shelf/inner slope versus outer slope/pelagic prey assemblages. Changes in the respective proportions likely occur in accordance with the sensitivity of snow petrels to prevailing sea-ice conditions in their foraging range.

After regurgitation the stomach oil undergoes some alteration by oxidation and bacterial activity, which is consistently found in deposits ranging from recent (surface scrapes) to older than 50 ka in age, indicating that degradation likely happens relatively soon after deposition. The conversion of un-saturated compounds leads to a loss of information on the composition of diet compared to fresh stomach oils. By defining the composition of diet in a paleoecological sense, which distinguishes a shelf (near shore) or pelagic (off-shore) prey assemblage, rather than trying to distinguish single species, we can infer past changes in the marine habitat of the snow petrels. In the fossil record we find region-specific differences in the lipids and isotopic signal of stomach oil deposits, likely reflecting regional characteristics of foraging grounds, such as the local shelf bathymetry (broad shelf vs. narrow shelf), ocean circulation, and seasonal distribution of sea ice and polynyas. Since the environmental histories of many coastal areas off East Antarctica are not well accessed by sedimentary records, we propose that future studies on stomach oil deposits will provide information on regional sea-ice and climate histories. Regional comparisons of the paleo-ecological diet will reveal potential variability of the foraging strategies and on long-term changes, ultimately providing understanding of ecosystem response to changing climate conditions.

## Data Availability Statement

Data presented in this publication can be accessed via Pangaea database (<https://doi.org/10.1594/PANGAEA.951357>) and from the supporting information to this article.

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