Paleoenvironmental insights into ice-ocean interactions in East Antarctica – The potential of mumiyo

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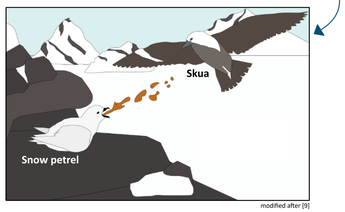
1. Introduction

Ice-ocean interactions in Antarctica are **strongly influenced by the presence of sea-ice**, the extent of which affects the marine food web, ocean-atmosphere heat exchange and deep water formation [1]. The extent of sea-ice during the Holocene has been investigated in several studies, which indicate a **mid-Holocene increase** in sea-ice in the coastal ocean off East Antarctica **after a period of reduced sea-ice cover** [e.g. 2; 3; 4]. However, the reasons for this increase are not fully understood yet and the timing of this change is not universal.

Past sea-ice extent can be inferred from archives such as marine sediment cores and ice cores, using proxies such as diatoms and lipid biomarkers [5]. One terrestrial archive that can be used to provide information about the Antarctic marine palaeoenvironment, i.a. sea-ice conditions, is **(Antarctic) mumiyo**. These are **lipid-rich deposits of stomach oil** from **snow petrels** (*Pagodroma nivea*) that form as a result of defences around their nesting sites in **ice-free areas** [6]. Until now, most studies have focused on the use of mumiyo as an indicator of ice retreat [6], but in recent years studies have been published on the use of mumiyo as an indicator of marine environmental conditions in the past [7; 8].

Stomach oil as defense mechanism against predators and competitors

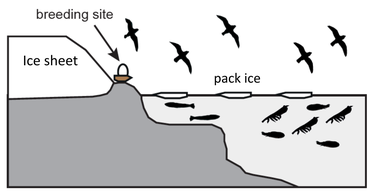


modified after [9]

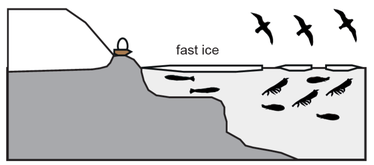
Video of fighting snow petrels spewing stomach oil at each other [10].

Snow petrels feed on **different species of fish and krill depending on the prevailing sea-ice conditions**. During periods of low sea-ice cover, prey from the shelf (fish) and from offshore (fish and krill) are consumed, whereas during periods of high sea-ice cover, a higher relative abundance of krill prevails [8]. The different lipid compositions of these organisms are reflected in the stomach oil, as the prey is **not metabolised** by the birds [11]. The lipid compounds can be analysed by chromatographic methods, e.g. gas chromatography coupled with mass spectrometry (**GC-MS**).

Relationship between sea-ice conditions and foraging range



Less sea ice – mixed feeding

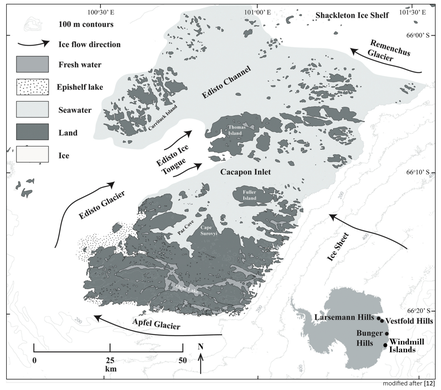


More sea ice – off-shore feeding

For this project, mumiyo deposits from several sites in East Antarctica will be analysed. These are sites in **Wilkes Land** (Bunger Hills and Windmill Islands) and **Prydz Bay** (Larsemann Hills and Vestfold Hills). Herewith, **initial data** are presented for **Bunger Hills**, which will be compared in a later stage with other sea-ice proxies, such as the relative abundance of sea-ice diatoms derived from sediment cores, to provide a better understanding of sea-ice conditions in these areas during the mid-Holocene.

2. Study area

Map of the Bunger Hills (Wilkes Land)



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3. Samples

A subset of samples from the southern Bunger Hills region was selected for further analyses based on their thickness and resulting potential to cover a long time scale, as well as their external appearance.

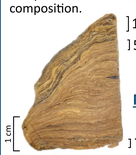
BH-MD -02 A, -131, -193 A, -213 } Partly radiocarbon dated

BH-MD -71-1, -71-2, -131/KUS9, -184 A-1, -214 A } Partly analysed for lipid composition

BH-MD-213

4. Radiocarbon ages

Radiocarbon ages were determined with *Calib 8.20* [13] using the marine radiocarbon age calibration curve *Marine 20* [14], whereby a marine reservoir effect of 1.3 kyr (ΔR = 750 yr) was assumed. The resulting ages are consistent with previous studies [15; 16], indicating an **occupation** of the area by snow petrels **since at least ca. 11 kyr BP**. Due to the coverage of the **mid-Holocene**, the samples will be analysed in the next step to infer their lipid composition.



1890 $^{+150}_{-150}$

5990 $^{+180}_{-140}$

7770 $^{+150}_{-130}$

BH-MD-131/KUS9

270 $^{+155}_{-150}$

3230 $^{+140}_{-160}$

5800 $^{+140}_{-160}$

7470 $^{+120}_{-140}$

9900 $^{+210}_{-200}$

BH-MD-214 A

Radiocarbon ages in yr cal BP
Median probability – 2 sigma range

Time span covered by Mumiyo samples from the Bunger Hills:

Verkulich and Hiller (1994):	< 0* – 10900 $^{+700}_{-700}$	Recalibrated
Ainley et al. (2006):	490 $^{+130}_{-135}$ – 10400 $^{+200}_{-200}$	ΔR = 750 yr
This study:	105 $^{+135}_{-135}$ – 9900 $^{+200}_{-200}$	

*Recalibration of the radiocarbon ages from [15] indicate that the assumed marine reservoir effect of 1.3 kyr in the Bunger Hills is an overestimate. A maximum reservoir age of 1.1 kyr is more likely, but needs to be confirmed by additional studies.

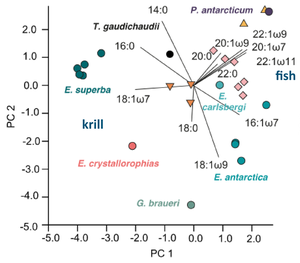
5. Methodological Approach

Mumiyo is composed of several lipid classes, including fatty acids (FA), fatty alcohols, sterols and wax esters (WE). These and triacylglycerols (TAG) are components of the snow petrel diet and have recently been reported in stomach oils of other birds of the order Procellariiformes [e.g. 17; 18].

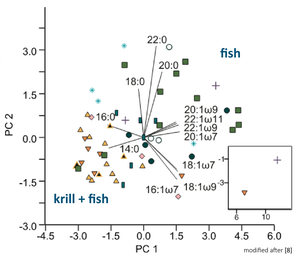
Previous studies [e.g. 7; 8] were mainly been based on the **fatty acid composition** of mumiyo. This allows conclusions to be drawn about the paleo-diet of snow petrels, as **specific** fatty acid distributions and in some cases specific fatty acids (e.g. 18:1ω7 for krill, 18:1ω9 for fish) **are typical of their diet**.

Principal component analysis of fatty acid compounds

Modern stomach oil and prey samples



Mumiyo from different regions



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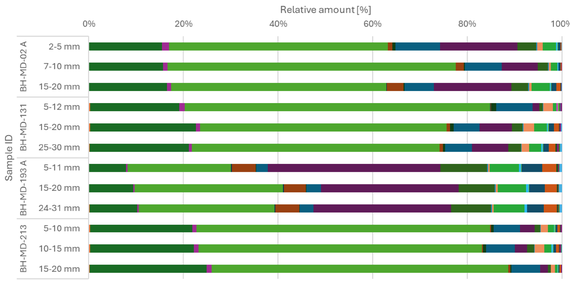
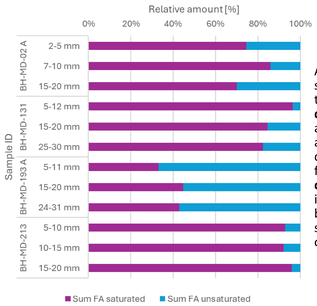
Fatty acid composition of several Bunger Hills samples

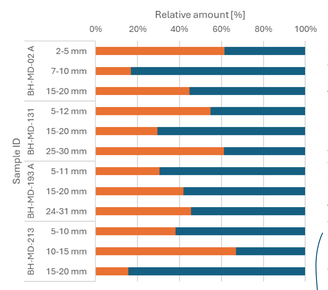


Saturated and unsaturated fatty acids



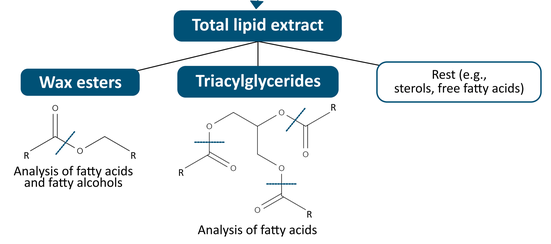
Analyses of mumiyo samples from several sites in East Antarctica have shown that there are **large differences in the fatty acid distributions of individual deposits**. In addition, the relative amounts of saturated and unsaturated fatty acids vary greatly within deposits from one location, as shown by data from Bunger Hills. This probably indicates **different stages of degradation** due to weathering of the material, with unsaturated fatty acids being degraded preferentially and converted to saturated carboxylic acids (e.g. by photo-oxidation [8; 19]).

Sources of fatty acids



Fatty acids in the samples are potentially free fatty acids (FFA) or part of intact phospholipids (PL), WE and TAG, respectively. They can also be isolated due to degradation of the latter compounds. So far the fatty acid composition of all lipid compounds has been analysed. In order to get a better picture of the paleo-diet, we want to **separate intact WE and TAG** as the main components of the prey [e.g. 17] from the other lipid compounds of the mumiyo by chromatographic methods. These will then be transesterified and the fatty acid composition, as well as the fatty alcohol composition of the WE, determined.

In addition, intact WE can be analysed for their compound-specific $\delta^{13}C$ values.

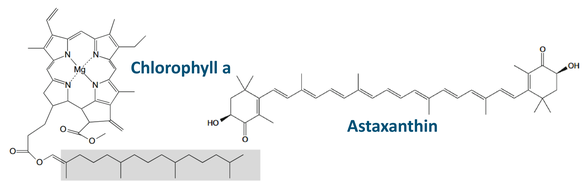


6. Future Work – Additional proxies

Pigments are additional components of mumiyo, as shown by previous studies [7; 20]. **Chlorophyll derivatives** are present **in our data** as isoprenoid acids derived from the phytol side chain. Potential carotenoid derivatives in mumiyo samples have been described by [7]. In future work we would like to **test** whether we can **detect carotenoid derivatives**, particularly of astaxanthin, by liquid chromatography coupled to mass spectrometry (LC-MS).

Euphausia superba [23]

Both chlorophyll and astaxanthin are derived from the **phytoplankton** on which crustaceans feed [21; 22]. Thus, the relative abundances of these compounds could serve as additional indicators of a **more krill-based diet**.



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7. Next steps

- Development of a protocol to separate WE and TAG from other compounds ☛ **Minimization of the degradation signal**
- Measurement of astaxanthin (derivates) by LC-MS ☛ **Additional krill-proxy**
- Lipid analysis of the dated Bunger Hills samples ☛ **Implications for the mid-Holocene**
- Radiocarbon dating and lipid analysis of Windmill Islands samples ☛ **Broader picture of Wilkes Land**
- Determination of $\delta^{13}C$ and $\delta^{15}N$ isotopic values ☛ **Inference of oceanographic conditions**

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