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Augustinus

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Holocene variation in the Antarctic coastal food web: linking δD and $\delta^{13}C$ in snow petrel diet and marine sediments

D. G. Ainley^{1,*}, K. A. Hobson², X. Crosta³, G. H. Rau⁴, L. I. Wassenaar⁵,
P. C. Augustinus⁶

¹H. T. Harvey & Associates, 3150 Almaden Expressway, Suite 145, San Jose, California 95118, USA

²Environment Canada, Canadian Wildlife Service, 115 Perimeter Road, Saskatoon, Saskatchewan S7N 0X4, Canada

³UMR-CNRS 5808 EPOC, Avenue des Facultés, Université de Bordeaux, 33405 Talence Cedex, France

⁴Institute of Marine Sciences, University of California, Santa Cruz, California 95064, USA

⁵Environment Canada, National Water Research Institute, 11 Innovation Place, Saskatoon, Saskatchewan S7N 3H5, Canada

⁶Departments of Geography and Geology, University of Auckland, Auckland 1030, New Zealand

ABSTRACT: Here we present first time evidence for concordant variation in the isotopic signature at both the base and the upper levels of the Antarctic coastal food web during the Holocene. Laminae in sub-fossil deposits of snow petrel *Pagodroma nivea* stomach oil, known as mumiyo, were collected from nest-sites in the Bunger Hills, East Antarctica. Mumiyo layers were sub-sampled, radiocarbon-dated, and analyzed for $\delta^{13}C$ and δD . The obtained values were compared to isotopic variability among layers of an ocean sediment core collected, and similarly dated, in nearby Dumont D'Urville Trough. Overlapping records extended from about 10 160 to 526 calendar years before present (cal yr BP). Mumiyo δD values remained relatively constant throughout the sampled period, in accordance with data from nearby ice cores. For ^{13}C , both mumiyo and sediment were enriched during the warmer mid-Holocene (ca. 7500 to 5500 cal yr BP). Isotopic concordance between the core and the mumiyo, and a significant correlation between mumiyo δD and $\delta^{13}C$, suggest that past $\delta^{13}C$ variation in plankton was transferred through diet to higher trophic levels and ultimately recorded in stomach oil of snow petrels. Divergence in signals during cold periods may indicate a shift in foraging by the petrels from ^{13}C -enriched neritic prey to normally ^{13}C -depleted pelagic prey, except for those pelagic prey encountered at the productive pack-ice edge during cooler periods, a shift forced by presumed greater sea-ice concentration during those times. Other air-breathing predators would likely respond in the same way.

KEY WORDS: Antarctica · Holocene climate change · Food webs · Isotopic analysis · Mumiyo · *Pagodroma nivea* · Sediment cores · Snow petrel

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INTRODUCTION

The climate history of the coastal Southern Ocean, and specifically the interplay between sea-ice cover and primary productivity during the Holocene, is becoming increasingly known through the analysis of isotopic variation in ocean sediment and glacial ice cores (e.g. Masson et al. 2000, Rosenthal et al. 2000, Stenni et al. 2001, Crosta & Shemesh 2002), as well as analysis of phytoplankton species composition in the sediment cores (e.g. Burckle & Cirilli 1987, Cunning-

ham et al. 1999). While this point will be expanded later in this paper, it is obvious that little is known about how the remainder of the coastal food web had responded to the indicated shifts in marine climate. What small amount is known in this regard has been derived from excavations of subfossil remains, specifically fish otoliths and cephalopod beaks, from abandoned Adélie penguin *Pygoscelis adeliae* colonies (e.g. Emslie & Woehler 2005, and references therein). These results have detected long-term patterns but without much recourse, owing to a lack of contextual informa-

*Email: dainley@penguinscience.com

tion, toward explaining why the penguin diet did or did not change. To further address that gap in knowledge, we present here an isotopic analysis of subfossil deposits of stomach oil from a seabird, the snow petrel *Pagodroma nivea*, which nested at coastal sites throughout the Holocene and longer.

The snow petrel is an exceptionally agile seabird that frequents ice-covered portions of the Southern Ocean. It forages by flying rapidly along the edges of ice floes, ice shelves and bergs, and related brash in search of its prey (Ainley et al. 1984). It has long been known that the species is rarely found more than one day's flight from sea ice, and usually much closer, as first noted by James Clark Ross (1847, p. 171) on 30 December 1840: 'A beautiful white petrel was seen in the evening, giving notice of our approach to a large body of ice, although we were not at the time aware that these birds never wander far from the main pack.' In fact, the 5-member pagophilic avian community of which this species is a part is the least varying in composition and has the strongest habitat affinities of any seabird community in the Pacific Ocean (Ribic & Ainley 1988/89, Raymond & Woehler 2003). So close is the snow petrel's association with sea ice that variation in winter ice extent inversely affects variation in its annual survival (Barbraud et al. 2000). In the looser pack ice of polynyas and the outer, large-scale edge of the ice pack, the snow petrel feeds mainly on fish, principally members of the family Myctophidae in pelagic waters and of the family Nototheniidae (especially *Pleuragramma antarcticum*) in neritic waters. It also feeds on krill (*Euphausia* spp.), which occupy a lower trophic level, and cephalopods (especially *Psychroteuthis glacialis*) in both habitats (Ainley et al. 1984, 1992).

Snow petrels nest mainly among the boulders of the talus slopes of nunataks that occur from the Antarctic coast to several hundred kilometers inland. At these sites, during November, they lay their eggs on the gravel of cavities and crevices well-protected from predatory skuas (*Catharacta maccormicki*; Brown 1966). The chicks, which hatch in early January, are left alone when several days old (once capable of maintaining body temperature), secure in the nesting cavities, while both parents forage at sea. At Pt. Géologie (140° E) in East Antarctica, snow petrels provisioning chicks made trips that lasted 35 to 120 h (mean 64 to 78 h depending on sex; Barbraud et al. 1999). Trips of such duration would allow the time for parents to feed over the entire continental shelf and slope and/or the entire ex-

pense of ice-influenced waters that exist during the spring and summer; such trips could easily extend several hundred kilometers from nest sites. Because the foraging of petrels often occurs long distances from nests, most petrel species reduce the prey ingested to high-caloric-value stomach oil, which they then feed to their chicks upon return to the nest (Warham 1977).

Although not the principal purpose of the stomach oil, fulmarine petrels defend themselves by spitting stomach oil at intruders or predators (Warham 1990). Predators may include skuas prospecting for food at the entrance to snow petrel nest cavities. Due to the nesting area's extreme aridity and cold temperatures, over time a stratified deposit of oil (lipid) builds up and is preserved frozen around the entrances of snow petrel nest cavities (Hiller et al. 1988, 1995; Fig. 1). These deposits of wax-like, yellowish brown or gray stomach oil are known as mumiyo (Hiller et al. 1995). Basal mumiyo layers have been radiocarbon-dated back to 34 000 calendar years before present (cal yr BP); these radiocarbon dates document a chronology of when terrain became ice free or when glacial advance or retreat occurred (Hiller et al. 1995, Steele & Hiller 1997). The rationale behind these ¹⁴C interpretations is that once suitable nesting terrain became ice free, it was colonized by the petrels.

Although the dating of mumiyo, thus far, has focused on basal layers, one feature of mumiyo deposits is their highly stratified nature. The cause of the laminations is not precisely known but each, as defined between bands of dust and sand, is presumed to reflect a period of snow petrel occupation of a particular nesting cavity. Occupation is apparently intermittent. We hypothesized that variation in stable isotope abundance in radiocarbon-dated layers of mumiyo would provide



Fig. 1. Snow petrel, incubating an egg in its nest, with mumiyo deposits covering the crevice entrance. Photograph by J. Clarke

insight into past isotopic variations in petrel diet, and thereby provide a proxy for changes in the marine ecosystem of coastal Antarctica during the Holocene. Mumiyo, of which the basal layers had been ^{14}C dated, was available from Bunger Hills, East Antarctica (Verkulich & Hiller 1994, Gore et al. 2001).

Accordingly, using funds from a small, exploratory grant, we report the $\delta^{13}\text{C}$ and δD values of extracted lipid layers in mumiyo samples from Bunger Hills, Wilkes Land, with basal layers that had been previously dated to 10 160 cal yr BP (Gore et al. 2001). We compare these results to the isotopic record of a sediment core obtained in near-by Dumont D'Urville Trough, off Adélie Land, theoretically within the snow petrels' foraging range from Bunger Hills. Samples were dated using accelerator ^{14}C analysis. Our objective was to determine if isotopic analysis of mumiyo, i.e. samples from an upper trophic level predator, could provide indications of climate and food web variation in the sea-ice-influenced portion of the Southern Ocean since the Last Glacial Maximum.

MATERIALS AND METHODS

Mumiyo samples. Field collection: Mumiyo stratigraphic samples were collected from sites in the Bunger Hills, East Antarctica (vicinity $66^{\circ}17'S$, $100^{\circ}47'E$; Fig. 2). Blocks of mumiyo, each from a different nest site, were broken out using a geologic hammer and cold chisel. Each sequence was then marked for orientation, wrapped in aluminum foil, sealed in a plastic bag and frozen at -20°C . Specimens were kept frozen during shipment from Antarctica to Australia and ultimately to Canada. Mumiyo samples were then subsampled in chronosequence from top to bottom at intervals of millimeters to centimeters for stable and radiocarbon analysis.

Stable isotope analyses: By working in a walk-in freezer, frozen (-20°C) mumiyo sub-samples corresponding to a cross section of a few laminae were obtained from the top, middle and bottom portions of each mumiyo slab using a pre-cleaned, 3 mm stainless steel biopsy punch. These mumiyo sub-samples were transferred into clean glass scintillation vials. Due to the occurrence of inorganic mineral material in the mumiyo (mostly quartz sand), we extracted and analyzed only the purified lipid fraction. This step prevented $\delta^{15}\text{N}$ analysis, since lipids contain little, if any, nitrogen. However, we reasoned that the purified

lipid fraction of the mumiyo could be unequivocally associated with historic snow petrel feeding at any given time horizon, assuming that any isotopic offset between lipids and the bulk diet had been constant during the Holocene.

Lipids were extracted from mumiyo sub-samples using a 2:1 chloroform:methanol solvent. Samples were soaked in solvent overnight in capped scintillation vials and agitated several times to aid dissolution of the lipids. The solvent containing the dissolved lipid samples was then filtered through a precombusted glass fiber filter to remove any insoluble sediment. The filtrate was transferred to an open glass vial and the solvent was evaporated by air drying in a fume hood. The residual purified lipid samples were then again stored frozen (-20°C). In addition to the mumiyo samples, we prepared butter (with modern ^{14}C) and grease (Apiazon[®]; undetectable ^{14}C present) samples to evaluate potential effects of our lipid solvent purification procedure on mumiyo radiocarbon ages.

All results are expressed in the typical delta notation, in units of per mil (‰), and normalized on the Vienna Standard Mean Ocean Water/Standard Light Antarctic Precipitation (VSMOW-SLAP) scale. For $\delta^{13}\text{C}$ analyses, 300 μg ($\pm 20 \mu\text{g}$) lipid samples were loaded into tin cups and combusted at 1050°C in a Eurovector elemental analyzer interfaced with a GV Instruments Isoprime[™]

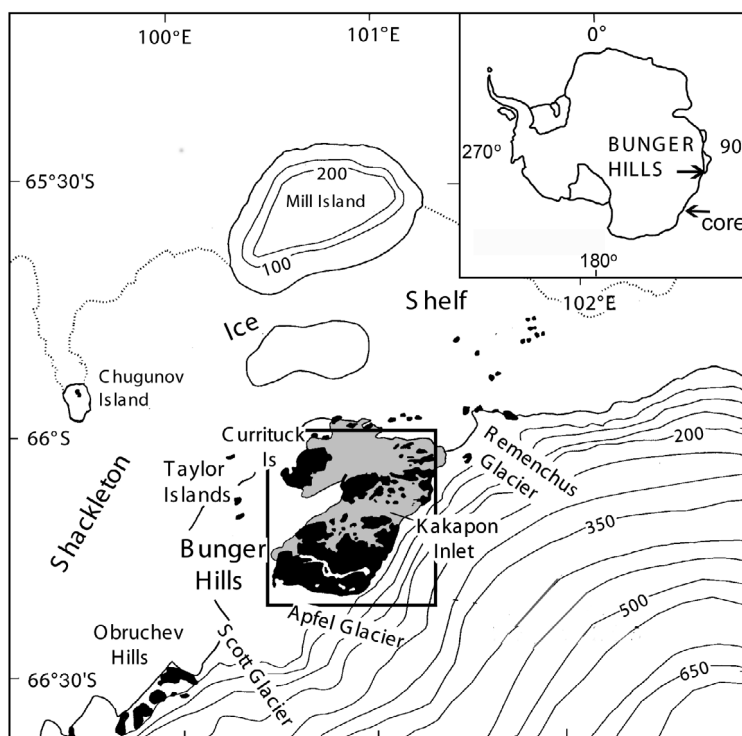


Fig. 2. Study area at the Bunger Hills, Antarctica, and approximate location of core MD03-2601

mass spectrometer configured in continuous-flow isotope ratio spectrometry (CF-IRMS) mode. All $\delta^{13}\text{C}$ results are reported relative to the Vienna Pee Dee belemnite (VPDB) international standard, and were calibrated by including primary International Atomic Energy Agency (IAEA) ^{13}C reference materials. Replicate analyses of reference materials yielded a measurement repeatability precision of approximately $\pm 0.18\%$ (SD).

For δD analyses, 150 μg ($\pm 20 \mu\text{g}$) lipid samples were loaded into Ag cups and pyrolyzed at 1275°C in a Eurovector elemental analyzer as described above. Stable hydrogen isotope measurements were performed on H_2 derived from the high-temperature flash pyrolysis of lipid samples. Pure H_2 was used as the sample analysis gas and the isotopic reference gas. The resolved H_2 sample pulse was introduced to the isotope ratio mass spectrometer (Isoprime™ with electrostatic analyzer) via an open-split capillary. Repeated analyses of hydrogen isotope reference material, IAEA-CH-7 (-100%), was routinely measured along with samples as a check, and yielded an external repeatability of better than $\pm 1.5\%$ (SD).

Radiocarbon dating: Lipid samples were prepared for accelerator mass spectrometry (AMS) radiocarbon dating by combusting purified lipid samples to CO_2 gas using the Dumas combustion procedure. Briefly, lipid samples ($\sim 4 \text{ mg}$) were weighed into Vycor boats and placed in 9 mm outer diameter (OD) Vycor tubes along with silver wire and excess cupric oxide. The sample tube was then evacuated and flame sealed. Sample tubes were combusted at 850°C for 2 h and allowed to cool slowly. Combustion gases were then separated cryogenically offline, CO_2 purified, frozen into 6 mm OD pyrex tubes and flame sealed. These CO_2 samples were then sent to the National Ocean Science Accelerator Mass Spectrometry (NOSAMS) dating facility for ^{14}C analysis and radiocarbon age determination. Radiocarbon ages for butter ($>$ modern) and grease (background), included as controls, confirmed that the lipid extraction technique did not introduce error into ^{14}C age measurements.

Raw radiocarbon dates were calibrated to cal yr BP by applying a marine reservoir correction factor of 1300 yr (Berkman et al. 1998) and using Bard's polynome (Bard et al. 1998; see Table 1).

Marine sediment record. Field collection: Piston core MD03-2601 was retrieved during the MD130-Images X cruise (CADO, Coring Adélie Diatom Oozes) in February 2003 on board the RV 'Marion Dufresne II'. It was retrieved at 66° 03.07' S, 138° 33.43' E in 746 m of water within the Dumont D'Urville Trough, about 60 km offshore of Adélie Land. The core was a 40.3 m sequence of diatom ooze. D'Urville Trough is about 800 km from the Bunger Hills and underlies typical

East Antarctic foraging habitat of the snow petrel during summer (Raymond & Woehler 2003).

Stable isotope analyses: For isotopic analysis, sediment was decarbonated with a 1 N HCl solution for 15 min at 65°C. The decarbonated organic fraction was then rinsed 3 times with Milli-Q water and dried in the oven. Carbon isotopic measurements were performed on a Carlo Erba 2500 elemental analyzer in line with a VG Isoprime at UMR EPOC (France). The mean standard deviation is $\pm 0.1\%$ for the carbon isotopic ratio. All results are reported in δ notation versus PDB and were checked for internal consistency using several calibrated laboratory standards, such as acetanilid, glycine and casein. Isotopic measurements were done every 4 to 8 cm along the 40 m core.

Radiocarbon dating: Accelerator mass spectrometry (AMS) radiocarbon dating was performed on the humic fraction of bulk organic matter at the Leibniz Laboratory, Kiel, Germany. The samples were checked and mechanically cleaned under the microscope. The residual material was then extracted with 1% HCl, 1% NaOH at 60°C and again with 1% HCl. The alkali extract (humic acid fraction) was precipitated with HCl, washed and dried. The combustion to CO_2 of all fractions was performed in a closed quartz tube together with CuO and silver wool at 900°C. The sample CO_2 was reduced with H_2 over about 2 mg of Fe powder as catalyst, and the resulting carbon/iron mixture was pressed into a pellet in the target holder. The ^{14}C concentration of the samples was measured by comparing the simultaneously collected ^{14}C , ^{13}C and ^{12}C beams of each sample with those of oxalic acid standard, CO_2 and coal background material. Conventional ^{14}C ages were calculated according to Stuiver & Polach (1977) with a $\delta^{13}\text{C}$ correction for isotopic fractionation based on the $^{13}\text{C}/^{12}\text{C}$ ratio measured by our AMS-system simultaneously with the $^{14}\text{C}/^{12}\text{C}$ ratio.

Raw radiocarbon dates were calibrated to cal yr BP by applying a marine reservoir correction factor of 1300 cal yr BP and using Bard's polynome (Bard et al. 1998; see Table 2).

RESULTS

Stable-hydrogen isotope values of mumiyo lipid ranged from -228 to -176% over the geologic time span represented in the core samples (mean $\delta\text{D} \pm \text{SE}$: $-201.59 \pm 1.67\%$, $n = 47$; Table 1), but showed no significant trend (Fig. 3A).

Stable-carbon isotope values of mumiyo ranged from -29.7 to -31.5% (mean $\delta^{13}\text{C} \pm \text{SE}$: $-30.79 \pm 0.06\%$, $n = 51$; Table 1). Our values were verified by independent stable carbon isotopic measurements associated with radiocarbon dating at 2 laboratories. Coverage in the

Table 1. Results of stable-carbon and hydrogen isotope analysis of mumiyo core samples relative to AMS and calibrated ages

Mumiyo core sample	Position	AMS age (cal yr BP) ^a ±1 SD	Calendar ages AR 1300 (cal yr BP) ^b	δ ¹³ C (‰)	δD (‰)
BH 125 A (M3)	A (top)			-31.2	-201
	B	4210 ± 50	3081	-31.1	-200
	C (base)	4480 ± 60 ^a	3426	-31.1	-201
BH 125 B	A (top)	2680 ± 30	1248	-30.9	-207
	B			-31.0	-209
	C	4180 ± 30	3042	-30.9	-209
	D (base)	4500 ± 30	3452	-30.8	-205
BH 183 (M6)	A (top)	1800 ± 30	452	-30.9	-193
	B			-30.9	-198
	C	2910 ± 35	1497	-31.0	-199
	D (base)	3080 ± 30	1690	-31.1	-193
BH 188	A (top)	3430 ± 30	2104	-31.3	-216
	B			-31.0	-213
	C	6430 ± 45	5840	-30.5	-203
	D			-30.7	-214
	E	8710 ± 35	8302	-30.7	-208
	F (base)	9180 ± 40	8792	-30.5	-208
BH 188 (M10)	A (top)	3240 ± 30	1877	-30.9	-196
	B			-30.9	-203
	C	6270 ± 40	5656	-30.5	-200
	D			-30.9	-198
	E (base)	9580 ± 80 ^a	9212	-30.9	-201
BH 192 (M12)	A (top)	1940 ± 25	527	-31.5	-220
	B			-31.0	
	C			-30.9	-218
	D	6410 ± 30	5820	-30.8	-205
	E (base)	8290 ± 70 ^a	7868	-31.0	-212
BH 214 A	A (top)	2220 ± 30	795	-30.2	-181
	B			-30.3	-184
	C			-30.1	-176
	D	7230 ± 40	6745	-30.4	-186
	E			-30.6	-190
	F			-30.5	-185
	G (base)	9630 ± 40	9260	-30.0	-186
BH 241 (M13)	A (top)	5380 ± 25	4853	-29.7	-208
	B			-29.9	-206
	C	8080 ± 40	7650	-30.6	-204
	D (base)	10100 ± 40	9803	-30.8	-213
BH 243 (M17)	A (top)			-31.3	-213
	B			-31.1	-221
	C			-31.2	-228
	D			-31.2	
	E			-30.3	
	F (base)	10400 ± 70 ^a	10160	-30.6	
BH 256 (M18)	A (top)			-31.2	-202
	B			-31.3	-200
	C			-31.4	-203
	D (base)	4240 ± 60 ^a	3119	-31.4	-201
BH 303 (M22)	A (top)			-30.2	-184
	B			-30.1	-183
	C (base)	9310 ± 80 ^a	8929	-30.8	-191

^aUncorrected ages from samples analyzed by Gore et al. (2001); others from NOSAMS

^bCorrection using a reservoir effect of 1300 yr and the technique of Bard et al. (1998)

mumiyo record was sparse between about 3500 and 5500 cal yr BP, but a δ¹³C trend was evident, which was significantly related to age of the mumiyo layer, with older samples being more enriched in ¹³C ($r = 0.4195$, $p < 0.05$). A step function is indicated, however, at about 4500 cal yr BP, when the relatively flat average for older samples changed from $-30.6 \pm 0.09\%$ ($n = 14$) to the relatively flat pattern for samples younger than about 3500 cal yr BP at an average $-31.0 \pm 0.09\%$ ($n = 13$; Fig. 3B). Except for 2 seemingly outlying data points from 1 mumiyo sample (BH 241), a significant correlation existed between δD and δ¹³C ($r = 0.6708$, $p < 0.01$; with the 2 data points, $r = 0.525$, $p < 0.05$; Fig. 4).

The isotopic record in the sediment core, which will be discussed in detail elsewhere (Crosta et al. in press), was more complete and of much finer resolution than that of the mumiyo ($n = 610$; Fig. 5). Values of δ¹³C in the sediment core ranged from about -24.8 to -26.6% . Sediments were depleted in ¹³C in the earliest portion of the record that overlapped the mumiyo, became more positive from 7500 to 5500 cal yr BP, and thereafter became more negative. As with the mumiyo, δ¹³C values showed much more variation in the early and late periods of the core. Actually, in comparison, the pattern of the mumiyo values tracked the pattern shown in the core quite well, thus indicating a pattern more complex than a mere one-step function (cf. Figs. 3 & 5). During cold periods before and after the mid-Holocene optimum, the mumiyo maintained its value relative to the longer-term decreases in sediment ¹³C. Accordingly, mumiyo values compared against a 9-point running mean of the core values, for dates when values for both records were available, were better correlated without values originating from the cold period of 8500 to 9500 cal yr BP when the 2 records widely diverged ($r = 0.5643$, $p < 0.01$, $n = 20$), than when values from all periods were compared ($r = 0.2881$, $p = 0.1$, $n = 24$).

DISCUSSION

General considerations related to isotopic variations

Hydrogen

Ocean water δD values are positively correlated with salinity and temperature (Jouzel 1999, Masson et al. 2000). The rather flat tem-

Table 2. Accelerator mass spectrometry ^{14}C ages from core MD03-2601. Dates were calibrated to calendar ages using Bard's polynome (Bard et al. 1998). cmbsf = cm below sea floor

Depth (cmbsf)	AMS age (^{14}C cal yr BP) ± 1 SD	Reservoir age (yr)	Calendar age (cal yr BP)
2	2350 \pm 70	1300	916
998	5175 \pm 60	1300	4314
1998	6310 \pm 100	1300	5703
2998	8775 \pm 40	1300	8369
3998	10855 \pm 45	1300	10742

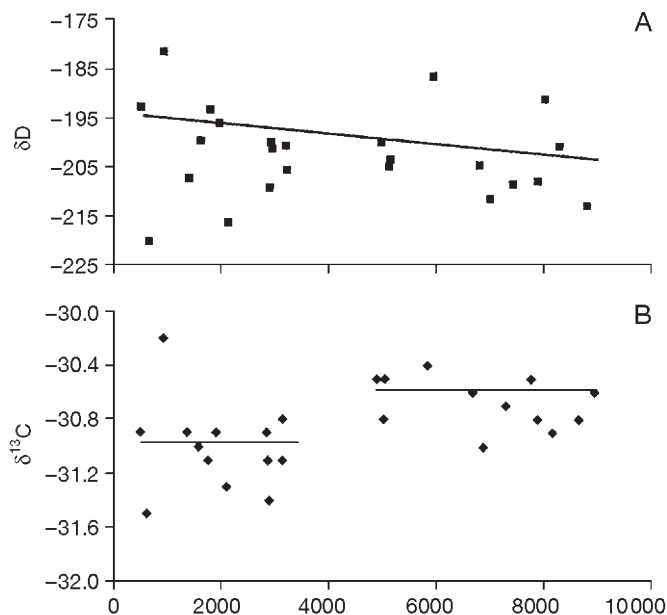


Fig. 3. Values of (A) δD (‰) and (B) of $\delta^{13}\text{C}$ (‰) related to corrected age of the mumiyo samples. The slopes of the trend line are not statistically significant

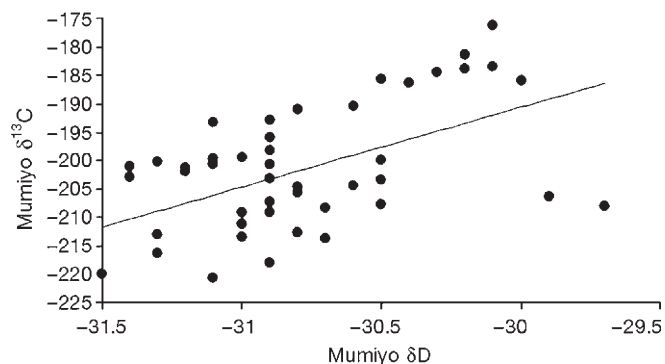


Fig. 4. Mumiyo values of $\delta^{13}\text{C}$ (‰) regressed against values of δD (data from Table 1). Excluding the 2 points below the line and >30 δD , both from the same sample (DH241 A and B), the regression line is $y = 20.8x + 439.3$ ($r^2 = 0.45$, $p < 0.01$; otherwise, with the 2 points, $r^2 = 0.27$, $p < 0.05$)

poral pattern to values of δD in the mumiyo over the time span of our samples is consistent with the pattern exhibited in δD from East Antarctic glacial ice cores for dates more recent than 9000 cal yr BP. The patterns are thought to represent relationships between sea surface temperatures and the oceanic moisture source of the ice (Masson et al. 2000, Stenni et al. 2001). The disparity in the mumiyo values (-180 to -225 ‰) relative to those of the ice cores (-320 to -450 ‰) may reflect the colder temperatures in the glacial ice (a function of higher elevations; see Masson et al. 2000) or may represent isotopic discrimination between mumiyo and the source of food-web hydrogen in the marine environment. δD may also be influenced by mixing of sea waters of different isotopic values ultimately associated with inputs from the terrestrial hydrologic cycle (www.giss.nasa.gov/data/o18data). As such, surface waters may have regional differences in deuterium content and may reflect the degree of deep-water mixing. In the Antarctic, however, there is very little change in water isotopic composition at full seawater salinity, from surface waters to hundreds of meters deep (Mackensen et al. 1994). Even though values of δD in marine food webs must be influenced by the δD contained in the associated oceanic waters, little is known about δD variability in open marine foodwebs of the Southern Ocean.

Carbon

With respect to $\delta^{13}\text{C}$, significant down-core variations in Southern Ocean marine sedimentary organic matter provide unambiguous evidence of past, fundamental changes in pelagic carbon biogeochemistry in this region, especially on glacial-interglacial time scales (e.g. Rosenthal et al. 2000, Crosta & Shemesh 2002). The effects of CO_2 concentration and primary production (among other variables) have been previously identified as important factors affecting oceanic food-web (planktonic) $\delta^{13}\text{C}$ and, by inference, that of the marine sedimentary record in East Antarctica (e.g. Lourey et al. 2004). However, empirical evidence is inconsistent in allowing universal interpretation of pelagic or sedimentary organic $\delta^{13}\text{C}$ variations in the context of one or a few variables. For example, while strong, opposing, southern-latitudinal gradients in CO_2 concentration and plankton $\delta^{13}\text{C}$ have been observed (arguing for significant influence of the former on the latter; e.g. Rau et al. 1989, Popp et al. 1999, Lourey et al. 2004), they have not been consistently observed within a given ocean regime (e.g. Popp et al. 1999, Villinski et al. 2000, Trull & Armand 2001). Therefore, if passive diffusion of CO_2 into phytoplankton cells is assumed to be the primary food-web carbon acquisi-

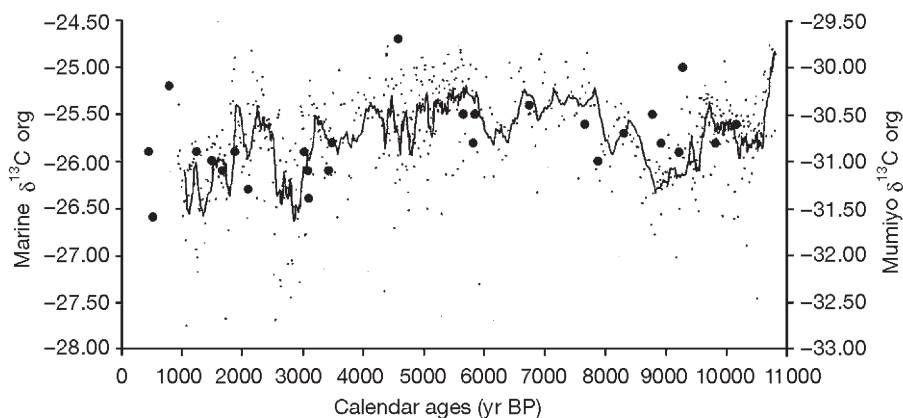


Fig. 5. Values of $\delta^{13}\text{C}$ (‰) in the mumiyo layers sampled at Bunger Hills, Wilkes Land (101°E ; large dots), compared to values in sediment core MD03-2601 taken in the D'Urville Trough, off Adélie Land (138°E ; small dots). A 9-point running mean is shown as a line for the sediment values. The correlation between mumiyo values and the corresponding point on the 9-point running mean for core values was $r = 0.2881$ ($p = 0.1$); excluding the period in the early Holocene (9500 to 8500 cal yr BP), when mumiyo and core values diverged (see text), the correlation was $r = 0.5643$ ($p < 0.01$)

tion pathway, then a range of factors such as growth rate, cell size, cell wall permeability, etc. will theoretically affect the downstream $\delta^{13}\text{C}$ of the organic matter produced (e.g. Rau et al. 1997) to perhaps confound pattern interpretation. Moreover, a significant fraction of inorganic carbon uptake by marine primary producers is via active rather than passive, cross-membrane transport (Laws et al. 2002, Cassar et al. 2004). Thus, until further research is conducted, interpreting past variations in $\delta^{13}\text{C}$ will be problematic, with the Antarctic and our study sites being no exception.

Specific considerations: water mass effects

Among factors that might directly affect food-web $\delta^{13}\text{C}$, past variation in coastal Antarctic dissolved inorganic ^{13}C can be inferred from analysis of carbonate (foraminifera shells) found in ^{14}C -dated sediments to 8450 cal yr BP (Shevenell & Kennett 2002). The magnitude of this variation, $\sim 1\%$, although also influenced by primary productivity and bottom water formation (Mackensen et al. 1994), is a significant fraction of the variation (1.8‰) seen in the mumiyo record over the same period (with the caveat related to sample size noted below). As in mumiyo and organic sediments, a general post-5000 cal yr BP decline in marine inorganic $\delta^{13}\text{C}$ was apparent. Thus, past isotopic variations in the inorganic carbon source for this food web, in addition to variations in isotopic fractionation within the food web, need to be considered when interpreting mumiyo and sediment $\delta^{13}\text{C}$. A closer examination of contemporaneous marine pelagic inorganic and organic/mumiyo $\delta^{13}\text{C}$ would be useful in this regard.

Water mass effects recorded in mumiyo $\delta^{13}\text{C}$ may also be indicated by the significant positive correlation between mumiyo $\delta^{13}\text{C}$ and δD . This correlation implies that a common factor or factors was influencing the stable isotope abundances of both elements. Since physical processes (i.e. precipitation, evaporation, seawater freezing and melting, end-member seawater mixing) are the primary determinants of ocean and, presumably, food-web δD , the preceding correlation implies that variations in similar or closely related processes have also been recorded in mumiyo $\delta^{13}\text{C}$.

Specific considerations: food web and diet effects

Within the context of the above discussion, the significant, corresponding trends and variability of $\delta^{13}\text{C}$ in our mumiyo lipid and marine sedimentary samples imply that changes have occurred in carbon sources, pathways and/or cycling within the coastal Antarctic food web. For example, significant changes in Holocene diatom species composition in this region are evident (e.g. Cunningham et al. 1999) which, when combined with observed phytoplankton species-specific ^{13}C selectivity in inorganic carbon uptake and photosynthesis (e.g. Popp et al. 1998), could have affected resulting food web $\delta^{13}\text{C}$. Such effects may explain the significant $\delta^{13}\text{C}$ variation, or lack thereof, among consumers within a given Antarctic marine food web (e.g. Rau et al. 1991, 1992). Isotopic variation in mumiyo lipids should represent variation in the $\delta^{13}\text{C}$ of the middle portion of the food web (fish, krill), including trophic or species variation in petrel diets, along with any (unknown) change in isotopic signature resulting from the parental food-to-oil processing. In

the current analysis, mumiyo $\delta^{13}\text{C}$ values were consistently lower than those reported for diatoms deposited through the Holocene (e.g. as recorded in sediment cores), consistent with the well-known isotopic discrimination against ^{13}C in the formation of lipids (Thompson et al. 2000). As expected, mumiyo values were also more ^{13}C depleted than the blood of snow petrels, thought to be feeding in pelagic waters, and measured in East Antarctica during modern times (mean $\delta^{13}\text{C} \sim -24.4\text{‰}$; Hodum & Hobson 2000).

It might be possible, therefore, to link variations in mumiyo $\delta^{13}\text{C}$ to past changes in the source of the snow petrel diet or to changes in the $\delta^{13}\text{C}$ signature of the food web itself. On average, an approximate 5‰ offset was indicated between mumiyo lipid and the sediment samples. Likewise, barring diagenetic isotope effects or selective preservation (e.g. Lourey et al. 2004), the $\delta^{13}\text{C}$ variations seen in the marine sediment core should also reflect those that occurred in past, overlying plankton communities. In this regard it is interesting to note that the range in sediment $\delta^{13}\text{C}$ variability from 400 to 10 200 cal yr BP (spanning the mumiyo record), 2.9‰, is larger than the $\delta^{13}\text{C}$ variability in the mumiyo lipid during the same period: 1.8‰. This could reflect the greater variation expected in the much larger marine data set, or it may reflect a broader range of oceanographic and food-web conditions occurring over the core site than was experienced by the near-ice food web sought by the snow petrel for feeding.

In the d'Urville Trough, sedimentary $\delta^{13}\text{C}_{\text{org}}$ appears to be related to variations in sea ice cover and seasonality that affect the diatom assemblages through time (Crosta et al. in press). Briefly, heavier $\delta^{13}\text{C}_{\text{org}}$ values during the warmer mid-Holocene period (8000 to 4500 cal yr BP) resulted from lessened sea ice cover and subsequent greater relative abundances of centric diatoms enriched in ^{13}C and lesser relative abundances of sea ice diatoms depleted in ^{13}C . Conversely, lighter $\delta^{13}\text{C}$ values during the cooler Neoglacial period (4500 to 900 cal yr BP) resulted from greater sea ice cover and subsequent lesser relative abundances of centric diatoms enriched in ^{13}C and greater relative abundances of sea ice diatoms depleted in ^{13}C .

The mumiyo and sediment $\delta^{13}\text{C}$ patterns match least well during colder periods of the Holocene (especially 8500 to 9500 cal yr BP) and perhaps variations in sea-ice cover could explain the differences. In recent decades, sea ice is present for 9 to 10 mo, and sea ice concentration is above 80% during 7 to 8 mo yr⁻¹ in the area (Schweitzer 1995). Sea-ice concentration >80% forces snow petrels to feed at the large-scale ice edge or in polynyas (Ainley et al. 1984) rather than the ice-pack interior, which overlies the sediment core site most of the year. Warmer temperatures and more divergent sea ice during the mid-Holocene would

lengthen the phytoplankton growing season, as well as allow the petrels to have greater or more extended access to food resources over the Antarctic continental shelf, the waters of which are more productive than pelagic waters, consistent with patterns elsewhere (Arrigo et al. 1999). In the absence of sea ice the petrels would feed in association with ice shelves, icebergs and brash resulting from their disintegration. Our observation of a decline in sediment $\delta^{13}\text{C}$ values before 8000 and after 5000 cal yr BP would be consistent with more ice cover and less productivity over the shelf; the greater ice cover would lead to increased foraging by petrels along the productive large-scale ice edge, compensating for the generally lower ^{13}C levels of the pelagic waters present there. Other air-breathing predators needing divergent sea ice in which to forage would likely exhibit the same shifts.

Specific considerations: climate effects

Hodell et al. (2001), studying a lower-latitude South Atlantic/Southern Ocean core, noted a decline in the $\delta^{13}\text{C}$ values of diatom-intrinsic organic matter after 5000 to 6000 cal yr BP, changing from variation centering around -21.0‰ to around -22.5‰ . On this basis and coincident with patterns shown by other climate proxies in their core, these authors concluded that a climatic shift at about 5000 cal yr BP corresponded to the end of the warm Hypsithermal and the onset of the cool Neoglacial. Such effects may also be reflected in our data but, more so, other studies have observed a mid-Holocene climate shift with a climate optimum between ~6000 and 3000 cal yr BP separating earlier and later cool periods (e.g. Cunningham et al. 1999, Masson et al. 2000, Masson-Delmotte et al. 2004). While the resolution of our mumiyo sampling is low, especially during this mid-Holocene period, a slight elevation in $\delta^{13}\text{C}$ values is apparent before 5500 cal yr BP, as in the more detailed mid-Holocene record in the sediment core, consistent with the existence of a warm mid-Holocene period developing at around 5500 cal yr BP into a neoglaciation in coastal East Antarctica and the Ross Sea.

The apparent mid-Holocene warming could account for the rapid increase in the presence of snow petrels in the Bunger Hills during this period (more cavities became occupied), as noted by Ingólfsson et al. (1998). First, melting of snow earlier in the season would provide more available breeding habitat (rock cavities), a process currently leading to population increase among cavity-nesting seabirds in the Arctic (Divoky 1998). Second, decreased sea-ice extent during winter would lead to increased annual survival in this species (Barbraud et al. 2000). Increased survival, all else being equal, would lead to population increase.

While there are a number of sediment core studies that show marine ecosystem change during the Holocene at the unicellular level, past changes in higher food-web elements have rarely been addressed and not by using stable isotopes (see Emslie & Woehler 2005, and references therein). We conclude that our analysis indicates that changes in the coastal Antarctic food web did occur (at the least, a spatial shift in upper-level predator pressure) with respect to a mid-Holocene period of warming and probably lessened sea ice cover, and that finer resolution isotopic analyses of mumiyo layers would likely provide increased details on ecosystem changes in the Southern Ocean—and those above the phytoplankton level—since the Last Glacial Maximum.

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