

Sources of organic matter and paleo-environmental implications inferred from carbon isotope compositions of lacustrine sediments at Inexpressible Island, Ross Sea, Antarctica

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Abstract The carbon isotopic composition of organic matter ($\delta^{13}\text{C}_{\text{org}}$) was determined in two sediment cores (IIL1 and IIL9) recovered from Inexpressible Island, Ross Sea, Antarctica, and analyzed to identify the sources of that organic matter. The $\delta^{13}\text{C}_{\text{org}}$ values of sediments of IIL9 were found to vary between -14.6‰ and -11.6‰ , with a mean of -13.4‰ ($n=48$). These values were significantly higher than those of IIL1 sediments which varied between -23.2‰ and -20.4‰ , with a mean of -21.8‰ ($n=55$). The variation in $\delta^{13}\text{C}_{\text{org}}$ values in these two sediment cores indicate different sources of organic matter. The relatively high $\delta^{13}\text{C}_{\text{org}}$ values in IIL9 are in accordance with a source from algae, while the low $\delta^{13}\text{C}_{\text{org}}$ values in IIL1 evince significant influence from penguin guano with algae as the secondary source. Compared with the reference data from other high-latitude lake sediments and plants, the $\delta^{13}\text{C}_{\text{org}}$ values in IIL9 were extremely high, a result likely related to intense competition for CO_2 assimilation among algal species during the growing season in this relatively shallow pond. These results indicate that sedimentary $\delta^{13}\text{C}_{\text{org}}$ is a reliable proxy for paleo-primary productivity in ponds at Inexpressible Island.

Keywords Inexpressible Island, Ross Sea, pond sediments, lake algae, carbon isotopic composition, paleo-environment

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1 Introduction

The formation of many ice-free areas in Antarctica occurred with climate warming and retreat of the ice sheets following the Last Glacial Maximum (LGM). Many of these ice-free areas contain a range of paleo-environmental records

which can provide information on both local history and global environmental changes^[1-3]. For example, sediments in lakes and ponds record responses in primary productivity to variations in temperature and precipitation, the advance and retreat of ice sheets, isostatic uplift of the continent, and relative sea level change^[4-8]. These records are valuable sedimentary archives with relatively high accumulation rates compared with terrestrial sedimentary successions^[9].

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Due to their short food chains, the ecosystems of Antarctic lakes are relatively simple compared with those of similar environments on other continents^[10]. Ecosystems of Antarctic lakes are often very sensitive and even slight changes in the ambient environment can induce significant fluctuations in their physical and chemical properties, and affect the organisms living within them. As these changes are often well preserved in lake sediments, paleo-limnological studies in the Antarctic region have become increasingly common^[11–14].

Multiple-proxies such as diatom species assemblage, biomarkers, mineralogy, magnetic properties, elemental/compound contents and ratios, isotopic composition, and grain size are commonly employed in research on Antarctic lacustrine sediments^[15–18]. Among these proxies, the organic carbon isotopic composition ($\delta^{13}\text{C}_{\text{org}}$) of lake sediments have been widely investigated to explore the origins of organic matter (OM) and carbon utilization/circulation^[19–21]. The $\delta^{13}\text{C}_{\text{org}}$ in lake sediments may be affected by ice cover, water depth, pH, temperature, nutrient input (salinity) and changes in the plants living in the lake and its catchment area^[20]. Studies of such changes have been widely applied in paleo-limnological research despite ambiguities in interpretation caused by these multiple confounding factors^[5, 22]. In the Ross Sea region, few studies have been conducted on sedimentary $\delta^{13}\text{C}_{\text{org}}$ as a proxy to identify sources of sedimentary organic matter and to reconstruct the paleo-environment^[23].

The purpose of this study is to investigate the applicability of lake sedimentary $\delta^{13}\text{C}_{\text{org}}$ analyses in paleo-environmental reconstruction. We recovered two sediment cores and aquatic algae samples from two small lakes at Inexpressible Island, Ross Sea region, to analyze and compare $\delta^{13}\text{C}_{\text{org}}$ values. We also compare these data with a wide range of $\delta^{13}\text{C}_{\text{org}}$ reference material from environmental samples collected in other high-latitude regions. Factors that influence the $\delta^{13}\text{C}_{\text{org}}$ values in lake sediments at Inexpressible Island, and the potential eco-environmental implications of these values are discussed.

2 Study area

Two pond sediment cores were collected on Inexpressible Island, which has an area of approximately 50 km², and is located in Terra Nova Bay, Victoria Land, Antarctica (Figure 1). The Ross Sea maintains open water all year because of the Terra Nova Bay polynya^[24]. The island is exposed to the marine environment and its climate is influenced by its location at the base of two merging continental glaciers and ice sheets. The western coast of Inexpressible Island is adjacent to the Nansen Ice Sheet, while the northeastern coast connects with the Hell's Gate Ice Shelf. Along the western margins of Inexpressible Island there are raised beaches with elevations ranging from 20–30 m above sea level (asl), and are truncated to the west by the Nansen Ice Sheet^[25]. During the LGM, ice inundated coastal areas possibly to as high as 500 m asl at Inexpressible Island^[26]. A large number of abandoned

Adélie penguin colonies have been located on Inexpressible Island, and a colony of ~40000 pairs occupies ice-free terrain surrounding Seaview Bay^[27] (Figure 1).

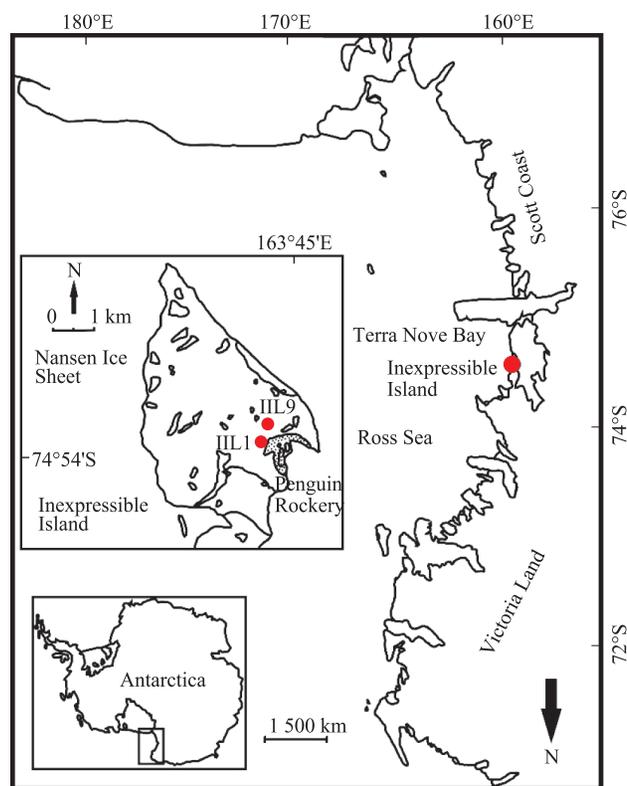


Figure 1 The study area showing the location of Inexpressible Island and the ponds where sediment cores IIL1 and IIL9 were collected.

According to meteorological data^[28], the interannual variation of the climate at Inexpressible Island is considerable. Average monthly temperatures are below 0°C, and the annual average ranges from -15.3°C to -18.7°C. The minimum temperature in winter (May to October) is -39.3°C with an average at -21.8°C. In October to December, the average temperature quickly rises to above 0°C, and the maximum temperature is up to 5.4°C. The downwind in the Inexpressible Island is strong and the wind direction is very stable. Precipitation is relatively low. Many freshwater lakes and ponds are found on Inexpressible Island, most with abundant benthic algal mats^[29]. The lacustrine sediments typically consist of black mud, which is interpreted as the remains of benthic microbial mats. The main components of the microbial mats are algae and cyanobacteria. These sediments are particularly suitable for paleo-limnological studies because there is no significant bioturbation and a limited season of open water when wind-induced mixing might encourage resuspension.

Cape Chocolate (77°56'S, 164°35'E) is located on the southern Scott Coast, southern Ross Sea, and also is highly sensitive to climate change. Cape Chocolate has no evidence of modern penguin activity or abandoned colonies. Across the cape, glacial erosion has left numerous small and shallow

ponds filled with algae. The ponds are ice-covered in winter. According to records of the neighboring McMurdo Station, the weather in this area is abrupt and severe. The mean annual temperature of this area is -18°C , and the temperatures may reach 8°C in summer and -50°C in winter. The average wind speed is 12 knots, but winds may exceed 100 knots on occasion.

3 Materials and methods

Sediment core IIL9 ($74^{\circ}53'18.98''\text{S}$, $163^{\circ}43'26.38''\text{E}$, Figure 1) was collected from a pond with a maximum depth of about 50 cm and a catchment perimeter of about 200 m. The pond was formed by glacial erosion, and is predominantly fed by snow-melt and local precipitation. Pond water is lost mainly through evaporation; no outlets were visible during sampling. Lake ice is absent from December to February^[30]. A large microbial mat (algae) occurs on the surface of the pond and the bedrock in the surrounding catchment is almost completely free of penguin colonies. Dried algae is abundant around the pond, which indicates that the depth of the water has changed over time. Algae, cyanobacteria and bacteria likely form the bulk of the biomass in the pond.

Sediment core IIL1 ($74^{\circ}53'46.61''\text{S}$, $163^{\circ}43'35.37''\text{E}$) was collected on Inexpressible Island from a small pond with a relatively low elevation (Figure 1). According to field surveys, the maximum depth of the pond is about 40 cm, and the catchment perimeter is about 150 m. There are small active penguin colonies near the southern side of the catchment area, and many ancient penguin colonies were found within the pond catchment.

In the laboratory, sediment cores were sectioned at 0.5 cm intervals. Throughout the IIL9 sediment core (48.5 cm long), the lithology has no obvious change, and as a whole it is comprised of black odiferous sapropelic sediments, indicative of a continuous sedimentary process. From the bottom to the top 10 cm, the sediments appear to contain more gravels and sands, whereas more abundant microbial deposition is observed in the surface 10 cm sediment layer, consistent with field observations of abundant dry and wet algae in and around the pond. Based on lithological observations, IIL1 (54 cm in length) comprise of ornithogenic sediments with a dark color and rancid odor, below 26 cm depth. Sediments between 26 cm and 20 cm depth appear to transition from ornithogenic to weakly ornithogenic deposition. The top 20 cm comprise of fine-grained sediments with a gray-yellow color. Overall, from bottom to top, the black, fine-grained ornithogenic layer seems to gradually transition into a brown clay unit. Penguin remains, including feathers and bones, were also recovered from the ornithogenic sediments of the core.

For comparison, a total of 18 microbial mat (freshwater algae) samples were collected from several small ponds at Cape Chocolate and Inexpressible Island. Algae were recovered from the water or collected from the shores of ponds and lakes, and placed in sealed bottles and plastic bags for transportation to the lab for analysis. Based on field observations, all algal samples were not noticeably influenced by penguin activity. All the sediment and algal samples were

freeze-dried for subsequent homogenization and sieving through a 200 mesh screen.

Organic carbon isotope analyses of acid-treated sediment samples were performed using the sealed tube combustion method at the State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry (LAPC), Institute of Atmospheric Physics, Chinese Academy of Sciences (Beijing, China), following the analytical methods of Wu et al.^[31]. The powdered samples were acid-treated ($1\text{ mol}\cdot\text{L}^{-1}\text{ HCl}$) to remove carbonates, and then freeze-dried to measure $\delta^{13}\text{C}_{\text{org}}$. The resulting CO_2 gas was measured using a MAT 253 mass spectrometer. Samples and standards were flash combusted and the gases were separated by a “purge and trap” adsorption column and sent to the IRMS (Isotope Ratio Mass Spectrometer) interface for analysis (MAT 253: Thermo Fisher Scientific). Stable isotope abundances were expressed in δ notation as deviations from standards in parts per thousand, $\delta^{13}\text{C}(\text{‰}) = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000$, where R is the corresponding ratio $^{13}\text{C}/^{12}\text{C}$. The R_{standard} values were based on the Vienna Pee Dee Belemnite (V-PDB) standard. The analytical precision (standard deviation) for the organic carbon isotopic measurements is better than $\pm 0.1\text{‰}$.

Contents of total organic carbon (TOC) and total nitrogen (TN) in the sediments were determined on homogenized sample aliquots. TOC was measured by the external heating-potassium dichromate oxidation-chemical volumetric method with a relative standard deviation (RSD) of 0.5% ^[32]. Total nitrogen content (TN) was determined by an elemental analyzer (FLASH, 2000 HT Elemental Analyzer, Thermo Fisher) with a relative standard deviation (RSD) of less than 1% ^[31].

4 Identification of sources of organic matter

Both the TN and TOC content in core IIL9 rapidly increased between 12 cm and 8 cm depth, and the values remain high above 8 cm, whereas below a depth of 12 cm, the TN and TOC values remain relatively low. The TN and TOC values in core IIL1 show a rapid decreasing trend at depths of 50 cm and below. The TN in core IIL1 increase between 50 cm and 25 cm depth but turn to decrease above 20 cm depth. The TOC values in core IIL1 increase from 50 cm to 39 cm depth, and the TOC values relatively decrease from 39 cm to the top (Figure 2). Overall, the depth profiles of TN and TOC proxies exhibit similar fluctuations in both cores (Figure 2). The TOC/TN values in the IIL9 and IIL1 sediment profiles differ greatly; the mean values of TOC/TN are 11.4 and 1.0 in cores IIL9 and IIL1, respectively, which indicate that the organic sources of the sediments of the two cores likely different.

The $\delta^{13}\text{C}_{\text{org}}$ values in IIL9 fluctuate from -14.6‰ to -11.6‰ with an average value of $-13.4 \pm 0.8\text{‰}$ ($n=48$, Figure 2, Table 1). The $\delta^{13}\text{C}_{\text{org}}$ values are generally more enriched in the sediments above 8 cm; the values remain

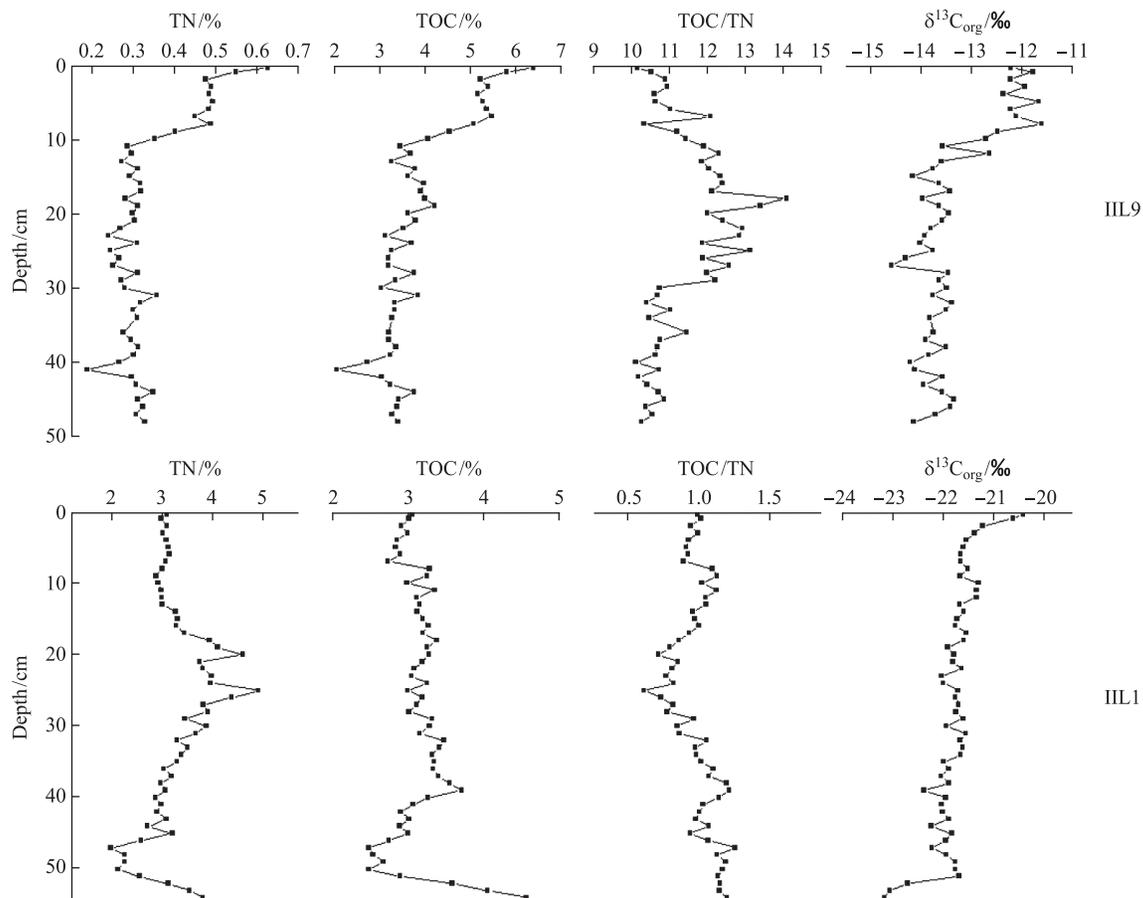


Figure 2 Stratigraphic profiles of biogeochemical proxies with depth in the two lacustrine sediment cores, IIL9 and IIL1, collected from Inexpressible Island.

relatively less enriched between 12 and 48 cm. $\delta^{13}\text{C}_{\text{org}}$ values in IIL9 display an increasing trend of enrichment between 11 and 8 cm. From the bottom to top, the $\delta^{13}\text{C}_{\text{org}}$ values display a gradual enrichment trend in IIL1 ranging from -23.2% to -20.4% with an average value of $-21.8 \pm 0.4\%$ ($n=55$, Figure 2, Table 1). The $\delta^{13}\text{C}_{\text{org}}$ values of algal samples from Cape Chocolate and Inexpressible Island range from -16.1% to -10.0% with a mean value of $-12.2 \pm 2.1\%$ ($n=6$) and from -17.2% to -10.6% with a mean value of $-13.3 \pm 1.8\%$ ($n=12$), respectively (Table 1).

We compared $\delta^{13}\text{C}_{\text{org}}$ values and the C/N ratio in IIL1 and IIL9 sediments and freshwater algae from Cape Chocolate and Inexpressible Island with those of Hodgson Lake sediments (a recently emerged Antarctic subglacial lake, Alexander Island, Antarctic Peninsula), Ablation Lake (Ablation Point, east coast of Alexander Island), Lake CF3

(northeastern Baffin Island, Canada), Moutonnée Lake (Ablation Point, on the east coast of Alexander Island), Lake Hoare (Taylor Valley) and reference data from a range of Antarctic substrates (Figure 3). These lakes all have similar values of $\delta^{13}\text{C}_{\text{org}}$ (Figure 3). In comparison, the sediments from IIL1 generally have lower C/N relative to other lake sediments, and also the $\delta^{13}\text{C}_{\text{org}}$ values of IIL1 lacustrine sediments are much lower. C/N values of algae from Cape Chocolate and Inexpressible Island are within the range of other freshwater algae. $\delta^{13}\text{C}_{\text{org}}$ values of algae are significantly higher than sediments in the IIL1 sediments, indicating the aquatic algae is not the main source of sedimentary organic matter in IIL1 pond. According to lithological observations, core IIL1 contains a large number of well-preserved penguin remains including feathers and bones. Liu et al.^[23] indicated that guano has very low carbon isotopic signature at about

Table 1 $\delta^{13}\text{C}_{\text{org}}$ values in different samples

$\delta^{13}\text{C}_{\text{org}}$ values /‰	IIL1 sediments ($n=55$)	IIL9 sediments ($n=48$)	IIL algae ($n=12$)	CC algae ($n=6$)
Minimum	-23.2	-14.6	-17.2	-16.1
Maximum	-20.4	-11.6	-10.6	-10.0
Mean \pm SD	-21.8 ± 0.4	-13.4 ± 0.8	-13.3 ± 1.8	-12.2 ± 2.1

Note: IIL algae and CC algae represent aquatic algae samples collected from Inexpressible Island and Cape Chocolate, respectively.

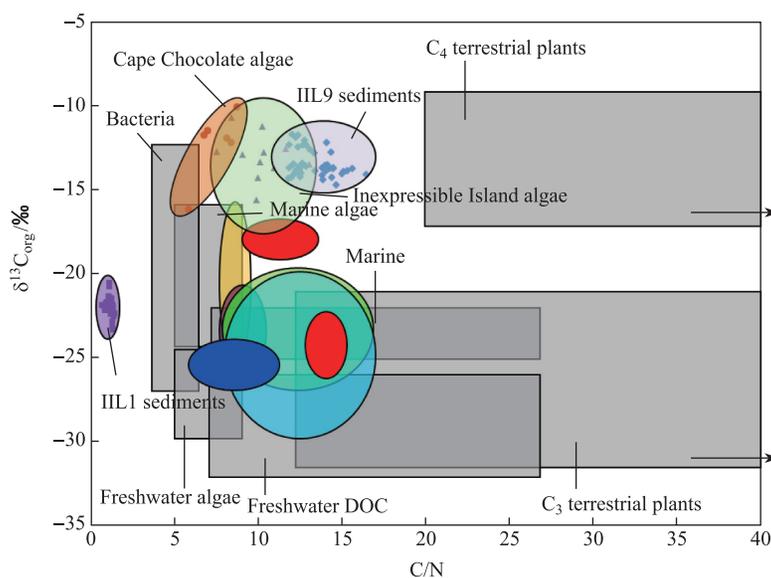


Figure 3 $\delta^{13}\text{C}_{\text{org}}$ and C/N values in the lacustrine sediments of Inexpressible Island and Hodgson Lake, Ablation Lake, Lake CF3, Moutonnée Lake, and Lake Hoare. Light purple area indicates pond sediments IIL9; purple area indicates pond sediments IIL1; light green area indicates Inexpressible Island algae; orange area indicates Cape Chocolate algae; red areas indicate mixed benthos from streams and melt ponds of Hodgson Lake^[22]; blue area indicates catchment gravel and fine-grained sediment at Hodgson Lake^[22]; yellow area indicates sediments from Ablation Lake^[34]; green area indicates sediments from Lake CF3^[35]; brown area indicates sediments from Moutonnée Lake^[34]; light blue area indicates sediments from Lake Hoare^[33]. $\delta^{13}\text{C}$ and C/N of Hodgson Lake sediments are within the ranges of blue and red areas.

–30‰. Therefore, the lower $\delta^{13}\text{C}_{\text{org}}$ values and lower C/N in IIL1 lacustrine sediments are likely derived from penguin guano.

The sediments from IIL9 generally do not show much difference in C/N with other lakes, but the $\delta^{13}\text{C}_{\text{org}}$ values of IIL9 lacustrine sediments are much higher than other regions in Antarctica^[22,33–35]. Core IIL9 mainly consists of algal and cyanobacterial residues, so to better understand this isotopic feature, we compared them with the $\delta^{13}\text{C}$ of algae (Figure 3). The stable carbon isotopes allow differentiation between C_3 and C_4 photosynthetic pathways. Generally, $\delta^{13}\text{C}_{\text{org}}$ values of C_3 plants range between –22‰ and –34‰ with an average of $-27 \pm 2\%$; $\delta^{13}\text{C}_{\text{org}}$ values of C_4 plants range between –9‰ and –19‰ with an average of $-13 \pm 2\%$. As shown in Figure 3, most plants in Antarctica have $\delta^{13}\text{C}_{\text{org}}$ values similar to that of C_3 plants, which is the case for the data from the mixed benthos from streams and melt ponds around Hodgson Lake and microbial mats in the other four reference lakes (Figure 3). However, the lacustrine sediments of IIL9 have much higher $\delta^{13}\text{C}_{\text{org}}$ than those of C_3 plants and some algae and bacteria. These $\delta^{13}\text{C}_{\text{org}}$ values are similar to the lake algae samples collected from the Cape Chocolate and Inexpressible Island, and are near the highest levels found in C_4 plants.

In summary, the lower TOC/TN ratio and lower organic $\delta^{13}\text{C}_{\text{org}}$ in IIL1 indicates that pond sediments contain high guano-derived materials. Sediment samples containing more algae-derived materials have a relatively low TOC/TN ratio and extremely high organic $\delta^{13}\text{C}_{\text{org}}$. Since the catchment

of IIL9 Pond is devoid of terrestrial vegetation, and soil formation is limited, the input of the organic matter from terrestrial vegetation and nutrients washed out of the soil are considered of limited significance, and the influence of recent human activity in the catchment is also negligible. Thus we suggest the organic matter in the IIL9 sediment profile is predominantly derived from endogenous microbial mats.

5 Potential paleoenvironmental implication

To further examine the environmental implication of $\delta^{13}\text{C}_{\text{org}}$ in the IIL9 and IIL1 cores, we compared our values with a series of $\delta^{13}\text{C}_{\text{org}}$ values in plants, microbial mats (mainly cyanobacteria) and organic matters (OM) from different sources (Figure 4). According to Burkins et al.^[36], the $\delta^{13}\text{C}_{\text{org}}$ of ornithogenic organic matter (OOM) is relatively low, ranging from –18.7‰ to –30.4‰ (NO. 28 in Figure 4). Additionally, Lorenzini et al.^[37] reported that the organic $\delta^{13}\text{C}_{\text{org}}$ values in guano samples varied from –28.9‰ to –24.0‰, and the mean value of modern guano samples is $-27.3 \pm 0.4\%$ (No. 31 in Figure 4), similar to the fresh penguin guano collected from Cape Bird^[23]. As mentioned above, the mean $\delta^{13}\text{C}_{\text{org}}$ value of pond algae at Inexpressible Island is –13.3‰, significantly more enriched than the guano samples. Based on comparative analysis, we suggest that the feature of $\delta^{13}\text{C}_{\text{org}}$ in IIL1 lacustrine sediments reflects a mixture source of organic matter from penguin guano and pond algae, with guano as the primary source. In other words,

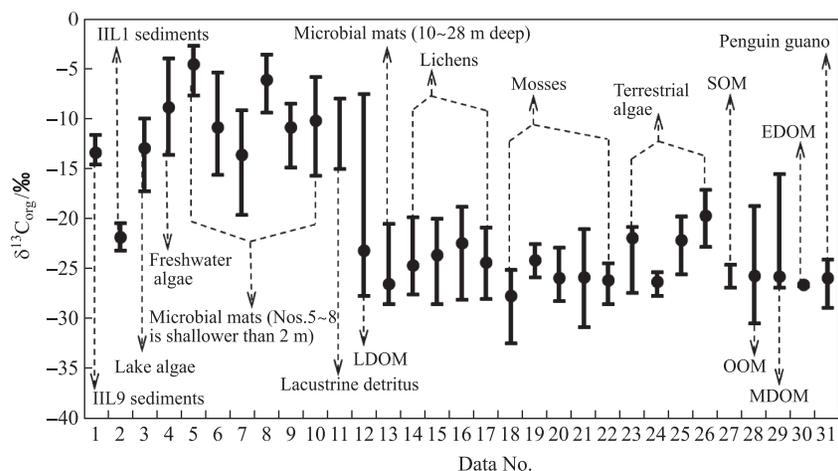


Figure 4 Comparison of $\delta^{13}\text{C}_{\text{org}}$ between Inexpressible Island ponds sediments and plants, microbial mats and SOM from different sources. Vertical lines in the figure represent ranges of $\delta^{13}\text{C}_{\text{org}}$ from different data; the dots are the mean values; the values on the x-axis stand for the following source regions; detailed data of the source regions of carbon isotopes represented by the numbers on the x-axis can be found in supplementary materials.

the change of sedimentary $\delta^{13}\text{C}_{\text{org}}$ was mainly controlled by the input of guano in the sediments, and thus the sedimentary $\delta^{13}\text{C}_{\text{org}}$ in the IIL1 pond can be used as a potential proxy to reconstruct the relative change of guano inputs, which is indicative of historical changes in the penguin population^[23].

Polar mosses, lichens and terrestrial algae (*Prasiola crista*) have relatively low $\delta^{13}\text{C}_{\text{org}}$ values, varying between -17.1‰ and -32.4‰ typical of C_3 plants (Nos. 14–26 in Figure 4), while freshwater algae have much higher $\delta^{13}\text{C}_{\text{org}}$ in the range of -13.6‰ to -4‰ (No. 4 in Figure 4). Studies of soil organic matter (SOM) from different sources and organic residues in lakes (East Antarctica) show similar results (No. 27 in Figure 4). According to Burkins et al.^[36], the $\delta^{13}\text{C}_{\text{org}}$ of marine-derived organic matter (MDOM) and endolith-derived organic matter (EDOM) are all relatively low, ranging from -15.5‰ to -26.9‰ (Nos. 29–30 in Figure 4), while the $\delta^{13}\text{C}_{\text{org}}$ values of lacustrine-derived organic matter (LDOM) have a larger range from -7.5‰ to -27.7‰ (No. 12 in Figure 4). The data show that the IIL9 sediments had some organic $\delta^{13}\text{C}_{\text{org}}$ overlap with LDOM, and agree well with values from the organic residues from lakes in the Dry Valleys (-8‰ to -15‰ , No. 11 in Figure 4) measured by Hopkins et al.^[38]. Comparison of the data shown in Figure 4 reveals significant differences in $\delta^{13}\text{C}_{\text{org}}$ values between terrestrial plants such as mosses and lichens, and aquatic plants such as freshwater algae and microbial mats. Even in freshwater lakes, there are significant differences in organic carbon isotopic compositions. Microbial mats in moats are enriched in $\delta^{13}\text{C}_{\text{org}}$ (about -2.7‰ to -19.6‰ , Nos. 5–10 in Figure 4), but in water of 10–28 m depth, the $\delta^{13}\text{C}_{\text{org}}$ of microbial mats drops to between -20.5‰ and -28.5‰ , approximately the same level as terrestrial plants (No. 13 in Figure 4). In brief, we suggest that the sedimentary carbon isotopic compositions in IIL9 are in accordance with those of microbial mats in the moats of lakes with seasonal lake ice, and have some overlap

with those of LDOM as well. The features of $\delta^{13}\text{C}_{\text{org}}$ suggest that the sedimentary organic matter in IIL9 is from a single source, mainly freshwater algae.

Figure 5 shows a comparison of the organic carbon isotopic compositions of lacustrine sediments of lakes in other polar regions. The $\delta^{13}\text{C}_{\text{org}}$ values of sedimentary organic matter in lakes of the East Antarctica, West Antarctica, and Arctic have similar ranges of about -15‰ to -30‰ , with most be lower than -20‰ . These values are close to the range of C_3 plants, and thus are indicative of the source of organic matter in lakes from these regions, which is comprised mainly of freshwater algae, mosses, lichens, and terrestrial algae carried into the lakes by melt water. As shown in Figure 5, analysis of $\delta^{13}\text{C}_{\text{org}}$ in Antarctic lake sediments showed that lakes with different geomorphic features have significantly different $\delta^{13}\text{C}_{\text{org}}$ values. The value of $\delta^{13}\text{C}_{\text{org}}$ in Figure 5 varied from -7.5‰ to -33.6‰ in lakes of the East Antarctica, West Antarctica, and Arctic. We found that most of the lakes with deep water and perennial ice cover, such as Lake Hoare, or at least ice cover for most of the year (e.g., 11 months for Ace Lake), have low $\delta^{13}\text{C}_{\text{org}}$ values in their sediments. However, White Smoke Lake in the Bunger Hills had very high sedimentary $\delta^{13}\text{C}_{\text{org}}$ values of -7.5‰ to -11.6‰ , mean -9.8‰ (No.3 in Figure 5), probably due to relatively thin lake ice and high light-use efficiency of organisms, a similar limnological environment exhibited by IIL9^[39]. These researchers interpreted the high $\delta^{13}\text{C}_{\text{org}}$ of lake sediments in East Antarctica as being a response to lake depth and seasonal ice cover. Bird et al.^[40] presented an example of where lower $\delta^{13}\text{C}_{\text{org}}$ corresponded to a greater lake depth; the $\delta^{13}\text{C}_{\text{org}}$ of sediments at a depth of 0.05 m in a melt water inflow was -10.8‰ , while values in sediments in shallow parts of the lake at 1.5 m and deeper at 6.7 m drop to -14.8‰ and -20.4‰ , respectively. The study of Burkins et al.^[36] on $\delta^{13}\text{C}_{\text{org}}$ of lacustrine organic matter at different depths showed the same trend: sediments in the shallow parts had a $\delta^{13}\text{C}_{\text{org}}$

of -7.5% to -11.5% ; $\delta^{13}\text{C}_{\text{org}}$ values of macrophytes at 10 m were $-19.9 \pm 0.3\%$ ($n=5$); microbial mats at 10–26 m and organic matter at 8–28 m had $\delta^{13}\text{C}_{\text{org}}$ of $-27.7 \pm 0.7\%$ ($n=5$) and $-25.0 \pm 2.9\%$ ($n=12$), respectively. Microbial mats in the moats of three lakes in the McMurdo Dry Valleys also had high $\delta^{13}\text{C}_{\text{org}}$ values ($-8.36 \pm 3.46\%$, $n=10$), consistent with benthic organic matter, with mean $\delta^{13}\text{C}_{\text{org}}$ values of -4.6% to -13.6% ($n=62$) being recorded in four lakes. In comparison, sediments collected from parts of the lakes with perennial ice-cover were much richer in ^{12}C , with $\delta^{13}\text{C}_{\text{org}}$ at -20.1% to -35% ^[20]. Taking all the data above into account, we suggest that the climatic conditions such as lake depth and ice-cover conditions likely have a significant impact on the $\delta^{13}\text{C}_{\text{org}}$ of sedimentary organic matter in the lakes of the Ross Sea region. The presence of seasonal (instead of perennial) lake ice and shallow moats could result in the occurrence of high $\delta^{13}\text{C}_{\text{org}}$ values in the sediments, and this might be caused by the high photosynthetic efficiency of aquatic plants under strong solar radiation.

The pond for IIL9 is a small seasonally ice-covered lake and its water depth is no more than 1 m. It is therefore necessary to investigate its specific catchment environment and in-lake ecosystem to determine the reasons for the extremely high $\delta^{13}\text{C}_{\text{org}}$ values in the pond sediments. As described above, freshwater algae residues are the main source of the organic matter in the core. Generally, the carbon isotopic composition of aquatic plants is affected by the photosynthetic pathway, temperature and pH of the water column, intensity of solar radiation, $\delta^{13}\text{C}$ of CO_2 in the atmosphere and the concentration of the dissolved inorganic carbon (DIC) in lakes^[41]. Isotopic fractionation caused by temperature is usually too small to be taken into account; according to studies on Antarctic ice cores, carbon isotopic variation in atmospheric CO_2 caused by historical $p\text{CO}_2$ change is less than 0.5% ^[42–43], so it is negligible as well. The catchment investigation can rule out the possibility of

influence from surrounding terrestrial plant input. Moreover, during the growing season of aquatic plants, the lake waters in the IIL9 pond are generally well mixed, allowing the CO_2 in the water to be exchanged completely with the atmosphere, thus the influence of CO_2 exchange was probably negligible. The reduction in fractionation and the resultant high $\delta^{13}\text{C}_{\text{org}}$ values in the IIL9 sediments are therefore interpreted as being the product of a CO_2 diffusion-limited environment caused by insufficient CO_2 supply and high photosynthetic efficiency^[4–5,40].

The surface albedo of the area of the IIL9 pond is very low in summer; the lake water is transparent and the lake ice melts completely. Under these favorable conditions, the freshwater algae in the IIL9 pond receives high levels of solar radiation. The extremely high $\delta^{13}\text{C}_{\text{org}}$ values of IIL9 sediments are therefore most likely controlled by the high productivity of pond algae. In spring and summer, optimal conditions of higher temperatures and sufficient solar radiation promote the growth of algae. Enhancement of photosynthesis by the increased algal biomass consumes dissolved CO_2 rapidly enough to surpass atmospheric replenishment and lead to CO_2 deficiency in the water column of the pond, thus, a CO_2 diffusion-limited environment is formed. Aquatic plants tend to preferentially use ^{12}C for photosynthesis under normal conditions, but in such the diffusion-limited environment, persistent photosynthesis can result in a decrease in ^{12}C -rich CO_2 in the pond water, and the availability of ^{12}C -rich carbon to the mat organisms gradually becomes limited. Eventually, the pond algae must assimilate more ^{13}C -rich CO_2 into the products of photosynthesis, which weaken, or even eliminate, the isotopic fractionation between reactants and resultants^[43–48]. In winter, pond ice cover affects sunlight transmission, gas exchange, mixing and deposition pathways, which also have a great impact on photosynthesis of algae in the pond. Although pond ice interrupts the replenishment of CO_2 from the atmosphere, weak sunlight could still penetrate the thin ice cover and provide energy for algal photosynthesis^[49–50]. More

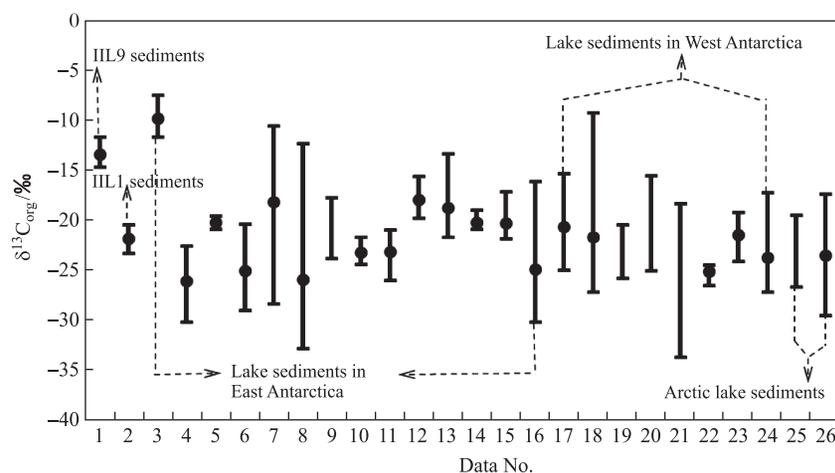


Figure 5 Comparison of $\delta^{13}\text{C}_{\text{org}}$ in the sedimentary organic matter of Inexpressible Island ponds and other lakes in polar regions. Vertical lines in the figure represent range of $\delta^{13}\text{C}_{\text{org}}$ from different data source; the dots are the mean values; the values on the x-axis stand for the following source regions; the dots are the mean values; detailed data of the source regions of carbon isotopes represented by the numbers on the x-axis can be found in supplementary materials.

depleted CO₂ would cause an even stronger diffusion-limited environment, and thus result in higher $\delta^{13}\text{C}_{\text{org}}$. In midwinter, some pond algae may die of insufficient carbon source and nutrient supply, but their residues with high $\delta^{13}\text{C}$ would be preserved well in the sediments. After the melt of the pond the following year, the remaining algae would begin another round of rapid growth. Thus, the sediments in the IIL9 pond contain a great deal of organic matter with extremely high $\delta^{13}\text{C}_{\text{org}}$ values.

The $\delta^{13}\text{C}_{\text{org}}$ values of IIL9 sediments fluctuate (by about 3.0‰) with depth. Based on the preservation of the core, under the extremely low-temperature conditions at Inexpressible Island, decomposition and diagenesis of organic matter are not expected to have had large effects on the carbon isotopic compositions of the sediments. Lawson et al.^[20] conducted research on the carbon isotopic composition of different species of algae and found that there were no statistical differences between them, which indicates that the fluctuation of $\delta^{13}\text{C}_{\text{org}}$ in the core is not related to variations among the aquatic plants. Therefore, if the extremely high $\delta^{13}\text{C}_{\text{org}}$ values of IIL9 are related to the intensified photosynthesis of algae, the fluctuation of $\delta^{13}\text{C}_{\text{org}}$ with depth may have been caused by changes in the pond's historical primary productivity. As described above, with an increasing algal biomass and sufficient solar radiation, intensified photosynthesis of algae allows the carbon source to diffuse and assimilate rapidly into algal cells. In this scenario, isotopic fractionation between the carbon substrates and the organic products was greatly weakened, which led to assimilation of more ¹³C into the plants. TOC and TN are basic proxies for the organic matter contents of lakes, and represent the level of lake primary productivity. Correlation analysis was used to explore the possible relationships between $\delta^{13}\text{C}_{\text{org}}$ and TOC, TN. The $\delta^{13}\text{C}_{\text{org}}$ values were found to have positive statistical correlations with both TOC ($R^2=0.74$) and TN ($R^2=0.77$) in core IIL9. However, $\delta^{13}\text{C}_{\text{org}}$ values have no strongly positive correlations with TOC ($R^2=0.22$) or TN ($R^2=0.004$) in core IIL1. These results indicate that the application of $\delta^{13}\text{C}_{\text{org}}$ may also contribute to a better understanding of the paleo-environment. Therefore, we suggest that the $\delta^{13}\text{C}_{\text{org}}$ values in the lacustrine sediments of the IIL9 pond are correlated with changes of pond primary productivity; higher $\delta^{13}\text{C}_{\text{org}}$ corresponds to more algae growth in the pond, and thus to higher productivity.

6 Conclusions

The lower $\delta^{13}\text{C}_{\text{org}}$ values in lacustrine sediments in the IIL1 pond are primarily the result of input from penguin guano. The extremely high $\delta^{13}\text{C}_{\text{org}}$ values of lacustrine sediments in the IIL9 pond are interpreted to have resulted from the formation of a CO₂ diffusion-limited state in the water column caused by the high photosynthetic efficiency in the pond, which may have resulted in a larger proportion of ¹³C being assimilated into algae. Therefore, the organic carbon isotope data can effectively distinguish the sedimentary

organic source of ponds and lakes at Inexpressible Island. Furthermore, the fluctuation of $\delta^{13}\text{C}_{\text{org}}$ with depth in the IIL9 sediment profile displayed significantly positive correlations with changes in TOC and TN, which are indicative of algal production. Thus $\delta^{13}\text{C}_{\text{org}}$ in the sediments predominately composed of pond algae can be used as a reliable proxy for changes in primary production, which are likely associated with climate change.

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Appendix Table 1 Specific types, numbers, locations and references for data in Figure 4

No.	Sample type	No. samples	Location	Reference
1	Lake sediments IIL9	48	Inexpressible Island	This Study
2	IIL1	54	Inexpressible Island	This Study
3	Lake algae	18	Cape Chocolate, Inexpressible Island	This Study
4	Freshwater algae	12	Schirmacher and Untersee Oases, King George Island and Thala Hills	Böttger et al. ^[41]
5	Microbial mats	31	Lake Fryxell, McMurdo Dry Valleys	Lawson et al. ^[20]
6	Microbial mats	9	Lake Hoare, McMurdo Dry Valleys	Lawson et al. ^[20]
7	Microbial mats	12	East Lake Bonney, McMurdo Dry Valleys	Lawson et al. ^[20]
8	Microbial mats	10	West Lake Bonney, McMurdo Dry Valleys	Lawson et al. ^[20]
9	Microbial mats	13	Hjorth Hill, McMurdo Dry Valleys	Hage et al. ^[49]
10	Microbial mats	11	Garwood Valley, McMurdo Dry Valleys	Hage et al. ^[49]
11	Lacustrine detritus	/	McMurdo Dry valleys	Hopkins et al. ^[38]
12	LDOM	24	Talyor Valley, McMurdo Dry Valleys	Burkins et al. ^[36]
13	Microbial mats	6	Lake Hoare, McMurdo Dry Valleys	Wharton et al. ^[33]
14	Lichens	7	Schirmacher and Untersee oases, King George Island and Thala Hills	Böttger et al. ^[41]
15	Lichens	24	Barton Peninsula, King George Island	Lee et al. ^[51]
16	Lichens	17	South Orkney Islands and South Shetland Islands	Galimov ^[52]
17	Lichens	9	Dronning Maud Land	Cocks et al. ^[53]
18	Mosses	9	Dronning Maud Land	Cocks et al. ^[53]
19	Mosses	23	South Orkney Islands and South Shetland Islands	Galimov ^[52]
20	Mosses	22	Barton Peninsula, King George Island	Lee et al. ^[51]
21	Mosses	11	North Baffin Bay	Blake ^[54]
22	Mosses	6	Schirmacher and Untersee oases, King George Island and Thala Hills	Böttger et al. ^[41]
23	Terrestrial algae	3	Schirmacher and Untersee oases, King George Island and Thala Hills	Böttger et al. ^[41]
24	Terrestrial algae	3	Barton Peninsula, King George Island	Lee et al. ^[51]
25	Terrestrial algae	7	South Orkney Islands and South Shetland Islands	Galimov ^[52]
26	Terrestrial algae	22	Léonie Islands Archipelago	Huiskes et al. ^[55]
27	SOM	30	Dronning Maud Land	Cocks et al. ^[53]
28	OOM	34	Talyor Valley, McMurdo Dry Valleys	Burkins et al. ^[36]
29	MDOM	35	Talyor Valley, McMurdo Dry Valleys	Burkins et al. ^[36]
30	EDOM	3	Talyor Valley, McMurdo Dry Valleys	Burkins et al. ^[36]
31	Penguin guano	82	Cape Bird, Cape Hickey, Cape Irizar, Cape Roberts, Cape Ross, Depot Island Peninsula, Dunlop Island, N Cape Day, Prior Island, South Harbord glacier	Lorenzini et al. ^[37]

Appendix Table 2 Specific types, numbers, locations and references for data in Figure 5

No.	Sample type	No. samples	Location	Reference
1	Lake sediments	48	Inexpressible Island	This Study
2	Lake sediments	54	Inexpressible Island	This Study
3	Lake sediments	8	DH7, White Smoke lake, Bunger Hills	Doran et al. ^[39]
4	Lake sediments	10	Lake Hoare (anoxic region), McMurdo Dry Valleys	Bishop et al. ^[5]
5	Lake sediments	10	Lake Hoare (oxic region), McMurdo Dry Valleys	Bishop et al. ^[5]
6	Lake sediments (using sediment traps)	12	Lake Hoare, McMurdo Dry Valleys	Wharton et al. ^[33]
7	Lake sediments (using sediment traps)	28	East Lake Bonney, McMurdo Dry Valleys	Lawson et al. ^[20]
8	Lake sediments (using sediment traps)	24	West Lake Bonney, McMurdo Dry Valleys	Lawson et al. ^[20]
9	Lake sediments	/	Windmill Islands	Kirkup et al. ^[56]
10	Lake sediments	5	Ace Lake, Vestfold Hills	Roberts et al. ^[57]
11	Lake sediments	23	Ace Lake, Vestfold Hills	Bird et al. ^[40]
12	Lake sediments	22	Organic Lake, Vestfold Hills	Bird et al. ^[40]
13	Lake sediments	26	Highway Lake, Vestfold Hills	Bird et al. ^[40]
14	Lake sediments	24	N island, Amanda Bay	Huang et al. ^[58]
15	Lake sediments	159	Lake Skallen Oike, the Syowa Station	Matsumoto et al. ^[15]
16	Lake sediments	143	Ross Island and Beaufort Island, Ross Rea	Liu et al. ^[23]
17	Lake sediments	140	Marguerite Bay, Antarctic Peninsula	Hodgson et al. ^[59]
18	Lake sediments	25	South Shetland Islands, Antarctic Peninsula	Watcham et al. ^[60]
19	Lake sediments	17	Moutonnée Lake, Alexander Island	Smith et al. ^[34]
20	Lake sediments	8	Ablation Lake, Alexander Island	Smith et al. ^[34]
21	Lake sediments	/	Long Lake, King George Island	Yoon et al. ^[61]
22	Lake sediments	3	Citadel Bastion Lake, West Antarctica	Roberts et al. ^[62]
23	Lake sediments	43	Fildes Peninsula	Liu et al. ^[63]
24	Lake sediments	115	Xihu Lake, Fildes Peninsula	Li et al. ^[64]
25	Lake sediments	/	Lake CF3, north-east Baffin Island, Canada	Briner et al. ^[35]
26	Lake sediments	4	Lake SS2, southern West Greenland	Anderson et al. ^[65]