Analysis of phosphorus forms in sediment cores from ephemeral ponds on Ardley Island, West Antarctica

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Abstract  The guano of penguins, other seabirds, and pinnipeds is an important source of phosphorus in the ecosystems of Antarctica. To study the vertical distribution of phosphorus in sediments influenced by penguins, we measured phosphorus forms in two sediment cores (G1 and Q2) from ephemeral ponds on Ardley Island. We also investigated the correlations between these phosphorus forms and physicochemical characteristics. Inorganic phosphorus was the main form of phosphorus in both cores. The vertical distribution patterns of phosphorus forms in G1 and Q2 differed, indicating different sedimentary sources. The G1 sediment profile was more influenced by penguin guano than the Q2 profile, and as a result sediments in the G1 core had higher total phosphorus, non-apatite inorganic phosphorus, and apatite phosphorus content. The findings from two ephemeral ponds on Ardley Island indicate that the contribution of penguin guano to organic matter in G1 core has increased in recent times, while Q2 showed a relatively larger contribution from mosses in ancient times, evident from the lithology and the vertical trend in organic matter.

Keywords    sediment, phosphorus forms, penguins


1 Introduction

There are many different water bodies in Antarctica, including ponds, streams, shallow lakes, and deep lakes. Shallow lakes and small ponds often appear when the ice retreats, and have key roles in moderating temperature fluctuation and increasing soil humidity in their vicinity[1-2]. The evolution of the Antarctic lacustrine ecosystem (including water bodies and lake sediments) has been little affected by human activity and has become a focus of paleoenvironmental studies in Antarctic ice-free areas[3-4].

In the cold and infertile Antarctic, organisms such as seals and penguins can transfer nutrients from sea to land, and these nutrients are crucial to support terrestrial and freshwater ecosystems in ice-free areas[5]. Because of differences in nutrient input by these organisms, nutrient conditions in Antarctic lakes and streams vary considerably, ranging from ultra-oligotrophic to extreme eutrophic[1-2,6-7]. In areas around the penguin colony at Admiralty Bay, Antarctica, the phosphorus (P) concentrations in freshwater streams and nearshore seawaters are 0.088–1.709 mg·L⁻¹ and 0.129 mg·L⁻¹, respectively, higher than the background value of freshwater (< 0.04 mg·L⁻¹)[8]. Therefore, penguin colonies increase the P concentration in freshwater bodies in their vicinity[5,9-10]. In addition, P input from penguin guano substantially alters the abundance and composition of microbial communities in the water[9], and P is significantly enriched in penguin ornithogenic sediments[10]. On Ardley Island, concentrations of P in sediments from lakes Y2, Y4, and G near penguin colonies are 25 093 mg·kg⁻¹,
31.988 mg·kg⁻¹ and 4.251 mg·kg⁻¹, respectively, much higher than those in proglacial sediments from Lake N1 on Nelson Island (611 mg·kg⁻¹), which are not affected by penguins[10-12].

The study of various P forms in the lake sediments of Antarctica can contribute to better understanding of the migration of P and its conversion processes. To date, P forms in soils and sediments have only been studied in the McMurdo Dry Valleys, East Antarctica[13-14], with few studies of P in lakes and other water bodies near areas of seabird activity. We used a harmonized sequential extraction method to investigate P forms in freshwater sediments from two ephemeral ponds near penguin colonies. We also compared P forms and their distribution patterns in the two cores, examined the correlation between P forms and sediment physicochemical characteristics, and investigated the organic matter sources of the sediments and their vertical changes.

2 Materials and methods

2.1 Study site and sample collection

Ardley Island (62°13′S, 58°56′W) is located in Maxwell Bay, King George Island, in the South Shetland Islands to the west of the Antarctic Peninsula. Ardley Island is connected to Fildes Peninsula by a fine gravel tombolo, 5–10 m wide at low tide. The island has an area of approximately 2 km², is relatively flat with low rocky hills that rise to 65 m above sea level, and is surrounded by raised beaches up to 15.5 m above sea level[15]. Approximately 80% of the island is densely covered with lichens and mosses[16]. Ardley Island has been designated an Antarctic Specially Protected Area (ASPA 150) by the International Scientific Committee on Antarctic Research (SCAR) because of the importance of its seabird colonies. The east coast has the largest penguin colonies among the South Shetland Islands, and mainly hosts gentoo penguins, chinstrap penguins, and Adélie penguins.

We collected two sediment cores, G1 and Q2, from moss-covered areas of Ardley Island close to penguin colonies (Figure 1). The G1 sediment core (62°12′36.9″S, 58°56′26.5″W) was collected during the 22nd Chinese National Antarctic Research Expedition from the northern shore of an ephemeral meltwater lake situated between raised beach ridges on the west coast of Ardley Island. The Q2 sediment core (62°12′49.06″S, 58°55′33.18″W) was collected during the 27th Chinese National Antarctic Research Expedition from another ephemeral meltwater lake occupying a depression at an altitude of 54 m. Because both lakes were shallow, the cores were collected in PVC pipes (11-cm diameter). After collection, both ends of the pipes were hermetically sealed and the cores were stored in the laboratory at −20°C.

2.2 Physicochemical analysis

The G1 core was 30-cm long and was sampled at 0.5-cm intervals. The top 0–15 cm of sediment produced 30 subsamples, but below 15.5 cm only odd-numbered subsamples were used. In total, 45 subsamples were obtained from G1. The Q2 core was 24 cm long and was

Figure 1 Map of sediment cores sampling from Ardley Island, West Antarctica.
sampled at 1-cm intervals to produce 24 subsamples. Parts of each subsample were used to determine water content. The remaining parts were freeze-dried, ground through a 170 mesh sieve, and stored hermetically in sample bags.

Loss on ignition at 550°C (LOI550°C) is widely used to determine organic matter content in sediments[17]. In the present study, LOI550°C was determined using the following procedure. A 0.3-g sample was placed in a weighing bottle, and dried at 105°C until it reached a constant weight. The sample was then transferred to a porcelain crucible and heated at 550°C for 5 h until it reached a constant weight. The measurement error was < 0.5%. To determine water content, about 1.0 g of wet sample was placed in a weighing bottle, and dried at 105°C until it reached a constant weight. An Elemental Vario EL III elemental analyzer (Vario Ltd) was used to measure total carbon (TC) and total nitrogen (TN) content. Samples were dried at 105°C for 2 h to constant weight, then 30 mg of sample was mixed with 10 mg of tungsten trioxide and wrapped in tinfoil. The measurement error was < 0.1%.

The analysis of the various P forms was performed using a harmonized sequential extraction method developed by the European Commission’s Standards, Measurements and Testing (SMT) Programme[18-19]. Five P forms were determined using the SMT protocol: non-apatite inorganic P (Fe/Al-P), apatite P (Ca-P), inorganic P (IP), organic P (OP), and total P (TP)[20]. The reagents and operating conditions are shown in Figure 2. One part of each sample was used for TP, a second for IP and OP, and a third for Fe/Al-P and Ca-P. In all cases, phosphate was determined using the spectrophotometric method, and absorbance measurements were performed at 880 nm. All samples were measured twice.

### Figure 2 The SMT extraction protocol.

<table>
<thead>
<tr>
<th>Extraction method</th>
<th>Phosphorus forms</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sample (0.2 g)</strong></td>
<td><strong>NaOH-P(Fe/Al-P)</strong></td>
</tr>
<tr>
<td>20 mL NaOH 1M</td>
<td>Extract</td>
</tr>
<tr>
<td>Shaking 16 h</td>
<td>4 mL HCl 3.5 M</td>
</tr>
<tr>
<td>Centrifugation</td>
<td>Shaking 16 h</td>
</tr>
<tr>
<td>Residue</td>
<td>Centrifugation</td>
</tr>
<tr>
<td>20 mL HCl 1M</td>
<td>Extract</td>
</tr>
<tr>
<td>Shaking 16 h</td>
<td>HCl-P(Ca-P)</td>
</tr>
<tr>
<td>Centrifugation</td>
<td><strong>OP</strong></td>
</tr>
<tr>
<td><strong>Sample (0.2 g)</strong></td>
<td><strong>IP</strong></td>
</tr>
<tr>
<td>20 mL HCl 1M</td>
<td>Extract</td>
</tr>
<tr>
<td>Shaking 16 h</td>
<td>IP</td>
</tr>
<tr>
<td>Centrifugation</td>
<td><strong>TP</strong></td>
</tr>
<tr>
<td>Calcination,450°C,3 h</td>
<td>Extract</td>
</tr>
<tr>
<td>20 mL HCl 1 M</td>
<td>TP</td>
</tr>
<tr>
<td>Shaking 16 h</td>
<td>TP</td>
</tr>
<tr>
<td>Centrifugation</td>
<td><strong>TP</strong></td>
</tr>
</tbody>
</table>

### 3 Results

#### 3.1 Sedimentary lithology

The G1 sediment core was black, and it contained penguin guano and other organic matter. The sediment in the top 5 cm was taupe arenose. Between 5 and 10 cm the sediment was fine sand and in the bottom 10 cm it was similar to taupe silt, with a finer grain size (Figure 3). The mean (range) LOI550°C of G1 was 5.36% (0.60%–15.39%). There was a decreasing trend with depth to the minimum value at 15 cm, with little change below 15 cm. TN, TC, and water content showed a similar trend to that of LOI550°C, with mean values of 0.24% (0.08%–0.80%), 1.70% (0.33%–6.20%), and 28.50% (14.63%–51.34%), respectively.

The Q2 sediment core contained abundant moss residues, especially from 7 cm to the bottom. The sediment was very black sand, mixed with nut-brown sand. The sediment in the upper 7 cm was very black sand. The means of LOI550°C, TN, TC, and water content of Q2 were 14.42% (3.96%–26.16%), 0.43% (0.12%–0.81%), 5.75% (1.18%–9.83%), and 39.77% (24.69%–55.07%), respectively. All four properties showed similar variation within the core with decreasing values from the surface to 7 cm, and increasing values from 7 cm to the bottom.

The vertical profiles of LOI550°C, TN, TC, and water content were similar within each core but differed between the G1 and Q2 cores. As mentioned above, in G1 the values
showed a decreasing trend from the surface to the bottom of the core while in Q2 values decreased from the surface to 7 cm, and then increased from 7 cm to the bottom. Consequently, the values of LOI$_{550^\circ C}$, TN, TC, and water content were higher in the bottom of the Q2 core than in the bottom of the G1 core.

### 3.2 Chemical states of P in the sediments

#### 3.2.1 P and Fe/Al oxide complex (Fe/Al-P)

In the Fe/Al-P complex, non-apatite inorganic P is mainly attached to the surface and interior of iron and aluminum oxides and hydroxides, and Fe/Al-P content will change as the oxidation-reduction state and temperature vary\[^{21-22}\]. Fe/Al-P content in the G1 core decreased from the surface to 5 cm, increased, and then decreased again to reach a relatively stable level. The mean Fe/Al-P content in the G1 core was $1571.95$ mg·kg\(^{-1}\) ($234.61–3484.85$ mg·kg\(^{-1}\)). The Q2 core was very different with a low Fe/Al-P content ($373.07–1170.26$ mg·kg\(^{-1}\)) showing a gradual increase with depth, with some fluctuations.

#### 3.2.2 P and Ca complex (Ca-P)

The Ca-P complex mainly refers to P forms related to authigenic apatite, lake sedimentary calcium carbonates, and animal bones\[^{23}\]. The mean Ca-P content in the G1 core was $571.95$ mg·kg\(^{-1}\) ($234.61–3484.85$ mg·kg\(^{-1}\)). The Q2 core was very different with a low Ca-P content ($373.07–1170.26$ mg·kg\(^{-1}\)) showing a gradual increase with depth, with some fluctuations.

#### 3.2.3 Organic P (OP)

The mean OP content in the G1 core was $162.12$ mg·kg\(^{-1}\) ($27.29–512.80$ mg·kg\(^{-1}\)), decreasing from the surface to 15 cm and remaining relatively unchanged below 15 cm. The OP content in the Q2 core showed a gradual increase with depth, with some fluctuations, and ranged from $112.04$ to $548.39$ mg·kg\(^{-1}\).

#### 3.2.4 Inorganic P (IP) and total P (TP)

In both G1 and Q2 cores, IP and TP content were closely related (Figure 4), with IP accounting for approximately 92% and 75% of TP, respectively. In the G1 core, IP and TP content varied considerably throughout the core and ranged from $1022.53$ to $4445.36$ mg·kg\(^{-1}\) and form $1032.04$ to $4897.88$ mg·kg\(^{-1}\), respectively. In the Q2 core IP and TP content varied less throughout the core, and showed a gradual increasing trend with depth, increasing from $831.57$ to $1650.51$ mg·kg\(^{-1}\), and from $959.92$ to $2126.59$ mg·kg\(^{-1}\), respectively.

### 3.3 Relative content of different P forms

As shown in Figure 5, in the G1 core the percentage of OP and Fe/Al-P in TP decreased gradually with depth to 15 cm (from 16.43% to 2.10% and from 72.44% to 23.90%, respectively), and below 15 cm showed an even more pronounced decrease. Conversely, in the Q2 core the percentage of OP and Fe/Al-P in TP increased gradually with depth, in particular in the layer below 7 cm, and ranged from 9.22% to 29.23% and from 33.04% to 56.36%, respectively.

The percentage of Ca-P in TP in the G1 profile tended
to increase with depth, increasing from 18.21% to 70.03%, but in Q2 it showed a gradual downward trend with depth, decreasing from 57.00% to 21.99%.

3.4 Correlation between different forms of P and physicochemical properties of sediments

Analyzing the correlations between different forms of P and between these forms and physicochemical properties of sediments will contribute to better understanding of the distribution of P\(^{24}\) in Antarctic lake sediments. As shown in Table 1, the contents of TP, Fe/Al-P, Ca-P, IP, and OP in the G1 core were significantly correlated, indicating that TP is not only linked to Fe/Al-P, Ca-P, and IP, but also to OP. However, the Q2 core was quite different. There were strong significant positive correlations between the contents of TP and IP and OP, but no correlation between TP and Ca-P, indicating that the main source of TP was Fe/Al-P and OP, not Ca-P. In addition, IP and Fe/Al-P, IP and Ca-P, and OP and Fe/Al-P were positively correlated, Fe/Al-P and Ca-P, and IP and OP were not correlated, and Ca-P and OP were negatively correlated.

As shown in Table 2, the five P forms in the G1 sediment core, Ca-P, Fe/Al-P, IP, OP, and TP showed strong significant positive correlations with LOI\(_{550^\circ C}\), water content, TN, and TC. In the Q2 core, Fe/Al-P, OP, and TP also showed significant positive correlations with all four physicochemical properties (LOI\(_{550^\circ C}\), water content, TN and TC), but Ca-P was negatively correlated with LOI\(_{550^\circ C}\), water content, TN, and TC. Moreover, Fe/Al-P showed no correlation with water content, and IP showed no correlation with any of the four physicochemical properties.

4 Discussion

4.1 Organic matter sources in the sediment cores

The LOI\(_{550^\circ C}\) is widely used to determine the content of
organic matter in sediments\cite{17}. TN, TC, and water content showed a similar vertical trend as LOI \textsubscript{550°C} in both cores, suggesting that they are also related to the content of organic matter rather than lithogenic matter. Therefore, to some extent these four proxies, TN, TC, and LOI \textsubscript{550°C} and water content, reflect the status of organic matter in sediments. The sediments in the bottom of the G1 core consisted mainly of silty deposits with low and relatively constant organic matter content, indicating minimal external material input. The sediments in the middle of the core had increased grain size and were black, consistent with the increasing organic C and P contents in this layer. Therefore, it is likely that penguin guano contributed to the organic matter in this layer. The bottom 7-cm layer of the Q2 core had high organic matter content. There were abundant moss residues in this bottom layer, suggesting that the organic matter in this layer was most likely derived from mosses. During the time period reflected in that part of the core, the soil of adjacent areas was fertile because of the input of penguin guano and there was abundant vegetation. Above the bottom layer in the Q2 core, organic matter decreased sharply and then increased, indicating a changed sedimentary environment. The nearby vegetation probably died, and sandy deposits increased.

We concluded that these significant differences in TN, TC, LOI \textsubscript{550°C} and water content between the G1 and Q2 cores resulted from differences in the contribution of penguin guano to organic matter in the pond. The vertical trend of LOI \textsubscript{550°C} in the Q2 core suggests a small contribution of lithogenic sediments to organic matter in ancient times, but a relatively large contribution from terrestrial mosses.

4.2 Characteristic P forms in the sediment
Fe/Al-P: In general, with increasing depth in sediments, amorphous minerals become more ordered and the binding capacity of iron oxides and hydroxides decreases\cite{25}. Furthermore, the reduction potential increases with depth, enhancing the conversion of ferric to divalent iron\cite{26}. As divalent iron is dissolving, bound P is released into the interstitial water and then enters the overlying water as a result of a concentration gradient\cite{27,28}. This process would result in reduced Fe/Al-P content after a certain depth, as seen in the G1 core (Figure 4). However, in the Q2 core, Fe/Al-P content did not reflect this phenomenon but increased in the layer containing abundant moss residues. Plants use a number of mechanisms to increase P solubility and availability. For example, organic acids such as citrate can complex iron and aluminum and displace phosphate anions from adsorption sites\cite{29}. Therefore, the upward trend in Fe/Al-P content in Q2 could be explained by the fact that it contained abundant organic matter from mosses in the middle and bottom layers.

Ca-P: Previous studies have shown that the application of poultry manure may cause the formation of dibasic calcium phosphate\cite{30}. In the present study, the G1 core had a higher Ca-P content, and the main form of TP was the Fe/Al-P of IP, followed by OP and Ca-P. In contrast, there was no significant correlation between TP and Ca-P in the

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Correlation between different forms of phosphorus</th>
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<tbody>
<tr>
<td></td>
<td>G1 profile (45 samples)</td>
</tr>
<tr>
<td>Fe/Al-P</td>
<td>1</td>
</tr>
<tr>
<td>Ca-P</td>
<td>0.681*(^{**})</td>
</tr>
<tr>
<td>IP</td>
<td>0.989*(^{**})</td>
</tr>
<tr>
<td>OP</td>
<td>0.731*(^{**})</td>
</tr>
<tr>
<td>TP</td>
<td>0.988*(^{**})</td>
</tr>
</tbody>
</table>

Note: *. Correlation is significant at the 0.05 level; **. Correlation is significant at the 0.01 level.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Correlation between phosphorus forms and the physicochemical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>G1 profile (45 samples)</td>
</tr>
<tr>
<td>LOI\textsubscript{550°C}</td>
<td>Water content</td>
</tr>
<tr>
<td>Fe/Al-P</td>
<td>0.652*(^{**})</td>
</tr>
<tr>
<td>Ca-P</td>
<td>0.216</td>
</tr>
<tr>
<td>IP</td>
<td>0.601*(^{**})</td>
</tr>
<tr>
<td>OP</td>
<td>0.690*(^{**})</td>
</tr>
<tr>
<td>TP</td>
<td>0.636*(^{**})</td>
</tr>
</tbody>
</table>

Note: *. Correlation is significant at the 0.05 level; **. Correlation is significant at the 0.01 level.
Q2 core. This difference is because the formation of Ca-P requires very high concentrations of phosphate, and leads to the formation of a crystal nucleus and crystal precipitation\[31]. The sediments in the G1 core were mainly affected by the input of penguin guano, which has higher P content than mosses. The sediments in the Q2 core were mainly affected by the input of mosses and as a result the Ca-P content was lower.

OP: Microbial mineralization of OP is an important mechanism to release P into overlying water\[32], and anaerobic conditions will facilitate the mineralization of OP\[33]. In addition, OP content increases as organic matter content increases\[34-35\]. Previous studies have shown that there are large amounts of plant and animal residues and humus in macrophytic lakes, and organic matter will undoubtedly increase the OP content of macrophytic lakes relative to other lakes\[36\]. In the present study, LOI550°C showed a highly significant positive correlation with OP in both sediment profiles, indicating that organic matter is a very important factor in determining OP content. This is consistent with the findings of previous studies\[36\]. Moreover, OP content in the Q2 core showed an increasing trend with depth, reflecting the large amount of moss residues below 7 cm.

IP: IP is very sensitive to changes in pH and redox conditions\[37\]. In the present study, IP was the main form of P and showed a similar vertical trend as TP in both sediment cores. This is because OP would mineralize and convert to IP under the effect of microorganisms or in anaerobic conditions, as discussed above.

TP: The vertical variation in TP in sediment cores provides information about the material sources at sampling sites and indicates how P inputs change across historical periods. TP content in the two sediment cores was relatively consistent with TN, TC, and LOI550°C. The TP concentration in fresh penguin guano (60 821 mg·kg\(^{-1}\)) is much higher than that in mosses (1 492 mg·kg\(^{-1}\))\[39\]. The G1 core had an average TP of 3 514.04 mg·kg\(^{-1}\), higher than that of the Q2 core (1 661.86 mg·kg\(^{-1}\)), and the latter is close to the P concentration in mosses. Therefore, we infer that the sediment in the G1 core was mainly affected by penguin guano, and the TP content in the G1 core reflects the historical fluctuations in penguin populations. In contrast, the sediment in the Q2 core was mainly affected by mosses.

5 Conclusions

In this paper, the SMT protocol was applied to study P forms and their distribution patterns in two sediment cores from Ardley Island, West Antarctica. IP was the main form of P in both cores. However, there were significant differences in TN, TC, LOI550°C, and phosphorus content between the G1 and Q2 cores, reflecting different levels of input from penguin guano between the two cores. Each core showed a vertical variation in these proxies, accounting for the different input of guano from penguin populations during different time periods. The contribution of penguin guano to the organic matter in the sediments in the pond where the G1 core was collected has been increasing in recent times, while the sediments in the pond where the Q2 core was collected show a relatively large contribution from mosses in ancient times.

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