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Depositional history of sedimentary sterols around Penguin Island, Antarctica

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Abstract: Lipid biomarkers are potential tools for identifying the sources, diagenesis and reactivity of organic matter (OM) in marine systems, including in Antarctica where the particular environmental characteristics have motivated several studies of organic markers. Sedimentary sterol distributions were determined in two sediment cores (PGI-1 and PGI-2) collected from the marine environment around Penguin Island, Antarctica, during the 2007–08 summer. The cores were sectioned at 1 cm intervals and the sterols were analysed using gas chromatography with flame ionization detection. The results indicate that the sterols were subjected to decades of degradation and transformation with depth in both cores. However, an expected progressive conversion of stenols to stanols (evaluated by 5α-stanols/Δ^5-stenols ratio) within the deepest sediment layers was not clear, suggesting low degradation rates. In PGI-1, the deposition of large quantities of penguin guano affected the distribution of sterols and, consequently, primary production was favoured by the ornithogenic soil input. The results contribute to the understanding of the current processes associated with primary sources and transformation of OM in this important region of the Antarctic environment.

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Key words: chlorophyll *a*, core, lipids, biomarkers, ornithogenic soil, primary productivity

Introduction

Antarctica is usually classified as a remote region and a symbol of the last great wilderness relatively untouched by human disturbance. Due to high seasonal primary productivity, the distance from major sources of human pollution, and characteristics such as low average temperature, strong seasonality and the absence of higher plants there is increasing interest in the local carbon cycle. Antarctica's carbon cycle may be expected to be different from those of urban sites and probably different from those of temperate and tropical oceans (Venkatesan 1988, Wisnieski *et al*. 2014).

The role of lipids in polar environments is of primary importance for understanding the global carbon cycle. Knowledge of the nature and quality of organic matter (OM) and relative rates of primary production for organism assemblages in the ocean and its interaction is important for understanding the overall impact of human activity and global changes in this area (Villinski *et al*. 2008, Wisnieski *et al*. 2014).

Penguin Island (62°06'S, 57°54'W; 1.7 km^2 in area) is on the south-eastern side of King George Island, South Shetland Islands, Antarctica (Fig. 1). It lies within a belt of inactive volcanoes in the Bransfield Strait. Geological studies (e.g. Birkenmajer 1979) suggest that the last volcanic activity may have occurred *c*. 100 years ago.

Almost the entire island is dominated by birds. In particular, *Pygoscelis antarctica* (Forster) (chinstrap penguin) and *P. adeliae* (Hombron & Jacquinot) (Adélie penguin); although the colonies decreased by 66% and 75%, respectively, between 1979–80 and 2003–04 (Sander *et al*. 2007). These birds contribute significantly to the island's large quantity of penguin guano, which influences the physical and chemical properties of ornithogenic soils. Ornithogenic soils present an acidic pH and are composed of clays containing secondary aluminous and ferriferous phosphates, thus constituting a rich source of N, P and Fe to the nearby environment (Nędzarek *et al*. 2015). Melt processes and freshwater inputs are responsible for transporting the soils and continental OM to the marine environment surrounding the island (Zhu *et al*. 2009).

Lipid biomarkers are important tools for identifying the sources, diagenesis and OM reactivity in aquatic systems. The environmental fate of lipids in sediments is well understood through studies of the degradation processes associated with herbivory, predation and diagenetic alteration (Villinski *et al*. 2008). These compounds

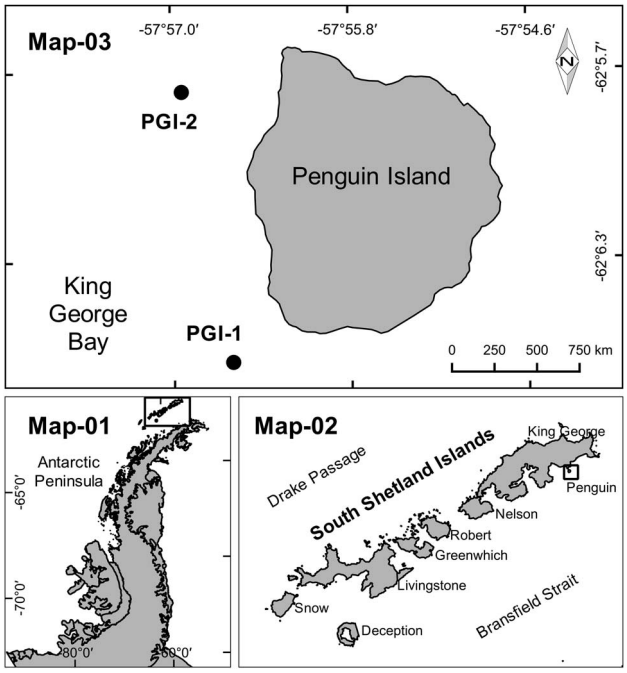

Fig. 1. Map 01: Antarctic Peninsula, Map 02: South Shetland Islands, and Map 03: location of sampling sites at Penguin Island (PGI-1 and PGI-2).

provide information about sources and OM quality that can be used to monitor habitat changes on a large scale (Matsumoto *et al.* 2006).

The aim of this study was to determine the sources, fates and transformations of OM in the marine environment around Penguin Island and the relative contribution of marine input through the analysis of lipid biogeochemical markers. Sedimentary sterols have been the basis for a variety of studies on biogeochemical reconstruction because they are relatively resistant to diagenetic change and retain the basic structure and details of the functional group (Eglinton & Eglinton 2008). By considering the signature of sedimentary sterols and the characteristics specific for the Penguin Island region, it is possible to obtain information on the potential sources and inputs of the sedimentary OM deposited on the sea floor.

Material and methods

Sampling and physical conditions of sample sites

Two sediment cores were taken with a mini-box corer (25 × 25 × 55 cm) during the 2007–08 summer at a water depth of 20–30 m. Core PGI-1 (62°06'S, 58°05'W) was collected 500 m offshore of the penguin colonies on southern Penguin Island, and core PGI-2 (62°02'S, 58° 02'W) was taken from King George Bay, 500 m offshore of the southern Giant Petrel colonies (Guerra *et al.* 2011).

The oceanographic conditions at the sites are quite different. Core PGI-1 was obtained from a relatively dynamic environment because it was collected from the side of the island that faces the Bransfield Strait. This region features complex interactions between circulation and topography, and is regulated by mechanisms of mesoscale jets and vortices intricately associated with wind forcing and baroclinic instability (Zhou *et al.* 2006). Core PGI-2 was collected close to King George Bay, a site protected from physical instability.

The cores were subsampled to a resolution of 1–2 cm and each sample was covered in pre-cleaned Al foil and stored at -20°C. The samples were freeze dried, carefully homogenized in a mortar, sieved through a stainless steel mesh (250 μm) and stored at room temperature in glass bottles until biomarker analysis.

Extraction and fractionation of sterols

More than 20 g of dry weight sediment from each subsample was extracted using a Soxhlet system for 8 h with 70 ml of ethanol. A surrogate standard (5α-cholestane) was added before each extraction. The extract was reduced to *c.* 2 ml using rotoevaporation and submitted to a clean-up procedure involving a column of 5% deactivated alumina and elution with 15 ml of ethanol. The extract was evaporated to dryness and derivatized using BSTFA (bis(trimethylsilyl)trifluoroacetamide) with 1% TMCS (trimethylchlorosilane; Supelco) for 90 min at 65°C.

Instrumental analysis and quality assurance

The instrumental analysis was performed with an HP 6890 gas chromatography (GC) instrument equipped with flame ionization detection and an Ultra-2 fused silica column coated with 5% diphenyl/dimethylsiloxane (30 m, 0.32 mm i.d. and 250 μm film thickness). The oven temperature was programmed to increase from 40–240°C at 10°C per min, then to 245°C (held for 5 min) at 0.25°C per min, and then to 300°C (held for 5 min) at 10°C per min. Samples were analysed for the following 15 sterols: i) faecal C_{27} sterols: 5β-cholestan-3β-ol (coprostanol), 5β-cholestan-3α-ol (epicoprostanol), ii) C_{27} sterols: $27\Delta^{5,22E}$ (cholesta-5,22E-dien-3β-ol), $27\Delta^{22E}$ (5α-cholest-22E-en-3β-ol), $27\Delta^{5}$ (cholest-5en-3β-ol, cholesterol), $27\Delta^{0}$ (5α-cholestan-3β-ol, cholestanol), iii) C_{28} sterols: $28\Delta^{5,22E}$ (24-methylcholesta-5,22E-dien-3β-ol), $28\Delta^{22E}$ (24-methylcholest-22E-en-3β-ol), $28\Delta^{5}$ (24-methylcholest-5-en-3β-ol), $28\Delta^{0}$ (24-methylcholestan-3β-ol), iv) C_{29} sterols: $29\Delta^{5,22E}$ (24-ethylcholesta-5,22E-dien-3β-ol), $29\Delta^{22E}$ (24-methylcholest-22E-en-3β-ol), $29\Delta^{5}$ (24-ethylcholest-5-en-3β-ol), $29\Delta^{0}$ (24-ethylcholestan-3β-ol), and v) C_{30} sterol: $30\Delta^{22E}$ (4α,22,23-trimethylcholest-22E-en-3β-ol).

The compounds were assigned by matching the retention times with results from standard mixtures of sterols within a range of 0.25–20.0 ng μl^{-1}. For the compounds without available commercial standards

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($27\Delta^{5,22E}$, $27\Delta^{22E}$, $28\Delta^{22E}$, 28Δ0, $29\Delta^{22E}$ and $30\Delta^{22E}$) assignment was carried out using GC-mass spectrometry (GC-MS).

Procedural blanks were performed and minor amounts of cholesta-5,22E-dien-3β-ol ($0.06 \pm 0.03\ \mu g\ g^{-1}$) and cholesterol ($0.05 \pm 0.02\ \mu g\ g^{-1}$) were found, which were subtracted from the results. Surrogate recovery ranged from 66–136% (average 107 ± 16). The sediment and blank samples were spiked with a mixture of sterols and the standard recovery ranged from 51–134% (average 100 ± 22). Detection limits (DL) were $< 0.01\ \mu g\ g^{-1}$ for all analysed compounds, and the precision ranged from 7.3–24.8% based on the analysis of five replicate samples from PGI-1. The measured concentrations of selected sterols in the IAEA-408 reference material were within 90–110% of the certified values provided by the International Atomic Energy Agency (IAEA).

Grain size analysis

Particle size distribution analysis was performed on raw subsamples by sieving for the coarse fraction and pipetting and screening the fine fraction. The Folk & Ward (1957) method was used to estimate the sediment parameters using SysGran software (version 3.0). The results consist of the sum of silt (62–4 μm) and clay (< 4 μm).

Magnetic susceptibility

Magnetic susceptibility measurements were performed on the entire unopened PVC cores using a Bartington MS-2C magnetic susceptibility meter equipped with a 90 mm diameter sensor. The measurements were made using a 0.1 detection range and readings were taken at 1 cm intervals with a resolution of 10^{-5} SI units. The measurements obtained from the top and the bottom core sections were discarded.

Dating of cores

The radionuclides in all samples (20 g dry weight) were counted for 90 000 and 120 000 s using a hyper-pure Ge detector (model GEM60190; EGG&ORTEC) with 1.9 keV resolution for the 1332.40 keV ^{60}Co peak.

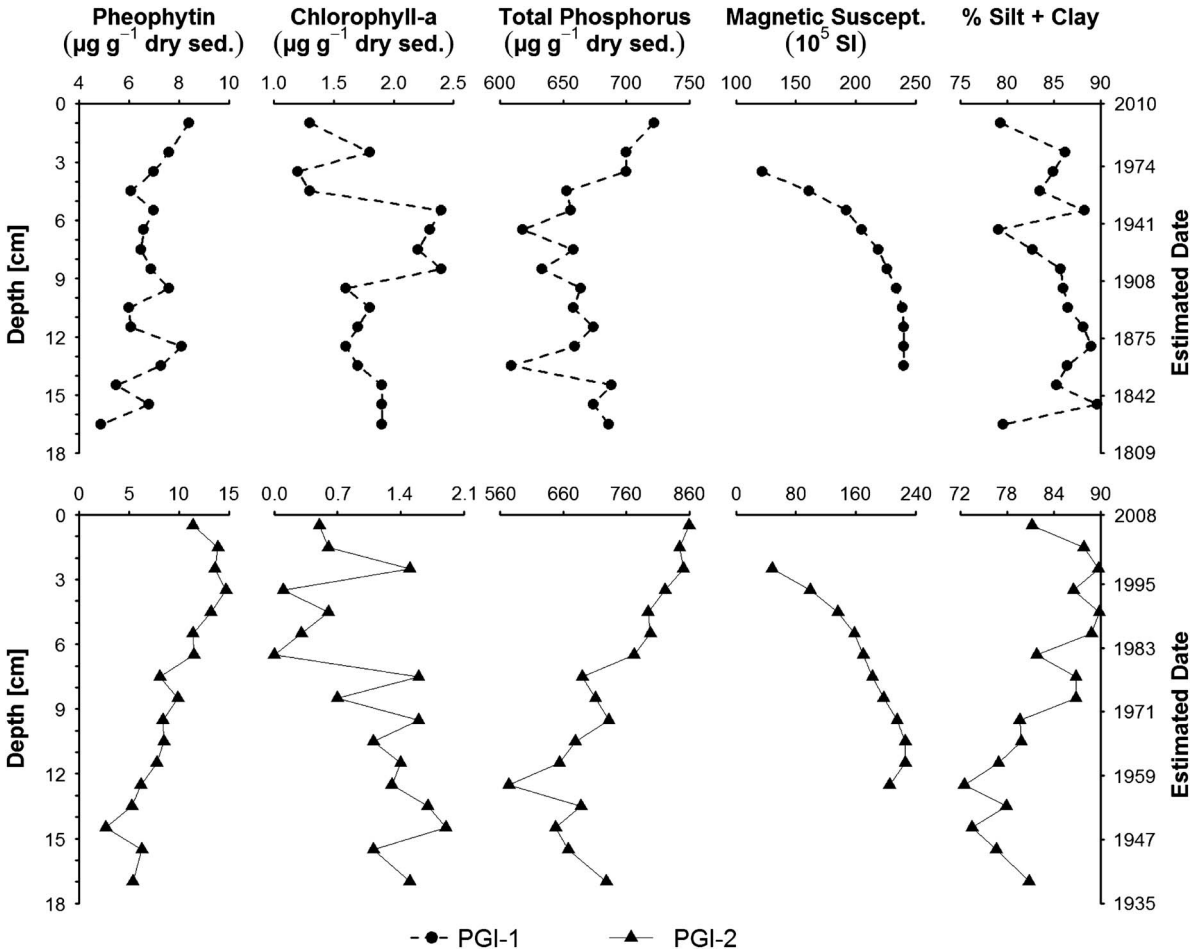

Fig. 2. Vertical profiles of the distribution of pheophytin and chlorophyll *a*, total P, magnetic susceptibility and proportion of silt and clay in the PGI-1 and PGI-2 cores.

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The ^{210}Pb activity was assayed by means of the photopeaks at 47 keV, 609 keV (^{214}Bi) and 661 keV, and the detailed method (calibration, detector counting efficiency and errors) has been fully described by Combi *et al.* (2013). To determine the detector counting efficiency in the radionuclide photopeak region, IAEA reference materials were employed.

Sedimentation rate estimates were based on the unsupported ^{210}Pb measurements and were made using the concentration initial constant model described by Appleby & Oldfield (1978). Based on the ^{210}Pb activity, the average sedimentation rate obtained was 0.091 ± 0.004 cm yr^{-1} (PGI-1) and 0.251 ± 0.010 cm yr^{-1} (PGI-2).

Total phosphorus, chlorophyll a *and pheophytin*

Approximately 0.2 g wet sediment was used for the total P analysis. The sample was first baked in a furnace for 2 h at 450°C. It was then shaken with 10 ml of 1.0 mol l^{-1} HCl for 16 h. After centrifugation (2500 rpm, 15 min), the liquid phase was subjected to colorimetric analysis following the method described by Grasshoff *et al.* (1983). Sedimentary P was quantified via a calibration curve from a stock solution of KH_2PO_4 (10 mmol l^{-1}), diluted to a range of 1.0–25.0 µmol l^{-1}. The procedural blanks did not reveal any contamination. Reproducibility was evaluated via extraction of five replicates of the same sample with a precision of 5.1%.

Chlorophyll *a* and pheophytin, a product of chl degradation, were analysed using *c.* 1.0 g wet sediment, acetone extraction and refrigeration for 24 h. After centrifugation (2500 rpm, 20 min), samples were measured using a SHIMADZU UV/V-1601 spectrophotometry via absorbance at 750 and 655 nm. To estimate the pheophytin, HCl (1 mol l^{-1}) was added to the extract and the absorbance at 750 and 655 nm measured. The difference in absorbance between the non-acidified and acidified samples corresponded to the absorbance of chl *a*.

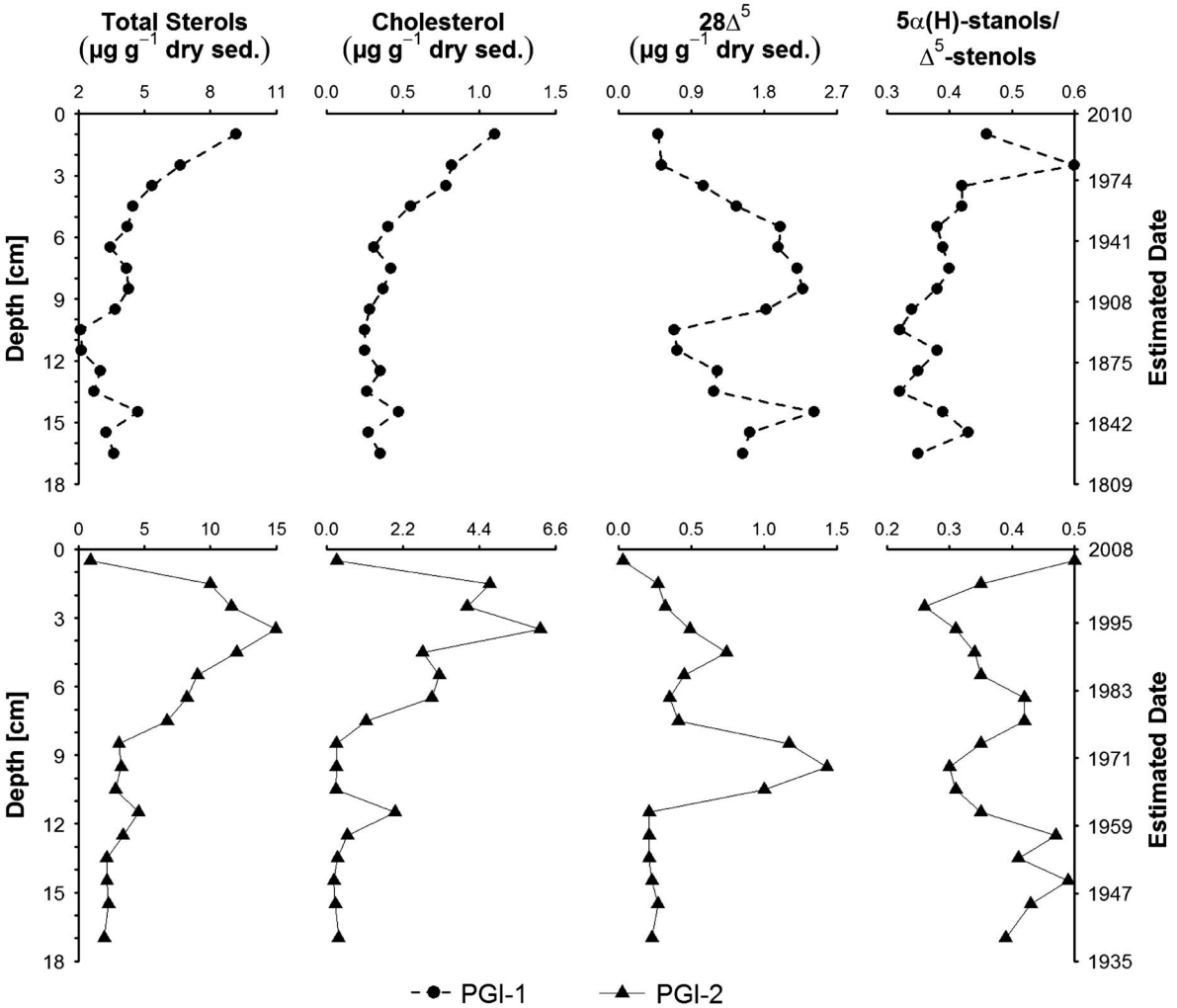

Fig. 3. Vertical profiles of the concentrations of total sterols, cholesterol and 28Δ^5 (µg g^{-1}) and the ratio of 5α-stanols/Δ^5-stenols in the PGI-1 and PGI-2 cores.

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Statistical analysis

Principal component analysis (PCA) was performed using the R package (version 3.0.3) to identify similarities and differences between the biomarkers in the sediments. A single matrix with the relative abundance of the variables studied was normalized prior to the PCA (value subtracted from the mean and divided by the standard deviation). Through linear combination, PCA assigns a loading value to each variable on each factor (principal component, PC), and the same assignment is given to the scores (in this case, subsample core section).

A multiple regression analysis with selection of the best statistical model through statistical Akaike Information Criterion (AIC) between biomarkers and selected parameters, including total P, chl *a*, pheophytin, fine sediments (% silt and clay), 5α-stanols/Δ^5-stenols and magnetic susceptibility, was performed using the R package (version 3.0.3) to verify any correlations among these parameters.

Results

Sedimentary parameters

The concentration of chl *a* (PGI-1 1.2–2.4 μg g^{-1}, relative standard deviation (RSD) 19.9%; PGI-2 < DL–1.9 μg g^{-1}, RSD 56.2%) was relatively low in the two cores compared with pheophytin (Fig. 2, Tables S1 & S2 found at http://dx.doi.org/10.1017/S0954102016000274). The concentration of pheophytin ranged from 5.0–8.4 μg g^{-1} (dry wt.) (RSD 13.5%) and 2.7–14.8 μg g^{-1} (RSD 36.4%) in PGI-1 and PGI-2, respectively (Fig. 2, Tables S1 & S2).

The cores featured a total P concentration (Fig. 2) of 609–722 μg g^{-1} (RSD 4.4%) in PGI-1 and 574–859 μg g^{-1} (RSD 11.2%) in PGI-2. The highest concentration was at the top of both cores. Magnetic susceptibility ranged

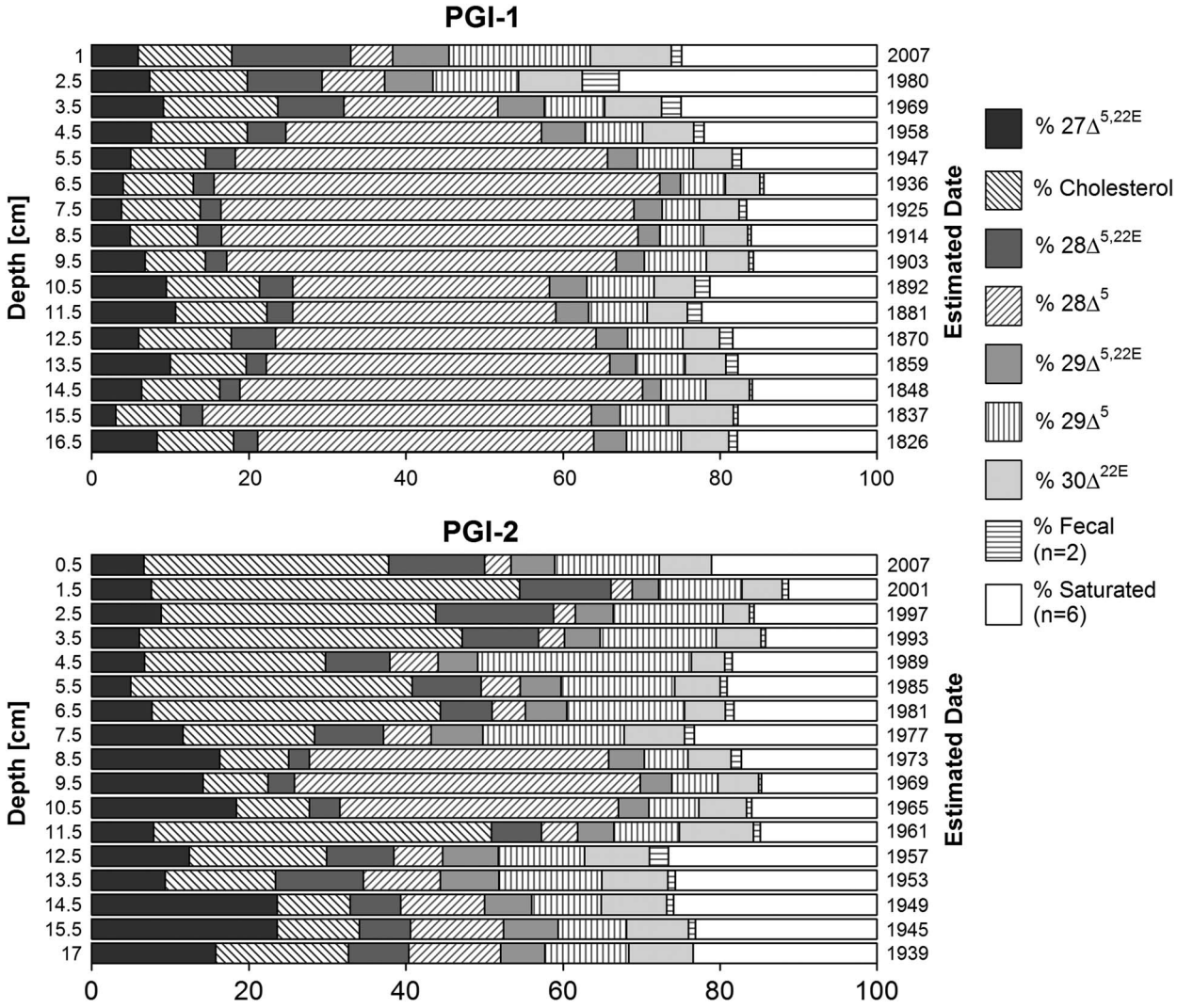

Fig. 4. Proportion of individual compounds in the PGI-1 and PGI-2 cores.

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from 122–240 × 10^{-5} SI (RSD 17.5%) in PGI-1 and 48–226.1 × 10^{-5} SI (RSD 31.6%) in PGI-2 (Fig. 2, Tables S1 & S2). The silt and clay content was 79.1–89.6% (RSD 3.8%) in PGI-1 and 72.5–89.8% (RSD 6.5%) in PGI-2 (Fig. 2, Tables S1 & S2).

Sterols

The total sterol concentrations in PGI-1 ranged from 2.11 (10–11 cm) to 9.19 μg g^{-1} (0–2 cm), with large contributions from 28Δ^5 (Fig. 3, Table S3). In PGI-2, the total sterol concentration ranged from 0.90 (0–1 cm) to 14.96 μg g^{-1} (3–4 cm), with a predominance of cholesterol (Fig. 3, Table S4).

PGI-1 had a lower concentration of cholesterol (0.25–1.10 μg g^{-1}, representing 8.2–15.0% of total sterols) than PGI-2, in which cholesterol was the most abundant sterol (0.20–6.15 μg g^{-1}, 8.2–47.3% of total sterols; Figs 3 & 4, Tables S3 & S4). The 27$\Delta^{5,22E}$ sterol exhibited a range of 0.10–0.54 μg g^{-1} in PGI-1 and 0.06–1.02 μg g^{-1} in PGI-2 (Tables S3 & S4), representing 3.1–10.8% and 5.1–24.2% of all sterols, respectively (Fig. 4).

The 28Δ^5 sterol ranged from 0.49–2.42 μg g^{-1} and 0.03–1.43 μg g^{-1} in PGI-1 and PGI-2, respectively (Fig. 3, Tables S3 & S4). The 28Δ^5 was the main individual sterol in the PGI-1 core, representing 5.4–57.1% of all sterols (Fig. 4). The other algal derived sterol was 28$\Delta^{5,22E}$, with a concentration of 0.07–1.39 μg g^{-1} in PGI-1 and 0.08–1.73 μg g^{-1} in PGI-2 (Tables S3 & S4), representing 2.5–15.3% of the total sterols in both cores (Fig. 4).

Furthermore, 29Δ^5 (0.16–1.65 μg g^{-1} in PGI-1 and 0.12–3.26 μg g^{-1} in PGI-2) and 29$\Delta^{5,22E}$ (0.09–0.66 μg g^{-1} in PGI-1 and 0.05–0.68 μg g^{-1} in PGI-2) (Tables S3 & S4) were also detected. The 30Δ^{22E} sterol was detected in lower concentrations than other sterols (0.11–0.95 μg g^{-1} in PGI-1 and 0.06–0.85 μg g^{-1} in PGI-2; Tables S3 & S4). Saturated sterols, such as cholestanol, 28Δ^0, 28Δ^{22E}, 29Δ^{22E} and 29Δ^0, were found in low concentrations compared to unsaturated sterols in both cores (Tables S3 & S4).

The values for the faecal sterol coprostanol ranged from < DL (< 0.01 μg g^{-1}) to 0.13 μg g^{-1} in PGI-1 and < DL–0.05 μg g^{-1} in PGI-2, and epicoprostanol ranged from 0.01–0.18 μg g^{-1} in PGI-1 and < DL - 0.06 μg g^{-1} in PGI-2.

5α-stanols/Δ^5-stenols ratio

The ratio values for all pairs of 5α-stanols/Δ^5-stenols (27Δ^{22E}/27$\Delta^{5,22E}$, 27Δ^0/27Δ^5, 28Δ^{22E}/28$\Delta^{5,22E}$, 28Δ^0/28Δ^5, 29Δ^{22E}/29$\Delta^{5,22E}$ and 29Δ^0/29Δ^5) were calculated and the mean values per section in the two cores varied from 0.32–0.62 (0.40 ± 0.07) in PGI-1 and 0.26–0.50 (0.38 ± 0.07) in PGI-2 (Tables S5 & S6).

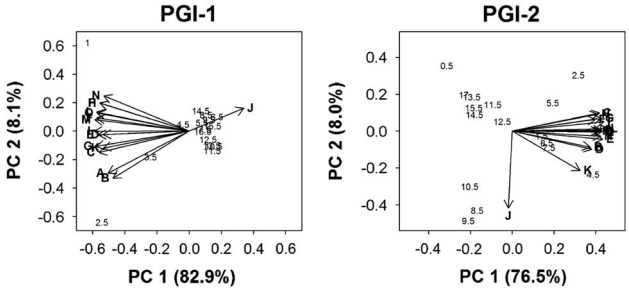

Fig. 5. Principal component analysis of the PGI-1 and PGI-2 cores based on sterols and core sections. A = coprostanol, B = epicoprostanol, C = 5β-cholestan-3-one, D = 27$\Delta^{5,22E}$, E = 27Δ^{22E}, F = cholesterol, G = 27Δ^0, H = 28$\Delta^{5,22E}$, I = 28Δ^{22E}, J = 28Δ^5, K = 28Δ^0, L = 29$\Delta^{5,22E}$, M = 29Δ^{22E}, N = 29Δ^5, O = 29Δ^0, P = 30Δ^{22E}.

Principal component analysis

As shown in Fig. 5, PC 1 from PGI-1 represented the variation in almost all the data (i.e. 83%), whereas PC 2 explained only 8% of the total variance. The PCA of PGI-2 produced a PC 1 that explained 76% of the raw data, whereas PC 2 explained only 8% of the total variance (Fig. 5). In general, PC 1 appropriately describes the variability of most biomarkers with depth in both cores.

Integrating sterols and sedimentary parameters

A multiple regression analysis with selection of the best statistical model was performed through the statistical AIC and a new measure of the badness of a statistical model with parameters determined with the method of maximum likelihood was then defined by the formula AIC = (-2) ln (maximum likelihood) + 2 (number of parameters), which is considered the best model with the lowest value of AIC.

The pheophytin, total P and magnetic susceptibility parameters explained the distribution of sterols in core PGI-1 (P = 0.004, R^2 = 0.61). In core PGI-2, the independent variables pheophytin and total P explained the distribution of sterols. The model was confirmed to be statistically significant (P = 0.002, R^2 = 0.67).

Discussion

Sedimentary parameters and sources of sterols

Chlorophyll *a* is the main pigment in photosynthetic organisms, while pheophytins are formed during the chl degradation and are usually found in zooplankton and protozoan faecal pellets (Bianchi 2007). Biological productivity in the Antarctic region may be limited by generally low Fe availability in the euphotic zone. Thus,

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the contribution of continental material can supplement the Fe supply, resulting in increased primary production. Therefore, an increase in chl *a* concentration was expected, as was observed for the pheophytin concentrations in the top sections of the PGI-1 and PGI-2 cores (Fig. 2), but it did not occur. One possible explanation is grazing pressure on the phytoplankton. Murray *et al*. (1998) observed that chl *a* concentrations decreased rapidly after the initial bloom, and with depth in Antarctic environments. Thus, after the initial bloom, the zooplankton predates the autotroph organisms producing pheophytins, so that little chl is preserved in sediment and the pheophytin concentrations are comparatively high. Schloss *et al*. (1999) also observed that the ratio chl *a*:pheopigments was higher in the water column than in sediment traps. The sections related to the period between 1930 and 1970 in two cores, presented relatively high concentrations of chl and low values of pheophytins, suggesting a lower predation pressure on phytoplankton and a consequent preservation of chl in the sediment.

These higher values of total P may reflect local productivity associated with OM recently deposited by the vertical and lateral movement of nutrients and faeces produced by the marine mammals and birdlife that historically inhabited the area. They may also reflect the typical conditions of oxic sediment layers, which tend to retain P in the sediment due to adsorption (Cha *et al*. 2005).

Magnetic susceptibility values are higher than those found by Salvi *et al*. (2006) for sediment samples from the Ross Sea, Antarctica, where the level ranged between $20–40 \times 10^{-5}$ SI. These results suggest that the past volcanic events on this island provided a large quantity of vulcanoclastic particles (such as ash and dust) rich in magnetic minerals (Srivastava *et al*. 2012), which were transported to the marine sediments by meltwater and Aeolian processes during periods of volcanic quiescence (Gray *et al*. 2003).

The morphological characteristics indicated by the grain size results are related to the variation in relative sea level during the Quaternary, the hydrodynamic processes that occur in these sheltered areas and the sources of marine sediments (i.e. the flux of terrigenous material, biological contribution and authigenic minerals) (Shozugawa *et al*. 2008). In the specific case of glacial environments, such as the environment of Penguin Island, fine sediment deposition is related to wind and glaciomarine processes (Srivastava *et al*. 2012).

Total sterol concentrations are in the same range as observed in other sediment cores collected in coastal Antarctic environments, such as Admiralty Bay (0.9–13.99 $\mu g\, g^{-1}$; Wisnieski *et al*. 2014) and McMurdo Sound (0.3–7.4 $\mu g\, g^{-1}$; Venkatesan 1988), but are higher than those observed in a marine Antarctic sediment core (0.25–0.40 $\mu g\, g^{-1}$; Venkatesan & Kaplan 1987).

The relative contributions of distinct sterols indicate the existence of multiple sources of sedimentary OM (Fig. 4), and these contributions could be assessed by grouping specific sterols related to zooplankton (e.g. cholesterol) and macro- and microalgae, including diatoms (e.g. $27\Delta^{5,22E}$ and C_{28} sterols), prymnesiophytes (cholesterol and $28\Delta^{5,22E}$) and dinoflagellates (e.g. $30\Delta^{22E}$) (Volkman 1986).

Cholesterol is traditionally thought to originate from zooplankton (Volkman 1986), with some contribution from phytoplankton (Rampen *et al*. 2010). Zooplankton species can promote dealkylation of C_{28} and C_{29} phytosterols to form cholesterol (Fernandes *et al*. 1996). Cholesterol has also been reported to be the most abundant sterol in *Cnidaria* collected near Elephant Island (Antarctic Peninsula, Nelson *et al*. 2001), krill species (especially *Euphausia triacantha* Holt & Tattersall and *E. frigida* Hansen), certain Antarctic salps (specifically *Salpa thompsoni* (Foxton)) and amphipods (Phleger *et al*. 2000). Because faecal material from different species of penguin is known to contain a high concentration of cholesterol (> 90%; Venkatesan & Santiago 1989), the relatively high concentrations in both cores may also come from penguin colonies that historically inhabit the site (Sander *et al*. 2007).

The $27\Delta^{5,22E}$ sterol is an intermediate in cholesterol synthesis and has been reported in Antarctic cnidarians (*Calycopsis borchgrevinki* (Browne), *Beroe cucumis* Fabricius, *Arctapodema ampla* (Vanhöffen) and *Periphylla periphylla* (Péron & Lesueur); Nelson *et al*. 2000) and salps (primarily *S. thompsoni* and *Ihlea racovitzai* (Van Beneden & Selys Longchamp); Phleger *et al*. 2000), as well as in the hyperiid amphipod *Themisto gaudichaudii* Guérin and in the Antarctic ice diatom *Nitzschia cylindrus* (Grunow) Hasle (Nelson *et al*. 2000), which is abundant in the Bransfield Strait water. The $28\Delta^{5}$ sterol is known as a marker for chlorophytes, diatoms, dinoflagellates, rotifers and mosses (Volkman 1986). The most common green alga in King George Bay, where PGI-1 was collected, is *Monostroma hariotii* Gain and the main mosses *Schistidium antarctici* (Card.) L. Savic. & Smirn, *Andreaea gainii* Cardot and *Sanionia uncinata* Loeske (Victoria *et al*. 2013). The other algal derived sterol $28\Delta^{5,22E}$ has been related to diatoms of Bacillariophyceae class, and may also be associated with prymnesiophytes (Volkman 2003).

Furthermore, $29\Delta^{5}$ have been found in several species of phytoplankton, such as diatoms, prymnesiophytes, chlorophytes and cyanobacteria (Volkman 1986, Laureillard & Saliot 1993, Volkman *et al.* 1998). Sea ice diatoms and macroalgae appear to be more probable sources of C_{29} sterols in the Antarctic environment than cyanobacteria or other algal groups (Nichols *et al*. 1993). The $30\Delta^{22E}$ sterol has been used as an indicator of a dinoflagellate contribution to marine sediments (e.g. Volkman 2003).

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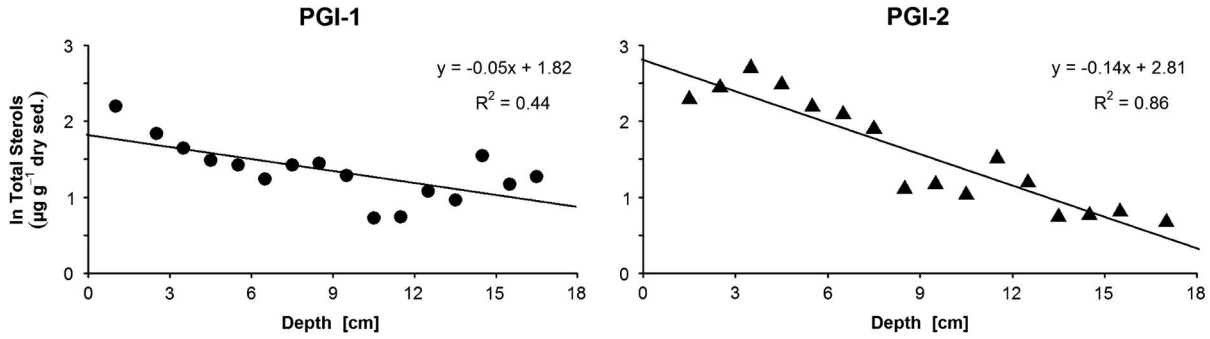

Fig. 6. Linear regression analysis based on the natural log (ln) of total sterols concentration versus depth to assess total sterol degradation in the PGI-1 and PGI-2 cores.

This sterol distribution was similar to the distributions found in other coastal Antarctic sediment cores. Venkatesan (1988) and Wisnieski *et al.* (2014) also found cholesterol as the main sterol, but followed by $29\Delta^{5}$, $30\Delta^{22E}$ and $28\Delta^{5,22E}$. This cholesterol predominance may indicate the importance of zooplankton and/or higher animals (such as penguins and seals) as OM sources in coastal environments. On the other hand, Venkatesan & Kaplan (1987) observed high levels of $30\Delta^{22E}$ and $27\Delta^{5,22E}$ in a sediment core from Maritime Antarctic, indicating the predominance of microalgae as an OM sources.

Saturated sterols come from the same sources as unsaturated sterols, and because they are formed via post-depositional processes they are indicative of the extent of geochemical transformation of OM (Wakeham & Canuel 2006).

The levels of faecal sterols were low and the mean concentrations of faecal sterols are similar to or less than values reported for other Antarctic regions near sewage inputs, e.g. McMurdo station, USA (0.01–0.05 µg g^{-1}, Venkatesan 1988), Rothera Station, UK (0.85 µg g^{-1}, Hughes & Thompson 2004), Carlini Station, Argentina (0.11 µg g^{-1}, Dauner *et al.* 2015) and of the same order of magnitude as the baseline limit calculated for Admiralty Bay (0.03–0.07 µg g^{-1}, Martins *et al.* 2014). Sewage input to the Penguin Island environment may be negligible because it is remote and located far from human activity. Therefore, these concentrations can be attributed to a natural environmental variability in marine mammal input (such as seals and whales; Venkatesan & Santiago 1989).

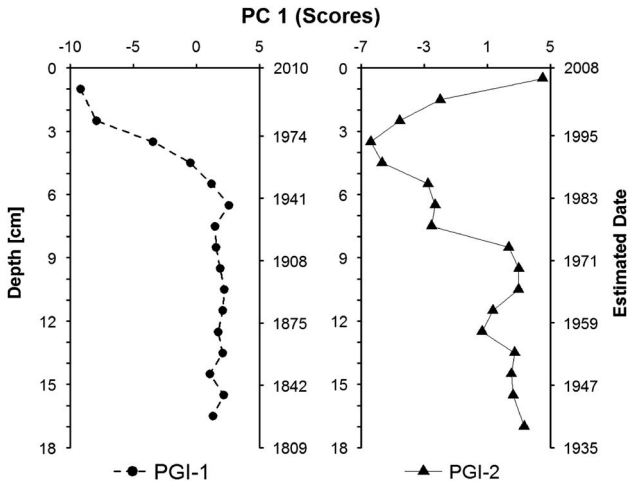

Fig. 7. Distribution of sterols versus depth based on PC1 scores obtained by principal component analysis of the PGI-1 and PGI-2 cores.

The 5α-stanols form within highly or permanently anoxic sediments via bacterial reduction of Δ^{5}-stenols (Nishimura & Koyama 1977). Consequently, the 5α-stanols/Δ^{5}-stenols ratio has been used to describe the redox conditions of the sediments to indicate microbial reduction in anaerobic environments and to identify OM degradation or preservation. The ratio values for all pairs of 5α-stanols/Δ^{5}-stenols between 0.1 and 0.5 indicate recently deposited OM with no significant diagenetic changes, whereas values >0.5 indicate an environment with conditions favourable for diagenetic processes, i.e. environments with a predominance of 5α-stanols (Wakeham & Canuel 2006). The results indicate well-oxygenated sediments and also show that the redox conditions of sediments appear to have been modified, as evidenced by the lower and higher values at several depths in both cores. This variation may reflect a change in water chemistry at the study sites at the time of deposition due to a general renewal of bottom water (Pinturier-Geiss *et al.* 2002).

Sterols are subject to a variety of chemical and microbial reactions in the surface layers of marine sediments. However, the slight increase in the 5α-stanols/Δ^{5}-stenols in PGI-2 and the absence of drastic variation in PGI-1 suggest relatively low rates of sterol degradation in sediments.

Because the most energetically favourable metabolic pathways for bacteria involve oxygen as an electron acceptor, OM degradation (and preservation) in sediments is strongly controlled by the average duration

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of OM exposure to oxygen (Wakeham & Canuel 2006). Therefore, it is possible that 5α-stanols are relatively less abundant at the surface than in the bottom core sections, mainly in PGI-2 core. This process of bacterial degradation occurs simultaneously with the progressive input of 5α-stanols from direct sources. For example, some dinoflagellates, diatoms and certain species of invertebrates can produce directly saturated compounds. This direct input of 5α-stanols helps to reduce the values of this ratio (Hudson *et al.* 2001).

The linear relationship between the natural log (ln) of the total sterol concentration and depth (R^2) was determined for both cores, assuming that the rate of degradation of sterols followed a typical kinetic mechanism of a first order reaction (Jeng *et al.* 1997). The relative decrease in the sterol concentrations toward the deeper layers (Fig. 6) showed the trend of degradation (rather than preservation) of organic compounds and, consequently, sedimentary OM in the deepest sections, what was not clearly based on 5α-stanols/Δ^5-stenols ratio.

Integrating sterols and sedimentary parameters with statistical approaches

The individual PCAs performed for PGI-1 and PGI-2 (Fig. 5) indicate that 28Δ^5 differed from the other sterols and was strongly associated with all core depths, suggesting a constant input over the years, with the exception of the surface layer (0–2 cm) of PGI-1 and the intermediate depths (2–8 cm) of PGI-2 where other biomarkers prevailed.

In PGI-1, the faeces-derived compounds were more abundant in the 2–3 cm and 3–4 cm sections. Higher concentrations of the remaining sterols were observed in the surficial layer. In PGI-2, the marine and faecal sterols were positively correlated with PC 1. The similarity in the distribution of all sterols throughout the core suggests the same environment factors control the input and deposition of sterols from distinct sources.

The majority of sterols (except 28Δ^5, which exhibited a unique distribution) exhibited a distribution similar to PC 1. Therefore, the PC 1 scores (sections) were used to show the general trends in biomarkers distribution versus depth (Fig. 7). The relatively low values in deep layers suggest OM degradation during the sediment deposition (positive scores), whereas OM preservation (negative scores) appeared to be limited to the recent sediment layers. However, relatively high values in certain sections were observed, primarily in PGI-2, and may represent immobilized OM, which may be related to increased OM input during periods with higher primary productivity.

Fluctuations in the natural supply of sterols over the years may affect the regular pattern of decreasing sterol concentration with depth, which explains the absence of a high R^2 value, especially for PGI-1 (Fig. 6). The degradation involves a decrease in compound concentration via the transformation of these compounds to other compounds (such as the conversion of Δ^5-stenols to 5α-stanols), decomposition to smaller compounds or incorporation into high molecular weight components. Because all of the processes decrease sterol concentration in the sediments (Jeng *et al.* 1997), the results suggest that OM diagenesis in the sediments around Penguin Island is an important environmental process for OM transformation, which is affected by the slow accumulation of sediments (i.e. relatively low sedimentation rate: 0.091 ± 0.004 cm yr^{-1} in PGI-1 and 0.251 ± 0.010 cm yr^{-1} in PGI-2), which may allow for a high rate of transformation of sterols.

A multiple regression analysis demonstrated that the distribution of sterols in PGI-1 was conditioned by

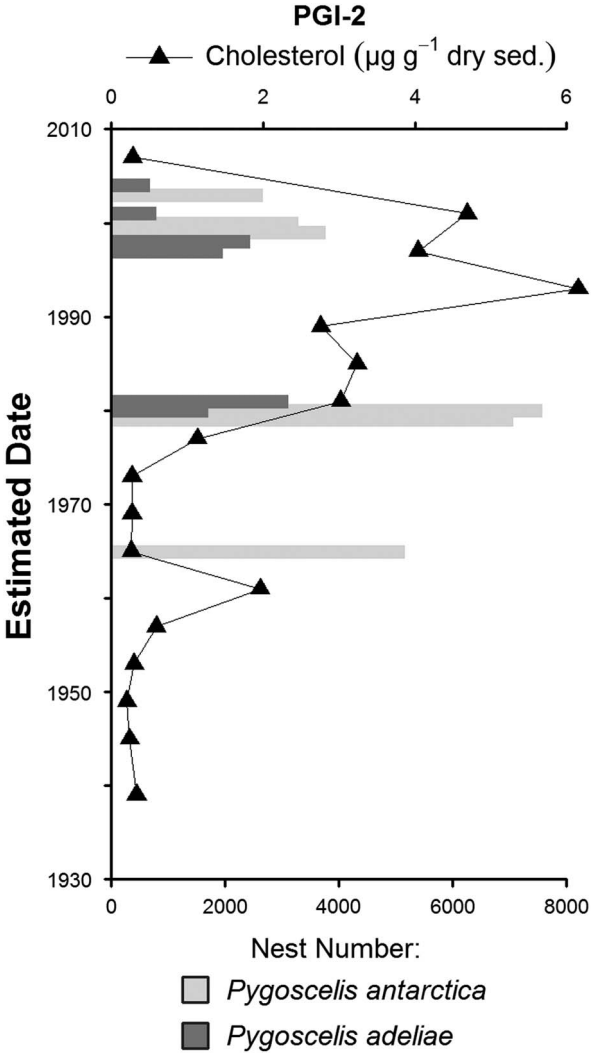

Fig. 8. Variation in the number of breeding pairs of *P. antarctica* and *P. adeliae* on Penguin Island (adapted from Sander *et al.* 2007) and cholesterol concentration versus estimated date for the PGI-2 core.

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primary production (represented by pheophytin), which is favoured by the runoff of nutrients (especially P) provided by penguin guano and magnetic minerals, which reflect the variation in sterol concentration. In PGI-2, magnetic susceptibility did not explain the sterol distribution, suggesting that the main source of P consumed by primary production was not only from bird colonies but also from the faeces of marine organisms, such as seals.

The highest concentration values of pheophytin and all sedimentary sterols in PGI-2 may represent high OM input and can be used as an indirect proxy of local marine primary productivity. The overall predominance of autochthonous OM in the sediments near Penguin Island was confirmed by the higher proportion of lipids derived from primary production and zooplankton throughout all the sections of the two cores.

Influence of ornithogenic material input on sterol distribution

The *Pygoscelis* spp. penguins are highly abundant, wide-ranging and central-place foragers, and have largely allopatric breeding ranges (e.g. Peña *et al.* 2014). Nine species of birds, including *P. adeliae* and *P. antarctica*, have historically occupied Penguin Island as a breeding area (Sander *et al.* 2007). A population increase in *P. antarctica* and *P. adeliae* was recorded in the 1960s and 1980s (Sander *et al.* 2007). The populations apparently stabilized before beginning to decrease in the 1990s (Fig. 8).

Cholesterol typically accounts for > 98% of the polar lipids in penguin droppings, and cholesterol level fluctuation may reflect variation in penguin numbers, thereby providing insight into the historic evolution of penguin population size. This approach has been used for the penguin colonies at Vestfold Hills, Antarctica, and was able to describe the fluctuation in penguin populations (Huang *et al.* 2010). By comparing the population variation and cholesterol profiles, we infer that the sharp decline seen in the surficial layer of PGI-2 coincided with the observed decline in the penguin population after 2000 (Sander *et al.* 2007), while other environmental factors may be important to explain the cholesterol trend in PGI-1. Considering the short distance between both sites, the effects of trophic and climatic factors on different short-term changes among penguin population changes may be negligible (Ciaputa & Sierakowski 1999). Therefore, the clear difference between cholesterol concentrations from PGI-1 and PGI-2 cores may be due to the distinct local hydrodynamic. While PGI-1 core was collected south-west of Penguin Island, near Bransfield Strait, PGI-2 was collected north-west of Penguin Island, in a protected region between the island and Turret Point (in King George Bay). This geographical configuration makes the PGI-2 area a depositional region for both organic and inorganic matter, which can be seen from the different sedimentation rates for the areas (PGI-1: 0.09 cm yr^{-1}, PGI-2: 0.25 cm yr^{-1}).

Conclusions

The sources and transformation of sterols in the marine environment and the relative contributions of marine inputs were assessed through analysis of sedimentary sterols, a specific group of lipid biogeochemical markers. The results showed that sterols were affected by degradation and transformation with depth and time (decades) in two cores collected from near Penguin Island. The linear regression relating total sterols and depth indicates that OM degradation was driven by low sedimentation rates, which resulted in the transformation of sterol compounds but not necessarily to 5α-stanols.

The C_{27} sterol cholesterol was the most abundant sterol in PGI-2 and was probably sourced from the faeces of marine mammals and penguins. The $28\Delta^5$ sterol was the main individual sterol in PGI-1 and was related to primary producers, such as chlorophytes, diatoms and mosses.

The statistical AIC applied to PGI-1 revealed that sedimentary parameters, such as pheophytin, total P and magnetic susceptibility, explained the distribution of sterols, suggesting that the distribution of biomarkers was conditioned by primary production. It is supported by the runoff of nutrients provided by the faeces of penguins that historically inhabit the region and even by the local marine fauna. However, PGI-2 showed a different pattern, suggesting that total P consumed by primary producers may be more associated with the faeces of marine organisms, such as seals.

Despite the geochemical complexity of the Penguin Island environment, the results of this work provide insight that aids understanding of the OM cycle in a particular region of the Antarctic Peninsula that is considered to be one of the most sensitive sites to global warming.

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Author contribution

Liziane M.M. Ceschim: laboratory analysis, manuscript writing, interpretation and conclusions. Ana L.L. Dauner: statistical analyses, elaboration of graphics and figures, discussion and manuscript editing. Rosalinda C. Montone: revision and discussion. Rubens C.L. Figueira: radionuclide analyses, dating of the cores and discussion. César C. Martins: project co-ordination, fieldwork, final revision and discussion.

Supplemental material

Supplemental tables will be found at http://dx.doi.org/10.1017/S0954102016000274.

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