2014-09

Characterization of sources and temporal variation in the organic matter input indicated by n-alkanols and sterols in sediment cores from Admiralty Bay, King George Island, Antarctica

Polar Biology, v. 37, p.483-486, 2014
http://www.producao.usp.br/handle/BDPI/46611

Polar Biol (2014) 37:483–496
DOI 10.1007/s00300-014-1445-6

ORIGINAL PAPER

Characterization of sources and temporal variation in the organic matter input indicated by *n*-alkanols and sterols in sediment cores from Admiralty Bay, King George Island, Antarctica

Edna Wisnieski · Márcia C. Bícego · Rosalinda C. Montone · Rubens C. L. Figueira · Liziane M. M. Ceschim · Michel M. Mahiques · César C. Martins

Received: 26 June 2013 / Revised: 27 December 2013 / Accepted: 31 December 2013 / Published online: 19 January 2014

Abstract The Antarctic continent is one of the most protected areas on the planet, but is dynamically responding to environmental change on a global scale. Change in the air temperature may affect the organic matter production in the area. Biomarkers such as sterols, *n*-alkanols and phytol in three sediment cores from Admiralty Bay, Antarctica, were determined to identify the type of organic matter, variation in input and possible relationship with general temperature changes over the past decades. The concentrations ranged from 0.91 to 13.99 μg g^{-1} (dry weight) of total sterols, 0.20–2.14 μg g^{-1} of total *n*-alkanols and 0.13–2.38 μg g^{-1} of phytol. Cholest-5-en-3β-ol was the most abundant sterol. The fecal sterols, 5β-cholestan-3β-ol and 5β-cholestan-3α-ol, occurred at low concentration (<0.01–0.15 μg g^{-1}), below the baseline values for this region. The lower carbon chain *n*-alkanols were more abundant, which suggested that algae, bacteria and zooplankton were the primary sources of the sedimentary organic matter. Phytol exhibited little variation across all of the cores, which appears to be the result of degradation. Variation in the concentration of compounds in one core was compared with the variation in mean air temperature (MAT) over time; this preliminary association showed a tendency toward increased concentration during the period in which the MAT was more elevated.

Keywords Sterols · Sediments · Antarctica · Organic matter · *n*-Alkanols

Introduction

The Antarctic continent is one of the most protected areas on the planet and is composed of ecological systems and a cryosphere that are capable of dynamically responding to environmental changes on a global scale (Monien et al. 2011). The Antarctic Peninsula is one of the sites that are warming faster than others on the planet, and the increase in temperature has been attributed to the decline in sea ice area (Turner et al. 2005). Therefore, it is important to establish the local environmental characteristics and to determine how these characteristics have been altered over time in order to understand how the environment may respond to future scenarios.

Geochemical markers have been extensively used to characterize the distribution of sources of sedimentary organic matter in different environments and timescales because they can be assigned to a specific source and are preserved after deposition (Birgel et al. 2004; Castaneda et al. 2011).

n-Alkanols and sterols are markers present in the polar fraction of lipid extracts of marine sediments, and they are directly related to primary production (Hudson et al. 2001). They are essential for marine organisms because they

Electronic supplementary material The online version of this article (doi:10.1007/s00300-014-1445-6) contains supplementary material, which is available to authorized users.

E. Wisnieski · C. C. Martins (✉)
Centro de Estudos do Mar, Universidade Federal do Paraná, Caixa Postal 61, Pontal do Paraná, PR 83255-976, Brazil
e-mail: ccmart@ufpr.br

E. Wisnieski · L. M. M. Ceschim
Programa de Pós-Graduação em Sistemas Costeiros e Oceânicos (PGSISCO), Universidade Federal do Paraná, Caixa Postal 61, Pontal do Paraná, PR 83255-976, Brazil

M. C. Bícego · R. C. Montone · R. C. L. Figueira · M. M. Mahiques
Instituto Oceanográfico, Universidade de São Paulo, Praça do Oceanográfico, 191, São Paulo, SP 05508-120, Brazil

function as key components in the composition of cell membranes and the specific regulation of metabolic processes (Laureillard et al. 1997). They are used to distinguish marine and terrestrial organic matter (OM) sources through sediment, generally by the number of carbon atoms in the aliphatic chain, according to the potential source organisms (Volkman 1986; Burns and Brinkman 2011; Faux et al. 2011; Oliveira et al. 2013).

Sterols can be used to characterize the input of fecal (excrement) material through the use of 5β-cholestan-3β-ol (coprostanol) and 5β-cholestan-3α-ol (epicoprostanol), which are produced in the intestines of mammals, including humans, and animals that comprise the Antarctic fauna, such as seals and whales (Venkatesan et al. 1986; Martins et al. 2002).

Because specific groups of organisms synthesize different *n*-alkanols and sterols, it is possible to identify the sources of OM in the region. The very cold average temperatures, a strong seasonality, lack of higher plants and occurrence of specific fauna relate to environmental conditions that ensure a high degree of specificity between the sources of organic compounds (Laureillard et al. 1997).

Changes in water temperature in the Antarctic Ocean have affected the structure of the ecosystems and OM production in the platform regions of the Antarctic Peninsula and have resulted in a decline in the species that are codependent on ice and an increase in tolerant species (Ducklow et al. 2007). Considering the high susceptibility of the Antarctic region to recent environmental changes, the aim of this study was to identify variation in the input and type of OM deposited in sediments from Admiralty Bay through the determination of sterols and *n*-alkanols as indicators of environmental change.

Materials and methods

Study area

Admiralty Bay is on King George Island (Fig. 1) and is the largest fjord in the South Shetland Islands, with a total area of 131 km^2. It is formed by a main channel >500 m in depth that divides it into three main inlets (Martel, Mackelar and Ezcurra); each inlet houses a research station (Majewski and Tatur 2009). The Martel and Mackelar inlets constitute the northern part of the bay, and the Ezcurra inlet is located on the western portion (Fig. 1).

The predominance of strong winds from the west–southwest and north–northwest, along with the tide, drives the water circulation inside the bay (Majewski and Tatur 2009); this plays an important role in the transport of OM, nutrients and trace metals (Ribeiro et al. 2011) that may influence primary production (Lange et al. 2007).

According to Rakusa-Suszczewski (1980), the flow of freshwater to Admiralty Bay originates in the glaciers. The Arctowski, Warzawa and Krakow ice fields are located around the bay, and many tidewater glaciers are distributed (Fig. 1) along the coastline (Braun and Gossmann 2002). The sedimentation is affected by melting and dispersed by the local circulation, carrying nutrients and decreasing the salinity of the water (Lange et al. 2007).

The presence of plants and animals, such as moss, algae, fungi, lichens, birds and aquatic mammals (Pinnipedia), represents a significant source of different classes of biomarkers. Specifically, marine mammals and birds contribute significantly to the baseline level of fecal sterols (5β-cholestan-3β-ol and 5β-cholestan-3α-ol) and cholest-5-en-3β-ol, respectively, and are the primary sources of these compounds in the Antarctic environment (Venkatesan and Santiago 1989).

Sampling

Three cores were collected between the austral summer of 2006–2007 and 2009–2010, one in each inlet of Admiralty Bay [Ferraz (FER), Barrel Point (BAR) and Refuge II (REF)] (Fig. 1). They were obtained using a box corer with a capacity to collect up to 50 cm of sediment. Aluminum tubes (25 mm diameter) were used to collect the samples, and the sediment columns were subsampled in 1-cm sections (except REF, for which the sections were 2 cm). The samples were placed in pre-cleaned aluminum foil at −20 °C. In the laboratory, the sediments were freeze-dried and were carefully homogenized in a mortar, sieved through a stainless steel mesh (250 μm) and stored in glass bottles until extraction.

Laboratory procedure

The analytical method was described by Readman et al. (1986) and Martins et al. (2011) with modifications for obtaining fraction three, which corresponds to *n*-alkanols and sterols. For analysis, 20 g of each sample was Soxhlet extracted (8 h) with 80 mL of 1:1 (v/v) *n*-hexane/dichloromethane (DCM) and 100 μL of a standard solution of 5α-androstanol (98 % purity, Sigma Aldrich) (20 ng μL^{-1}). Copper, previously treated with HCl 2 mol L^{-1}, was added to the extraction solvent.

After this step, the concentrated samples were collected and the lipids were purified and fractionated using 5 % deactivated silica (silica gel 60, 0.063–0.200 mm) and alumina (aluminum oxide 90 active, 0.063–0.200 mm) column chromatography. The samples were eluted with 10 mL of *n*-hexane for the first fraction (aliphatic hydrocarbons—not analyzed), 15 mL of 7:3 (v/v) *n*-hexane/DCM for the second fraction (aromatic hydrocarbons—not

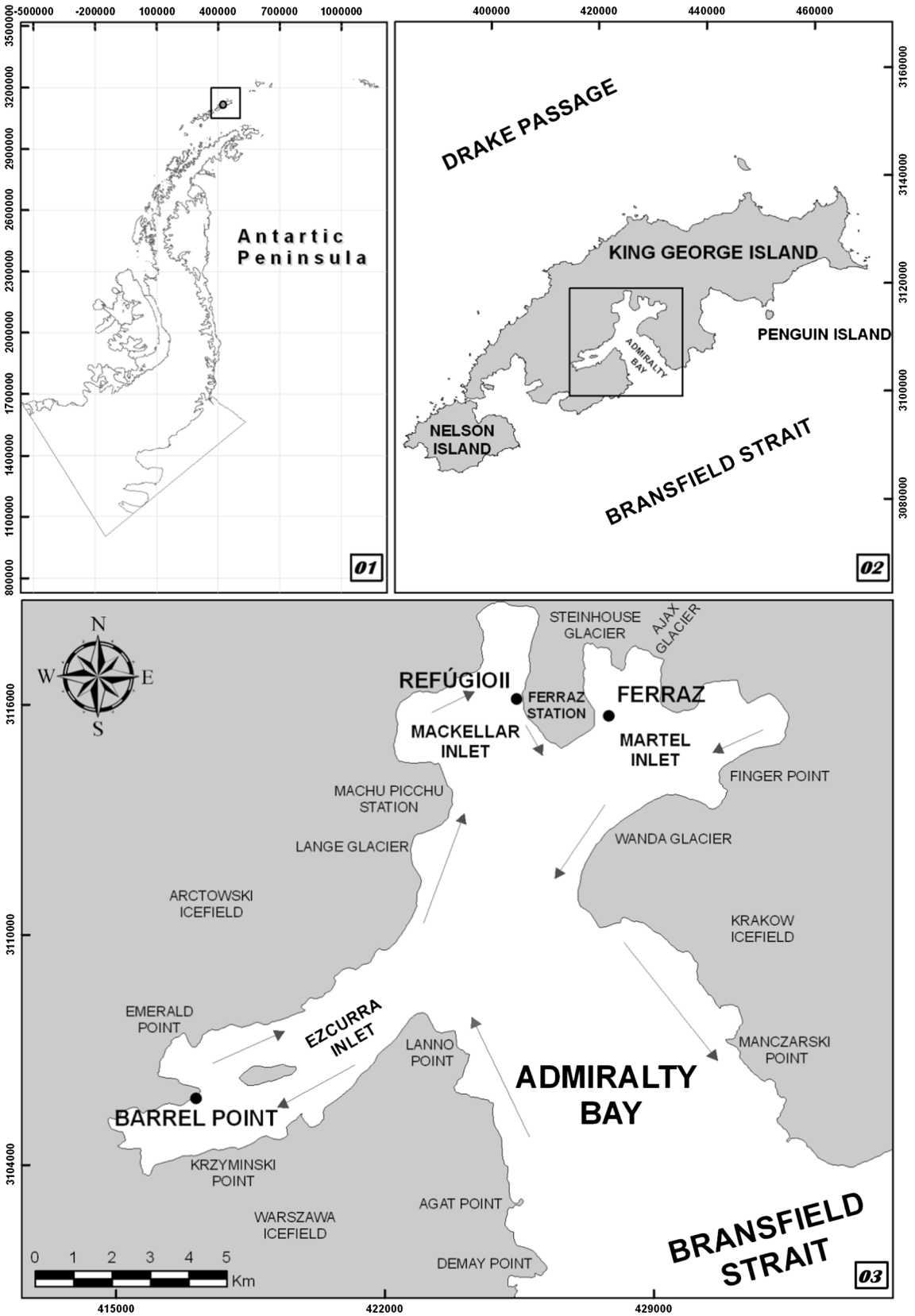

Fig. 1 Map of the studied region with three sampling points in Admiralty Bay. The *arrows* indicate the direction of circulation within the Bay (Rakusa-Suszczewski 1980). The UTM coordinates are related to zone 21

analyzed) and 5 mL of 1:9 (v/v) ethanol/DCM followed by 20 mL ethanol for the third fraction (*n*-alkanols and sterols). The third fraction was then derivatized (90 min in a water bath at ca. 70 °C) by adding 40μL of 99:1 (v/v) BSTFA/TMCS (*N*,*O*-bis(trimethylsilyltrifluoroacetamide)/trimethylchlorosilane).

Instrumental analysis

The instrumental analysis has been described by Montone et al. (2010) and was performed by Agilent 7890A (Agilent Technologies, Palo Alto, CA, USA) gas chromatography (GC) equipped with a flame ionization detector (FID) and a Agilent HP-5 column (50.0 m × 0.32 mm i.d. × 0.17 μm film thickness). The injector and detector temperatures were 300 and 325 °C, respectively. The GC oven heating program was 40–240 °C at 10 °C min^{-1}, then to 245 °C at 0.25 °C min^{-1}, and then to 300 °C at 10 °C min^{-1} (held 9.5 min). Samples (1 μL) were injected in the split mode using H_2 as carrier gas. The flow rates to the detector was 30 mL min^{-1} for H_2, 350 mL min^{-1} for synthetic air and 30 mL min^{-1} for N_2 (make up).

Calibration curves for the compounds were created using external standard solutions of *n*-alkanols [*n*-C_xOH (x = 13–30)] and sterols (5β-cholestan-3β-ol, 5β-cholestan-3α-ol, cholest-5-en-3β-ol, 5α-cholestan-3β-ol, 24-methylcholest-5-en-3β-ol, 24-ethylcholesta-5,22E-dien-3β-ol, 24-methylcholesta-5,22E-dien-3β-ol, 24-ethylcholest-5-en-3β-ol and 24-ethylcholestan-3β-ol) at a concentration ranging from 0.25 to 20.0 ng μL^{-1}. All components had a Pearson's linear correlation index that was equal to or greater than 99.5 % (r^2 0.995); this criterion was used for acceptability. All standards used were purchased at Sigma Aldrich, with purity between 94 and 98 %, except 24-methylcholest-5-en-3β-ol (~65 % purity).

HP Chemstation software (G2070BA) was used for quantification and for determining the response factor of each compound in the standard solutions. Component assignment was performed by comparing the retention times of the peaks with those of the external standards. For quantification, peak area was multiplied by the response factor for each compound present in the calibration curve, in relation to the ratio of the mass/area of the pattern of the standard added to each sample at the beginning of each extraction.

Quality control

After every 20 samples, a blank sample was extracted to assess the external contamination during analysis. The only peak observed in the blank samples corresponded to *n*-C_{20}OH retention time and was identified using gas chromatography–mass spectrometry (GC–MS) to be a phthalate, so *n*-C_{20}OH was excluded from further discussion.

The recovery of the surrogate standard ranged from 63.7 to 186.6 %, with a mean of 119.2 ± 4.8 % for the *n*-alkanols and sterols; only 14 % of the samples had a recovery outside the acceptable range (60–140 %). Sediment and blank samples were spiked with a mixture of *n*-alkanol and sterol standards, and the recovery was 52.3–66.7 % (mean 53.1 ± 5.2 %) and between 42.9 and 140.8 % (mean 95.2 ± 29.5 %), respectively.

The detection limit (DL) was defined as three times the standard deviation of five samples spiked with the external standards (Wade and Cantillo 1994) and ranged from 0.002 to 0.006 μg g^{-1}, with an average of 0.005 μg g^{-1} for the sterols; and it ranged between 0.011 and 0.020 μg g^{-1}, with an average of 0.017 μg g^{-1} for the *n*-alkanols. The concentration for the reference material IAEA-408 revealed that 80 % of the sterols were within the range of acceptable values (85–115 % of set value). A precision test was performed by analyzing five replicates of the same sample and exhibited less than 20 % of variability for the sterols and *n*-alkanols.

Estimated date of core sections

For estimating the sedimentation rate, what was determined in previous studies (Martins et al. 2010a, 2014; Ribeiro et al. 2011), sediment samples (20 g) were counted for 90,000–120,000 s using a hyper-pure Ge detector (model GEM60190 by EGG&ORTEC) with a 1.9 keV resolution for the 1,332.40 keV ^{60}Co peak. Cesium-137 activity was assayed by means of its peak at 661 keV. The detailed method (calibration, detector counting efficiency and errors) was fully described in Martins et al. (2010b). International Atomic Energy Agency (IAEA) reference materials were employed to determine the detector counting efficiency in the radionuclide photopeak region. The estimated age for each section of the cores was based on the maximum activity of ^{137}Cs, corresponding to 1963–1965, the period of maximum fallout in the southern Hemisphere due to atmospheric nuclear weapons testing (Abril 2003). The sediment thickness between the depth of maximum ^{137}Cs activity and the core top was used to estimate the mean sedimentation rate for this period.

The sedimentation rate was as follows: 0.35 ± 0.03 cm $year^{-1}$ for FER, 0.25 ± 0.01 cm $year^{-1}$ for REF (Crepin Point) and 0.33 ± 0.01 cm $year^{-1}$ for BAR, and consistent with mean sedimentation rate estimated by the diffusion–convection model presented by Ferreira et al. (2013). In addition, Yoon et al. (2000) found a mean sedimentation rate of 0.23 cm $year^{-1}$ (since 1200 cal. year BP)

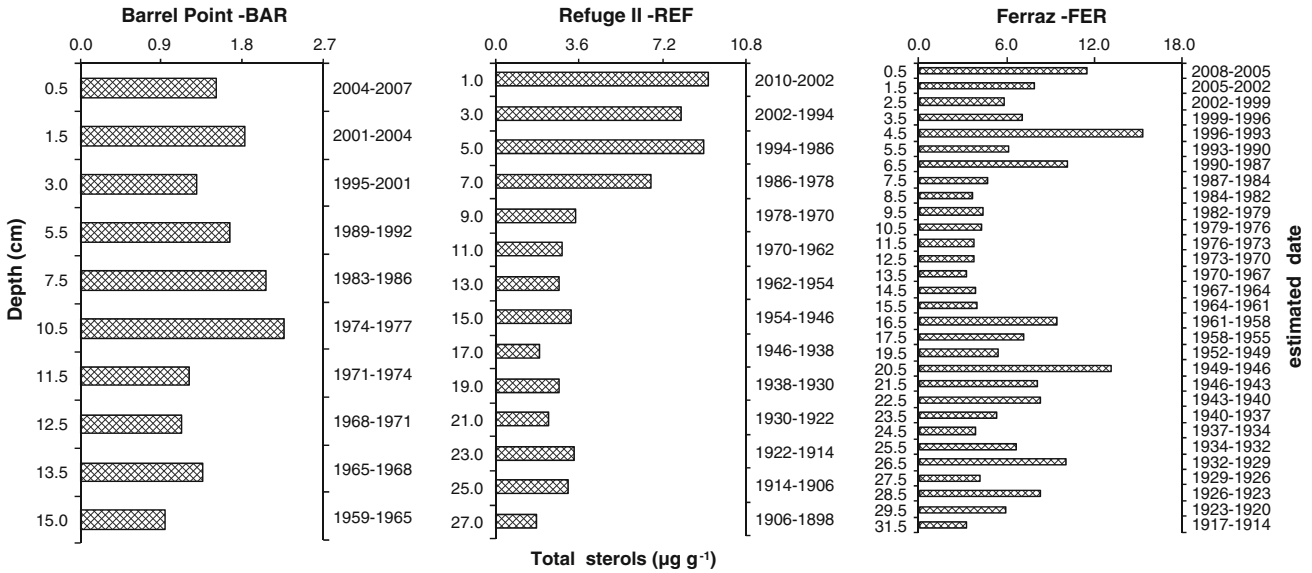

Fig. 2 Vertical profile of the concentration of total sterols (in µg g^{-1}) in the studied samples from Admiralty Bay, Antarctica

from ^{14}C-dating, relatively close to our data. Based on these values above sedimentation rates, the estimated date for each section of the three cores was calculated using the following equation:

$$\text{Estimated date} = a - (b/c)$$

where "estimated date" refers to the year of the section, "*a*" is the year in which the core was collected, "*b*" depth of the section in the core and "*c*" the sedimentation rate of each core.

Results and discussion

Concentration and source of sterols

In total, 15 sterols were identified including (1) C_{27}-sterols: cholest-5,22E-dien-3β-ol ($27\Delta^{5,22E}$), 5α-cholesta-22E-en-3β-ol ($27\Delta^{22E}$), cholest-5en-3β-ol ($27\Delta^{5}$), 5α-cholestan-3β-ol ($27\Delta^{0}$); (2) C_{28}-sterols: 24-methylcholest-5,22E-dien-3β-ol ($28\Delta^{5,22E}$), 24-methyl-5α-cholestan-22E-en-3β-ol ($28\Delta^{22E}$), 24-methylcholest-5-en-3β-ol ($28\Delta^{5}$), 24-methyl-5α-cholestan-3β-ol ($28\Delta^{0}$); (3) C_{29}-sterols: 24-ethylcholest-5,22E-dien-3β-ol ($29\Delta^{5,22E}$), 24-methyl-5α-cholestan-22E-en-3β-ol ($29\Delta^{22E}$), 24-ethylcholest-5-en-3β-ol ($29\Delta^{5}$), 24-ethyl-5α-cholestan-3β-ol ($29\Delta^{0}$); (4) C_{30}-sterol: 4α,22,23-trimethylcholest-22E-en-3β-ol ($30\Delta^{22}$) and (5) the fecal sterols 5β-cholestan-3β-ol and 5β-cholestan-3α-ol. Their distribution reflects the diversity of organisms living in a region with different environmental conditions, such as Admiralty Bay (Jaraula et al. 2010).

The total sterol concentration (total OLs) ranged from 0.91 to 2.17 µg g^{-1} (BAR), 1.63 to 8.59 µg g^{-1} (REF) and 2.64 to 13.99 µg g^{-1} (FER). The average concentration and standard deviation were 1.47 ± 0.40 µg g^{-1} (BAR), 4.03 ± 2.47 µg g^{-1} (REF) and 5.76 ± 2.83 µg g^{-1} (FER). The concentration versus the depth is presented in Fig. 2.

The vertical profile of total OLs in BAR shows a higher concentration between 7 and 11 cm depth, with lower concentration in the deeper sections. In REF, the highest concentration occurs at 7 cm. FER shows a varying profile, with a lower concentration in the interval corresponding to the period between 7 and 16 cm (Fig. 2).

These variations over the vertical profiles in the cores may reflect fluctuation in the supply of OM, where the sections with a higher concentration indicate a greater contribution of material and/or higher rate of preservation, whereas sections with lower values indicate a reduction in the amount of OM and/or higher rate of degradation (Meyers 1997). The variations may occur due to environmental changes, which affect the contribution, burial, preservation and/or degradation of the OM (Faux et al. 2011), or they may be the result of natural variability. The decrease in concentration with depth, although not constant, can also result from diagenesis (Burns and Brinkman 2011).

The highest concentration of sterols in specific sections, 4–5 and 20–21 cm in FER, 10–11 cm in BAR and 4–6 cm in REF (Fig. 2; Tables S1, S2 and S3—Tables are presented as Supplementary Material), may indicate a greater efficiency in accumulating OM, a higher level of primary production or low extent remineralization of the OM in the

water column and sediments (Meyers 1997). For example, the differences in particle size in the sample from REF, which has 90 % fine sediment (silt and clay) in the surface sections, and from BAR, which had the lowest concentration at 78 % may explain the spatial variability. This hypothesis is supported by Jeng and Chen (1995), who highlighted the effect of grain size and stated that an increase in concentration would occur in finer sediments.

Cholest-5-en-3β-ol (cholesterol; $27\Delta^{5}$) and cholesta-5,22E-dien-3β-ol ($27\Delta^{5,22E}$) represented 12–36 % (BAR), 10–33 % (REF) and 15–60 % (FER), and 4–6 % (BAR) 2–10 % (REF) and 1–3 % (FER) of the total OLs, respectively. These compounds are indicators of the contribution from the phytoplankton and zooplankton. The phytoplankton community is comprised of diatoms, dinoflagellates, prymnesiophytes, cyanobacteria and other photosynthetic organisms, while zooplankton comprises, among others, copepods (ca. 18 species identified, the most abundant being *Oithona similis*), krill (*Euphausia superba*, *Euphausia crystallorophias*) and salps (*Salpa thompsoni*), which mainly contribute to the cholest-5-en-3β-ol for this the environment (Phleger et al. 2000; Volkman 2005). In addition to the above sources, cholest-5-en-3β-ol may represent contributions from higher animals, such as the penguin species *Pygoscelis adeliae, Pygoscelis papua* and *Pygoscelis antarctica*, and from marine mammals, especially Pinnipedians such as elephant seals (*Mirounga leonina*) and seals (*Lobodon carcinophagus, Leptonychotes weddelli, Hydrurga leptonyx* and *Arctocephalus gazella*), which inhabit Admiralty Bay and have colonies mainly on Telefon Point, Thomas Point, Llano Point and Demay Point (Fig. 1) (Sierakowski 1991). All of these points are located near BAR and, depending on the movement within the bay, the material produced in these colonies may possibly be carried and deposited in BAR and reach REF (Rakusa-Suszczewski 1980).

The 24-methylcholesta-5,22E-dien-3β-ol ($28\Delta^{5,22E}$) and 4α,23,24-trimethylcholesta-22E-en-3β-ol (dinosterol; $30\Delta^{22}$) were also significant at 6–14 % and 7–12 % (BAR), from 2 to 10 % and 3 to 10 % (REF), from 1 to 4 % and 2 to 11 % (FER), respectively; the 24-methylcholesta-5,22E-dien-3β-ol is a marker for diatoms (representing 90 % of the total OLs from such organisms; Volkman 1986), with the most representative species in Admiralty Bay being *Thalassiosira, Fragilariopsis, Pseudo-nitzschia* and *Chaetoceros*. This compound is also very abundant in cyanobacteria (primarily present in the bay in *Nostocales* and *Oscillatoriales*) and cryptophyta algae, indicating that OM is contributed by these organisms (Volkman 2006). It has been reported that 4α,23,24-trimethylcholesta-22E-en-3β-ol is a specific indicator of dinoflagellates (Volkman 1986) and specimens of *Prorocentrum* spp., *Gymnodinium* spp, *Amphidinium* sp. and *Protoperidinium* spp. have been observed in the region (Kopczynska 2008) and are most likely its source here. It has also been identified, but only as a minor component, in some species of diatoms (Volkman 2006).

The FER sample exhibited some particularities, such as high concentrations of cholest-5-en-3β-ol and relatively lower concentration of 24-methylcholesta-5,22E-dien-3β-ol. The relatively high concentration of cholest-5-en-3β-ol (Tables S1) may be associated with increased local productivity due to a flow and concentration of nutrients (e.g., N and P) from the activity of the "Comandante Ferraz" Brazilian Station (Martins et al. 2012). The effluent represents an important, but punctuated, source of OM deposited in the sediments and contributing to an increase in local productivity and thereby an important OM input to sediments. The low proportion of 24-methylcholesta-5,22E-dien-3β-ol may be due to a lesser presence of organisms that biosynthesis at that location versus other areas of Admiralty Bay. The concentration differences between the study sites may also reflect the variation in abundance of the organisms in different places, indicating that their distribution in the environment is not always homogeneous (Skerratt et al. 1995).

The 24-ethylcholest-5-en-3β-ol (sitosterol; $29\Delta^{5}$) was the second most abundant sterol, representing from 13 to 19 % of the total OLs in BAR, 10–20 % in REF and 2–8 % in FER. Its origin in aquatic environments is not clear because GC-FID does not allow assignment of the 24-ethyl stereochemistry. The 24α-isomer (clionasterol) is derived from plankton, whereas the 24β-isomer is produced by higher plants (Volkman 2006).

In Admiralty Bay, terrestrial sources are limited to two specimens of vascular plants, *Deschampsia antarctica* and *Colobanthus quitensis*, found in the ice-free areas (Harris et al. 2011), moss (primarily S*anionia uncinata, Syntrichia princeps* and *Brachytecium* sp.) and also lichens (primarily the Usnea genus). Macroalgae of the Chlorophyta genus (seven specimens) identified in Admiralty Bay (Oliveira et al. 2009) are sources of the 24-ethylcholest-5-en-3β-ol (Volkman 1986), such as diatoms, cyanobacteria and prymnesiophyte algae.

The 24-ethylcholesta-5,22E-dien-3β-ol (stigmasterol; $29\Delta^{5,22E}$) was observed in a proportion ranging from 4 to 12 % of the total OLs in BAR, 4 to 16 % in REF and 2 to 6 % in FER, which reveals it is one of the least abundant in the sediments of the Martel Inlet. Possible sources of this sterol are the macroalgae of the Chlorophyta genus, prymnesiophytes and cryptophytes algae (Volkman 1986).

One of the sterols in lower concentration in the samples from the Ezcurra and Mackelar inlets was 24-methylcholest-5-en-3β-ol (campesterol; $28\Delta^{5}$), which comprised 1–6 % of the total OLs in BAR and 1–8 % in REF. In FER, it was the third most abundant, at 2–10 % of the total OLs.

It is associated with terrestrial plants or prymnesiophytes (Volkman 1986). However, the low relative concentration in some areas of Admiralty Bay may be related to the absence of organisms that biosynthesize.

One method to identify the predominance of terrestrial or marine sterols is through the ratio between 24-methylcholest-5-en-3β-ol, 24-ethylcholesta-5,22E-dien-3β-ol and 24-ethylcholest-5-en-3β-ol. Values between 1.0:1.4:4.0 and 1.0:1.6:6.0 are attributed to a terrestrial source, whereas values below these limits suggest marine-based source for these compounds (Laureillard and Saliot 1993; Carreira et al. 2009).

However, the concentration of 24-methylcholest-5-en-3β-ol was close to the DL, so calculation of the ratio in sections of the samples from BAR and REF (Tables S2 and S3) could result in misinterpretation. Therefore, the ratio of 24-ethylcholesta-5,22E-dien-3β-ol and 24-ethylcholest-5-en-3β-ol was calculated, where values between 1.0:2.9 and 1.0:3.9 indicate a terrestrial origin and values below these suggest a marine origin for these compounds. The results for the BAR samples ranged from 1.0:1.1 to 1.0:4.3 (mean 1.0:2.5 ± 1.2), and only in the sections near the top (0–1 and 2–4 cm) did the values indicate a contribution from land-based sources. In other sections, these compounds were primarily of marine origin. In the core from REF, the values ranged from 1.0:0.7 to 1.0:4.8 (mean 1.0:2.0 ± 0.1), and only in the 6–8 cm section did the values indicate some contribution from a terrestrial source.

The concentration of 24-methylcholest-5-en-3β-ol in the FER region was relatively higher (Table S1); the ratio indicated that the compounds were of marine origin because the values ranged between 1.0:0.2:0.4 and 1.0:2.7:4.1 (mean 1.0:0.8 ± 0.4:1.1 ± 0.7). The values suggest a higher contribution of OM from a terrestrial source only for the 5–6-cm section of the core from the FER region.

Fecal sterols (5β-cholestan-3β-ol and 5β-cholestan-3α-ol) had a concentration near or below the DL in different sections of the cores, representing <1–2 % in BAR and 1–3 % of total OLs in FER and REF.

According to Green and Nichols (1995), there are three primary sources for these sterols in the Antarctic marine environment: (1) human feces, generated by the sewage from the research stations, (2) marine mammal feces and (3) in situ formation in a reducing environment (cholest-5-en-3β-ol → 5β-cholestan-3β-ol), such as anoxic water from the bottom of fjords.

To differentiate between the contributions of human or natural fecal sterols, Venkatesan and Santiago (1989) proposed using specific values of 5β-cholestan-3β-ol/5β-cholestan-3α-ol (cop/e-cop). Values <2.5 suggest contributions from marine mammals, whereas values >2.5 are related to sewage input. The values varied here and were ca. 1.0 in BAR, between 0.3 and 2.0 (mean 0.8 ± 0.4) in REF and between 0.8 and 2.3 (mean 1.2 ± 0.3) in FER, which indicates that the fecal sterols are predominantly of natural origin or from mammalian origin, as mentioned above.

The absolute concentration values varied between less than <DL to 0.01 μg g^{-1} (mean 0.010 ± 0.004 μg g^{-1}) in BAR, from 0.01 to 0.06 μg g^{-1} (mean 0.03 ± 0.01 μg g^{-1}) in REF, and from 0.03 to 0.15 μg g^{-1} (mean 0.05 ± 0.03 μg g^{-1}) in FER (Tables S1, S2 and S3), similar than found by Martins et al. (2014). The values are lower than that established by Montone et al. (2010) at Martel inlet (0.19 μg g^{-1}) as indicative of a sewage contribution, which indicates an insignificant contribution of sterols from sewage and confirms the natural origin of the sterols.

5α(H)-stanols (cholesta-22E-en-3β-ol, 5α-cholestan-3β-ol, 24-methylcholesta-22E-en-3β-ol, 24-methylcholestan-3β-ol, 24-ethylcholesta-22E-en-3β-ol and 24-ethylcholestan-3β-ol) occur in smaller relative proportions than those of their unsaturated analogues. They are associated with the same sources as their respective parent sterols via diagenesis. They represented between 20 and 34 % of the total OLs in BAR, 20 and 45 % in REF, and 16 and 49 % in FER. Their presence, even at low concentration (Tables S1, S2 and S3), indicates that the reduction in double bond (Δ^5) in the parent sterols occurs in the sediments (Volkman et al. 2008).

Concentrations and sources of *n*-alkanols

In total, 14 *n*-alkanols, ranging from C_{12} to C_{30}, were found, including *n*-C_{12}OH to *n*-C_{20}OH, *n*-C_{24}OH, *n*-C_{26}OH to *n*-C_{28}OH and *n*-C_{30}OH.

In the BAR sample, the total concentrations varied from 0.20 to 0.58 μg g^{-1} (mean 0.35 ± 0.11 μg g^{-1}; Fig. 3). Short chain *n*-alkanols (C_{12}–C_{20}) varied between 0.18 and 0.56 μg g^{-1} (mean 0.32 ± 0.11 μg g^{-1}), whereas the concentration of long chain *n*-alkanols (C_{22}–C_{30}) varied between 0.01 and 0.06 μg g^{-1} (mean 0.03 ± 0.02 μg g^{-1}) (Table S4).

In REF, the mean concentration was 0.80 ± 0.47 μg g^{-1}, with values between 0.33 and 2.14 μg g^{-1} (Fig. 3). Similar to the sample from BAR, the short chain *n*-alkanols were more abundant, with a mean concentration of 0.70 ± 0.45 μg g^{-1} and a total concentrations ranging from 0.29 to 2.06 μg g^{-1} (Table S4). The concentration of the long chain *n*-alkanols varied between 0.04 and 0.29 μg g^{-1} (mean 0.10 ± 0.07 μg g^{-1}) (Table S5).

The concentration of total *n*-alkanols from FER ranged from 0.22 to 1.97 μg g^{-1}, with a mean concentration of 0.67 ± 0.39 μg g^{-1} (Fig. 3). The short chain *n*-alkanols dominated the long chain ones, with values between 0.11 and 1.26 μg g^{-1} (mean 0.48 ± 0.20 μg g^{-1}) for the short chain ones and 0.04 to 1.41 μg g^{-1} (mean 0.20 ± 0.32 μg g^{-1}) for the long chain ones (Table S6).

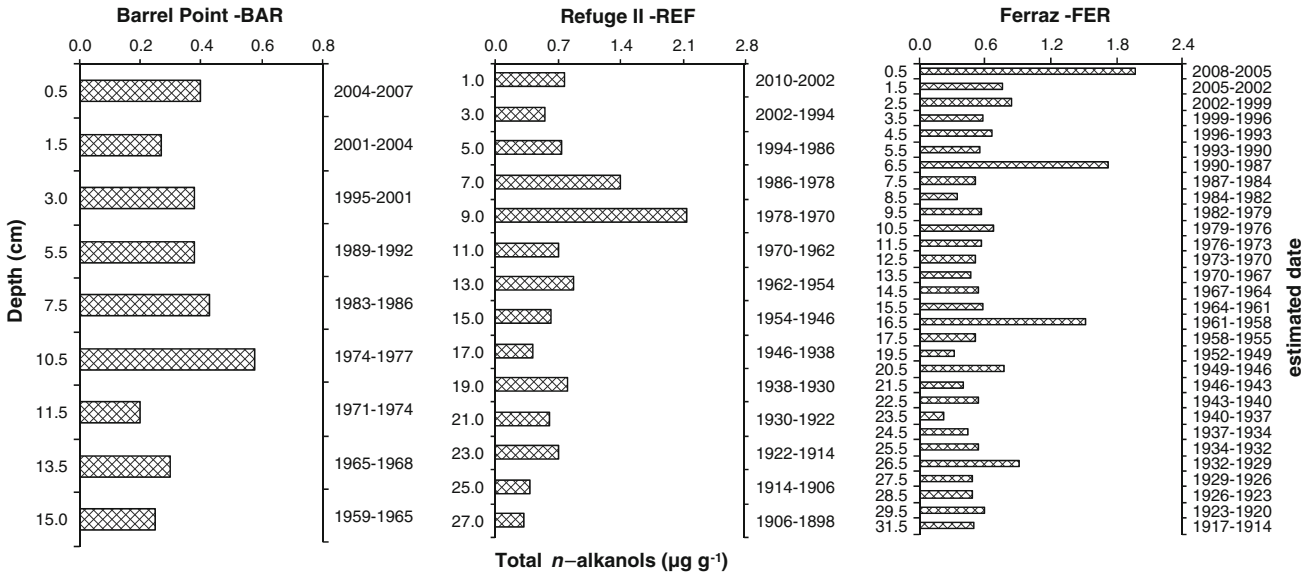

Fig. 3 Vertical profile of the concentration of total *n*-alkanols (in µg g^{-1}) in the studied samples from Admiralty Bay, Antarctica

The concentration of total *n*-alkanols versus depth is presented in Fig. 3. The vertical profile of total *n*-alkanols from BAR is similar to the total OLs, with the highest concentration in the sections between 7 and 11 cm. In REF, the highest concentration occurred between 7 and 9 cm, whereas in FER, the three most significant peaks were at 16.5, 6.5 and 0.5 cm. As for total OLs, the variation in the depth profiles may reflect variation in the OM input from sources that biosynthesis these compounds or conditions favorable for preserving the deposited OM (Meyers 1997).

The short chain *n*-alkanols suggest a contribution from marine organisms, including aquatic algae and bacteria (Meyers 2003; Xiong et al. 2010), zooplankton (Burns and Brinkman 2011) and the hydrolysis of esters of zooplankton, which results in saturated alcohols (Volkman 2006). The long chain *n*-alkanols indicate an input of terrestrial origin, but in the Antarctic environment, such sources are limited to two regional specimens of vascular plants, which include lichens (source of *n*-C_{24}OH) and moss (especially *n*-C_{28}OH) (Wang et al. 2007).

The predominance of short chain *n*-alkanols in all the samples indicates that the OM is primarily from marine organisms, such as algae. Although present in low concentration, the presence of long chain *n*-alkanols reflects a less significant contribution of terrestrial OM from lichens and mosses in the region.

Vertical distribution of phytol concentrations

Phytol, derived from the degradation of chlorophyll-*a* (Volkman et al. 2008), occurred in all the samples and has been used as a marker of photosynthetic organisms (Huang et al. 2010). In the case of the Antarctic region, its contribution is related to vascular plants (*D. antarctica* and *C. quitensis*), including lichens, moss and algae (Wang et al. 2007).

The concentration distribution versus depth is presented in Fig. 4. In BAR (Table S4), it ranged from 0.17 to 0.26 µg g^{-1} (mean 0.21 ± 0.03 µg g^{-1}), being fairly constant and near the DL. For the REF samples (Table S5), it ranged from 0.13 to 2.39 µg g^{-1} (mean 0.47 ± 0.59 µg g^{-1}). In FER, the mean concentration was 0.37 ± 0.21 µg g^{-1}, with values ranging from 0.24 to 1.26 µg g^{-1} (Table S6). A higher concentration was observed in the more recent sediments near the top of the core, whereas in the remaining sections, there was a more homogeneous distribution.

There are no studies of phytol in Admiralty Bay marine sediments and only a few in the Antarctic region. Huang et al. (2010, 2011) evaluated the distribution of phytol in cores from Antarctica, but their cores were collected on land. Therefore, comparing the concentrations from the previous study with the results of this work is difficult. In both of the latter studies, the concentration reached ca. 50 µg g^{-1} (Huang et al. 2010) and ca. 600 µg g^{-1} (Huang et al. 2011), higher than in our study, is most likely because these studies used continental samples, where the contribution of plants is considerably more significant. In addition, the degradation of phytol may be more significant for our marine sediments as a result of aerobic and anaerobic biodegradation, photodegradation and sulphurization (Rontani and Volkman 2003; Volkman et al. 2008) at the sediment–water interface.

The expected pattern for the distribution of phytol is the highest concentration occurring at the surface and decreasing with depth (Fig. 4), due to degradation. Because

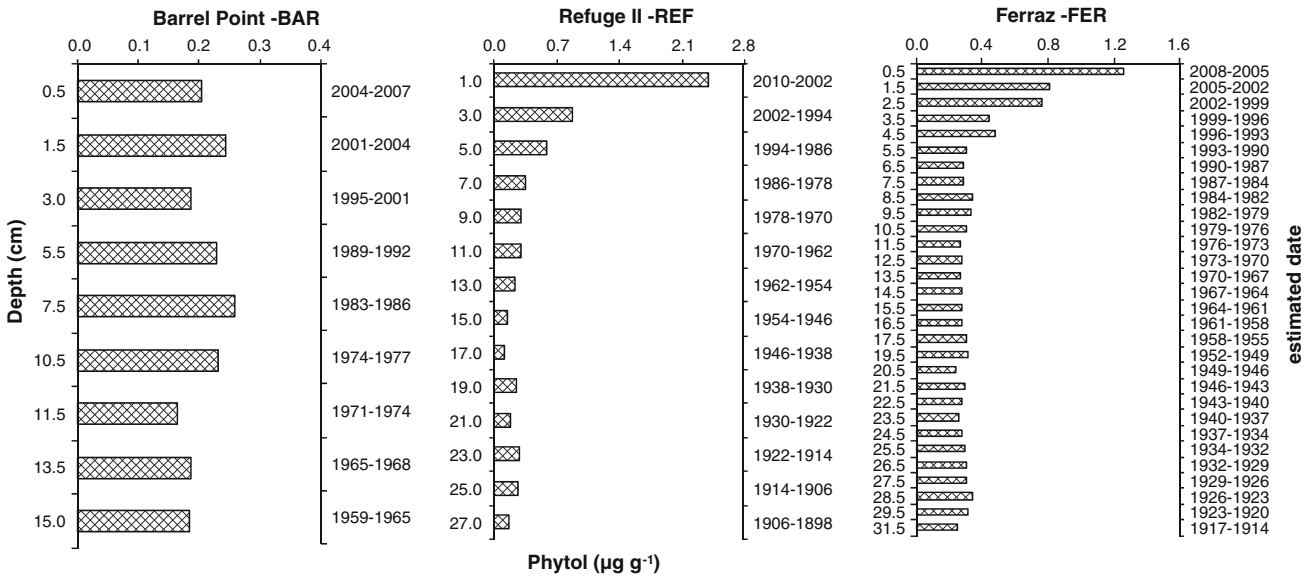

Fig. 4 Vertical profile of the concentration of phytol (in µg g^{-1}) in the studied samples from Admiralty Bay, Antarctica

there was little change versus depth in our case, we conclude that there was no significant change in input (Burns and Brinkman 2011).

Diagenetic alteration of OM indicated by 5α(H)-stanols/Δ^5-stenols ratio

The 5α(H)-stanols/Δ^5-stenols ratio may be used to evaluate the effect of diagenesis because 5α(H)-stanols in marine sediments occur as a result of the bacterial reduction in unsaturated sterols (stenols), which helps identify degradation processes or preservation of OM in sediments (Jeng and Han 1996).

The ratio for all pairs of 5α(H)-stanols/Δ^5-stenols was calculated [cholesta-22E-en-3β-ol/cholesta-5,22E-dien-3β-ol ($27\Delta^{22E}/27\Delta^{5,22E}$); 5α-cholestan-3β-ol/cholest-5-en-3β-ol ($27\Delta^0/27\Delta^5$); 24-methylcholesta-22E-en-3β-ol/24-methylcholesta-5,22E-dien-3β-ol ($28\Delta^{22E}/28\Delta^{5,22E}$), 24-methylcholestan-3β-ol/24-methylcholest-5-en-3β-ol ($28\Delta^0/28\Delta^5$); 24-ethylcholesta-22E-en-3β-ol/24-ethylcholesta-5,22E-dien-3β-ol ($29\Delta^{22E}/29\Delta^{5,22E}$) and 24-ethylcholestan-3β-ol/24-ethylcholest-5-en-3β-ol ($27\Delta^0/27\Delta^5$)]. Low values between 0.1 and 0.5 indicate recently deposited OM with no significant diagenetic change, whereas values >0.5 indicate an environment with conditions favorable for occurrence of diagenetic processes, i.e., with a predominance of 5α(H)-stanols (Wakeham and Canuel 2006; Carreira et al. 2011).

For a discussion of the changes, the mean values per section for all cores were used (Fig. 5). For BAR, the values ranged from 0.3 to 1.0 (Table S7); however, along the core, they ranged from ca. 0.3 to 0.6, indicating a Δ^5-stenol predominance and suggesting low post-depositional conversion in almost all the samples (Volkman et al. 2008). Only at the bottom was a value of 1.0 observed, suggesting that the environmental conditions favored OM conversion for this period (Muri et al. 2004). In REF, the values were between 0.3 and 1.1 (Table S8), with the highest predominance of values below or close to 0.5 only in the most surficial sections, which suggests the presence of "fresh" OM or conditions for the preservation of material deposited during the corresponding periods. However, in deeper sections, the predominance of higher values suggests significant changes with a conversion of the unsaturated to saturated isomers, which indicates the degradation of this material. In FER, the values ranged between 0.3 and 1.0 (Table S9). The reason for these lower values is as for REF, with a predominance between 0.3 and 0.6 in the upper layers to the middle of the core, from where there is a predominance of values >0.8. This profile also indicates the presence of "fresh" organic matter in the surface sections, whereas conditions for its preservation are evident in the intermediate layers. In the older sediments, there was a significant change, where the 5α(H)-stanols prevailed in all sections, from conversion of the unsaturated.

The increase in the ratio observed in REF and FER versus depth has been reported elsewhere (Muri et al. 2004; Lu and Zhai 2006) and indicates that by the time the reduction in Δ^5-stenols to 5α(H)-stanols (Arzayus and Canuel 2004) occurs with greater intensity, most likely due to time, the environmental conditions in both samples favored such a conversion (Canuel and Martens 1993; Christodoulou et al. 2009).

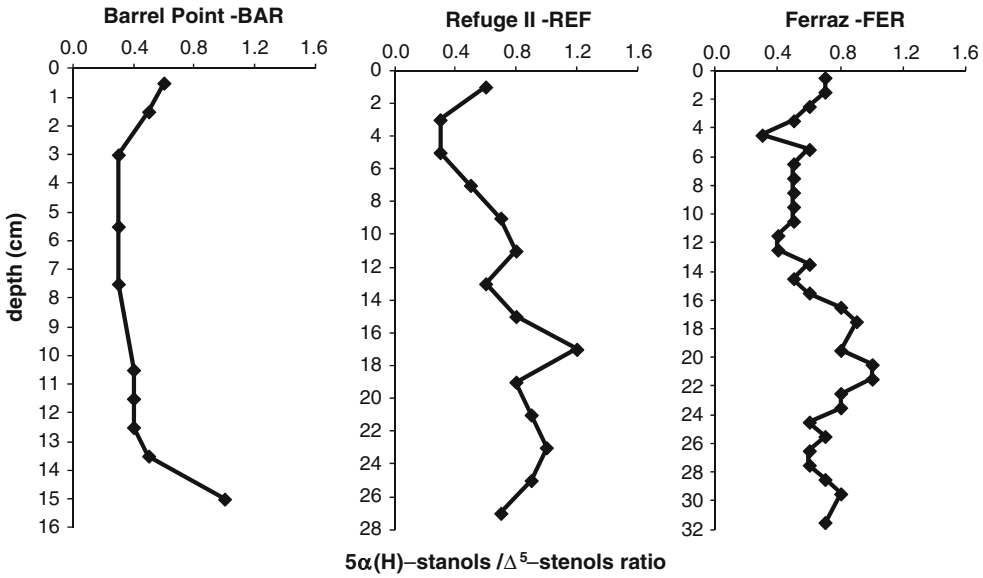

Fig. 5 Values of the ratios 5α(H)-stanols/Δ^5-stenols along the three analyzed samples

Distribution of organic markers in different ages and relation to temperature variations

The date for each section of the FER sample was estimated using the sedimentation rate; and this sample was chosen because its sections involve shorter time intervals, which improves the temporal resolution. These sections were then grouped at depth intervals in accord with the variation in the concentration of the markers, being classified as periods A (recent sediments), B, C, D and E (older sediments).

The temporal series of mean air temperature (MAT) presented by Setzer and Romão (2008) for Admiralty Bay, provided some assistance in the comparison between the fluctuations in air temperature with the variation in the vertical profile of some sterols during the period from 1949 to 2007. The same trend in MAT was observed in the time series presented by Ferron et al. (2004) to King George Island.

The distribution of the concentration of compounds was established throughout the FER sample is presented in Fig. 6.

Period E corresponds to the time between 1914 and 1926. No continuous temporal data series for MAT in the region was found for this period. Jones (1990) compiled information from scientific expeditions since the early 1900s, which could assist interpretation. Although the report provides an average for the entire Antarctic Peninsula region, its data reflect the average trend at the time and can be used as a basis for comparison. From this information, it was possible to observe an average minimum temperature of −4.8 °C in 1915 and −3.3 °C in 1921 (Jones 1990), resulting in an average temperature of −4.1 ± 0.8 °C ($n = 2$) during the interval corresponding to period E. These oscillations appear to have no influence on the OM supply because no significant variations in the concentrations of the most of compounds were observed. During period D, 1926 to 1961, cholest-5-en-3β-ol exhibited a concentration peak in 1929–1932 and another peak in 1946–1949. The sterol 4α,23,24-trimethylcholesta-22E-en-3β-ol also had relatively higher values in 1949–1952; however, considering the range of concentration, this variation seems not to be significant (Fig. 6) and the punctual contribution of cholest-5-en-3β-ol from pinnipedians and penguins cannot be excluded. Other compounds maintained a relatively constant concentration, with a few oscillations, without much significance. The pattern may suggest that the sources of sterols in that period did not experience any disturbance. According to the information from Jones (1990), in 1935, the average temperature in the region was −4.6 °C, which was slightly higher than in previous years. However, the lack of more MAT data to this period does not let a precise comparison.

The FER sample in period C, from 1961 to 1987, presented the average temperature of −2.0 ± 0.7 °C ($n = 7$) and a relatively constant concentration of cholest-5-en-3β-ol was lower than in previous periods. Other sterols, such as indicators of phytoplankton, algae and plants, exhibited a distribution with no significant variations (Fig. 6). A relatively constant supply of cholest-5-en-3β-ol in period C coincides with a period (between 1962 and 1977) during which average temperature was more constant, around −2.5 to −2.0 °C. Thereafter, a more pronounced change occurred in average temperature, which becomes as high as −0.5 °C in 1985. This increase at the beginning of the 1980s coincides with reports of a declining population of penguins in the Antarctic region since the mid-1980s (Sander et al. 2007; Trivelpiece et al. 2011). In period B, which corresponds to 1987–1999, the average temperature

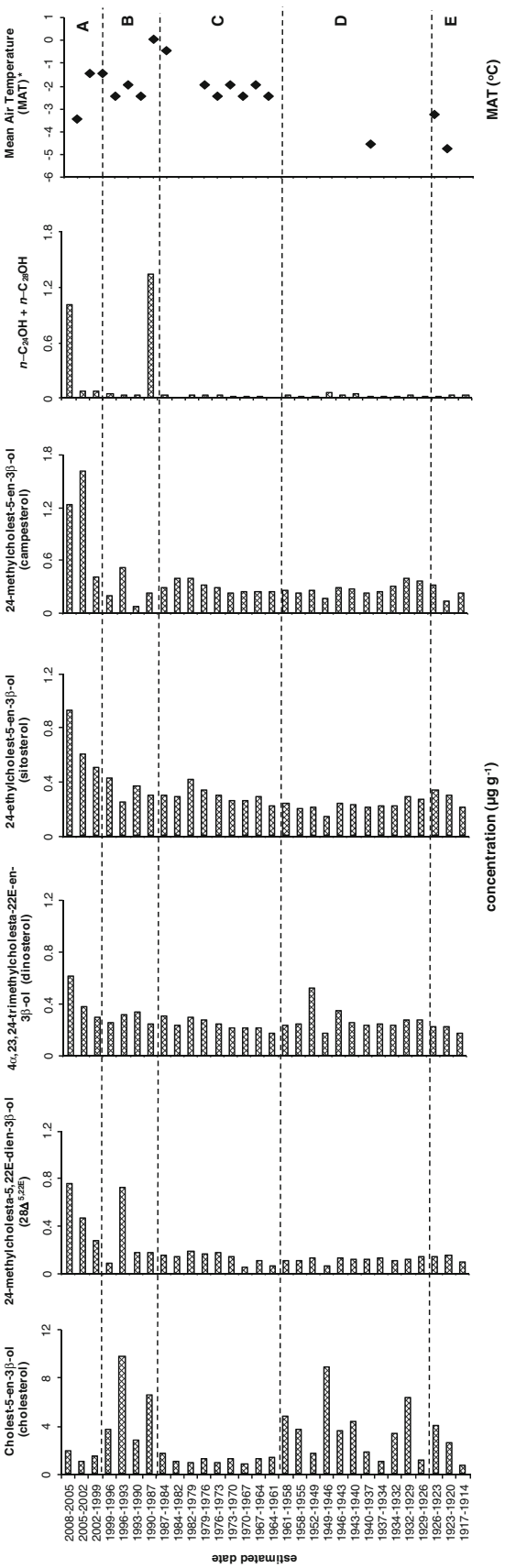

Fig. 6 Concentration of sterols and *n*-alkanols (in µg g^{-1}) in the sample from Ferraz, Admiralty Bay, Antarctica. The *dotted lines A–E* correspond to the following periods: *A* (2008–1999), *B* (1999–1987), *C* (1987–1961), *D* (1961–1926) and *E* (1926–1914). Mean air temperature (MAT) based on Setzer and Romão (2008), Ferron et al. (2004) and Jones (1990). Mean MAT and standard deviation (in °C) for each period are *A* (−2.2 ± 0.9 °C; $n = 3$), *B* (−1.8 ± 1.0 °C; $n = 4$), *C* (−2.0 ± 0.7 °C; $n = 7$) and *E* (−4.1 ± 0.8 °C; $n = 2$)

was −1.8 ± 1.0 °C ($n = 4$). A slightly higher concentration of cholest-5-en-3β-ol and *n*-alkanols was observed (Fig. 6). During this period, the annual average temperature was slightly higher, peaking at 0 °C in 1989, the highest average temperature recorded. This increase may have generated a more intense process of melting, which consequently carried more particulate matter into the bay and resulted in a greater availability of nutrients to the marine environment. The increase in temperature generated the largest expanse of ice-free areas on the continent, which may favored the growth of terrestrial plants (Clarke et al. 2007; Huang et al. 2010), as evidenced by the increase in the concentration of *n*-alkanols. The increase in temperature between 1987 and 1990 was followed by a decrease in the concentration of cholest-5-en-3β-ol (1990–1993), when the temperature decreased to lower than −2.5 °C in 1991, which relates to a smaller contribution of this sterol to the sediment. The decrease is also observed in the profile of 24-methylcholest-5-en-3β-ol and *n*-alkanols, although the differences in their concentrations may not be significant (Fig. 6).

Furthermore, during period B, the concentration of the compounds began to increase between 1993 and 1996, where the highest peak in cholest-5-en-3β-ol, 24-methylcholesta-5,22E-dien-3β-ol and 24-methylcholest-5-en-3β-ol (Fig. 6) was recorded. Other compounds maintained their concentrations at the same scale. During this period, the temperature was ca. −2.5 °C, which then increased to −1.5 °C in 1994 and returned to −2.5 °C in 1996 (Setzer and Romão 2008). In period A, which corresponds to 1999–2008, the highest average temperature was recorded (ca. −1.5 °C), and only in 2007 was a lower average of −3.5 °C measured (Setzer and Romão 2008), with an average temperature of −2.2 ± 0.9 °C ($n = 3$). This decrease in 2007 was also observed by Schloss et al. (2012) in Potter Cove, Maxwell Bay, which has a similar environment and is relatively close to Admiralty Bay (Khim et al. 2001). With the exception of cholest-5-en-3β-ol, all the other compounds had a relative increase in concentration (Fig. 6).

Several authors have reported warming in the region of the Antarctic Peninsula, at least in the last 50 years (Turner et al. 2005; Schofield et al. 2010; Simms et al. 2011). From comparison of the variation in temperature and the

concentration of the compounds, it appears that the increased concentration of sterols is related to the increases in MAT, which can enhance melting. Primary production may increase with melting as a function of generating new areas free of ice (icebergs, glaciers and ice shelves) and the weathering of rocks, promoting greater stability in the water column (decreasing salinity and stratification) or greater availability of trace metals and micronutrients (carried from mainland by defrost waters), such as Fe, which, at low concentration, limits primary production in the Southern Ocean (Clarke et al. 2007; Ducklow et al. 2007). Bertolin and Schloss (2009) observed that the emergence of new ice-free areas with the collapse from the Larsen ice shelf in the Weddell Sea region favored an increase in primary production (phytoplankton) in the area. This increase and consequent secondary production (zooplankton) would be reflected in a greater supply of OM, culminating in the highest concentration of sterols in the cited periods with higher temperature. In addition, some variations in the sterols concentrations in middle/upper layers agreed with the trace metals distribution obtained in sediment cores collected in Admiralty Bay (Ribeiro et.al. 2011).

Furthermore, a relatively increase in the concentration of the n-C_{24} and n-C_{28} alkanols indicates an increased contribution from moss and lichens. Warmer weather and more ice-free areas may promote their growth and melt water that carries terrigenous material into the bay.

However, in period A, where the temperature was higher, cholest-5-en-3β-ol had a lower concentration and may represent an adverse effect of increased temperature on organisms. Recent studies (Atkinson et al. 2004; Schofield et al. 2010) indicate that, with increasing temperature in the Antarctic region, a change in the composition of phytoplankton occurred, which affected other trophic levels. Majewski and Tatur (2009) identified in sediments of Admiralty Bay the foram *Cribroelphidium webbi*, a type of organism that is associated with areas of shrinkage of glaciers and hence melting. The presence of this organism in sediments may be related to events that occurred 30 or 50 years ago and are not directly the result of a single melting event, but rather a consequence of the increase in average temperature during the past 50 years.

Moline et al. (2004) observed that the cryptophyte algae dominate the environment versus diatoms in less saline and warm water, typical of the occurrence of defrosting. This change in the composition of phytoplankton leads to a reduction in the biomass of krill (Schofield et al. 2010), which graze on larger cells, such as diatoms but are inefficient in "grazing" on very small cells, such as cryptophyta, thereby, favoring the growth of the salp population, which in turn feeds on cryptophyta.

Krill biosynthesis cholest-5-en-3β-ol and represents a significant source of this compound in sediment OM, so a reduction in the size of the population krill may alter the concentration of cholest-5-en-3β-ol in sediments. Furthermore, 24-methylcholesta-5,22E-dien-3β-ol is primarily found in diatoms, but it is also found in cryptophyta algae and is a primary sterol biosynthesized by salps (Phleger et al. 2000). Additionally, the presence of these organisms could alter the concentration of 24-methylcholesta-5, 22E-dien-3β-ol in sediments.

The reduction in cholest-5-en-3β-ol may also be related to the population of higher animals, such as penguins, as reported for the Antarctic region (Sander et al. 2007; Trivelpiece et al. 2011).

Acknowledgments This work is resulted of PALEOANTAR project (Identification of abrupt climate changes in Antarctica during the Upper Quaternary through sedimentary record) supported by the Antarctic Brazilian Program (PROANTAR), the Secretaria da Comissão Interministerial para os Recursos do Mar (SECIRM), Ministério de Ciência, Tecnologia e Inovação (MCTI) and National Council for Scientific and Technological Development (CNPq) (Grant codes: 550014/2007-1 and 305763/2011-3 to C.C. Martins, 557044/2009-0 to M.M. Mahiques). We also thank CAPES (Coordenação de Aperfeiçoamento de Pessoal de Ensino Superior) for a MSc scholarship to E.Wisnieski and for grant by Ciências do Mar-09/2009. We are grateful to R.S. Carreira [Department of Chemistry, Pontifícia Universidade Católica (PUC-RJ)] and M.C. Bernardes [Department of Geochemistry, Universidade Federal Fluminense (UFF)] for assistance with the preliminary evaluation of this article and the two anonymous reviewers for constructive comments which substantially improved the manuscript. This work contributes to the National Institute of Science and Technology for Environmental Research Antarctic (INCT–APA, CNPq 574018/2008-5 and FAPERJ E-16/170023/2008).

References

Abril JM (2003) Constraints on the use of ^{137}Cs as a time-marker to support CRS and SIT chronologies. Environ Pollut 129:31–37

Arzayus KM, Canuel EA (2004) Organic matter degradation in sediments of the York river estuary: effects of biological versus physical mixing. Geochim Cosmochim Acta 69:455–463

Atkinson A, Siegel V, Pakhomov E, Rothery P (2004) Long-term decline in krill stock and increase in salps within the southern Ocean. Nature 432:100–103

Bertolin ML, Schloss IR (2009) Phytoplankton production after the collapse of the Larsen A ice shelf, Antarctica. Polar Biol 32:1435–1446

Birgel D, Stein R, Hefter J (2004) Aliphatic lipids in recent sediments of the Fram Strait/Yermak Plateau (Arctic Ocean): composition, sources and transport processes. Mar Chem 88:127–160

Braun M, Gossmann H (2002) Glacial changes in the areas of Admiralty Bay and Potter Cove, King George Island, maritime Antarctica. In: Beyer L, Bolter M (eds) Geoecology and Antarctic ice-free coastal landscapes. Springer, Berlin, pp 75–89

Burns K, Brinkman D (2011) Organic biomarkers to describe the major carbon inputs and cycling of organic matter in the central Great Barrier Reef region. Estuar Coast Shelf S 93:132–141

Canuel EA, Martens CS (1993) Seasonal variations in the sources and alteration of organic matter associated with recently-deposited sediments. Org Geochem 20:563–577

Carreira RS, Ribeiro PV, Silva CEM, Farias CO (2009) Hydrocarbons and sterols as indicators of source and fate of organic matter in sediments from Sepetiba Bay, Rio de Janeiro. Quim Nova 32:1805–1811

Carreira RS, Araújo MP, Costa TLF, Spörl G, Knoppers BA (2011) Lipids in the sedimentary record as markers of the sources and deposition of organic matter in a tropical Brazilian estuarine-lagoon system. Mar Chem 127:1–11

Castaneda IS, Werne JP, Johnson TC, Powers LA (2011) Organic geochemical records from Lake Malawi (East Africa) of the last 700 years, part II: biomarker evidence for recent changes in primary productivity. Palaeogeogr Palaeoecol 303:140–154

Christodoulou S, Marty JC, Miquel JC et al (2009) Use of lipids and their degradation products as biomarkers for carbon cycling in the northwestern Mediterranean sea. Mar Chem 113:25–40

Clarke A, Murphy EJ, Meredith MP, King JC, Peck LS et al (2007) Climate change and the marine ecosystem of the western Antarctic Peninsula. Philos T Roy Soc B 362:149–166

Ducklow HW, Baker K, Martinson DG et al (2007) Marine pelagic ecosystems: the west Antarctic Peninsula. Philos Trans R Soc B 362:67–94

Faux JF, Belicka LL, Harvey HR (2011) Organic sources and carbon sequestration in Holocene shelf sediments from the western Arctic Ocean. Cont Shelf Res 31:1169–1179

Ferreira PAL, Ribeiro AP, Nascimento MG, Martins CC, Mahiques MM et al (2013) ^{137}Cs in marine sediments of Admiralty Bay, King George Island, Antarctica. Sci Total Environ 443:505–510

Ferron FA, Simões JC, Aquino FE, Setzer AW (2004) Air temperature time series for King George Island, Antarctica. Pesq Antarct Bras 4:155–169

Green G, Nichols PD (1995) Hydrocarbons and sterols in marine sediments and soils at Davis station, Antarctica: a survey for human-derived contaminants. Antarct Sci 7:137–144

Harris CM, Carr R, Lorenz K, Jones S (2011) Important bird areas in Antarctica: Antarctic Peninsula, South Shetland Islands, South Orkney Islands—final report. Prepared for bird Life International and the Polar Regions Unit of the UK Foreign & Commonwealth Office. Environmental Research and Assessment Ltd. Cambridge

Huang J, Sun L, Huang W, Wang X, Wang Y (2010) The ecosystem evolution of penguin colonies in the past 8,500 years on Vestfold hills, East Antarctica. Polar Biol 33:1399–1406

Huang J, Liguang S, Wang X et al (2011) Ecosystem evolution of seal colony and the influencing factors in the 20th century on Fildes Peninsula, West Antarctica. J Environ Sci 23:1431–1436

Hudson ED, Parrish CC, Helleur RJ (2001) Biogeochemistry of sterols in plankton, settling particles and recent sediments in a cold ocean ecosystem (Trinity Bay, Newfoundland). Mar Chem 76:253–270

Jaraula CMB, Brassel SC, Morgan-Kiss RM, Doran PT, Kenig F (2010) Origin and tentative identification of tri to pentaunsaturated ketones in sediments from Lake Fryxell, East Antarctica. Org Geochem 41:386–397

Jeng WL, Chen M (1995) Grain size effect on bound lipids in sediments off northeastern Taiwan. Org Geochem 23:301–310

Jeng WL, Han BC (1996) Sedimentary coprostanol in Kaohsiung Harbour and Tan-Shui Estuary, Taiwan. Mar Pollut Bull 28:494–499

Jones PD (1990) Antarctic temperatures over the present century: a study of the early expedition record. J Clim 3:1193–1203

Khim B, Yoon HI, Kim Y, Shin IC (2001) Late Holocene stable isotope chronology and meltwater discharge event in Maxwell and Admiralty bays, King George Island, Antarctica. Antarct Sci 13:167–173

Kopczynska EE (2008) Phytoplankton variability in Admiralty Bay, King George Island, South Shetland Islands: 6 years of monitoring. Pol Polar Res 29:117–139

Lange PK, Tenenbaum DR, Braga ES, Campos LS (2007) Microphytoplankton assemblages in shallow waters at Admiralty Bay (King George Island, Antarctica) during the summer 2002–2003. Polar Biol 30:1483–1492

Laureillard J, Saliot A (1993) Biomarkers in organic matter produced in estuaries: a case study of the Krka estuary (Adriatic Sea) using the sterol marker series. Mar Chem 43:247–261

Laureillard J, Pinturier L, Fillaux J et al (1997) Organic geochemistry of marine sediments of the subantarctic Indian Ocean sector: lipid classes—sources and fate. Deep-Sea Res Pt II 44: 1085–1108

Lu X, Zhai S (2006) Distributions and sources of organic biomarkers in surface sediments from the Changjiang (Yangtze River) Estuary, China. Cont Shelf Res 26:1–14

Majewski W, Tatur A (2009) A new Antarctic foraminiferal species for detecting climate change in sub-recent glacier-proximal sediments. Antarct Sci 21:439–448

Martins CC, Venkatesan MI, Montone RC (2002) Sterols and linear alkylbenzenes in marine sediments from Admiralty Bay, King George Island, South Shetland Islands. Antarct Sci 14:244–252

Martins CC, Bícego MC, Rose NL, Taniguchi S et al (2010a) Historical record of polycyclic aromatic hydrocarbons (PAHs) and spheroidal carbonaceous particles (SCPs) in marine sediment cores from Admiralty Bay, King George Island, Antarctica. Environ Pollut 158:192–200

Martins CC, Bícego MC, Mahiques MM, Figueira RCL et al (2010b) Depositional history of sedimentary linear alkylbenzenes (LABs) in a large South American industrial coastal area (Santos Estuary, Southeastern Brazil). Environ Pollut 158:3355–3364

Martins CC, Bícego MC, Mahiques MM, Figueira RCL et al (2011) Polycyclic aromatic hydrocarbons (PAHs) in a large South American industrial coastal area (Santos Estuary, Southeastern Brazil): sources and depositional history. Mar Pollut Bull 63:452–458

Martins CC, Aguiar SN, Bícego MC et al (2012) Sewage organic markers in surface sediments around the Brazilian Antarctic station: results from the 2009/10 austral summer and historical tendencies. Mar Pollut Bull 64:2867–2870

Martins CC, Aguiar SN, Wisnieski E et al (2014) Baseline concentrations of faecal sterols and assessment of sewage input into different inlets of Admiralty Bay, King George Island, Antarctica. Mar Pollut Bull 78:218–223

Meyers PA (1997) Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. Org Geochem 27:213–250

Meyers PA (2003) Applications of organic geochemistry to paleolimnological reconstructions: a summary of examples from the Laurentian Great Lakes. Org Geochem 34:261–289

Moline MA, Claustre H, Frazer TK et al (2004) Alteration of the food web along the Antarctic Peninsula in response to a regional warming trend. Glob Change Biol 10:1973–1980

Monien P, Schnetger B, Brumsack HR, Hass HC, Kuhn G (2011) A geochemical record of late Holocene palaeoenvironmental changes at King George Island (maritime Antarctica). Antarct Sci 23:255–267

Montone RC, Martins CC, Bícego MC, Taniguchi S et al (2010) Distribution of sewage input in marine sediments around a maritime Antarctic research station indicated by molecular geochemical indicators. Sci Total Environ 408:4665–4671

Muri G, Wakeham SG, Pease TK, Faganeli J (2004) Evaluation of lipid biomarkers as indicators of changes in organic matter delivery to sediments from Lake Planina, a remote mountain lake in NW Slovenia. Org Geochem 35:1083–1093

Oliveira EC, Absher TM, Pellizzari FM, Oliveira MC (2009) The seaweed flora of Admiralty Bay, King George Island, Antarctic. Polar Biol 32:1639–1647

Oliveira DRP, Cordeiro LGMS, Carreira RS (2013) Characterization of organic matter in cross-margin sediment transects of an upwelling region in the Campos Basin (SW Atlantic, Brazil) using lipid biomarkers. Biogeochemistry 112:311–327

Phleger CF, Nelson MM, Mooney B, Nichols PD (2000) Lipids of Antarctic salps and their commensal hyperiid amphipods. Polar Biol 23:329–337

Rakusa-Suszczewski S (1980) Environmental conditions and the functioning of Admiralty Bay (South Shetlands Islands) as part of near shore Antarctic ecosystem. Pol Polar Res 1:11–27

Readman JW, Preston MR, Mantoura RFC (1986) An integrated technique to quantify sewage, oil and PAH pollution in estuarine and coastal environments. Mar Pollut Bull 17:298–308

Ribeiro AP, Figueira RCL, Martins CC et al (2011) Arsenic and trace metal contents in sediment profiles from the Admiralty Bay, King George Island, Antarctica. Mar Pollut Bull 62:192–196

Rontani JF, Volkman JK (2003) Phytol degradation products as biogeochemical tracers in aquatic environments. Org Geochem 34:1–35

Sander M, Balbão TC, Costa ES, Santos CR, Petry MV (2007) Decline of the breeding population of *Pygoscelis antarctica* and *Pygoscelis adeliae* on Penguin Island, South Shetland Antarctica. Polar Biol 30:651–654

Schloss IR, Abele D, Moreau S, Demers S et al (2012) Response of phytoplankton dynamics to 19 year (1991–2009) climate trends in Potter Cove (Antarctica). J Marine Syst 92:53–66

Schofield O, Ducklow HW, Martinson DG, Meredith MP, Fraser WR (2010) How do polar marine ecosystems respond to rapid climate change? Science 328:1520–1523

Setzer A, Romão M (2008) Atenção pesquisador: caiu a temperatura nos últimos 11 anos em Ferraz. XVI simpósio Brasileiro Sobre Pesquisa Antártica. Universidade de São Paulo, São Paulo, pp 7–8 (in Portuguese)

Sierakowski K (1991) Birds and mammals in the region of SSSI No. 8 in the season 1988/89 (South Shetlands, King George Island, Admiralty Bay). Pol Polar Res 12:25–54

Simms AR, Milliken KT, Anderson JB, Wellner JS (2011) The marine record of deglaciation of the South Shetland Islands, Antarctica since the last glacial maximum. Quat Sci Rev 30:1583–1601

Skerratt JH, Nichols PD, McMeekin TA, Burton H (1995) Seasonal and inter-annual changes in planktonic biomass and community structure in eastern Antarctica using signature lipids. Mar Chem 51:93–113

Trivelpiece WZ, Hinke JT, Miller AK, Reiss CS, Trivelpiece SG, Watters GM (2011) Variability in krill biomass links harvesting and climate warming to penguin population changes in Antarctica. Proc Natl Acad Sci USA 108:7625–7628

Turner J, Colwell S, Marshall GJ, Lachlan-Cope TA, Carleton AM, Jones PD, Lagun V, Reid PA, Iagovkina S (2005) Antarctic climate change during the last 50 years. Int J Climatol 25: 279–294

Venkatesan MI, Ruth E, Kaplan IR (1986) Coprostanols in Antarctic marine sediments: a biomarker for marine mammals and not human pollution. Mar Pollut Bull 17:554–557

Venkatesan MI, Santiago CA (1989) Sterols in oceans sediments: novel tracers to examine habitats of cetaceans, pinnipeds, penguins and humans. Mar Biol 102:431–437

Volkman JK (1986) A review of sterol markers for marine and terrigenous organic matter. Org Geochem 9:83–100

Volkman JK (2005) Sterols and other triterpenoids: source, specificity and evolution of biosynthetic pathways. Org Geochem 36: 139–159

Volkman JK (2006) Lipid markers for marine organic matter. In: Volkman JK (ed) Handbook of environmental chemistry reactions and processes 2 (N). Springer, Berlin, pp 27–70 2

Volkman JK, Revill AT, Holdsworth DG, Fredericks D (2008) Organic matter sources in an enclosed coastal inlet assessed using lipid biomarkers and stable isotopes. Org Geochem 39:689–710

Wade TL, Cantillo AY (1994) Use of standards and reference materials in the measurement of chlorinated hydrocarbon residues. Chem Workb NOAA Tech Memo NOS ORCA 77:59

Wakeham SG, Canuel EA (2006) Degradation and preservation of organic matter in sediments. In: Volkman JK (ed) Handbook of environmental chemistry reactions and processes 2 (N), vol 2. Springer, Berlin, pp 295–321

Wang J, Wang Y, Wang X, Sun L (2007) Penguins and vegetations on Ardley Island, Antarctica: evolution in the past 2,400 years. Polar Biol 30:1475–1481

Xiong Y, Wu F, Fang J, Wang L, Li Y, Liao H (2010) Organic geochemical record of environmental changes in Lake Dianchi, China. J Paleolimnol 44:217–231

Yoon HI, Park BK, Kim Y, Kim D (2000) Glaciomarine sedimentation and its paleoceanographic implications along the fjord margins in the South Shetland Islands, Antarctica during the last 6000 years. Palaeogeogr Palaeocol 157:189–211