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THE ROLE OF EARLY DIAGENESIS IN THE SEDIMENTARY STEROIDS AROUND PENGUIN ISLAND, ANTARCTICA

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Abstract: *The role of lipids in polar environments is of primary importance for understanding the cycling of carbon organic and associated elements. Thus, the knowledge of the nature and quality of organic matter is necessary to evaluate the overall impact in this area and to model the carbon cycle. The aim of this study was to determine the transformations of organic matter in the marine environment by analysis of a specific group of lipid biogeochemical markers, the sedimentary steroids. Sediment cores were collected during the 2007/08 austral summer in the vicinity of the Penguin Island (2 cores). In general, the cores were sectioned at 1 cm intervals and the steroids analyzed by gas chromatography with flame ionization detection (GC-FID), after Soxhlet extraction, adsorption column chromatography and derivatization. The results showed that organic matter had been subjected to extensive degradation and transformation with depth in the two corers and the general increase of the stanol/stenol ratio may have represented the progressive reduction of stenols to stanols within the deepest sediment layers. According to the linear regression (R^2) applied, the process at Penguin Island is governed by a natural supply, and a random pattern in the concentration values with increasing depth. These results contribute to the understanding of the current processes of organic matter transformation in this important region of Antarctic environment.*

Keywords: steroids, sediments, organic matter, Antarctica

Introduction

Advanced studies about biogeochemical cycles in the relatively unpolluted areas of the world, such as Antarctica, have been of great interest. Thus, the Southern Ocean appears an attractive region due to the distance from major sources of human pollution, very cold average temperatures, a strong seasonality and the almost complete absence of higher plants (Laureillard *et al.,* 1997).

The role of lipids in polar environments is of primary importance for understanding the cycling of carbon organic and associated elements. Knowledge of the nature and quality of organic matter, assemblages of organisms and relative rates of primary production for those communities in the ocean and its interactions with chemical and biological systems is important to evaluate the overall impact in this area and modeling the world carbon cycle (Mudge & Norris, 1997; Villinski *et al.,* 2008).

Based on this expectation, this work has the purpose to investigate different organic compounds in the marine sediments to determine the transformations of organic matter in the Antarctic environment by analysis of a specific group of lipid biogeochemical markers, the sedimentary steroids.

Material and Methods

Study area

Penguin Island (62° 06' S and 57° 54' W; area 1.7 km^2) is situated on the southeastern side of King George Island, South Shetland Islands, Antarctica (Figure 1). It lies within a belt of inactive volcanoes that developed in the Bransfield Strait (Birkenmajer, 1982).

Almost all this island is dominated by species of birds and according to Sander *et al.* (2007) nine bird species nest on Penguin Island, among them *Pygoscelis antarctica* (chinstrap penguin) and *Pygoscelis adeliae* (adélie penguin). These populations contribute significantly to a large amount of guano, influencing strongly the physical and chemical properties of local soils, producing ornithogenic soil (Michel *et al*., 2006; Zhu *et al.,* 2009).

Sampling

Sediment cores were taken by mini-box corer (25 × 25 × 55 cm) during the 2007/08 austral summer. In general, the cores were sectioned on board to a resolution of 1-2 cm prior to sub-sampling for chemical and physical characterization, and placed into pre-cleaned aluminum foil and stored at –20 °C until analyzed in laboratory.

Extraction and fractioning of sterols

In the present study, all samples were analyzed for 17 different steroids, including 15 sterols and 2 ketones. The laboratory procedure was based on a method described by Kawakami and Montone (2002). This consists of analysis by gas chromatography with flame ionization detection (GC-FID), after Soxhlet extraction, adsorption column chromatography and derivatization with BSTFA/TCMS.

Data was subject to quality control procedures, like the analysis of spiked samples (4 replicates), precision tests (4 replicates) and evaluation of the instrumental performance (response factors). Analysis of procedural blanks (6 replicates) indicated minor amounts of dehidrocholesterol and cholesterol, which were subtracted from the samples. Surrogate recoveries (5α-cholestane) ranged from 66-132%. Sediment and blank samples were spiked with a mixture of steroids and the standard recoveries ranged from 99-139 %. Detection limits (DL) were < 0.01 μg.g^{-1} for all compounds analyzed.

Results and Discussion

The ratio between stanol/stenol has been used to indicate microbial reduction in anaerobic environments. Studies about redox effects on organic matter degradation/preservation have shown that the residence times for organic compounds present in marine sediments can vary as a result of environmental conditions such as bioturbation, physical mixing and the presence or absence of oxygen and other electron acceptors (Wakeham & Canuel, 2006).

Stanols may be formed within the sediments by bacterial reduction of stenols in highly or permanently anoxic sediments (Nishimura & Koyama, 1977). Consequently, the stanol/stenol ratio has been used to describe the redox conditions of the sediments (Gagosian *et al.*, 1980). Since stanols are synthesized by some plankton, notably dinoflagellates (Robinson *et al.,* 1984) and diatoms (Barrett *et al.,* 1995), changes in the distribution of marine phytoplankton through time may provide an additional source of variability in the sedimentary stanol/stenol ratio.

Sterols undergo a variety of chemical and microbial reactions in the surface layers of marine sediments. It is seems evident that they have been subjected to degradation and transformation with depth in the two corers (Figure 2), mainly PGI-2. The general increase of the stanol/stenol ratio may illustrate the progressive reduction of stenols to stanols within the deepest sediment layers (Shanchun *et al.,* 1994; Fernandes *et al.,* 1999), showing that the rates of sterol degradation in sediments are a group of several processes, which the hydrogenation appears to be relatively more important (Volkman *et al.,* 1987).

Once the most energetically favorable metabolic pathways for bacteria involve oxygen as the electron acceptor, the organic carbon degradation (and preservation) in sediments is strongly controlled by the average time that organic matter is exposed to oxygen (Wakeham & Canuel, 2006). Hence, it is feasible that stanols are relatively less abundant at the surface than at the bottom sections of the PGI-1 and PGI-2 corers.

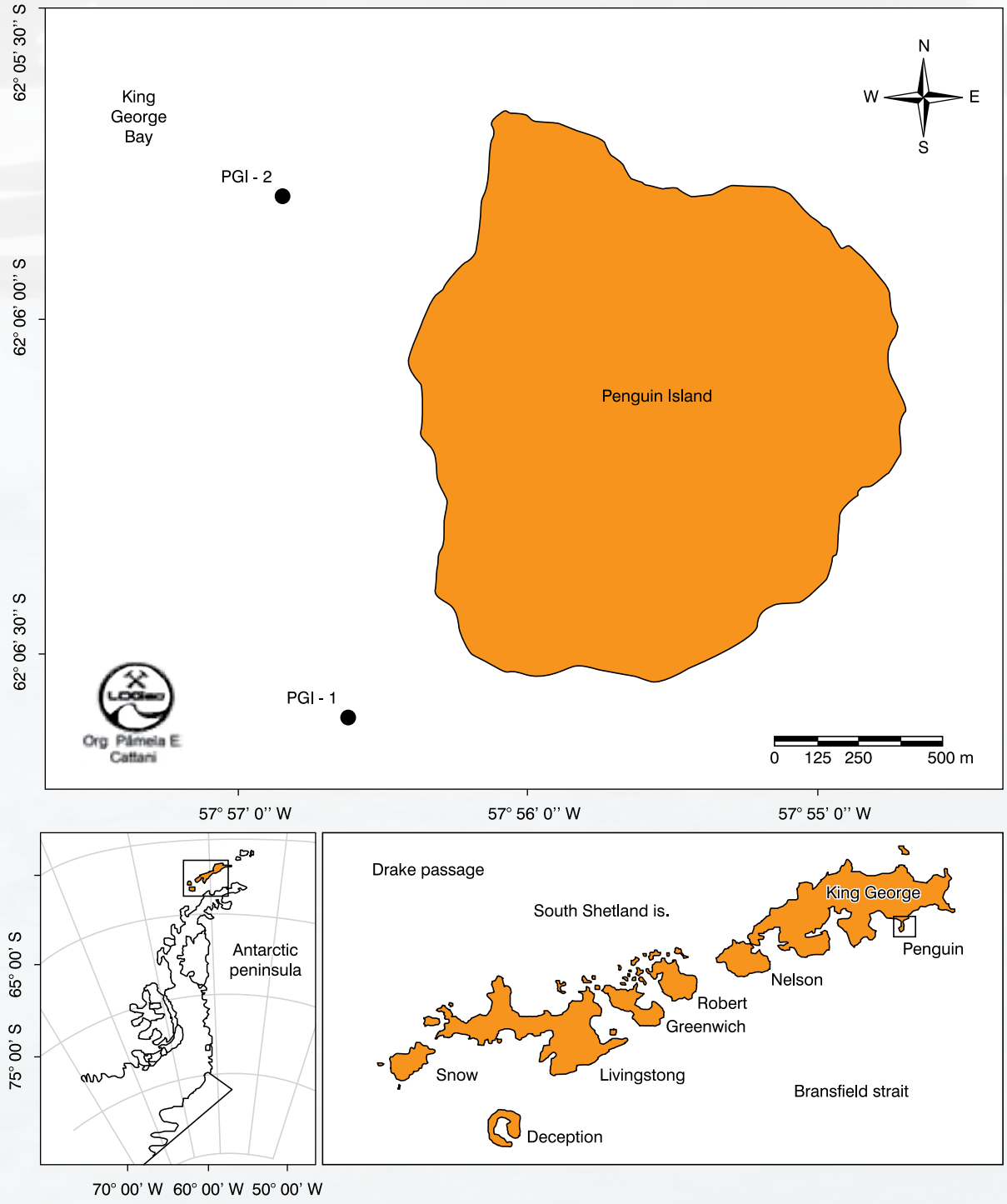

Figure 1. Location of sampling stations (PGI-1 and PGI-2) in the Antarctic continent and the South Shetland Islands.

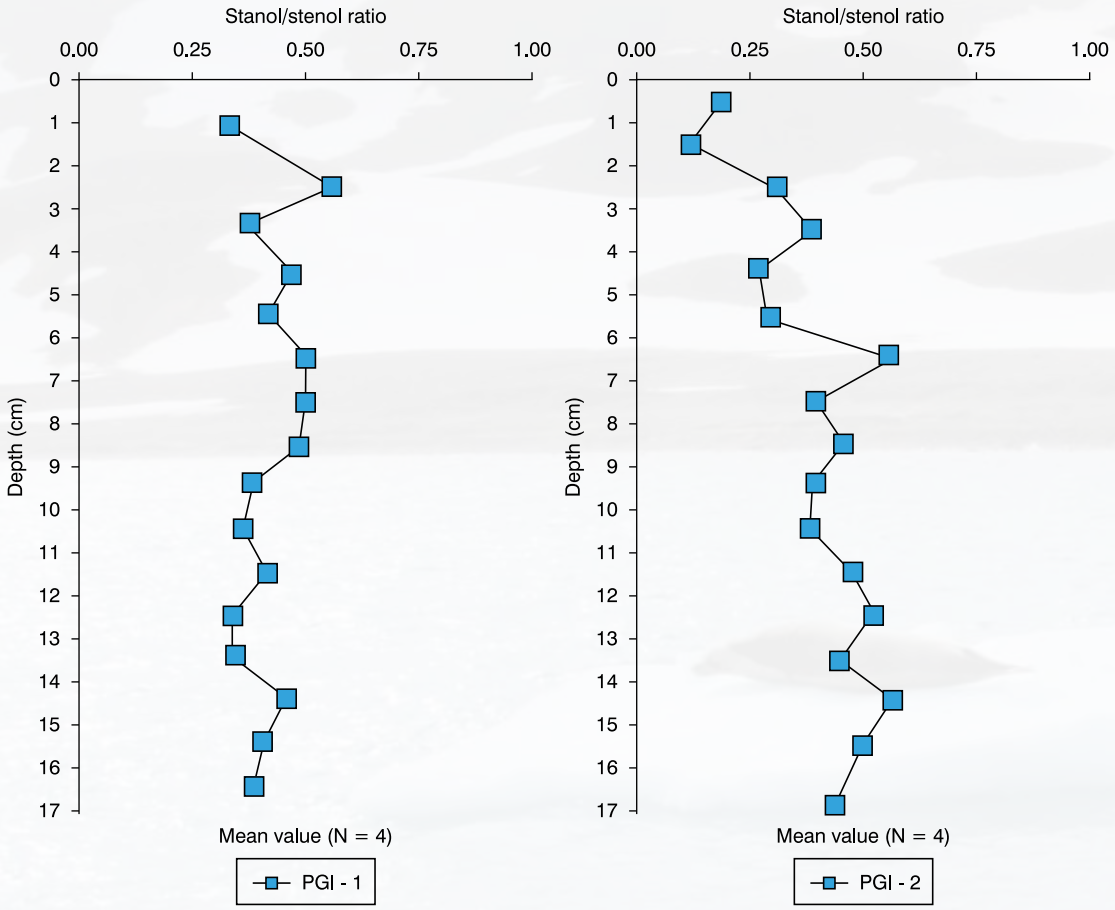

Figure 2. Mean value of four pairs of stanol/stenol rate in PGI-1 and PGI-2.

This process occurs in opposition to the progressive input of stanols from potentially new sources of biogenic saturated molecules being identified by different studies, such as dinoflagellates, diatoms and some species of invertebrates, usually represented by low values in the ratio (Hudson *et al.,* 2001; Ternois *et al.,* 1998).

According to Wakeham and Canuel (2006), values of the stanol/stenol ratio varied between 0.1 and 0.2 for oxic water columns and between 0.6 and 1.2 in sub-oxic and anoxic interfaces in the water column from the Cariaco Trench (Caribbean shelf) and Black Sea. In the present study, the ratio varied from 0.33 to 0.57 (0.43 ± 0.07) (PGI-1) and 0.11 to 0.57 (0.39 ± 0.12) (PGI-2) indicating well oxygenated sediments. The results also show that the redox conditions of sediment appear to have been potentially modified, as is noted by the reduction and increase in the values at several depths of both corers. This variation may reflect the change of water chemistry of the site at the time of sediment deposition due to a general renewal of bottom water and thus its re-oxygenation (Pinturier-Geiss *et al.*, 2002).

Jeng *et al.* (1997) analyzing sediment cores of the coast of Taiwan, found that the rate of degradation of sterols follows a typical kinetic mechanism of 1st order reaction. To this evaluation, the linear relation between the natural logarithm (ln) of total sterols concentration and depth (along the cores) was determined. In order to complement the results obtained, graphs of linear regression (R^2) for both cores (Figure 3) were done. It is possible to observe a decrease in the concentration of sterols toward the lower depth layers, for most points in the sedimentary columns. These results

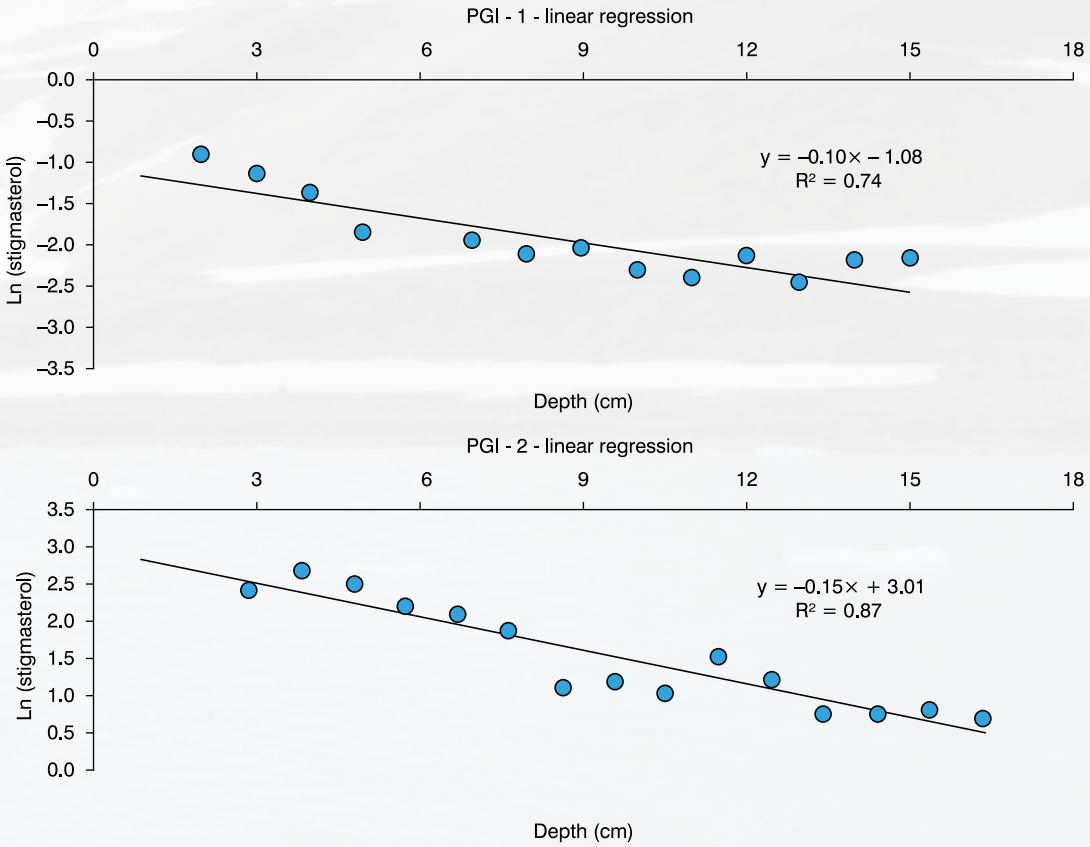

Figure 3. Sterol degradation model indicated by linear regression between Ln stigmasterol concentration vs depth to PGI-1 and PGI-2 sediment cores.

confirm the trend of degradation over the preservation of organic compounds and, consequently, of sedimentary organic matter, which is of fundamental importance for understanding the processes prevailing in this environment.

In both corers, the linear regression values showed that the degradation occurs according to kinetic mechanism of 1st order ($R^2 < 0.75$). Fluctuations in the natural supply of sterols and over the years may change the regular pattern with increased depth, which explains the absence of a perfect linear correlation, especially in PGI-1. The degradation can be defined as the decrease of compound concentration by transformation into other molecules (such as conversion of stenols to stanols), decomposition into smaller molecules, or incorporation into high molecular weight components. As all processes are related with removal of extractable sterols from the sediments (Jeng *et al.,* 1997), the results suggest that the diagenesis of organic matter in sediments around Penguin Island is an important environment process of organic matter transformation.

Conclusion

According to the values found for the stanol/stenol ratio, the sediments around Penguin Island are well oxygenated. However, some changes were detected along the sedimentary column and may have resulted by change of water chemistry related to the time-scale of sediments deposition and the general renewal of bottom water and thus its re-oxygenation. Linear regression analysis confirmed the degradation trend over the preservation of sedimentary organic matter. This information helps a better understanding of the processes related to contribution and the transformation of organic matter around Penguin Island.

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