PROGRAMA DE DOCTORADO EN CIENCIAS DEL MAR

Universitat Politècnica de Catalunya (UPC)
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Organic matter in sediments of Antarctic continental shelves under the influence of climate change

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Barcelona, Mayo de 2010

Contents

En los últimos 60 años las temperaturas del océano y del aire en la Antártida aumentaron por encima del promedio global (Vaughan et al., 2001; Gille, 2002). Como consecuencia, se ha observado un incremento en el retroceso de los glaciares (Cook et al., 2005) y la reducción del espesor de las plataformas de hielo (Shepherd et al., 2003; Whingham et al., 2009). Con ello, la desintegración de plataformas de hielo en la Antártida se ha hecho más frecuente, como demostraron el colapso en 2008 de la plataforma de hielo Wilkins y el colapso en 2010 del glaciar Mertz. En 1995 se desintegraron 4200 km^2 de la plataforma de hielo Larsen A y en 2002, 3200 km^2 de la plataforma de hielo Larsen B (Rack and Rott, 2004). Tres episodios de retroceso 1400, 2100 y 3800 años A.C. precedieron la desintegración de la plataforma de hielo Larsen A (Brachfield et al., 2003), a diferencia de la plataforma de hielo Larsen B que empezó a colapsar en 1947 después de 10000 años de estabilidad (Domack et al., 2005a). Durante la expedición Antártica ANT-XXIII/8 tuvimos la oportunidad de llegar a las Bahías Larsen A y B frente a la costa oriental de la Península Antártica (PAO) y muestrear la parte superior (los primeros 30 cm) de la columna de sedimento. Uno de los objetivos de este trabajo fue el estudio de la acumulación de la materia orgánica (MO) en el sedimento antes y después del colapso de las plataformas de hielo. No es común tener la oportunidad de analizar el sedimento en áreas donde la producción primaria y el flujo de MO hacia el fondo del mar empiezan a desarrollarse pocos años antes que el muestreo tenga lugar. Las bahías Larsen A y B representan un "laboratorio natural" donde fue posible investigar la llegada reciente de MO a un sustrato relativamente pobre. La cantidad y la calidad química de la MO encontrada en los sedimentos de la PAO se compararon con las características de la MO analizada en sedimento muestreado al Norte de la Península Antártica Norte (NPA) y en el Mar de Weddell Sur Oriental (MWSO), regiones que desde hace miles de años no han estado cubiertas por plataformas de hielo (Ingólfsson et al., 1998; Anderson et al., 2002). Otro objetivo fue identificar qué constituyente de la MO entre pigmentos (PG), aminoácidos (AA), ácidos grasos (AG), carbohidratos totales (CHO), lípidos totales (LPD) y proteínas totales (PRT) es mejor utilizar como biomarcador de cambios ambientales. Un tercer objetivo fue identificar las relaciones entre las características químicas del sedimento y la estructura de las comunidades bentónicas para obtener una idea general de cómo está cambiando el ecosistema bajo las antiguas plataformas de hielo. Para alcanzar este objetivo se estudiaron la abundancia, biomasa y diversidad de la macrofauna béntica en la PAO y en el MWSO. Para completar la información sobre el origen de la MO obtenida con los resultados de AA y AG se

contaron también las valvas de diatomeas presentes en los sedimentos de la PAO y de la NAP. El exceso de la actividad del ^{210}Pb en los testigos de sedimento se midió para desarrollar una cronología radioquímica de los eventos sedimentarios recientes en la PAO y en la NPA.

En la NPA las concentraciones de PG y AA fueron mayores que en la PAO a lo largo de la columna sedimentaria. Las valvas de diatomeas, la actividad del ^{210}Pb, la distribución vertical de los PG y de los AA indicó un flujo menos intenso y más corto de MO lábil en la PAO que en la NPA. En la PAO sólo se encontró MO lábil en los 2 cm superiores de la columna de sedimento. La cantidad y la calidad química de las variables biogénicas demostraron que la presencia de las plataformas de hielo efectivamente impide el flujo vertical de MO lábil al sedimento. Los perfiles del número de valvas de diatomeas y la concentración de PG sugieren que esto se debe principalmente a una producción primaria baja. El origen de los constituyentes de la MO que se depositó recientemente tanto en la PAO como en la NPA está relacionado principalmente con las diatomeas. La MO lábil encontrada en la PAO llegó al suelo marino principalmente a través de transporte vertical desde la zona eufótica, mientras que los CHO refractarios y los AG de cadena media se acumularon principalmente por advección lateral durante años de cobertura por las plataformas de hielo y la ausencia de un flujo de MO lábil. La ausencia de Chl*b* en el área de estudio confirmó la falta de aporte terrestre de MO desde el continente Antártico y la ausencia de AG de los tipos *iso*- y *anteiso*-, hidroxilados, y de 18:1(n-7) evidenció la ausencia de MO de origen bacteriana. Los PG resultaron ser los mejores marcadores para identificar la deposición de MO después del colapso de las plataformas de hielo Larsen A y B en la PAO. La baja proporción de AG poli-insaturados y la ausencia de AG poli-insaturados indicadores de diatomeas tanto en la PAO como en la NPA reflejaron una rápida degradación de estos compuestos incluso en este ambiente polar y sugirieron que por lo menos en el presente estudio, los AG poli-insaturados no se pueden usar como indicadores de MO de origen fitoplanctónica a plazo medio (años). Los CHO, PRT, LPD y la sílice biogénica no se mostraron buenos indicadores para trazar cambios recientes en la columna de agua ya que no son específicos para ninguna fuente de material. La macrofauna béntica de la PAO presentó abundancia y biomasa relativamente bajas. Típicas especies pioneras pertenecientes a la clase Polychaeta y al filum Echinodermata incrementaron la diversidad en esta región. Los perfiles de concentración de PG, abundancia de valvas de diatomeas y actividad de ^{210}Pb demostraron que este tipo de de comunidades bentónicas no produjo bioturbación

importante en el sedimento subsuperficial.

In the last 60 years air and oceanic temperatures increased in Antarctica above global average (Vaughan et al., 2001; Gille, 2002). As a consequence, the increase of glaciers retreat (Cook et al., 2005) and the thinning of ice shelves (Shepherd et al., 2003; Whingham et al., 2009) have been observed. Furthermore, ice shelf collapses became more frequent in Antarctica, as exemplified by the collapse in 2008 of Wilkins ice shelf and in 2010 of Mertz glacier. In 1995 and 2002, 4200 km^2 and 3200 km^2 of the sections A and B of the Larsen Ice shelf disintegrated, respectively (Rack and Rott, 2004). Larsen A ice shelf disintegration was preceded by three retreat episodes in 1400, 2100 and 3800 year BP (Brachfield et al., 2003), whereas ice shelf Larsen B started collapsing in 1947 after 10000 years of stability (Domack et al., 2005a). During Antarctic expedition ANT-XXIII/8 we had the opportunity to reach the Bays Larsen A and B off the Eastern Antarctic Peninsula (EAP) and sample the sediment column (the upper 30 cm). One of the objectives of the present work was to study organic matter (OM) accumulation in the sediment before and after ice shelf collapses. It is not usual to have the opportunity to analyze sediment from areas in which primary production and OM flux to the seafloor started just some years before sampling takes place. The bays Larsen A and B represented “a natural laboratory” where it was possible to investigate the recent arrival of OM onto a rather poor seabed. The quantity and the chemical quality of the OM found in EAP sediments were compared to the characteristics of the OM analyzed in sediments off the Northern Antarctic Peninsula (NAP) and the South Eastern Weddell Sea (SEWS), where no ice shelves developed at least for a thousand years (Ingólfsson et al., 1998; Anderson et al., 2002). Another objective was to identify which OM constituent among pigments (PG), amino acids (AA), fatty acids (FA), total carbohydrates (CHO), total lipids (LPD) and total proteins (PRT), was better to use as biomarker to record environmental changes. A third objective was to identify relationships between sediment chemical characteristics and benthic communities’ structure aiming to produce a comprehensive picture of the changing Antarctic ecosystem under extinct ice shelves. To accomplish with this objective abundance, biomass and diversity of the benthic macrofauna from EAP and SEWS were studied. Microscopical counts of diatom valves were carried out on EAP and NAP sediment samples to complete the information on OM sources available from data on amino acids and fatty acids. Excess ^{210}Pb activity was also measured to develop a radiochemical chronology of sedimentary events in NAP and EAP.

In NAP, pigment and amino acid concentrations were higher than in EAP throughout the sediment cores. Diatom valves, ^{210}Pb activity, pigment and amino acid vertical distributions indicated a lower input of labile OM to the seafloor and a shorter period of accumulation in EAP than in NAP. Labile OM was only found in the upper 2 cm of the sediment column in EAP. The quantity and chemical quality of the biogenic variables throughout the sediment column demonstrated that the presence of ice shelves effectively hamper the vertical input of labile OM to the seabed. Diatom valves and pigment profiles strongly suggested that this is mainly the consequence of rather limited primary production. Recently deposited OM constituents were mainly originated from diatoms in both EAP and NAP. Labile OM was vertically transported from the euphotic zone, while refractory CHO and mid-chained FA most likely accumulated by lateral advection during years of ice shelf coverage and lack of fresh OM supply. In the study area the absence of Chl*b* confirmed the lack of terrestrial inputs of OM from the Antarctic continent and the absence of *iso*- and *anteiso*-FA, hydroxylated FA and 18:1(n-7) evidenced the lack of OM of bacterial origin. Pigments revealed as the best markers to identify the deposition of OM after Larsen A and B ice shelf collapses in EAP. The very low proportion of polyunsaturated fatty acids (PUFA) and the absence of diatom PUFA, in both EAP and NAP reflected a rapid PUFA degradation even in this polar environment and suggested that, in the case of the present study, PUFA cannot be used as indicators of phytoplankton debris or fresh OM in a mid-term (years). Total CHO, PRT, LPD and biogenic silica were not good indicators to track recent changes in the water column because they are not specific to any source of material. Benthic macrofauna in EAP presented relatively low abundance and biomass. Typical pioneer species belonging to the class Polychaeta and the phylum Echinodermata increased diversity in this region. PG, diatom valves and ^{210}Pb activity profiles demonstrated that this type of benthic assemblage did not produce important bioturbation in subsurface sediment.

Polar science is receiving increasing attention due to ongoing climate change. Among other aspects, Polar Regions have shown evident signs of their sensitivity to the increase in atmospheric and oceanic temperatures, such as the dramatic reduction of seasonal sea-ice extent in the Arctic and disintegration of ice shelves in Antarctica. As an example of the efforts of the society to generate conscience and scientific information to understand and attempt to ameliorate the rapid ecosystem change in the Poles, the International Polar Year (IPY) was launched in 2007. Within the frame of this initiative, several international groups joined efforts to cover broader fields of Polar Research and make the results closer to the general public. The present work is part of such initiative and is focused on the effects that climate change imprints on the continental shelf environments in Antarctica.

In the last 60 years atmospheric and oceanic temperatures increased in the Antarctic Peninsula above the world average (Vaughan et al., 2001; Gille, 2002). This trend caused the ice shelves to retreat (Vaughan et al., 2003; Cook et al., 2005). A study of the tendency of 244 glaciers in the last 61 years showed that 75 % of the glaciers retreated from 2000 to 2004 while only 38 % of the glaciers retreated from 1945 to 1954 (Cook et al., 2005). Furthermore, from 1992 to 2001 ice shelf thickness diminished 0.27±0.11 meters par year (Shepherd et al., 2003). At the Eastern Antarctic Peninsula, in 1995 and 2002, 4200 Km^2 and 3200 Km^2 of the sections A and B of Larsen ice shelf, respectively, collapsed and rapidly disintegrated (Rott et al., 1996; Skvarca et al 1999). Ice shelf collapses in Antarctica are developing faster than predicted, as recently exemplified in March 2008 by the collapse of the Wilkins Ice Shelf, by the thinning of Pine Island Glacier further south along the Peninsula (Wingham et al., 2009) and the disintegration of ~ 2500 Km^2 of the Mertz Glacier in February 2010. After the collapses of the Larsen ice shelves, the rather stable conditions for at least a thousand years (Domack et al., 2005a) drastically changed. Primary production started developing (Bertolin and Schloss, 2009) and consequently a flux of fresh organic matter to the seafloor. This flux will enrich the surface sediment with nutritive material, which presumably will set the basis for benthic colonization. Palaeoecological studies of recolonization beneath the Amery Ice Shelf (East Antarctica) after an ice sheet retreat at the end of the last glaciation showed that benthic colonisation in the Antarctic shelf is

very low (~ 9000 yr) (Post et al., 2007). Thus, studying colonization processes at early stages in the Larsen bays will also provide insights into the evolutionary history of the abundant and highly diverse benthic communities found elsewhere in the Weddell Sea (Brey and Gerdes, 1997; Gili et al., 2006).

These communities at the southeastern Weddell Sea (SEWS) are threatened by iceberg scouring, which represents a strong source of disturbance. This mechanism is rather frequent in the Weddell Sea where 42% to 70% of SEWS bottom presents signs of iceberg disturbance and it has been catalogued as one of the five most significant sources of natural disturbance on large ecosystems (Gutt and Starmans, 2001). Iceberg scouring is likely to increase in parallel to iceberg calving induced by global warming. Evident differences in the benthic community have been observed in the Antarctic continental shelf between areas affected by iceberg scouring and undisturbed areas (Gerdes et al., 2003). After iceberg scouring events, the recovery time for an Antarctic mature benthic community is comprised between 230 and 500 yr (Gutt et al., 1996; Gutt and Starmans, 2001), with early recovery stages that may take up to 10 yr long (Teixidó et al., 2004). Recovery stages in disturbed areas in SEWS may present common patterns with those taking place off the eastern Antarctica Peninsula.

Based on the idea that climate change forces the environmental characteristics that ultimately modify the ecosystem, in this work we investigate how Antarctic continental shelf ecosystems respond to climate change through the comparison of the composition and the concentration of different organic matter constituents in the upper sediment column (approximately 30 cm depth) and macrobenthic communities from the Eastern Antarctic Peninsula (EAP), where recently ice shelf collapses occurred, and the Northern Antarctic Peninsula (NAP) and the Southeastern Weddell Sea (SEWS) continental shelves, where no ice shelves developed at least for thousands of years (Ingólfsson et al., 1998; Anderson et al., 2002).

The present work represents the first study analyzing in detail (5 mm resolution) the upper centimetres of the sediment column below recently (~10 yr) extinct ice shelves, which reflect the latest changes at the sea surface. Further, it relates chemical changes

at the sediment column presumably triggered by the disintegration of ice shelves with the actual benthic communities and describes the present state of this transforming benthic ecosystem.

Principal objectives

1. To analyze contrasting conditions in organic matter composition and accumulation in regions with and without influence of ice shelves.

Ice coverage hampers primary production (PP) (Arrigo et al., 2002; Arrigo and Dijken, 2003) and consequently the organic matter (OM) flux to the seafloor. Even if some authors studying the Ross Ice Shelf suggested that under ice shelves chemosynthesis may provide a small amount of energy for benthic organisms (Horrigan, 1981), PP under ice shelves is considered to be very low (Grebmeir and Barry, 1991; Thomas et al., 2008) making laterally advected OM the principal food input for benthic communities (Grebmeir and Barry, 1991). After Larsen A and B ice shelf collapses, PP started developing in the water column (Bertolin and Schloss, 2009) and consequently a phytoplankton detritus flux to the seafloor (Domack et al., 2005a). Based on the hypothesis that the evident changes at the sea surface will trigger changes at the seafloor through the arrival of fresh OM, this work aims to analyze the distribution of OM in the sediment column in several stations in the bays Larsen A and B to assess the lability and biological availability of the most recently deposited OM and contrast them with those in sediment samples form NAP and SEWS.

2. To identify the best OM constituents from a pool of biomarkers to record environmental changes.

With Antarctic expedition ANT-XXIII/8 we had the opportunity to reach two regions recently affected by ice shelf collapses. It is not usual to have the opportunity to analyze sediment from areas in which primary production and OM flux to the seafloor started just some years before sampling takes place. In this study, bays Larsen A and B represented “a natural laboratory” where it was possible to investigate the recent arrival of OM onto a rather poor seabed. The concentration profile vs. depth of each OM constituent is different depending on its source, consumption and also on its lability. With this work we

attempt to identify which OM constituent is better to use as biomarker to record environmental changes.

3. To identify relationships between OM distribution in the sediment and the macrobenthic community.

The relationship between benthos and the quality of the OM in the sediment is tight; thus, is difficult to distinguish which factor determines the other if there is any stronger than the other. Here, we attempt to relate sediment chemical characteristics and benthic communities' structure to produce a comprehensive picture of the changing Antarctic ecosystem under extinct ice shelves. Based on the contrast between areas with different environmental characteristics and disturbance pressures we try to identify animal-environment relationships and to understand how ongoing climate change affects and ultimately modifies the continental shelf benthic communities in Polar regions.

In addition to this General Introduction and Objectives, the thesis is composed of six Chapters, where each chapter is the edited version of a future publication in scientific journals, a Comprehensive Discussion, which summarizes the main arguments of the Discussion of each chapter in an inclusive format and as a corollary a Conclusions section. To avoid redundancy with this General introduction section a detailed Introduction dealing with the scope of each chapter is included at the beginning of the correspondent chapter. In Chapter 1 pigment concentration in sediments from the EAP and NAP is discussed. The analyzed pigments were Chl*a*, Chl*b*, Chl*c*, Pheo*a*, Pheo*b* and Pheo*c*. The quantity and the quality of OM in EAP and NAP sediments based on total hydrolyzable amino acids (THAA) and enzymatically hydrolizable amino acids (EHAA) concentrations is discussed in Chapter 2. In Chapter 3, the relationship between the amount of total carbohydrate, protein and lipid concentrations in the sediment and the abundance, biomass and diversity of the macrofaunal benthic community is studied in EAP and SEWS. The origin and the lability of the OM in EAP and NAP sediments is treated in Chapter 4, where the occurrence of particular fatty acids that are diatom indicators is compared with the total number of diatom valves counted with microscopical observations. Chapter 5 is a Short Note where the abundance of diatom valves in sediment from NAP and EAP is compared with the percentage of biogenic

silica in the same regions. In Chapter 6, the profiles of the studied OM constituents are compared with the profiles of excess ^{210}Pb activity.

Pigments in sediments beneath recently collapsed ice shelves: the case of Larsen A and B shelves, Antarctic Peninsula.

Edited version of E. Sañé, E. Isla, A. Grémare, J. Gutt, G. Vétion. Pigments in sediments beneath recently collapsed ice shelves: the case of Larsen A and B shelves, Antarctic Peninsula.

Submitted to Journal of Sea Research (SEARES-D-09-00065)

1.1 Introduction

Chlorophyll-*a* (Chl*a*), the most abundant phytoplanktonic pigment, is commonly used to estimate phytoplankton biomass in the water column, whereas the amount of its degradation product, Pheophytin-*a* (Pheo*a*), is indicative of phytoplankton physiological status (Mantoura and Llewellyn, 1983; Sun et al., 1994). Chlorophyll is degraded to phaeophytin predominantly during grazing (Shuman and Lorenzen, 1975; Hawkins et al., 1986; Bianchi et al., 1988). The longer the organic matter remains in the water column the longer it is exposed to degradation (Furlong and Carpenter, 1988; Leavitt, 1993; Bianchi et al., 2002). However, the formation of phytoplankton aggregates and diatom inclusion into faecal pellets prevents pigment degradation in the water column (Smetacek, 1985; Tallberg and Heiskanen, 1998). Chl*a* degradation is also reduced when living diatoms settle onto the seafloor (Josefson and Hansen, 2003; Lee, 1992). Both mechanisms enable the use of Chl*a* concentration in the sedimentary record as an indicator of primary production in the water column (Furlong and Carpenter, 1988; Stephens et al., 1997; Villanueva and Hastings, 2000). Nevertheless, degradation pigments are the predominant form of pigments in sediments (Repeta and Gagosian, 1987).

Pigment degradation in sediment depends on several factors such as pigment specific lability (Cariou-Le Gall and Blanchard, 1995), microbial activity (Bianchi et al., 1988), light, oxygen (Leavitt, 1993) and sedimentation rate (Lee, 1992). Bacteria decompose organic matter while microbial grazers are responsible of organic matter remineralization, which is higher in oxic than in anoxic sediments (Lee, 1992; Sun et al., 1993b; Andersen, 1996). Anoxia and high sedimentation rates limit microbial grazing (Lee, 1992) and consequently enhance organic matter preservation. Sediment mixing by bioturbation in the upper centimeters causes an oxygen gradient redistribution that controls organic matter degradation (Sun and Dai, 2005). Bioturbation is mainly driven by deposit feeders and infauna, which also actively participate in chlorophyll degradation (Bianchi et al., 1988; Ingalls et al., 2000). Physical events such as intense sedimentation can also modify oxygen availability burying the organic matter originally settled at the upper ventilated layers of the seabed into deeper anoxic layers (Sun and Dai, 2005). Chl*a* and Pheo*a* are subject to the same mixing processes but Pheo*a* is less labile and degrades slower than Chl*a* (Sun et al., 1993a; Stephens et al., 1997; Kowalewska and Szymczak, 2001). Furthermore,

Pheo*a* is subject to production over the entire core depth (Barranguet et al., 1997). Chl*a* to Pheo*a* ratio is commonly used as an indicator of Chl*a* preservation, where high values indicate a good preservation of Chl*a* (Reuss et al., 2005). The Chl*a* to Chl*c* ratio is used to estimate the proportion of organisms in the water column producing Chl*c* such as dinoflagellates, diatoms and crysophytes. However, this approach is subject to misinterpretations due to the different degradation rates of both pigments (Gillan and Johns, 1980).

In polar areas, it has been observed that Chl*a* persists longer in the sedimentary record due to low temperature and substrate concentration (Mincks et al., 2005). Ice coverage limits primary productivity in the surface layers of the water column by reducing available space for algal blooms to develop (Arrigo et al., 2002; Arrigo and van Dijken, 2003). Therefore, a small pigment concentration in underlying sediments is expected.

In January 1995, 4200 km^2 of the Larsen A ice shelf collapsed (Rott et al., 1996). This event was preceded by three retreat episodes in 3800, 2100 and 1400 yr BP (Brachfield et al., 2003). Ice shelf Larsen B started collapsing in 1947 after 10000 years of stability (Domack et al., 2005a). In March 2002, 3200 km^2 of the Larsen B ice shelf collapsed within 33 days. These events were connected to the recent temperature increase in the atmosphere (Vaughan et al., 2001) due to anthropogenic climate change (Marshall et al., 2006), which causes a reduction of the ice shelf thickness and the retreat of the glacier front (Shepherd et al., 2003; Cook et al., 2005). Ice shelf collapses at the Antarctic Peninsula are developing faster than predicted, recently exemplified in March 2008 by the collapse of the Wilkins Ice shelf further South in the Peninsula. The study of Larsen A and B sediment represents a great opportunity to investigate ecological changes generated by ice shelf collapses induced by global anthropogenic change since the last time such events occurred in these regions took place just seven years ago. Therefore, those ecosystems present early stages of reaction.

Palaecological studies of recolonization beneath the Amery Ice Shelf (East Antarctica) after an ice sheet retreat at the end of the last glaciation showed that benthic

colonisation in the Antarctic shelf is very low (~ 9000 yr) (Post et al., 2007). Recolonization after iceberg disturbance seems to be slower in the Antarctic than in the Arctic (Conlan et al., 1998; Gutt and Starmans, 2001). Off the Eastern Antarctic Peninsula (EAP) where seasonal sea ice duration is reducing (Vaughan et al., 2003) and ice shelf retreats are increasing (Scambos et al., 2000), benthic recolonization should be intensively developing. At short time scales sudden changes at the sea surface like an increase of the flux of phytoplankton detritus can be rapidly reflected in the benthic realm producing evident reactions at early stages of recolonization (Post et al., 2007).

Based on the hypothesis that after the collapse of the ice shelves primary production develops in the water column and that this change will be reflected in the seabed we expected to find evidences of such activity in the upper layers of the sediment column. Here, we present results for the first time on the pigment concentration in the sediment column beneath collapsed ice shelves and compare them with results from Antarctic shelf sediment representing ice shelf-free conditions for at least a thousand years with the aim to identify early ecosystem changes after the ice shelf collapse.

1.2 Materials and methods

In the austral summer 2006-2007, during the oceanographic cruise ANT XXIII/8, the R/V Polarstern reached the areas in the Eastern Antarctic Peninsula (EAP) where the former Larsen A and B ice shelves existed. Sediment samples were taken using a multi-corer (Barnett et al., 1984) with an inner diameter of 10 cm and up to 40 cm long. Limited by meteorological and logistical constraints five stations could be performed in the Larsen bays and two stations at the NAP, 1 off Elephant Island and 1 off the South Shetland Islands (Fig. 1.1). Six stations were located on the continental shelf within a depth range from 250 to 450 m water depth and one in the axis of a glacial trough at 850 m depth in the Larsen B embayment. Station coordinates, depth and overlying waters temperature are listed in Table 1.1. All the cores were analyzed from the top to 12 cm depth except that of Larsen A which was only 5 cm long. Cores were subsampled onboard in slices 0.5 cm thick from the top to 10 cm depth and in slices 1 cm thick from 10 to 12 cm depth. Subsamples were stored in plastic bags at -20ºC until analysis in the laboratory.

Chl*a,* Chl*b* and Chl*c* and Pheo*a*, Pheo*b* and Pheo*c* were assessed on triplicates using the spectrofluorometric technique of Neveux and Lantoine (1993). Samples (~ 0.5-1 g wet weight) were extracted in 5 ml of 90 % acetone (final concentration) at 4 ºC and in darkness for 12 h. Samples were centrifuged at 3000 rpm for 5 min and extracts were

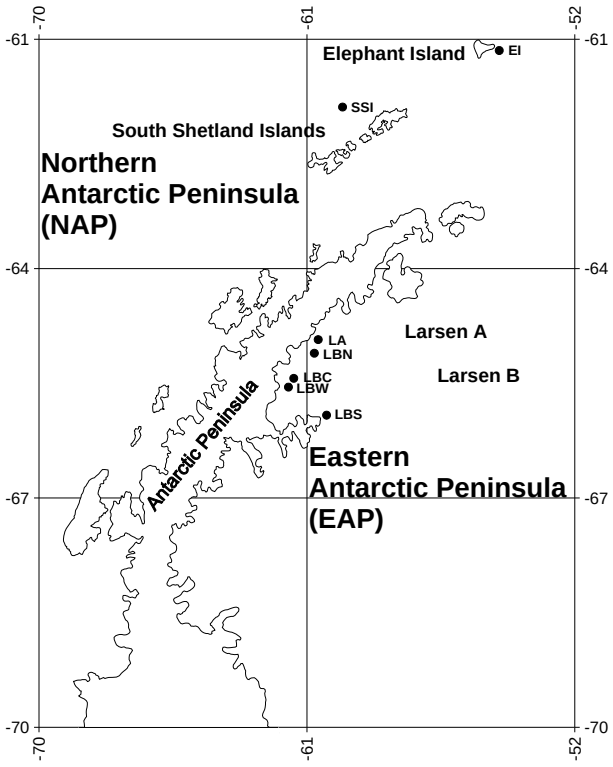

Fig. 1.1 Study area with sampling stations.

analyzed in a Perkin-Elmer Luminescence Spectrometer LS55 FL. Pigment concentrations are expressed in micrograms of pigment per gram of wet sediment. Grain size analyses were carried out using a Mastersizer 2000 (Malvern®) laser micro-granulometer.

Data were statistically treated through a multivariate analysis using PRIMER 6 software (Clarke and Gorley, 2006). Variables were normalised and a resemblance matrix was created through the measurement of Euclidean distances. A two-dimensional Non-metric Multi-Dimensional Scaling (MDS) plot was created and the ANOSIM test was runned in order to quantify differences between a priori-defined groups (Clarke, 1993). When the “Global R” statistic value, generated by ANOSIM in PRIMER, is zero (0)

there is no difference among groups, while when it is one (1) all samples within groups are more similar to one another than any samples from different groups (Clarke and Gorley, 2006).

Table 1.1 Coordinates, depth and overlying waters temperature relative of the seven sampling sites.

Core station	Lat	Long	Depth (m)	T(ºC)
Elephant Island (PS69-609)	61° 9,32' S	54° 32,27' W	404	-0.44
South Shetland Islands (PS69-675)	61° 53,10' S	59° 48,16' W	358	-0.68
Larsen B South (PS69-700)	65° 55,11' S	60° 20,14' W	446	-1.89
Larsen B West (PS69-703)	65° 33,00' S	61° 37,15' W	297	-1.98
Laesen B Central (PS69-711)	65° 26,12' S	61° 26,73' W	849	-1.89
Larsen B North (PS69-715)	65° 6,40' S	60° 45,01' W	322	-1.90
Larsen A (PS69-725)	64° 55,73' S	60° 37,23' W	239	-1.88

1.3 Results

Superficial sediment (0-1 cm) Chl*a* concentrations were similar in NAP and EAP cores (~ 0.6-0.8 µg g^{-1} WW) but diminished with depth more slightly in NAP than in EAP cores where they reduced near to zero below the upper 2 cm of sediment (Fig. 1.2). Among Larsen cores, superficial Chl*a* concentration was highest in Larsen B Central and North (~ 1.1-1.4 µg g^{-1} WW) and lowest in Larsen B West (~ 0.4 µg g^{-1} WW) (Fig. 1.2). Chl*b* was absent in both NAP and EAP cores. Chl*c* concentration both in Elephant Island and South Shetlands cores was < 0.1 µg g^{-1} WW (Fig. 1.3). Among Larsen cores, superficial Chl*c* concentration was highest in Larsen B Central and Larsen B North cores (~ 0.2-0.4 µg g^{-1} WW), whereas below the upper 2 cm of sediment the values were close to zero (Fig. 1.3).

Pheo*a* superficial concentrations were higher in NAP (~ 9 µg g^{-1} WW) than in EAP cores (~ 6 µg g^{-1} WW) (Fig. 1.2). Among Larsen cores, Pheo*a* superficial concentration was highest in Larsen B North and Larsen B Central (~ 6-7 µg g^{-1} WW) and lowest in Larsen B West (~ 1.5 µg g^{-1} WW) (Fig. 1.2). In all Larsen cores Pheo*a* concentration decreased with depth (Fig. 1.2).

Pheo*b* superficial concentration varied between 0.2 and 0.4 µg g^{-1} in NAP cores, whereas in the EAP samples no Pheo*b* was found.

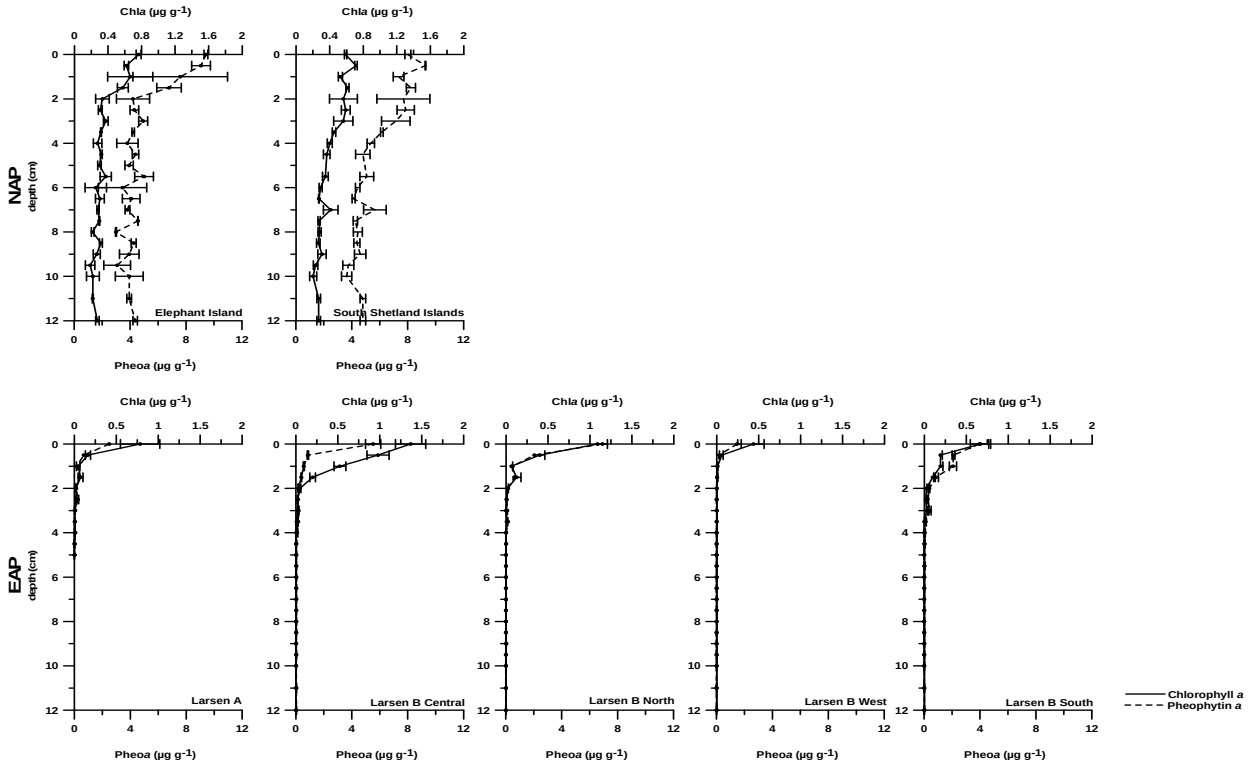

Fig. 1.2 Concentrations of Chl*a* and Pheo*a* in NAP and EAP cores from 0 to 12 cm depth (in Larsen A core, from 0 to 5 cm depth). Horizontal bars are SD.

In NAP Pheo*c* superficial sediment concentration presented values between 8 and 12 µg g^{-1} WW and decreased slightly with depth (Fig. 1.3). In Larsen B Central, Larsen B North and Larsen B South superficial concentrations of Pheo*c* were comparable to those of NAP (~ 6-9 µg g^{-1} WW) whereas they were lower in Larsen B West and A (~ 2 µg g^{-1} WW) (Fig. 1.3). In all Larsen cores there was not Pheo*c* below the upper 3 cm (Fig. 1.3).

The superficial Chl*a* to Pheo*a* ratio was ~ 0.1 in NAP cores and remained practically constant with depth (Fig. 1.4). In Larsen A, Larsen B North, Larsen B West and Larsen B South Chl*a* to Pheo*a* ratio in surface sediment was ~ 0.2-0.4 and decreased with depth whereas in Larsen B Central there was a subsurface (0.5 cm depth) peak that reached the value of ~ 1.2 (Fig. 1.4).

Chl*a* to Chl*c* ratio decreased in all cores with depth (Fig. 1.5). Superficial Chl*a* to Chl*c* ratio was ~ 180 in Elephant Island, ~ 10 in South Shetlands and ~ 6-8 in Larsen A and B samples, whereas subsurface peaks were only present in South Shetlands, Larsen A and Larsen B Central. Sediment grain size depth distribution was similar in Elephant Island and South Shetland Islands cores (80 % < 63 µm and 5 % > 200 µm) (Fig. 1.6). In Larsen B West and Larsen A the percentage of particles > 200 µm was highest (~ 10-20 %) while in Larsen B North 100 % of sediment was < 200 µm (Fig. 1.6). In Larsen B South and Central there was an increase of coarse sediment (> 63 µm) in the upper ~4 cm (Fig. 1.6).

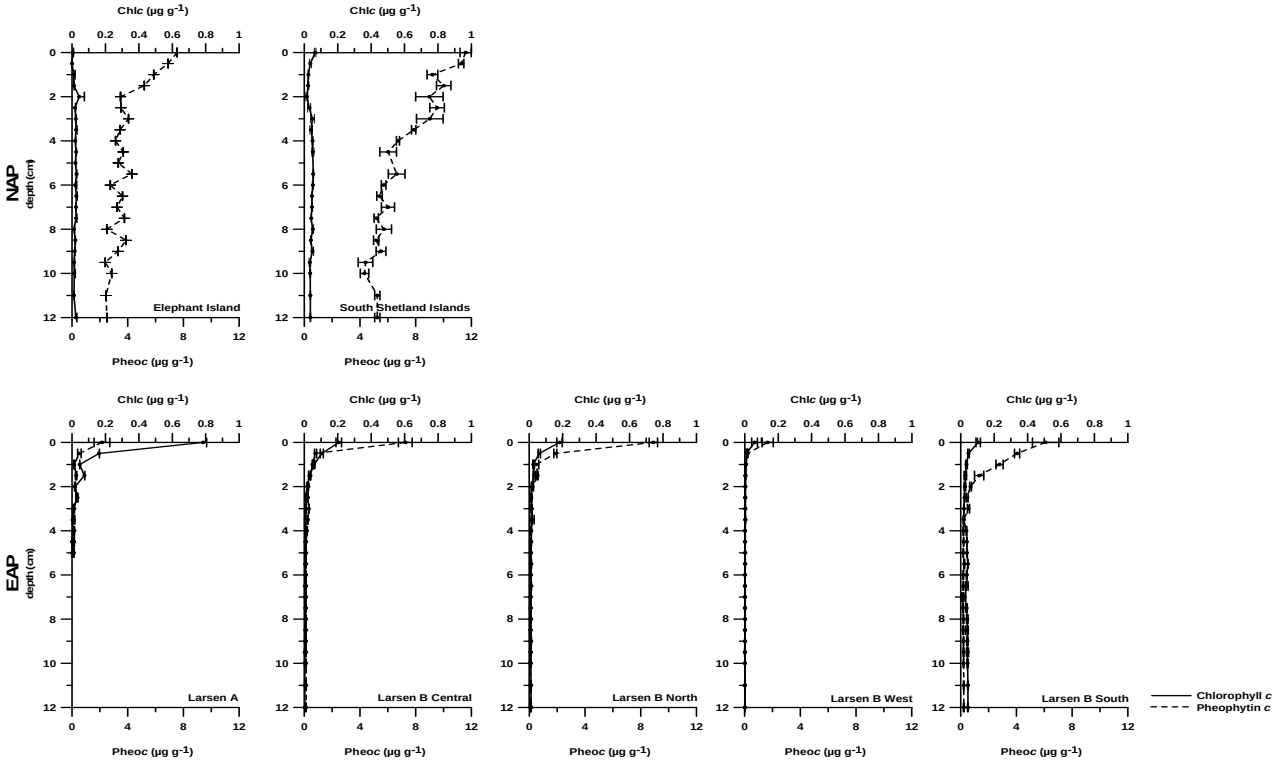

Fig. 1.3 Concentrations of Chl*c* and Pheo*c* in NAP and EAP cores from 0 to 12 cm depth (in Larsen A core, from 0 to 5 cm depth). Horizontal bars are SD.

No significant relationship was found between grain size and pigment concentrations (R^2=0.016).

To find differences in pigment distributions througout the cores among regions MDS and ANOSIM tests were performed for every core depth including all pigment variables and their ratios. Chl*b* and Pheo*b* were excluded due to the little abundances found.

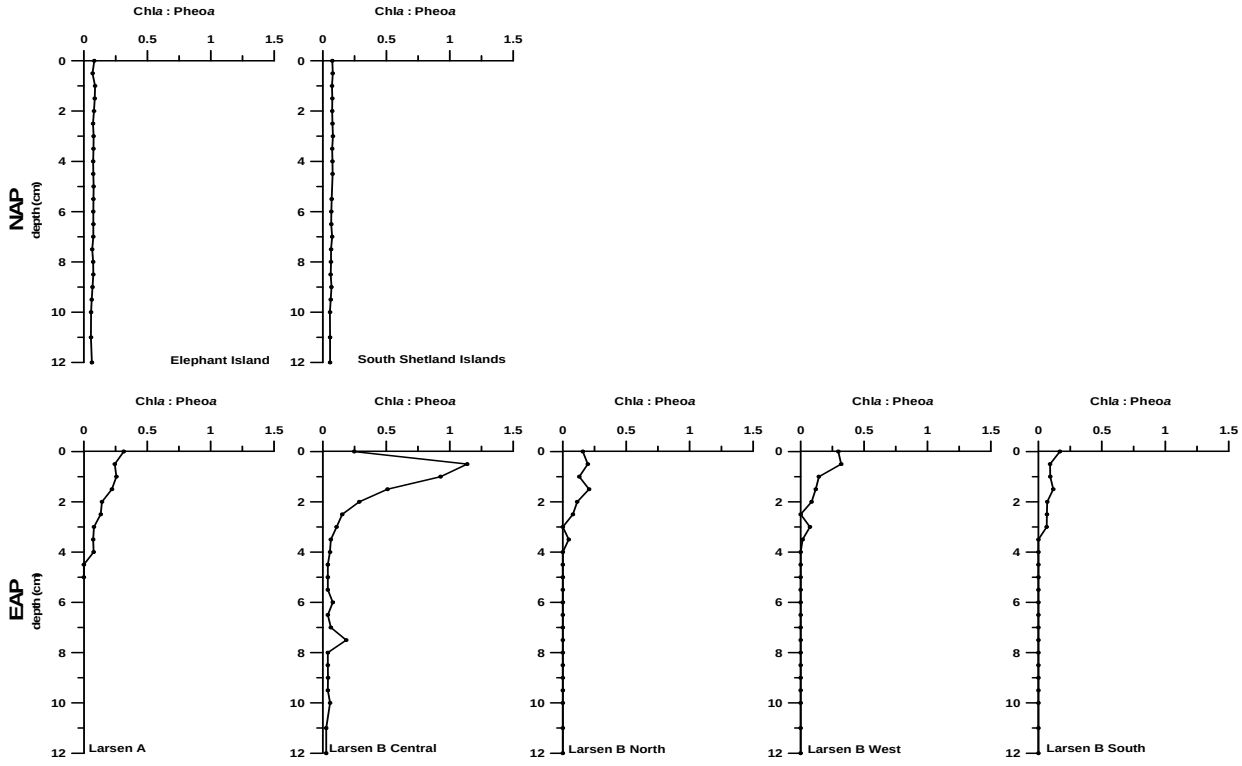

Fig. 1.4 Chl*a*:Pheo*a* ratios in NAP and EAP cores from 0 to 12 cm depth (in Larsen A core, from 0 to 5 cm depth).

The statistical tests confirmed that pigment concentrations in NAP and EAP cores were similar in the upper 1 cm (Table 1.3). Based on these criteria samples were divided into regions and the 1 cm depth horizon was used to create the groups NAP-sup, NAP-deep, EAP-sup and EAP-deep. Again MDS (Fig. 1.7) and ANOSIM tests confirmed that these divisions using the 1 cm depth horizon were effective (Global R: 0.886).

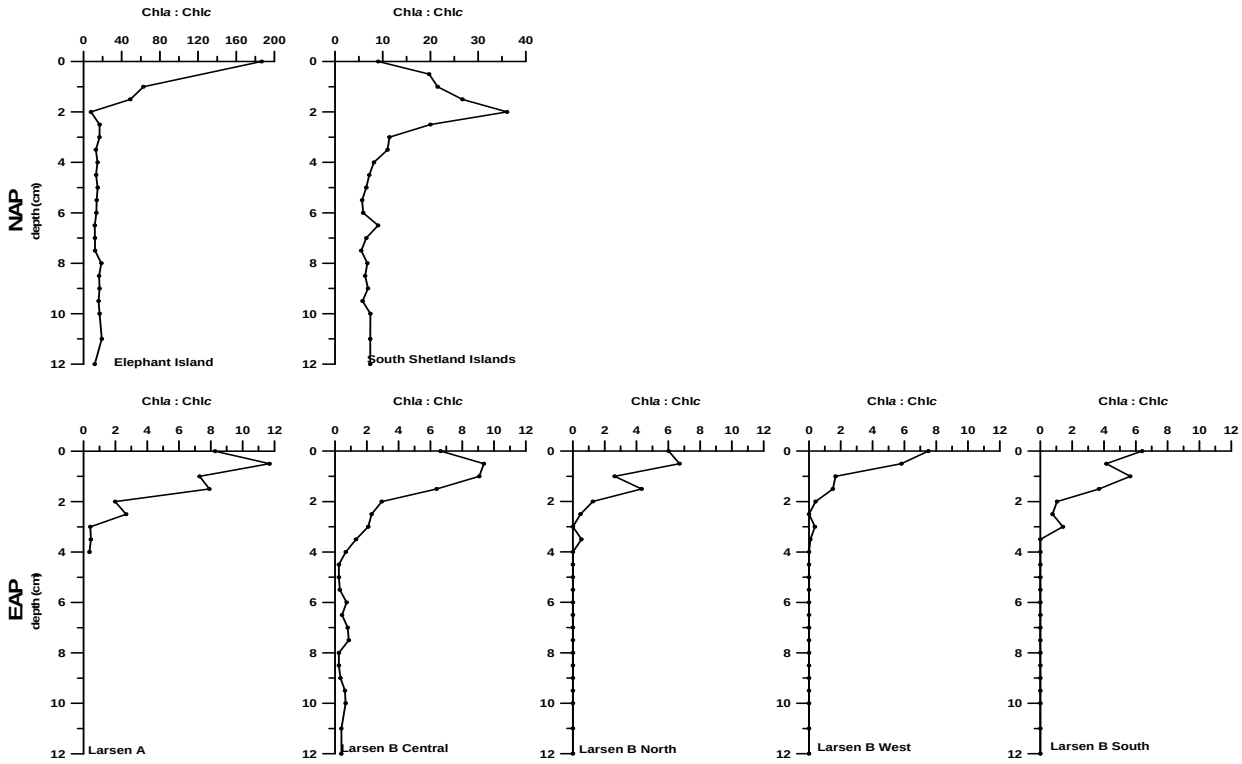

Fig. 1.5 Chl*a*:Chl*c* ratios in NAP and EAP cores from 0 to 12 cm depth (in Larsen A core, from 0 to 4 cm depth). Note that scale of horizontal axis in EAP differs from that in NAP.

1.4 Discussion

1.4.1 Sediment grain size

We showed grain size percentages related to the 63 µm and the 200 µm grain size fractions (Fig. 1.6). On the one hand, the 63 µm grain size limit is the physical threshold used to differentiate fine and coarse sediment. Higher organic contents are known to be better associated to fine sediments, due to the high surface to volume ratio (Mayer, 1994). On the other, the 200 µm fraction represents the grain size suitable to capture by filter feeders due to their anatomical limitations (Gili et al., 2001).

In all samples the sediment fraction with a grain size < to 200 µm was higher than 76%. This characteristic is favourable for the future development of filter feeder communities that correspond to the most advanced level in a benthic succession (Gutt and Piepenburg, 2003; Post et al., 2007). 63 and 200 µm grain size percentages were relatively constant with depth in all cores except in Larsen B South and Larsen B Central stations, where the fine sediment fraction was more than 95 % below the upper

4 cm (Fig. 1.6). These particular profiles suggest a recent sedimentation of coarse sediment reasonably linked to the poorly sorted sediment released by the ice after the Larsen B ice shelf collapse. In our samples, the sediment fraction < to 200 µm and

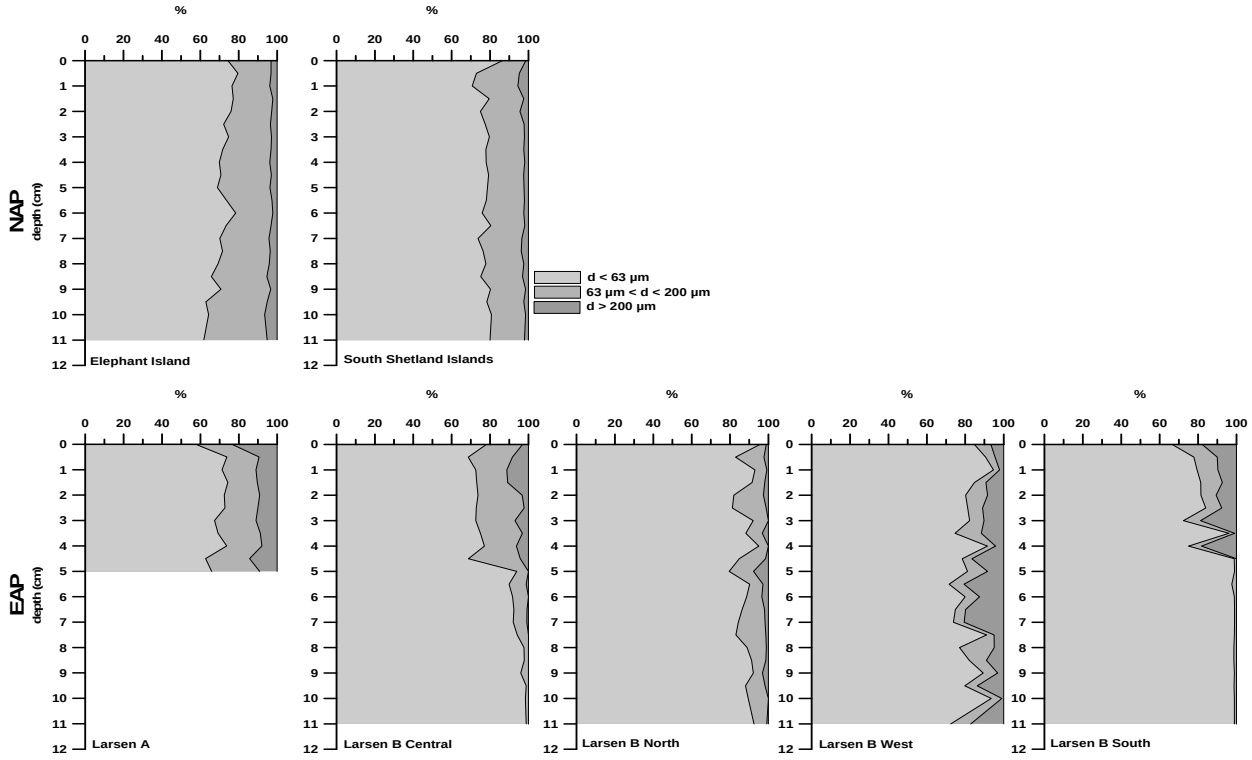

Fig. 1.6 Sediment grain size in NAP and EAP cores from 0 to 12 cm depth (in Larsen A core, from 0 to 5 cm depth).

Chl*a* values were pooorly correlated (R^2=0.016). This poor correlation indicates that differences between regions are not the consequence of sediment grain size.

1.4.2 Origin of pigments in NAP and EAP sediment columns

The last major collapse of the Larsen A ice shelf occurred in 1995, whereas in Larsen B took place in 2002 (Shepherd et al., 2003). Before these dates study areas in Larsen A and B were covered by ice sheets, which greatly limited light and consequentely

Table 1.2 Chl*a* concentration and Chl*a*:Pheo*a* ratio in a global context.

Chl*a*	Chl*a*:Pheo*a*	Location	Depth	Sampling	Technique	Reference
8.72 µg g^{-1} (0-0.5 cm)	no Pheo*a* data	Atlantic Ocean (UK)	mid-tide level	spring-summer	Fluor.	Anderson et al., 1981
48.25 µg g^{-1} (0-1 cm)	41.538	Atlantic Ocean (USA)	subtidal	spring	HPLC	Sun and Dai, 2005
75 µg g^{-1} (0-0.2 cm)	no Pheo*a* data	Atlantic Ocean (USA)	58 m	winter	Fluor.	Radziejewska et al., 1996
2.29 µg g^{-1} (box corer)	no Pheo*a* data	Atlantic Ocean (USA)	785	summer	Spectr.	Cahoon et al., 1994
2.42 µg g^{-1} (0-1 cm)	(Chl*a*/TPheo) 0.626	Atlantic Ocean (Africa)	50 m	spring	Spectr.	Berghuis et al., 1993
50 µg g^{-1} (0-1 cm)	(Chla/Pheoa_{1+2})	Gulf of Mexico (USA)	mudflat	summer	HPLC	Buffan-Dubau and Carman, 2000
480 µg g^{-1} (0-1 cm)	no Pheo*a* data	Pacific (central Chile)	< 100 m	autumn	Fluor.	Gutierrez et al., 2000
0.06 µg g^{-1} (0-0.5 cm)	0.08	Equatorial Pacific	4300-4400 m	autumn	HPLC	Smith et al., 1996
0.1 µg g^{-1} (0-0.2 cm)	0.092	Central Equat Pacific	4412 m	autumn	HPLC	Stephens et al., 1997
14.05 µg g^{-1} (0-0.25 cm)	0.52	Deception Island	155 m	spring	Fluor.	Baldwin and Smith, 2003
3.07 µg g^{-1} (0-0.5 cm)	no Pheo*a* data	Western Antarctic Peninsula	550-625 m	summer	Fluor.+HPLC	Mincks et al., 2005
0.27 µg g^{-1} (0-0.5 cm)	no Pheo*a* data	(Crozet Isles) Southern Ocean	4200 m	summer	HPLC	Hughes et al., 2007
90 µg g^{-1} (0-0.5 cm)	~ 0.04	Southern Ocean (Indian sector)	~ 4700 m	autumn	Spectrofluor.	Riaux-Gobin et al., 1997
0.4 µg g^{-1} (0-1 cm)	no Pheo*a* data	Ross Sea	567 m	spring-summer	Fluor.	Fabiano and Danovaro, 1998
0.59-0.77 µg g^{-1} (0-0.5 cm)	**~ 0.05-0.2**	**NAP**	**~ 400 m**	**spring-summer**	**Spectrofluor.**	**Sañé et al., present work**
0.44-1.37 µg g^{-1} (0-0.5 cm)	**~ 0.2-1.2**	**EAP**	**~ 400 m**	**spring-summer**	**Spectrofluor.**	**Sañé et al. present work**
20 µg g^{-1} (0-1 cm)	no Pheo*a* data	North Sea	~ 25 m	spring	HPLC	Stoeck and Kröncke, 2001
10.7 µg g^{-1} (0-1 cm)	no Pheo*a* data	North Sea	20 m	summer	HPLC	Dauwe and Middelburg, 1998

primary production in the water column (Thomas, 1963). After the ice shelf collapsed, the sea surface became partially covered by ice sheet debris and seasonal sea ice. Remaining ice-free areas provided suitable conditions for phytoplankton to develop. The consequent blooms increased the concentration of Chl*a* in the water column as detected via satellite and by the increase in diatom abundances in the sedimentary record (Domack et al., 2005a; Sañé et al. *d*-CAP.4). In our results, the relatively high Chl*a* to Pheo*a* ratio showed that fresh Chl*a* is present in the upper millimetres of the seabed in the continental shelf at both Larsen regions followed by a drastic decrease below the upper 2 cm layer (Fig. 1.4). The Larsen A and B regions are under the influence of the Weddell Gyre current regime, which is able to transport fine sediment particles from higher latitudes at the southeast up to the tip of the Antarctic Peninsula (Diekmann and Kuhn, 1999). Supposing that pigments were coming from the more productive regions at the southeast (Moore and Abbott, 2000) a currentward, decreasing concentration pattern in surface sediment would be expected. However, the geographical distribution of surface sediment concentrations did not show any clear pattern. In addition, the high Chl*a* to Pheo*a* ratios indicate a small degree of degradation making unlikely that the provenance of phytoplankton pigments is far from the deposition sites. Thus, suggesting that pigment occurrence in the upper millimetres of the seabed is the result of the input of local primary production. However, to develop a comprehensive explanation on the organic matter distribution in the surface sediment within the bay a complete set of current measurements is needed.

The sediment recovered at 800 m depth in a sea floor depression in the axis of a glacial trough (station Larsen B Central) presented the highest surface sediment concentrations, suggesting that the trough acts as a sediment trap that concentrates pigments from adjacent regions (Isla et al., 2004).

The obvious lack of terrestrial inputs from the Antarctic continent confirmed by the absence of Chl*b* made evident the algal origin of the pigments found in EAP (Furlong and Carpenter, 1988; Stephens et al., 1997).

Chl*a* to Chl*c* ratio, used to estimate the proportion of dinoflagellates, diatoms and crysophytes, in NAP showed the highest values (Fig. 1.5), also corresponding to the highest abundance of Pheo*c* (Fig. 1.3). These results together with the lower chemical stability of Chl*c* relative to Chl*a* (Gillan and Johns, 1980) and the well developed

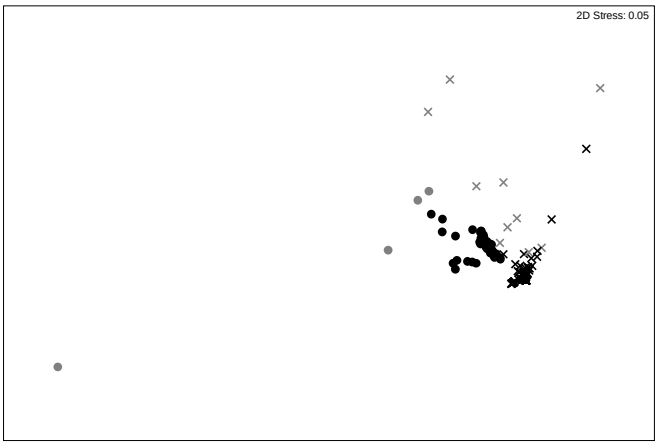

Fig. 1.7 MDS plot of the 7 stations pigment data considering the four groups of samples NAP-sup (gray dot), NAP-deep (black dot), EAP-sup (gray cross) and EAP-deep (black cross) (*sup*: from 0 to 1 cm, *deep*: from 1 cm to the bottom of the core). Variables included in the statistical test are: Chl*a*, Chl*c*, Pheo*a*, Pheo*c*, Chl*a*:Pheo*a* and Chl*a*:Chl*c*. The Global R of the ANOSIM test is 0.886.

Table 1.3 Results of the ANOSIM test to verify differences between NAP and EAP samples from 0 to 5 cm depth. Variables included in the statistical test are: Chl*a*, Chl*c*, Pheo*a*, Pheo*c*, Chl*a*:Pheo*a* and Chl*a*:Chl*c*.

Deep	Global R
0-0.5 cm	0.655
0.5-1 cm	0.564
1-1.5 cm	0.818
1.5-2 cm	1
2-2.5 cm	0.945
2.5-3 cm	1
3-3.5 cm	1
3.5-4 cm	1
4-4.5 cm	1
4.5-5 cm	1

benthic community in NAP (Piepenburg et al., 2002) in contrast to the scarce benthic fauna in EAP (Sañé et al. *c*-CAP.3) indicate that there is a more active degradation of Chl*c* in NAP than in EAP.

1.4.3 Vertical distribution of pigments in the sediment column

Pigment concentrations in surface sediment (upper 10 mm) in Larsen A and B regions were similar or even higher than those found in the NAP (Fig. 1.2 and 1.3). However, pigment profiles below this depth were different between the two regions with a sharp decline in EAP sediment. Except for Larsen B Central, all samples were collected on the continental shelf (250 to 450 m water depth). Thus, degradation in the water column, assuming that the transport to the seabed had a larger vertical than lateral component, should have been similar among most of the core sites. Assuming this, several hypotheses arise to explain differences in Chl*a* profiles.

The first hypothesis is that photosynthesis has been developing for the last hundreds of years in the NAP water column, whereas in the Larsen A and B regions, local phytoplankton productivity began only after the ice shelves collapsed. The second is that in the present time primary productivity is higher in the NAP than in the EAP causing higher accumulation rates and a consequent deeper penetration of Chl*a* in the sediment column. The third is that bioturbation is more active in NAP sediment producing a thicker upper mixed layer. However, the most realistic scenario is a combination of factors which we suggest are responsible for the differences between the vertical distribution of Chl*a* in NAP and EAP cores.

1st hypothesis: Photosynthesis pigments start settling onto the seabed only after the ice shelf collapsed

To verify the first hypothesis it would be necessary to estimate organic matter accumulation rates in the sea floor. Unfortunately, we lack such information. However, previous studies under ice shelves showed that the scarce benthic life in those environments depends on the organic matter advected from the open ocean where photosynthesis can be performed (Horrigan, 1981; Castellini et al., 1984). For example, no chlorophyll pigments were found in water samples beneath the Ross Ice Shelf in an area of 40 m ice thickness and about 20 km from the open sea (Littlepage and Pearse, 1962). In the present study the core sites were located between 14 km and 30 km from the ice shelf edge in Januray 2002, which was more than 200 m thick (Doake et al., 1998; personal observation), making photosynthesis unlikely to occur above the sampling sites before 2002.

Chl*a* may accumulate deeper than 2 cm in the sediment column (Cahoon et al., 1994; Villanueva and Hastings, 2000; Stoeck and Kröncke, 2001; Reuss et al., 2005) suggesting that the lack of Chl*a* below the upper 2 cm in Larsen sediments reflects the recent supply of pigments to the sediment column.

2rd hypothesis: Primary production is higher in the NAP

Assuming that degradation in the water column is similar in EAP and NAP areas we hypothesize that primary production is higher in NAP than in EAP.

Albeit chlorophyll concentration in the upper cm of the sediment was similar in both regions (with the exception of Larsen Central and North), the deeper penetration of chlorophyll in NAP sediment indicates a more abundant supply of organic matter that maintain the higher amount of chlorophyll measured along the 12 cm-long sediment cores. Although the ice shelf collapse opened space at the EAP sea surface enabling phytoplankton blooms, the large amount of icebergs that calved from the ice shelves and the seasonal sea ice bridging them together greatly reduced the available ice-free areas (personal observation) drastically limiting primary production (Arrigo et al., 2002; Arrigo and van Dijken, 2003). Primary production off the South Shetland and Elephant Islands is rather moderate to low (Bodungen et al., 1986; Holm-Hansen and Mitchell, 1991; Holm-Hansen et al., 1997) but the region has been free of ice shelves for more

than a thousand years (Ingólfsson et al., 1998; Anderson et al., 2002). Thus, it seems that the constant supply of organic matter to the NAP seabed during a longer time span has developed a larger chlorophyll inventory in the sedimentary record and that the ice coverage in the Larsen regions still limits primary production to a greater extent.

3nd hypothesis: Bioturbation is more active in NAP sediment

In the NAP cores, the vertical distribution of pigments showed a relatively constant pattern (Fig. 1.2 and 1.3). This distribution strongly suggests that efficient biological mixing occurs, making particle transport in the sediment column faster than deposition (Sun et al., 1994). Bioturbation has been identified as an element that increases sediment mixing (Sun and Dai, 2005) and enhances Chl*a* degradation (Bianchi et al., 2000) especially in the superficial sediment (Ingalls et al., 2000), increasing sediment porosity and creating space for microbial grazers (Lee, 1992). In the continental slope off North Carolina, bioturbation was responsible for the distribution of viable diatoms and Chl*a* throughout the upper 14 cm of the sediment column (Cahoon et al., 1994). The higher degradation status demonstrated by a lower Chl*a* to Pheo*a* ratio and the higher Pheo*c* concentrations found in NAP sediment gives support to the hypothesis that bioturbation is most likely responsible for the vertical distribution pattern in those sites. Deposit-feeder ingestion rates are positively related to the amount of organic matter supplied to the sediment (Taghon and Jumars, 1984) thus a high pigment flux reaching NAP seafloor would lead to an enhanced deposit feeder degradation activity and bioturbation.

The case of Larsen B Central is different to the rest of the sediment cores. This core showed an evident subsuperficial peak in the Chl*a* to Pheo*a* ratio profile. Subsurface peaks can be generated by several factors: a) a pulsed deposition after an algal bloom combined with higher decomposition rates at surface than at deeper layers (Sun et al., 1991); b) the domination of non-diffusive mixing over vertical transport of Chl*a* through “conveyor-belt” feeding type (Boudreau, 1986); c) a massive sediment deposition event that may develop an anoxic layer specially in submarine canyons or sea floor depressions similar to site Larsen B Central (Paull et al., 2003; Puig et al., 2004).

The latter process most likely ocurred at Larsen B Central site developing higher Chl*a*:Pheo*a* ratios as a consequence of higher Chl*a* fluxes enhanced by particle

trapping within the trough that increases the organic matter concentrations in the upper centimeters of the sediment column.

Based on the three hypotheses we suggest that pigment distributions in EAP cores reflect the relatively short period of time transcurred since phytoplanktonic activity start developing, the low primary production and bioturbation intensity resulting in a thin sediment mixed layer.

1.4.4 Relationships to benthic ecology

In EAP, the high chlorophyll concentration in surface sediment, the good preservation state of Chl*a* given the Chl*a* to Pheo*a* ratio and the low Pheo*c* concentration suggest that fresh organic matter is reaching the sea bed and undergoing low degradation. Clearly, benthic consumers in Larsen A and B regions are surface deposit feeders, such as holothurians, whereas in the NAP are burrowers, which feeding behavior tend to homogenize and deepen the sediment upper mixed layer (Diaz et al., 1994). The pigment profiles in EAP strongly suggest abscence of bioturbation driven by infauna, which would transport the organic matter deeper in the sediment column, as observed in NAP and also in the continental slope off North Carolina (Cahoon et al., 1994; Díaz et al., 1994). The lack of benthic infauna in the EAP coincided with observations under more than 400 m of ice in the Ross Ice Shelf, where an assemblage of amphipods, isopods and fish was present but no infauna was found (Lipps et al., 1979). This characteristic would represent the still early stage of benthic recolonization on Larsen A and B continental shelves, which is characterized by the occurrence of mobile deposit feeders (Gutt and Piepenburg, 2003).

Before Larsen A and B ice shelf collapsed primary production in the upper meters of the water column was limited by light. Under this condition only organisms adapted to a low food regime such as those found at the deepsea inhabited the seafloor as observed from ANT XXIII/8 ROV images (Gutt et al., submitted). After the ice shelf collapses in 1995 and 2002 light could penetrate in the water column in the embayments Larsen A and B enhancing the phytoplanktonic activity and presumably icreasing the organic matter supply to the seafloor which started a benthic community

succession. Benthic successions have been deeply studied in the Arctic and in the Antarctic continental shelves after iceberg scouring (Gutt et al., 1996; Conlan et al., 1998; Gerdes et al., 2003; Gutt and Piepenburg, 2003). In the polar regions this is a frequent cause of benthos disturbance above 350 m depth (Gutt, 2000; Gutt and Starmans, 2001). Benthic successions studied after iceberg scouring are up to date the only available tool to predict changes and future development of the benthic fauna beneath collapsed ice shelves. The continental shelf below the former ice shelves presented a heterogeneous pattern of areas affected by iceberg scourings lacking of benthic fauna and areas without scours and scattered mobile fauna. This mixture of environments is similar to that found in other Antarctic continental shelf regions with the difference that areas without the influence of ice shelves present benthic communities at higher stages of recolonisation at the border of the scours. It seems that in Larsen A and B areas reconolisation will start with the typical early stage of succession represented by mobile deposit feeders but also by a few sessile pioneer species (Gutt and Piepenburg, 2003; Gutt et al., submitted; Sañé et al. *c*-CAP.3). Based on the structure of benthic communities developing at the eastern Weddell Sea, the succession pattern will follow the sequence of colonization by polychaetes and then by filter feeders like sponges and bryozoans (Gutt and Starmans, 2001; Teixidó et al., 2004: Post et al., 2007).

In Table 1.2 we reported some Chl*a* values from different geographical regions including NAP and EAP results of the present study. NAP and EAP Chl*a* values are similar to those from sediments recovered at approximately 600 m of depth in the Ross Sea (Fabiano and Danovaro 1998) and to those from deep sea sediments (Smith et al., 1996; Stephens et al., 1997; Hughes et al., 2007). In Larsen areas, like in the deep sea, these concentrations can only sustain mobile deposit feeder communities characteristic of the first benthic succession stages (Gutt and Piepenburg, 2003). In the actual scenario of increasing atmospheric temperatures it is likely that primary production rates will increase in the Larsen regions by blooming in new open, ice-free areas. Consequentely more organic matter will arrive to the benthic realm. These conditions may lead to the establishment of the rich benthic communities found in the southeastern Weddell Sea. Clearly the desintegration of ice shelves is opening space for benthic colonization of the Antarctic continental shelf.

1.5 Conclusions

Phytoplankton pigments were found in sediment cores recovered below the former Larsen A and B ice shelves. The distribution of pigments throughout the sediment cores showed evident differences between NAP and EAP regions leading to hypothesize that the flux of phytoplankton pigments to the continental shelf in the Larsen embayments is only recent and still weak. However, the presence of fresh pigments in the upper 10 mm of the sediment column in the Larsen areas indicates they originate in local primary production. The surface pigment concentrations found in the Larsen embayments are similar to those found in deep-sea environments. These characteristics set conditions for the recolonization of the continental shelf under the recently desintegrated ice shelves. Disintegration of ice shelves is opening space for the development of benthic communities on the Antarctic continental shelves.

Amino acids in sediments from the Northern Antarctic Peninsula and the Larsen A and B bays off the Eastern Antarctic Peninsula: evidence of fresh organic matter deposition after ice shelf collapses.

Edited version of E. Sañé, E. Isla, A. Grémare, K. Escoubeyrou. Amino acids in sediments from the Northern Antarctic Peninsula and the Larsen A and B bays off the Eastern Antarctic Peninsula: evidence of fresh organic matter deposition after ice shelf collapses.

Submitted to Journal of Marine Systems (MARSYS-D-10-00031)

2.1 Introduction

Biogenic particulate matter produced in the euphotic zone of the oceans sinks down to the seabed, where it is mineralized and ultimately get buried and preserved in the sedimentary record. However, more than 90% of the organic matter (OM) produced in the euphotic zone of the open ocean is degraded in the mesopelagic zone before it reaches deeper waters (Bishop et al., 1978; Knauer and Martin, 1981). Sediment trap studies in the North and Equatorial Pacific have shown that only ~15% and ~1% of the OM of phytoplanktonic origin was still present at 100 and 4000 m depth, respectively, whereas ~ 40 % of the amino acids were lost between 100 and 1000 m depth (Martin et al., 1987; Lee and Wakeham, 1988; Wakeham et al., 1997). OM degradation is also intense in highly productive waters (Lee and Cronin, 1984), as in the Peru upwelling region where almost 90 % of amino acids are decomposed witin the upper 50 m of the water column (Lee and Cronin, 1982). In spite of such an intense degradation in the water column, a small fraction of the amino acid pool reaches the seafloor and is incorporated in the sediment column (Wakeham et al., 1997), both in shallow and in deep waters and sediments (Hedges et al., 2001). OM inclusion into fecal pellets and the formation of diatom aggregates enhance OM preservation (Tallberg and Heiskanen, 1998; Josefson and Hansen, 2003) through a reduction of particles surface/volume ratio which increases sinking velocity (Ploug et al., 2008). Amino acid concentrations in the sedimentary record give information about the state of degradation of OM and on its sources (Ingalls et al., 2003). Most of amino acid analyses in the literature refer to total hydrolysable amino acids (THAA) (Burdige and Martens, 1988; Cowie and Hedges, 1992b; Cowie et al., 1992; Horsfall and Wolff, 1997; Keil et al., 1998; Ingalls et al., 2003; García and Thomsen, 2008), which correspond to the amino acids hyrolysed after a complete acidic digestion (HCl 6N, 100°C) that releases all the amino acids into a solution, whereas analyses of enzymatically hydrolysable amino acids (EHAA), which correspond to the fraction of amino acids potentially digested by organisms, are less common (Gupta and Kawahata, 2004). EHAA:THAA ratio is indicative of the digestibility (lability) of particulate organic matter (POM) (Mayer et al., 1995; Dauwe et al., 1999; Medernach et al., 2001; Grémare et al., 2003).

As a consequence of global warming, 4200 km^2 of the Larsen A ice shelf collapsed in 1995 (Rott et al., 1996) and 3200 km^2 of the Larsen B ice shelf collapsed in 2002 (Rack and Rott, 2004). These collapses opened space at the sea surface setting the basis for new primary production through photosynthesis, which was negligible below ice shelves (Littlepage and Pearse, 1962). Our working hypothesis was that such an increase in primary production at the sea surface should enhance amino acids deposition onto the seabed below the previously existing ice shelves. The present study aims at analyzing the distribution of amino acids in the sediment column at several stations within the Larsen A and B embayments, recently affected by ice shelf collapses, and drawing comparisons with the North Atlantic Peninsula, where no ice shelf has been present for thousands of years (Ingólfsson et al., 1998; Anderson et al., 2002).

2.2 Materials and Methods

2.2.1 Sediment collection and preparation

During the expedition ANT XXIII/8 in austral summer 2006-2007 onboard the R/V *Polarstern,* sediment cores were collected at 7 stations, 2 in the Northern Antarctic Peninsula (NAP) off Elephant Island (EI) and South Shetland Islands (SSI), and 5 off the Eastern coast of the Antarctic Peninsula (EAP), within the Larsen A (LA) and B (LB) embayments (Fig. 2.1). All stations were located on the continental shelf at a water depth between 200 and 400 m, except for station Larsen B Central (LBC), which was 849 m deep in the axis of a glacial trough. As stated above, EI and SSI stations have been free of ice shelf influence for thousands of years while the Larsen area was previously covered by an ice shelf, which recently collapsed due to global warming.

At each station, a sediment core (10 cm in diameter and up to 19 cm long) was collected using a multi-corer (Barnett et al., 1984) and sliced on board (slices were 0.5 cm thick from 0 to 10 cm depth and 1 cm thick from 10 to 19 cm depth). After slicing samples were immediately frozen and stored at -20ºC. Back at the laboratory, they were freeze dried and stored at ambient temperature prior to analysis. Sediment grain size analyses were carried out using a Mastersizer 2000 (Malvern®) laser micro granulometer.

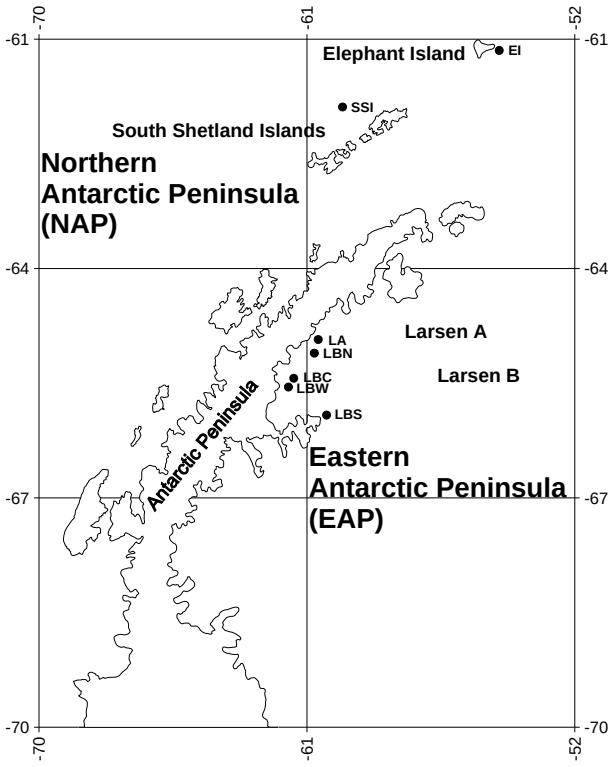

Fig. 2.1 Study area with sampling stations.

2.2.2 THAA and EHAA

THAA and EHAA were assayed using High Performance Liquid Chromatography (Lindroth and Mopper, 1979; Cowie and Hedges, 1992a). For THAA analyses, 15 mg DW of sediment were submitted to a strong acid hydrolysis (500 µl of 6NHCl, 100°C, 24h, under vacuum). Subsamples of the hydrolyzates (0.4 ml) were neutralized with 0.4 ml of 6N NaOH and buffered with 0.8 ml of H_3BO_3 (0.4M, pH 8). Fluorescent derivatives were obtained by adding 6 µl of an orthophtaldialdehyde solution (125 mg in 2.5 ml of methanol and 0.125ml of mercaptoethanol) and 400 µl of H_3BO_3 to 100 µl of those samples. THAA identification was based on retention times within an HPLC column (Lindroth and Mopper, 1979) and achieved through comparison with a standard containing 21 amino acids. Homoserine and s-methyl cysteine were also used as internal standards to help amino acid identification. THAA quantification was based on

fluorescence measurements (excitation wavelength: 335 nm, emission wavelength: 450nm).

EHAA were extracted following the biomimetic approach proposed by Mayer et al (1995). Digestion was mimicked through the addition of proteinase-K (1 mg ml^{-1}) to quantify the available fraction of the amino acid pool. Approximately 200 mg DW of sediment were poisoned with 1 ml of a solution containing 2 inhibitors of bacterial active transport systems (0.1M sodium arsenate and 0.1mM pentachlorophenol within a pH 8 sodium phosphate buffer). This mixture was let to incubate for 1 h. 100 µl of proteinase K solution (1mg ml^{-1}) were then added and the samples incubated for 6 h at 37°C. Samples were then centrifuged to discard remaining particulate material. Pure TCA (75 µl) was added to 750 µl of supernatant to precipitate macromolecules, which are considered to be non suitable for absorption by the benthic fauna. The supernatant (750 µl) was then hydrolyzed and processed as described for THAA. In addition, a blank accounting for possible degradation of the enzyme was carried out.

We quantified the concentrations of 15 amino acids (Medernach et al., 2001), namely: aspartic acid (ASP), glutamic acid (GLU), histidine (HIS), arginine (ARG), lysine (LYS), alanine (ALA), glycine (GLY), threonine (THR), isoleucine (ILEU), leucine (LEU), phenylalanine (PHE), serine (SER), valine (VAL), tyrosine (TYR) and taurine (TAU). THAA and EHAA concentrations were expressed in nanomoles of amino acids per miligram dry weight of sediment (nmol mg^{-1}DW). When comparing with literature data, we used and average molecular weight of 132 g for conversion in weight units (Grémare et al., 2002).

2.2.3 Lability indices

The enzymatically hydrolyzable amino acids to total hydrolyzable amino acids ratio (EHAA:THAA) (Medernach et al., 2001; Grémare et al., 2002, 2003), and the index proposed by Dauwe et al (1999) were both used as lability indices. The Dauwe's index (DI) is based on a principal component analysis (PCA) carried out on a THAA spectra measured on a large variety of POM sources differing by their lability. Its computation consists in a correction and a summation of the factor coefficients for each amino acid along the first axis (i.e., the one reflecting most degradation) of the PCA. Methionine was not included in corresponding computations due to detection problems.

2.2.4 Statistics

Relationships between amino acid contents and sediment grain size were assessed using simple linear regression models linking the proportion of fines and either THAA or EHAA concentrations.

Comparisons of relationships between THAA and EHAA and depth in the sediment column among stations were assessed using covariance analyses (ANCOVAs). At EI and SSI, changes in concentrations with depth showed continuous exponentially decreasing patterns. ANCOVAs were thus carried out on $\log_{10}$ transformed concentrations of the whole vertical profiles. At all 5 Larsen stations, THAA and EHAA profiles showed typical discontinuous patterns characterized by higher values and sharper decreases in the top of the sediment column. ANCOVAs were thus carried out on untransformed data and separately for the surface and deep layers. The delimitation between these two layers was based on the Chlorophyll-*a* (Chl*a*) and Chlorophyll-*c* (Chl*c*) concentrations reported by Sañé et al. (*a.*-CAP.1) for the same sediment cores. Comparison of interceptions in the surface layers model was used to assess differences in surface concentrations between stations, whereas comparisons of slopes both in the surface and deep layers models were used to assess differences in the decrease of concentrations with depth in the sediment column.

Correlation analyses (simple linear regression models) were used to assess changes in EHAA:THAA ratio and DI with depth in the sediment column at each station.

THAA spectra was classified using non parametric Multidimensional Scaling (MDS) (Euclidean distance) based on percent contributions. The effects of stations and depth in the sediment column on THAA spectra were assessed using a Two-Way ANOSIM test.

The overall significance of the difference in THAA and EHAA spectra was assessed using non parametric Multidimensional Scaling (MDS) (Euclidean distance based on percent contributions) and the associated One-Way ANOSIM test.

Relationships between EHAA:THAA ratios and DIs were assessed using simple linear regression models.

The preferential association of each individual amino acid with the EHAA fraction was assessed through the proportion of samples (i.e., combination of stations and depths in the sediment columns) where the relative contribution of a particular amino acid was higher in EHAA than in THAA. We used simple linear regression models to assess the

relationship between these proportions and individual amino acid scores provided by Dauwe et al. (1999).
All procedures were carried out using either the Primer 6® (Clarke, 1993; Clarke and Gorley, 2006) or the Statgraphics® software.

2.3 Results

All stations were muddy with proportions of fines (i.e., particles less than 63 µm in diameter) in surface sediment between 58% (LA) and 96% (LBN). Changes in the proportion of fines along the sediment column differed between stations (Fig. 2.2). This proportion was almost constant at SSI, LBN, LBW and LA. Sediments were finer at depth at LBC and LBS, whereas they tended to be coarser at EI. There were significant negative correlations between the percentage of fines and both THAA (N=115, r^2=0.095, p<0.001) and EHAA (N=115, r^2=0.043, p=0.026) concentrations, however the proportions of the variances explained by corresponding linear regression models were very low.

THAA and EHAA concentrations decreased along the sediment column at all 7 studied stations (Fig. 2.3 and 2.4). At EI and SSI, changes in THAA and EHAA were best described using simple exponential regression models (Table 2.1). Surface THAA concentration was significantly higher in SSI than in EI (ANCOVA, p<0.001) and there was no significant difference in the decrease in THAA concentration along the sediment column at these two stations (ANCOVA, p=0.234). Surface EHAA concentration was significantly higher at SSI than at EI (ANCOVA, p<0.001). The decrease in EHAA concentration along the sediment column was higher at EI (ANCOVA, p=0.014).

All Larsen stations were characterized by sharp declines in THAA and EHAA concentrations in the top of the sediment column and lower ones in deep sediment layers. The thickness of the portion of the top sediment column featuring those declines was 2 cm at all stations but LBW where it was only 1 cm. Surface concentrations of THAA and EHAA significantly differed between Larsen stations (Table 2.1, ANCOVAs,

p<0.001 and p=0.017, respectively). Surface THAA concentration was lower at LBW, intermediate at LA and higher at LBS, LBN and LBC. There was no significant difference among stations in the decrease of THAA and EHAA concentrations with depth in the top sediment column (Table 2.1, ANCOVAs, p=0.734 and p=0.559, respectively). In deep sediments, there were significant differences in the intercepts (Table 2.1, p<0.001 for both THAA and EHAA) and the slopes (Table 2.1, p=0.005 and p<0.001 for THAA and EHAA, respectively) of the regression models linking concentrations with depths in the sediment column. These slopes were higher at LA, LBS and LBC for THAA and at LBW, LA and LBS for EHAA (Table 2.1). THAA and EHAA concentrations deep in the sediment column were less than 1.5 $nmol.mg^{-1}$DW both at LBS and LBW, which hampered both the computation of EHAA:THAA ratios and the analysis of amino acid spectra. Corresponding samples were thus excluded of the following analyses.

EHAA:THAA ratios tended to decrease with depth in the sediment column at all stations but LBC (N=21, r=0.703, p<0.001) (Fig. 2.5, Table 2.2).

THAA spectra differed significantly between stations (Fig. 2.6) and depths within the sediment column (Two-Way ANOSIM, R=0.626 and R=0.387, respectively p<0.001 in both cases). THAA spectra thus tended to be similar for sediment layers of similar depth and belonging to the same station.

DI correlated negatively with depth in the sediment column at all stations except at LBS and LA (Fig. 2.7, Table 2.3). EHAA:THAA ratio and DI correlated positively only at stations SSI (N=19, r=0.477, p=0.039) and LA (N=12, r=0.733, p=0.007) (Table 2.4).

In spite of the confounding effect of stations and depths within the sediment column, there were, significant differences in THAA and EHAA spectra (Fig. 2.8, One-way ANOSIM, R=0.745, p<0.001). Average THAA and EHAA spectra are shown in Fig. 2.9. ARG, GLY, HIS and ASP contributed more to THAA than to EHAA. Conversely, LEU, ILEU, PHE, VAL and ALA contributed more to EHAA than to THAA. EHAA enrichment factors were between 0 (ARG) and 1 (LEU, ILE, PHE, ALA and VAL). They did not correlate significantly with the individual amino acid scores reported by Dauwe et al. (1999) (Fig. 2.10; N=12, p=0.234).

Table 2.1 Main characteristics of the regression models linking THAA and EHAA with depth within the sediment column. Significant negative correlations are in bold. Abbreviations are the same as in **Fig. 2.1**.

THAA

Station	Model	Layer	n	r	p	intercept	slope
EI	exponential	whole core	19	-0.810	<0.001	1.941	-0.059
SSI	exponential	whole core	19	-0.905	<0.001	1.088	-0.019
LBS	linear	0-2 cm	5	-0.786	0.115	7.663	-2.008
LBS	**linear**	**2.5-11 cm**	**11**	**-0.635**	**0.036**	**2.318**	**-0.227**
LBW	linear	0-1 cm	4	-0.884	0.116	3.121	-1.118
LBW	**linear**	**1.5-11 cm**	**11**	**-0.657**	**0.028**	**1.864**	**-0.147**
LBC	linear	0-2 cm	5	-0.852	0.066	8.746	-2.520
LBC	**linear**	**2.5-19 cm**	**16**	**-0.844**	**<0.001**	**5.945**	**-0.212**
LBN	linear	0-2 cm	5	-0.658	0.227	6.585	-1.403
LBN	**linear**	**2.5-11 cm**	**12**	**-0.646**	**0.026**	**3.703**	**-0.128**
LA	linear	0-2 cm	3	-0.886	0.306	5.123	-0.906
LA	**linear**	**2.5-7 cm**	**9**	**-0.829**	**0.006**	**4.752**	**-0.267**

EHAA

Station	Model	Layer	n	r	p	intercept	slope
EI	**exponential**	**whole core**	**19**	**-0.903**	**<0.001**	**0.903**	**-0.103**
SSI	**exponential**	**whole core**	**19**	**-0.918**	**<0.001**	**0.548**	**- 0.028**
LBS	**linear**	**0-2 cm**	**4**	**-0.957**	**0.043**	**1.762**	**-0.503**
LBS	linear	2.5-11 cm	11	-0.510	0.109	0.908	-0.072
LBW	linear	0-1 cm	4	-0.734	0.226	1.120	-0.349
LBW	**linear**	**1.5-11 cm**	**11**	**-0.653**	**0.029**	**0.958**	**-0.100**
LBC	linear	0-2 cm	5	-0.809	0.097	3.076	-1.036
LBC	**linear**	**2.5-19 cm**	**16**	**-0.561**	**0.024**	**1.799**	**-0.043**
LBN	linear	0-2 cm	5	-0.435	0.464	1.929	-0.224
LBN	linear	2.5-11 cm	12	-0.161	0.617	0.933	-0.018
LA	linear	0-2 cm	3	-0.868	0.331	1.397	-0.325
LA	linear	2.5-7 cm	9	-0.565	0.113	1.189	-0.084

2.4 Discussion

Studies regarding biogeochemical variables beneath ice shelves are scarce (Littlepage and Pearse, 1962; Lipps et al., 1979). The few existing observations have shown that chlorophyll pigment concentrations in the water column are negligible below thick ice shelves and that the few but diverse benthic fauna living beneath these shelves depend on a food supply made of detrital material originating beyond the shelf boundaries (Littlepage and Pearse, 1962; Lipps et al., 1979; Riddle et al., 2007). The recent collapse of the Larsen A and B ice shelves provides a unique opportunity to track changes on the benthic realm linked to drastic changes at the sea surface. We compared THAA and EHAA concentrations in continental shelf sediments from: (1) EAP, where two ice shelf collapses recently occurred, and (2) NAP, which has been free of ice shelves for thousands of years (Ingólfsson et al., 1998; Anderson et al., 2002). With this approach we tried to find out whether fresh OM reaches the seabed in

the EAP region (Wakeham et al., 1997; Ingalls et al., 2003). Our results showed the lack of any clear relationship between sediment grain size and amino acid concentrations. Thus, differences in sediment granulometry do not explain the distribution of THAA and EHAA at our sampling stations.

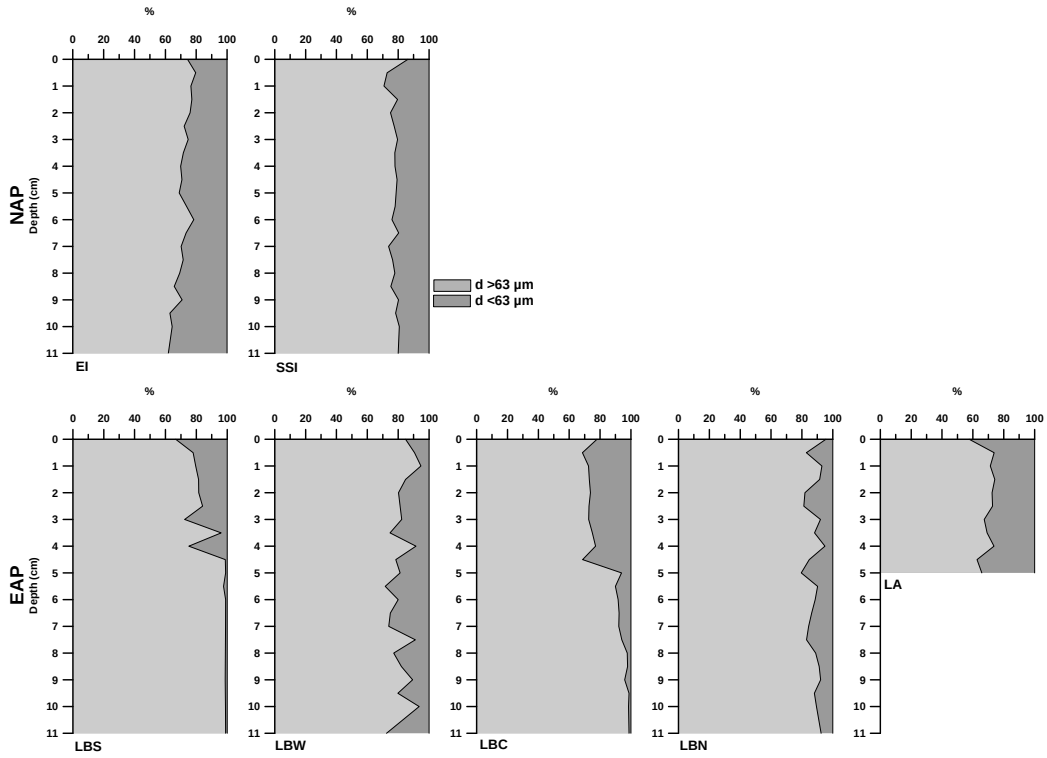

Fig. 2.2 Vertical profiles of the proportions of fines at the 7 sampling stations. Same abbreviations as in **Fig. 2.1.**

2.4.1 Impact from ice shelf collapses: comparison with literature data and pigment distribution in NAP and EAP

We have compiled values of THAA and EHAA concentrations in the upper sediment column (varying from 5 mm to 5 cm) from several regions and environment (Table. 2.5). THAA and EHAA superficial concentrations in NAP and EAP were similar to those measured in the NW Mediterranean continental shelf at ~300 m depth (Grémare et al., 2002) and in the deep NE Atlantic Ocean at 4850 m depth (Horsfall and Wolff, 1997). They were higher than those measured in the NE Pacific Ocean continental shelf at

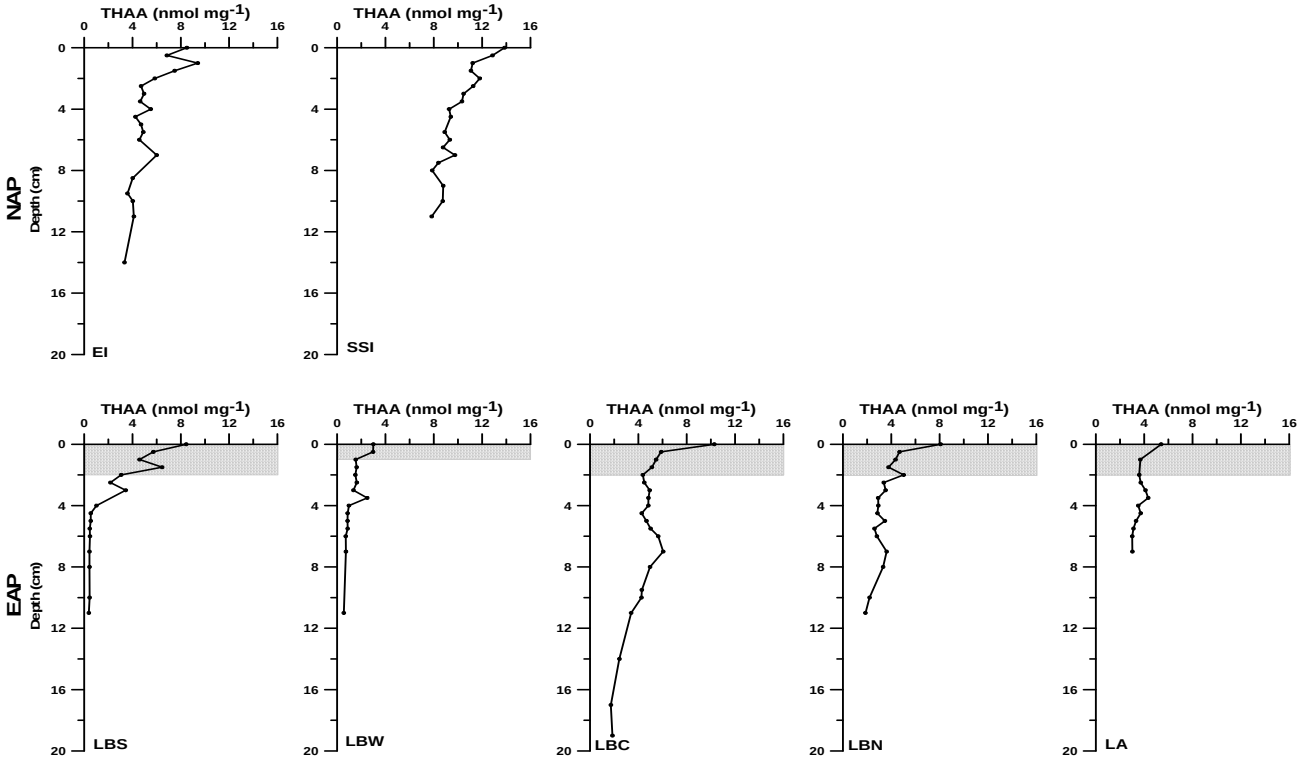

Fig. 2.3 Vertical profiles of THAA concentrations at the 7 sampling stations. Same abbreviations as in **Fig. 2.1.**.

170 m depth where most of the analyzed material was of continental origin (Degens et al., 1964) and lower than those reported for the silt deposit north of Quinault Canyon, at 133 m depth off the Washington coast, where the Columbia River constitutes an important source of POM to the shelf (Keil et al., 1998). EHAA values from the upper 5 cm depth were within the range of those measured at 10-20 m depth in a New Caledonian coastal lagoon characterized by a very low lability of sedimentary organics (Dalto et al., 2006) (Table 2.5). NAP and EAP superficial sediment (0-0.5 cm depth) EHAA:THAA ratios were similar to those recorded in a NW Mediterranean coastal lagoon (Carlier et al., 2007), and at 17 m depth in the Gulf of Lions where, based on isotopic evidence, phytoplankton was presumably the main source of OM (Grémare et al., 2002; Carlier et al., 2007). These comparisons suggest that THAA and EHAA concentrations are similar in the studied area and in lower latitude environments where

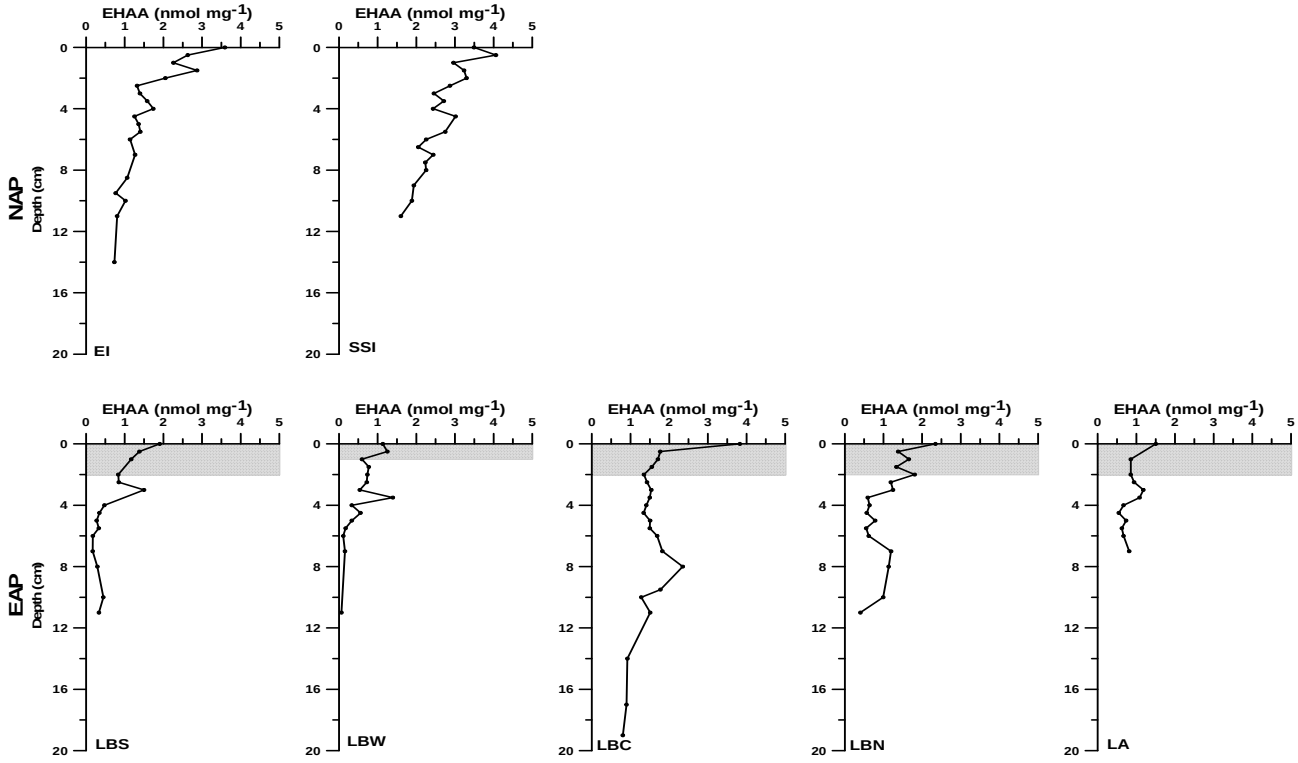

Fig. 2.4 Vertical profiles of EHAA concentrations at the 7 sampling stations. Same abbreviations as in **Fig. 2.1**.

the OM supply to the seabed is of local origin, not limited by ice and vary seasonally. This supports the hypothesis that recently produced THAA and EHAA are reaching the seabed in EAP due to the ongoing production of OM following the collapse of ice shelves. EHAA concentrations in NAP and EAP indicate that the seabed receives OM usable by benthic organisms as in shallow low latitude areas, where the high lability of OM reflects recent particle deposition (Grémare et al., 2003; Dalto et al., 2006). The high proportion of labile OM in both NAP and EAP superficial sediments may be linked to the fast transport of OM from the sea surface thereby supporting the idea of a developing primary production in this area. Comparisons of NAP and EAP with other shallow coastal areas and post-bloom conditions (Grémare et al., 2003; Ingalls et al., 2003) show that OM lability in NAP and EAP sediments is rather high, which further suggests a switch from a non productive state due to the limiting effect of ice shelves to a more productive regime after their collapse.

This interpretation is further supported by the comparison of amino acid and

Table 2.2 Main characteristics of the regression models linking EHAA:THAA with depth within the sediment column. Significant positive correlations are in bold. Abbreviations are the same as in **Fig. 2.1**.

Station	Model	Layer	n	r	p	intercept	slope
EI	linear	whole core	19	-0.767	<0.001	0.354	-0.013
SSI	linear	whole core	19	-0.529	0.020	0.287	-0.005
LBS	linear	whole core	4	0.988	0.012	0.228	0.023
LBW	linear	whole core	7	0.364	0.422	0.405	0.015
LBC	**linear**	**whole core**	**21**	**0.703**	**<0.001**	**0.291**	**0.009**
LBN	linear	whole core	17	-0.076	0.772	0.303	-0.002
LA	linear	whole core	12	-0.329	0.296	0.256	-0.006

chloropigment profiles recorded in NAP and EAP sediments (Sañé et al. *a.*-CAP.1). Chloropigment profiles clearly differ in NAP and EAP. In EAP, Chl*a* and Chl*c* concentrations are higher in the upper (from 0 to 2 cm depth in LBS, LBC, LBN and LA, and from the 0 to 1 cm depth in LBW) than in the lower part of the sediment. Conversely, in NAP pigment concentration decrease with depth is less evident (Sañé et al. *a.*-CAP.1). These differences can be interpreted as resulting from the initiation of an enhancement of benthic/pelagic coupling in EAP after ice shelf collapses (Sañé et al. *a.*-CAP.1). THAA and EHAA vertical profiles were similar to chloropigment ones with higher concentrations in the surface than in the deep sediment in EAP and a steady decline with depth in NAP. Even if primary production in the EAP region is probably still be limited by the large number of icebergs (personal observation), which greatly reduce the space for phytoplankton to bloom (Arrigo et al. 2002; Arrigo and van Dijken, 2003), our results suggest a significant increase in OM deposition after ice shelf collapses within the Larsen areas.

2.4.2 The particular case of LBC

The high EHAA:THAA ratio values found below 8 cm depth in the sediment column at LBC (Fig. 2.5) suggest the presence of labile material originating from a different source than phytoplankton based on the fact that pigment analyses showed that Chl*a* and Pheo*a* were exhausted in the upper 2 cm of the sediment column (Sañé et al. *a.*-CAP.1). A plausible explanation is linked to the contribution of labile amino acids from the low- activity cold seep located in the immediate vicinity of LBC, which showed anaerobic methane oxidation as deep as 1 m in the sediment column (Niemann et al.,

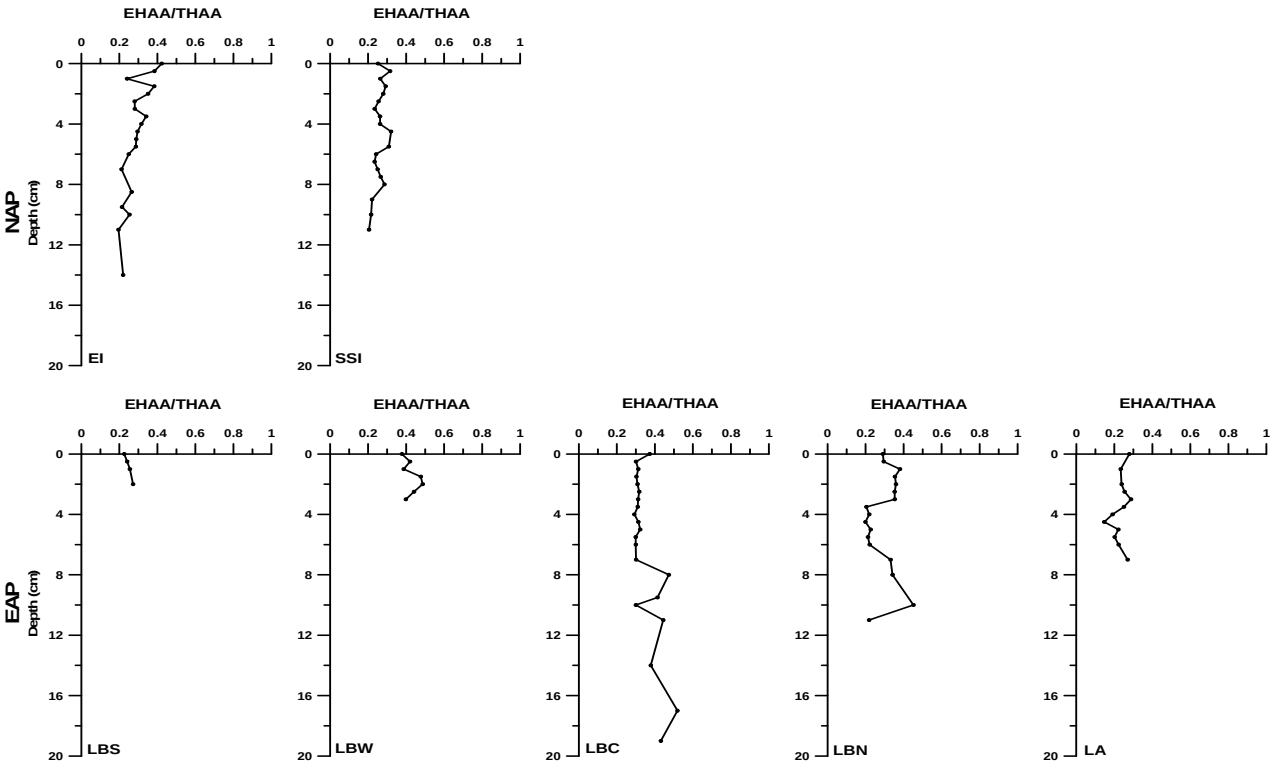

Fig. 2.5 Vertical profiles of EHAA/THAA ratios at the 7 sampling sites. Same abbreviations as in **Fig. 2.1**.

2009). It is remarkable that the Larsen B Central station in the axis of a glacial trough is acting as a sediment trap that accumulates OM of good lability with similar characteristics or even better than the adjacent continental shelf despite being more than 800 m deep. Similar results were obtained in a submarine canyon from 300 to 500 m depth in the Western Iberian Margin which accumulates more phytodetritus and bioavailable OM than the open slope (García and Thomsen, 2008).

2.4.3 Comparison between EHAA and THAA spectra and between lability indices

There were significant differences in THAA and EHAA spectra. The five most abundant THAA and EHAA (Gly, Ala, Ser, Glu and Asp) (Fig. 2.9) were the same in NAP and EAP. Moreover these amino acids are also predominant in the western Pacific section of the Southern Ocean (Ingalls et al., 2003), in the NW Atlantic Ocean (Burdige and Martens, 1988), the Peru upwelling region (Henrichs et al., 1984) and the Bay of Bengal (Unger et al., 2005). This suggests that these amino acids are the most abundant in marine sediments.

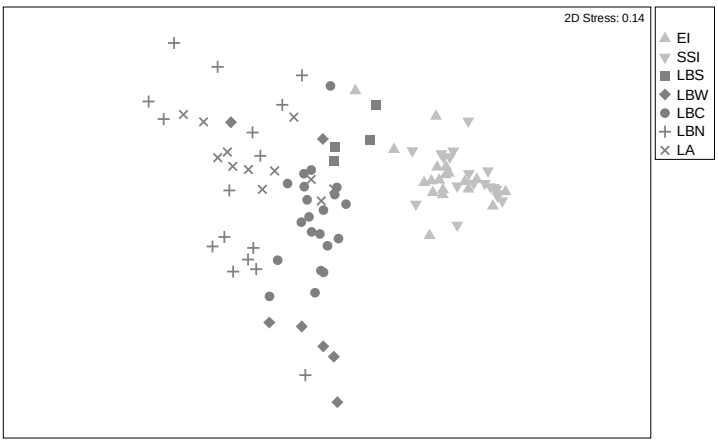

Fig. 2.6 MDS plot of THAA spectra. Same abbreviations as in **Fig. 2.1**.

Amino acid concentration in the sediment column depends on the source and the degradation status of OM (Ingalls et al., 2003). Gly, Ser and Thr are associated with biogenic opal (King, 1974, 1977; Kröger et al., 1996, 1999) since diatom cell walls have a protein-silica complex enriched in these particular amino acids (Hecky et al., 1973; Siezen and Mague, 1978). The similar contribution of Thr (THAA) in NAP (6.70%) and EAP (7.71%) could suggest a similar abundance of diatoms in the sediment in both regions (Brown and Landry, 2001; Ingalls et al., 2003). Conversely, Gly (THAA) and Ser (THAA) relative abundances were higher in NAP (20.54% and 11.21%, respectively) than in EAP (17.84% and 8.20%, respectively) superficial sediment. High concentrations of Gly can also be related to bacteria cell-walls, which have a peptidoglycan highly enriched in Gly (Salton, 1960; Bidle and Azam, 1999; Ingalls et al., 2003). The $CaCO_3$-associated THAA (Asp and Glu) relative abundances in the superficial sediment were similar in NAP (15.44% for Asp and 10.08% for Glu) and in EAP (16.46% for Asp and 12.71% for Glu) suggesting no difference between NAP and EAP in the occurrence of calcareous plankton in the sediment (e.g., foraminiferans, coccolithophorids or pteropods) (King, 1974, 1977; Ittekkot et al., 1984).

Table 2.3 Main characteristics of the simple linear regression models linking DI with depth within the sediment column. Significant negative correlations are in bold. Abbreviations are the same as in **Fig. 2.1**.

Station	n	r	p	intercept	slope
EI	**19**	**-0.507**	**0.027**	**0.630**	**-0.036**
SSI	**19**	**-0.733**	**<0.001**	**0.486**	**-0.042**
LBS	4	-0.401	0.503	1.211	-0.207
LBW	**7**	**-0.860**	**0.013**	**-0.207**	**-0.685**
LBC	**21**	**-0.647**	**0.002**	**0.090**	**-0.051**
LBN	**17**	**-0.529**	**0.029**	**0.437**	**-0.154**
LA	12	-0.386	0.215	0.137	-0.062

THAA represent the totality of amino acids present in the sediments whereas EHAA represent the fraction of THAA, which can potentially be digested by benthic organisms (Mayer et al, 1995). Significant differences between THAA and EHAA spectra have been found in NAP and EAP sediments, which supports previous results in the NW Mediterranean (Medernach et al., 2001). Asp (acidic), Arg (basic) and His (basic) together with Gly (neutral) contributed more to THAA than to EHAA. Our results thus suggest that these amino acids (in prevalence charged) are associated to the most refractory fraction of OM. Conversely, the neutral Leu, Ileu, Phe, Val and Ala, contributed more to EHAA than to THAA, thereby suggesting that they are associated to the most labile fraction of OM. Even if basic amino acids (His, Arg and Lys) are sometimes considered less stable than acidic ones (Asp and Glu) (Degens et al., 1964), it is often suggested that all charged amino acids are strongly adsorbed onto clay minerals and are therefore less susceptible to degradation than neutral ones (Weiss, 1969; Theng, 1974), which is in accordance with our results. Neutral Gly was preserved in diatom cell walls (Hecky et al., 1973), while Ala instability was linked to

Table 2.4 Main characteristics of the simple linear regression models linking EHAA/THAA with DI at the 7 sampling stations. Significant positive correlations are in bold. Abbreviations are the same as in **Fig. 2.1**

Station	n	r	p	intercept	slope
EI	19	0.225	0.356	0.168	0.960
SSI	**19**	**0.477**	**0.039**	**-0.427**	**2.709**
LBS	4	-0.993	0.007	5.022	-16.687
LBW	7	-0.307	0.503	1.380	-6.121
LBC	21	-0.269	0.238	0.348	-1.679
LBN	17	0.420	0.094	-1.736	5.071
LA	**12**	**0.733**	**0.007**	**-1.515**	**6.117**

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the easily broken peptide linkages related to this neutral amino acid (Schroeder and Bada, 1976). The cellular Tyr, Phe and Glu are easily degraded by trophic activity (Lee and Cronin, 1984; Lee and Wakeham, 1989).

THAA spectra differed significantly between stations and depths within the sediment column, which allowed for the computation of DI. We found a significant positive correlation between DI and EHAA:THAA ratio only at SSI and LA stations. The concordance between these two lability indices was thus rather low, which can be partly explained by the fact that EHAA:THAA ratios and DI do not account for the same range of lability. According to Dauwe et al. (1999), EHAA:THAA ratio is considered a good indicator of lability predominantly during initial or intermediate states of degradation. Nevertheless, and from a more mathematical standpoint, the lack of correlation between EHAA:THAA ratios and DI was due to the lack of correlation between the contribution of each individual amino acid to DI (Dauwe et al 1999) and their EHAA enrichment factors (present study). The comparison between these two parameters allowed for the identification of several amino acids whose contributions to THAA are problematic to interpret in terms of OM lability (i.e., namely His, Tyr, Thr, Ala and Val). Further studies are now clearly needed to: (1) unravel the particular status of these amino acids relative to OM lability, and (2) test the possible use of THAA spectra to assess OM lability within the same range as EHAA:THAA ratios.

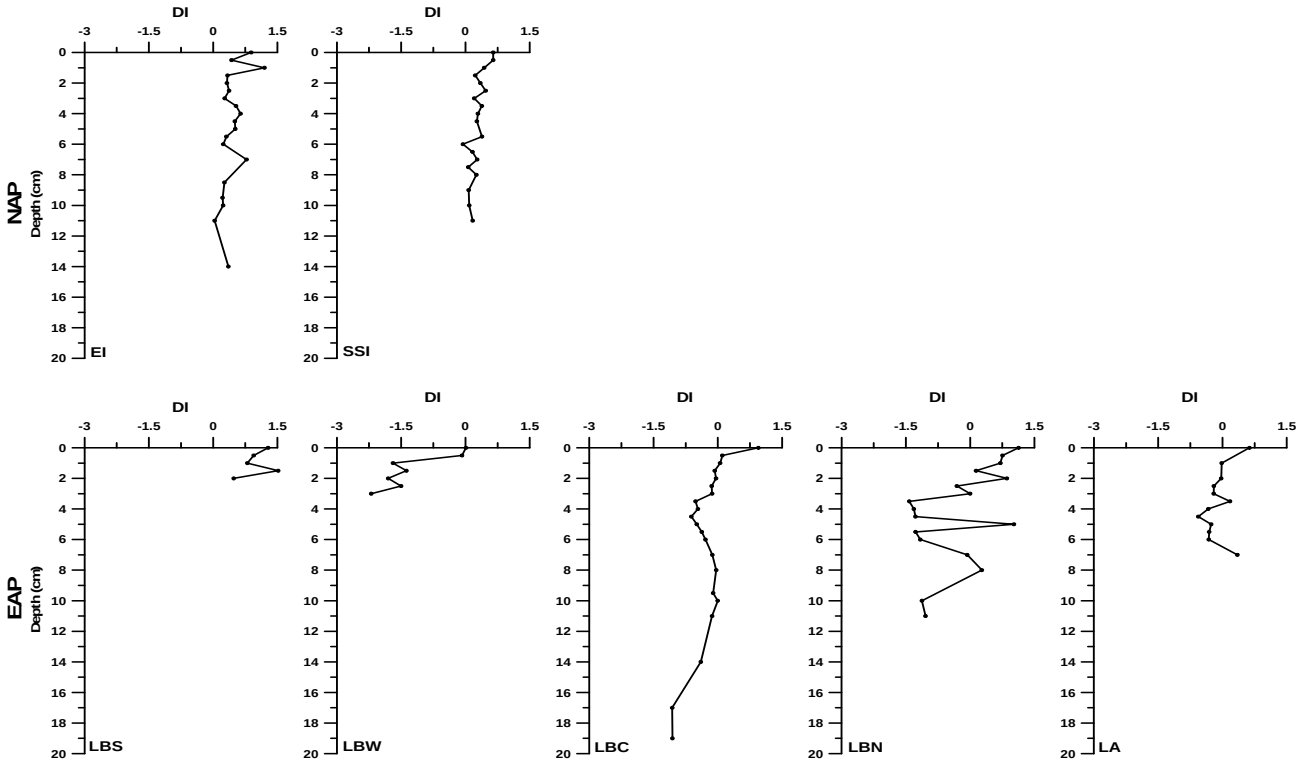

Fig. 2.7 Vertical profiles of DIs at the 7 sampling stations. Same abbreviations as in **Fig. 2.1**.

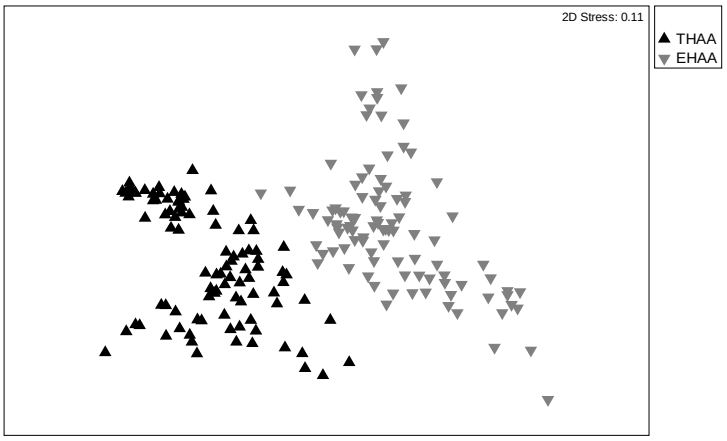

Fig. 2.8 MDS plot of THAA and EHAA spectra.

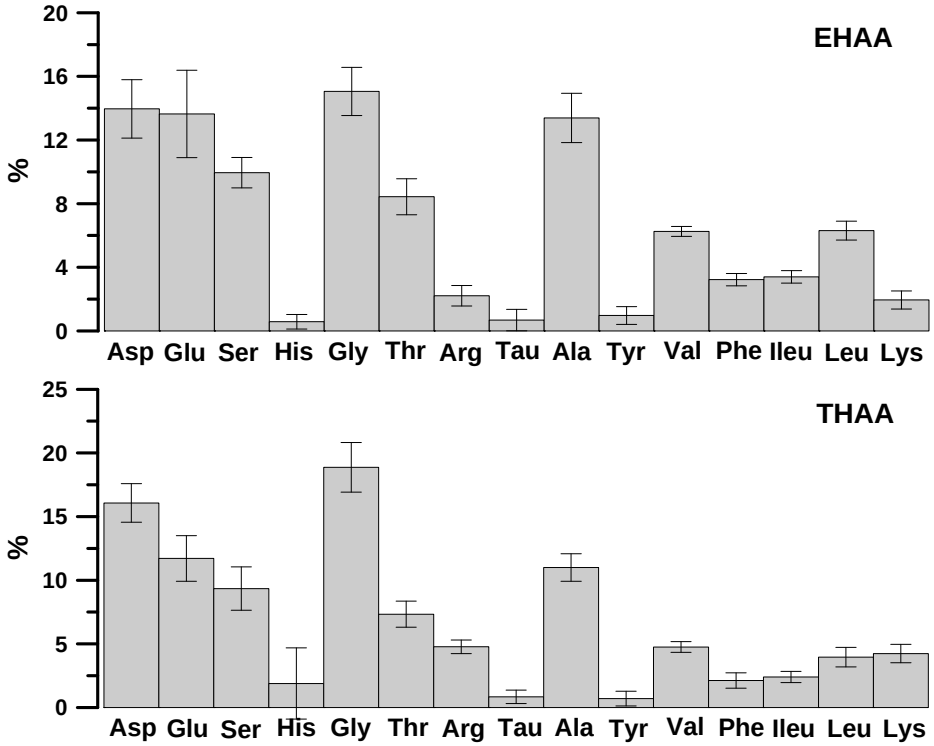

Fig. 2.9 Average THAA and EHAA spectra of all samples analyzed during the present study. Vertical bars are standard deviations.

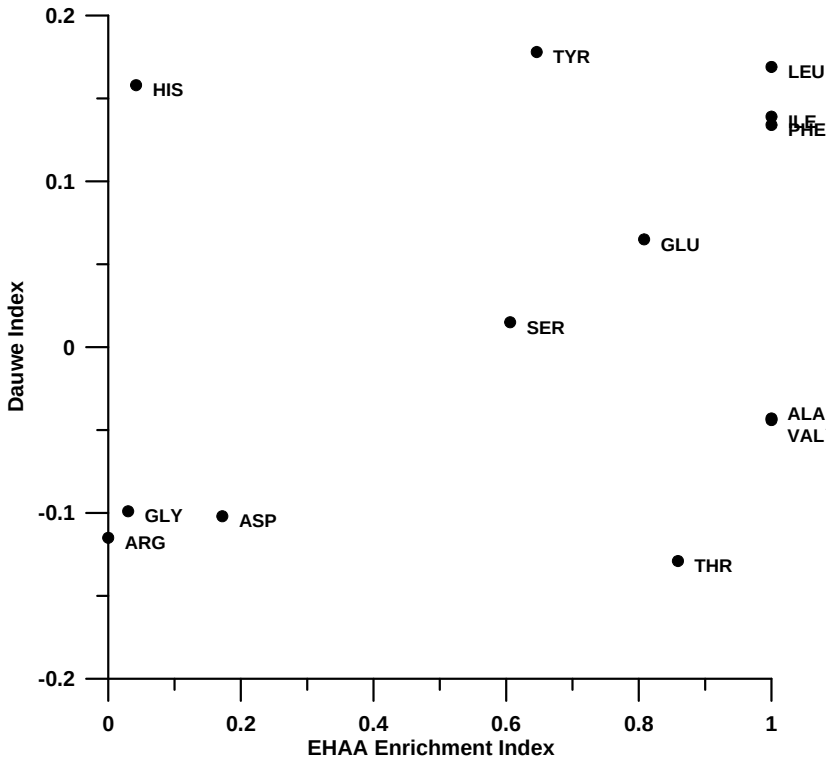

Fig. 2.10 Relationships between individual amino acid scores reported by Dauwe et al. (1999) and the individual amino acid EHAA enrichment factors computed during the present study.

Table 2.5 Comparison of EHAA and THAA measured during the present study and literature data.

EHAA (nmol mg^{-1})	THAA (nmol mg^{-1})	% EHAA:THAA	location	depth (m)	core depth (cm)	reference
no data	~9	no data	NE Atl. Oc.	4850	1-2	Horsfall and Wolff, 1997
no data	~28	no data	NE Atl. Oc.	130	0-5	Keil et al., 1998
no data	51-76	no data	NE Atl. Oc.	17	0-2	Henrichs and Farrington, 1987
no data	0.166	no data	NW Atl. Oc.	5454	0-8	Whelan, 1977
no data	~22-151	no data	Oslofjord	~100-150	0-2	Haugen and Lichtentaler, 1991
2.5-3	12.5-14.8	16.9-29.6	NW Med.	240-380	0-1	Grémare et al., 2002
3.03	12.47	24.3	NW Med.	340	0-1	Grémare et al., 2005
15.2	46.8	~40	NW Med.	0.6	no data	Carlier et al., 2007
no data	~27-72	no data	W Med.	300-5000	sed. aggr.	García and Thomsen, 2008
~1.9-5.7	no data	no data	NW Pac. Oc.	~23	no data	Lesen, 2006
no data	~121.2	no data	NE Pac. Oc.	210	0-1	Cowie et al., 1992
no data	~2.7	no data	NE Pac. Oc.	170	surface	Degens et al., 1964
no data	310	no data	SW Pac. Oc.	~270	0-3	Henrinchs et al., 1984
2.29-7.70	16.2-50.1	8-21 (summer)	Pac. Oc.	10-20	0-5	Dalto et al., 2006
no data	33.1 µmol THAA C/g	no data	Ant.	2885	0-0.5	Ingalls et al., 2003
1.13-3.83	**3.00-13.86**	**23-42**			**0-0.5**	
1.19-3.78	**2.99-13.36**	**23-41**			**0-1**	
0.94-3.44	**2.28-12.26**	**24-41**	**Ant.**	**200-400**	**0-2**	**Present Study**
0.80-3.05	**1.80-11.16**	**24-45**			**0-5**	
0.68-3.10	**1.58-11.15**	**23-43**			**1-2**	

2.5 Conclusions

Sediment grain size does not explain amino acids distribution throughout the sediment cores from both EAP and NAP regions. EAP THAA and EHAA profiles in the sediment column may be linked to Larsen A and B ice shelf collapses, in fact, Larsen A and B amino acid concentrations are higher in the upper than in the lower part of the sediment cores and the upper part could correspond to OM deposition after ice shelf collapses, as suggested in a previous work on pigments in Larsen sediments. The high EHAA:THAA ratio in LBC below 8 cm depth could be the result of the contribution of labile amino acids from the low-activity cold seep found in the area. NAP and EAP amino acid concentrations are similar to those reported for lower latitude environments where the OM supply to seabed is of local origin, not limited by the ice and vary with seasonal restrictions. As regards OM quality, based on the EHAA:THAA ratio, amino acids undergo similar degradation in NAP and EAP sediments and comparisons with other geographical regions indicated that in a global context OM quality is relatively high (high lability) in NAP and EAP sediments and comparable to shallow areas at lower latitudes. Fresh OM material reaches the seabed in EAP and NAP suggesting an efficient vertical transport and making evident the developing of primary production at the sea surface.

Biochemical characterization of sediments and benthic macrofauna characteristics off the Eastern Antarctic Peninsula and the South Eastern Weddell Sea.

Edited version of E. Sañé, E. Isla, D. Gerdes, A. Montiel, I. Fiorillo, J.-M. Gili. Biochemical characterization of sediments and benthic macrofauna characteristics off the Eastern Antarctic Peninsula and the South Eastern Weddell Sea.

3.1 Introduction

The quantity and quality of the organic matter (OM) reaching the seabed are important for benthic communities (Thompson and Nichols, 1988; Graf, 1989; Dugan et al., 2003) since are the principal factors regulating benthic biomass (Grebmeier et al., 1988).

Benthic community abundance and diversity are positively correlated with protein (PRT), carbohydrate (CHO) and lipid (LPD) concentrations in the sediment (Fabiano and Danovaro, 1999; Albertelli et al., 1999; Dell'Anno et al., 2000; Medernach et al., 2001; Neira et al., 2001b; Grémare et al., 2002). PRT and diatom storage CHO are easily degraded by bacteria in the water column and in the superficial sediment (Handa and Yanagi, 1969; Berland et al., 1970; Liebezeit, 1984; Ittekkot and Arain, 1986) while LPD and water-insoluble CHO have a higher chemical stability (Handa and Tominaga, 1969; Toth and Lerman, 1977).

In polar regions, ice coverage at the sea surface hampers primary production (Arrigo et al., 2002; Arrigo and van Dijken, 2003) limiting the OM flux to the seafloor, whereas iceberg scouring events disturb benthic communities (Gutt et al., 1996). As a consequence of the recent temperature increase in the atmosphere (Vaughan et al., 2001) and in the ocean (Gille, 2002), 4200 km^2 of the Larsen A ice shelf disintegrated in January 1995 (Rott et al., 1996) and 3200 km^2 of the Larsen B ice shelf collapsed within 33 days in March 2002.

Based on the idea that climate change forces the environmental characteristics that ultimately modify the ecosystem, we investigate how Antarctic continental shelf ecosystems respond to climate change by comparing the sediment biochemical characteristics and the macrofauna off the Eastern Antarctic Peninsula (EAP) coast, where Larsen A and B ice shelf collapses recently occurred, and the South Eastern Weddell Sea (SEWS) continental shelf which has not been covered by shelf ice at least for thousands of years (Ingólfsson et al., 1998; Anderson et al., 2002). In SEWS two adjacent regions off Atka Bay (SEWS I) and off Austasen (SEWS II) characterized by different environmental settings (e.g. transit of icebergs) have been investigated.

3.2 Materials and Methods

3.2.1 Samples collection

Sediment and macrobenthic samples were collected from board RV POLARSTERN during expeditions ANT-XXI/2 and ANT-XXIII/8 in the austral summers of 2003-2004

and 2006-2007 respectively. Sediment cores and macrobenthic samples were collected in the South Eastern Weddell Sea at four stations (76, 77, 80, 82) on the continental shelf off Atka Bay (SEWS I) during ANT-XXI/2 and at four stations (700, 703, 714, 725) on the Eastern Antarctic Peninsula (EAP) shelf during ANT-XXIII/8 (Fig. 3.1 and Table 3.1). Sediment cores were taken with a multi-corer (Barnett et al., 1984) and macrobenthic samples were taken with a multi-box corer (Gerdes, 1990). During ANT-XXI/2 sediment and macrobenthic samples were also collected with a multi-box corer (Gerdes, 1990) at four stations (105, 106, 116 and 197) on the continental shelf off Austasen (SEWS II) (Fig. 3.1 and Table 3.1).

3.2.2 Sediment biochemistry

Biochemical analyses were carried out on the homogenized superficial 5 cm of the sediment column. Samples were stored at -20ºC until analyses in the laboratory. Before biochemical analyses sediment was freeze dried (P=0.1 mbar and T=-80ºC) for 24 hours. Each sample was analyzed on triplicates and for each sample a blank (sediment treated during 4 hours at 450ºC) analysis was also performed. LPD were quantified following the Barnes and Blastock procedure (Barnes and Blastock, 1973) using cholesterol as a standard, CHO following the Dubois procedure (Dubois et al., 1956) using glucose as a standard and PRT following the Lowry procedure (Lowry et al., 1951) as modified by Rice (1982) using albumine as a standard. Absorbance was measured with a Shimadzu spectrophotometer at 520 nm for LPD, 485 nm for CHO and 750 nm for PRT. Concentrations of LPD, CHO or PRT were expressed as mg g^{-1} sediment dry weight (DW) and should be considered as cholesterol, glucose and albumine equivalents, respectively.

3.2.3 Macrobenthos

The samples were sieved over 500 µm mesh size and preserved in a 4% formaldehyde-seawater solution buffered with hexamethylentetramine. All macrobenthic specimens were counted and their wet weight was determined using a Sartorius balance (model R 180 D).

Table 3.1 Sampling expedition, year and season, region, station, coordinates and depth.

expedition	sampling year and season	region	station	latitude	longitude	depth
ANT XXIII/8	2006-2007 -summer	EAP	700	-65° 55,11'	-60° 20,14'	446
ANT XXIII/8	2006-2007 -summer	EAP	703	-65° 33,00'	-61° 37,15'	297
ANT XXIII/8	2006-2007 -summer	EAP	714	-65° 6,40'	-60° 45,01'	322
ANT XXIII/8	2006-2007 -summer	EAP	725	-64° 55,73'	-60° 37,23'	239
ANT XXI/2	2003-2004 -summer	SEWS I	76	-70º 22.97'	-9º 22.32'	489
ANT XXI/2	2003-2004 -summer	SEWS I	77	-70º 26.08'	-09º 15.32'	311
ANT XXI/2	2003-2004 -summer	SEWS I	80	-70º 28.27'	-09º 11.71'	343
ANT XX/2	2003-2004 -summer	SEWS I	82	-70º 31.51'	-09º 06.28'	421
ANT XXI/2	2003-2004 -summer	SEWS II	105	-70º 56.50'	-10º 32.01'	295
ANT XXI/2	2003-2004 -summer	SEWS II	106	-70º 56.64'	-10º 32.03'	304
ANT XXI/2	2003-2004 -summer	SEWS II	116	-70º 56.81'	-10º 32.87'	321
ANT XX/2	2003-2004 -summer	SEWS II	197	-70º 56.29'	-10º 30.32'	253

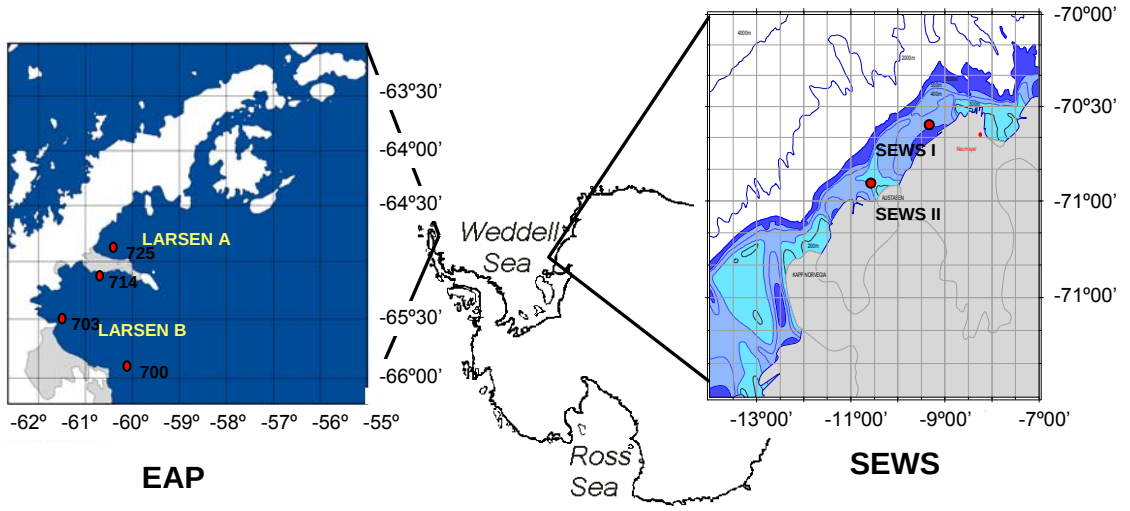

Fig. 3.1 Study area: Eastern Antarctic Peninsula (EAP), South Eastern Weddell Sea off of Austasen (SEWS II) and South Eastern Weddell Sea off of Atka Bay (SEWS I) regions.

Number of organisms (N m^{-2}) and wet biomass (mg WM m^{-2}) were calculated for each station and their average values were also calculated for each region. The macrobenthic organisms were subdivided into 35 taxonomic units: Porifera, Hydrozoa, Anthozoa, Bryozoa, Polyplacophora, Aplacophora, Bivalvia, Gastropoda, Scaphopoda, Polychaeta, Acari, Pantopoda, Amphipoda, Cumacea, Harpacticoidea, Cirripedia, Isopoda, Tanaidacea, Ostracoda, *Crustacea* spp., Echinoidea, Holothuroidea, Asteroidea, Ophiuroidea, Crinoidea, Tunicata, Brachiopoda, Sipunculida, Turbellaria, Nemertinea, Priapulida, Clitellata, Echiurida, Hemichordata and unidentified. This set was subdivided into 8 major taxonomic groups: sponges (Porifera), cnidarians (Hydrozoa and Anthozoa), bryozoans (Bryozoa), molluscs (Polyplacophora, Aplacophora, Bivalvia, Gastropoda and Scaphopoda), polychaetes (Polychaeta), crustaceans (Acari, Pantopoda, Amphipoda, Cumacea, Harpacticoidea, Cirripedia, Isopoda, Tanaidacea, Ostracoda and *Crustacea* spp.), echinoderms (Echinoidea, Holothuroidea, Asteroidea, Ophiuroidea and Crinoidea), tunicates (Tunicata) and others (Brachiopoda, Sipunculida, Turbellaria, Nemertinea, Priapulida, Clitellata, Echiurida, Hemichordata and one unidentified). In the present work "taxonomic groups" will refer to these 8 major taxonomic groups. Based on their feeding strategy all the organisms included in the 35 taxonomic units were subdivided in suspension feeders, deposit feeders and carnivores. Porifera, Hydrozoa, Anthozoa, Bryozoa, Brachiopoda, Turbellaria, Bivalvia, Scaphopoda, Cirripedia, Holothuroidea, Crinoidea, Hemichordata and Tunicata were grouped as suspension feeders; Sipunculida, Priapulida,

Polyplacophora, Aplacophora, Clitellata, Echiurida, Acari and Echinoidea were included as deposit feeders and Nemertinea, Gastropoda, Polychaeta, Pantopoda, Amphipoda, Cumacea, Harpacticoidea, Isopoda, Tanaidacea, Ostracoda, Crustacea spp., Asteroidea and Ophiuroidea were counted as carnivores. The percentage of contribution of each of the 8 taxonimic groups and the percentage of contribution of each feeding guild to the total biomass were calculated. The Simpson diversity index (Margalef, 1958; Menhinick, 1964) was also calculated for biomass of SEWS I, SEWS II and EAP benthic communities.

3.2.4 Sediment granulometry

Grain size analyses of the upper 5 cm were carried out using a Mastersizer 2000 (Malvern®) laser micro-granulometer. Sediment grain size analyses with the laser micro-granulometer required a previous exclusion of the sediment with a grain size higher than 2000 µm.

3.2.5 Statistical analysis

A one-way ANOVA comparison with a post-hoc Scheffé test was applied to compare biochemical characteristics of EAP, SEWS I and SEWS II sediments. CHO, PRT and LPD data were statistically treated using STATISTICA software.

Macrofauna data were statistically treated through a multivariate analysis using PRIMER 6 software (Clarke and Gorley, 2006). Taxon biomass data were fourth root transformed to reduce the effects of highly dominant taxa and the SIMPER test was performed to describe the contribution of taxonomic units to similarities within and dissimilarities among regions.

3.3 Results

3.3.1 Sediment biochemistry

Station and average values for each region of all biochemical variables are shown in Table 3.2.

The average concentration of LPD was 0.25±0.18 mg g^{-1} DW in SEWS II, 0.41±0.31 mg g^{-1} DW in EAP and 2.56±1.89 mg g^{-1} DW in SEWS I (Table 3.2). Regarding CHO, the average concentration was 1.25±0.49 mg g^{-1} DW in SEWS I, 1.81±0.62 mg g^{-1} DW in EAP and 4.48±1.88 mg g^{-1} DW in SEWS II (Table 3.2), whereas the average concentration of PRT was 0.52±0.38 mg g^{-1} DW in EAP, 0.60±0.17 mg g^{-1} DW in SEWS

I and 1.92±0.25 mg g^{-1} DW in SEWS II (Table 3.2).

3.3.2 Macrobenthos

Macrobenthos abundance and biomass are listed in Table 3.3. The mean total number of organisms in SEWS II (3993±1489 N m^{-2}) was more than three times the mean total number of organisms in EAP (1213±561 N m^{-2}) while the mean total number of organisms in SEWS I (2337±533 N m^{-2}) doubled the mean total number of organisms in EAP (Table 3.3). The mean total biomass in SEWS II (1842.0±2154.7 g WM m^{-2}) was almost two orders of magnitude higher (~88 times higher) than the mean total biomass at EAP (20.9±11.3 g WM m^{-2}) while the mean total biomass in SEWS I (97.2±94.0 g WM m^{-2}) was almost five times the mean total biomass at EAP (Table 3.3).

The contribution of the 8 major taxonomic groups to the total biomass is shown in Fig. 3.2. The average relative biomass of sponges was ~24 % in EAP, ~33 % in SEWS I and ~93 % in SEWS II, of polychaetes ~19 % in EAP, ~23 % in SEWS I and ~3 % in SEWS II, of echinoderms ~21 % in EAP, ~20 % in SEWS I and ~1 % in SEWS II, of crustaceans ~7 % in EAP, ~6 % in SEWS I and ~1 % in SEWS II, of molluscs ~3 % in EAP, ~6 % in SEWS I and ~1 % in SEWS II (Fig. 3.2). Cnidarians, bryozoans and tunicate average biomass was lower than 4% in the three regions (Fig. 3.2).

The average percentage of suspension feeders was ~44 % in EAP, ~47 % in SEWS I and ~95 % in SEWS II, of deposit feeders ~10 % in EAP, ~16 % in SEWS I and 0.25 in SEWS II, and of carnivores of ~43 % in EAP, ~40 % in SEWS I and ~5 % in SEWS II (Fig. 3.3).

Simpson index values are presented in Table 3.4. The average Simpson index was 0.34 in EAP, 0.28 in SEWS I and 0.62 in SEWS II (Table 3.4).

3.3.3 Sediment granulometry

The percentage of sediment with a grain size < 63 µm (silt and clay) ranged in EAP from ~70 % (stn. 725) to ~89 % (stn. 714), in SEWS I from ~28 % (stn. 82) to ~58 % (stn. 77) and in SEWS II from ~24 % (stn. 116) to ~66 % (stn. 105) (Fig. 3.4). The average percentage of sediment with a grain size < 63 µm was highest in EAP (80.93 %) (Fig. 3.4). A poor linear correlation between fine sediment and LPD (R^2=0.229), CHO (R^2=0.190) and PRT (R^2=0.041) concentrations was found.

Table 3.2 LPD, CHO and PRT concentration (mg g^{-1} DW) at stations 700, 703, 714 and 725 (EAP), stations 76, 77, 80, 82 (SEWS I) and stations 105, 106, 116, 197 (SEWS II).

Station	LPD (mg g-1 DW)	CHO (mg g-1 DW)	PRT (mg g-1 DW)	Region	LPD (mg g-1 DW)	CHO (mg g-1 DW)	PRT (mg g-1 DW)
700	0.50±0.24	1.11±0.29	1.04±0.59	EAP	0.41±0.31	1.81±0.62	0.52±0.38
703	0.09±0.07	1.52±0.20	0.20±0.14				
714	0.25±0.17	2.06±0.26	0.30±0.15				
725	0.80±0.59	2.54±0.27	0.54±0.15				
76	3.77±1.52	1.80±0.53	0.36±0.24	SEWS I	2.56±1.89	1.25±0.49	0.60±0.17
77	1.36±0.78	0.74±0.12	0.75±0.36				
80	4.53±1.03	1.50±0.62	0.66±0.18				
82	0.57±0.49	0.96±0.19	0.64±0.21				
105	0.22±0.29	5.54±0.39	2.19±0.45	SEWS II	0.25±0.18	4.48±1.88	1.92±0.25
106	0.27±0.13	4.50±0.53	1.99±0.46				
116	0.05±0.02	1.82±0.37	1.91±0.50				
197	0.48±0.71	6.05±0.83	1.60±0.34				

Table 3.3 Abundance and biomass at stations 700, 703, 714 and 725 (EAP), stations 76, 77, 80, 82 (SEWS I) and stations 105, 106, 116, 197 (SEWS II).

Station	Abundance (N m^{-2})	Biomass (g WW m^{-2})	Region	Mean Abundance (N m^{-2})	Mean Biomass (g WW m^{-2})
700	2014	8.6	EAP	1213±561	20.9±11.3
703	812	14.6			
714	1191	27.0			
725	836	33.4			
76	2728	56.7	SEWS I	2337±533	97.2±94.0
77	1577	33.3			
80	2683	237.0			
82	2361	61.8			
105	4129	238.0	SEWS II	3993±1498	1841.9±2154.7
106	3356	198.4			
116	2497	4765.9			
197	3993	2165.6			

3.3.4 Statistical analysis

Significant differences were found in CHO and PRT concentrations between SEWS II and both EAP and SEWS I (Table 3.5), whereas LPD concentration was significantly different only between SEWS I and SEWS II (Table 3.5).

SIMPER analysis showed that the average macrofauna biomass similarity within regions was 72.41 % in EAP, 74.72 % in SEWS I and 74.07 % in SEWS II (Table 3.6). In EAP and SEWS I polychaetes (21.67 % in EAP and 22.00 % in SEWS I) contributed most to the similarity, whereas in SEWS II sponges (31.98 %) were the most important contributors to similarity. The average macrofauna biomass dissimilarity was 23.19 % between EAP and SEWS I, 30.59 % between EAP and SEWS II and 29.53 % between SEWS I and SEWS II (Table 3.6). In the three cases the taxonomic group which contributed most to dissimilarity was that of sponges (16.76 % between EAP and SEWS I, 19.34 % between EAP and SEWS II, and 18.62 % between SEWS I and SEWS II).

3.4 Discussion

3.4.1 Biochemical characteristics of sediment

3.4.1.1 Sediment biochemistry differences between EAP and SEWS

EAP and SEWS stations were sampled during the austral summer, therefore, differences in the sediment OM contents linked to the marked Antarctic seasonality at the sea surface (Clarke, 1988) should be negligible. The main difference between the

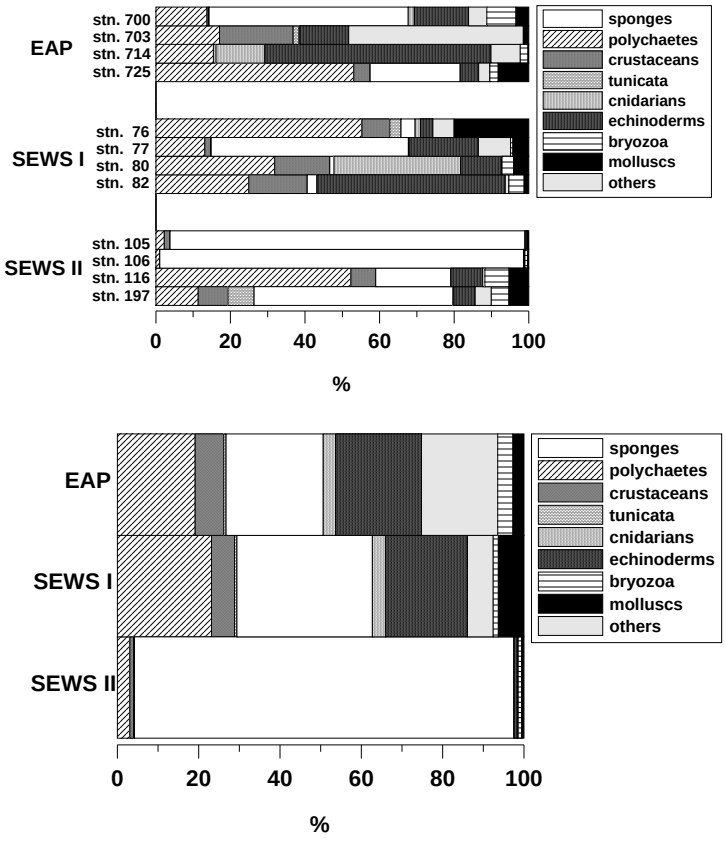

Fig. 3.2a Relative biomass of principal taxonomic groups at stations 700, 703, 714, 725 (EAP), stations 76, 77, 80, 82 (SEWS I) and stations 105, 106, 116, 197 (SEWS II). **3.2b** Relative biomass of principal taxonomic groups in EAP, SEWS I and SEWS II regions.

two regions regarding OM supply to the seabed, is that EAP has been free of an ice shelf influence since a decade, whereas SEWS region for at least a thousand years (Ingólfsson et al., 1998; Anderson et al., 2002).

Ice coverage hampers primary production (PP) (Arrigo et al., 2002; Arrigo and Dijken, 2003) and consequently the OM flux to the seafloor. Even if some authors studying the Ross Ice Shelf suggested that under ice shelves chemosynthesis may provide a small amount of energy for benthic organisms (Horrigan, 1981), PP under ice shelves is considered to be very low (Grebmeier and Barry, 1991; Thomas et al., 2008) making

laterally advected OM the principal food input for such benthic communities (Grebmeier and Barry, 1991). After Larsen A and B ice shelf collapses, PP in EAP water column started developing (Bertolin and Schloss, 2009) and consequently the phytoplankton detritus flux to the seafloor (Domack et al., 2005; Sañé et al. *a.*-CAP.1). This flux represents a high percentage of the POM reaching the seafloor (Fisher et al., 1988) and is typically composed by heterotrophic bacteria and abundant unicellular algae (Arrigo et al., 1995), which are released during pack ice breakage and melting (Legendre et al., 1992). Although the ice shelf collapse opened space at the EAP sea surface enabling phytoplankton blooms, the large amount of icebergs that calved from the ice shelves greatly reduced the available ice-free areas (personal observation) drastically limiting primary production (Arrigo et al., 2002; Arrigo and van Dijken, 2003). As a consequence of the recent Larsen A and B ice shelf collapses, we suggest the OM input to the seafloor to be lower in EAP than in SEWS. The lower input of fresh OM to the seafloor in EAP and SEWS can explain the lower LPD and PRT concentration in EAP than in SEWS sediments (Table 3.2). CHO was the largest fraction of the measured OM in EAP sediments (Table 3.2). We suggest that refractory structural CHO (Liebezeit, 1984) accumulated under Larsen A and B ice shelves during years of ice coverage and lack of fresh OM supply. In fact, CHO are generally considered as compounds characteristic for deep-sea habitats (Danovaro et al., 1993) and oligotrophic environments (Rodil et al., 2007) where the supply of fresh OM is limited. Furthermore, water column observations showed that structural CHO concentration increases with depth due to their resistance to biological attack (Handa and Tominaga, 1969). CHO synthesis by bacteria (Klok et al., 1984a, b) may represent another source of CHO in EAP sediments but we lack of bacterial abundances to corroborate its contribution. On the contrary, the CHO in SEWS I and SEWS II could origin both from fresh diatom storage compounds. Diatoms are protected and isolated by structural hydrophilic CHO (Hecky et al., 1973), thus these algae also supply CHO to the sediment. Nevertheless, diatoms are not very abundant in EAP (Sañé et al. *d.*-CAP.4) excluding them as sources of CHO in EAP sediments. The low abundance and biomass of the macrofauna found in EAP (Table 3.3) strongly suggest that in this region benthic consumption of OM does not control the concentration of LPD, CHO and PRT in the sediment.

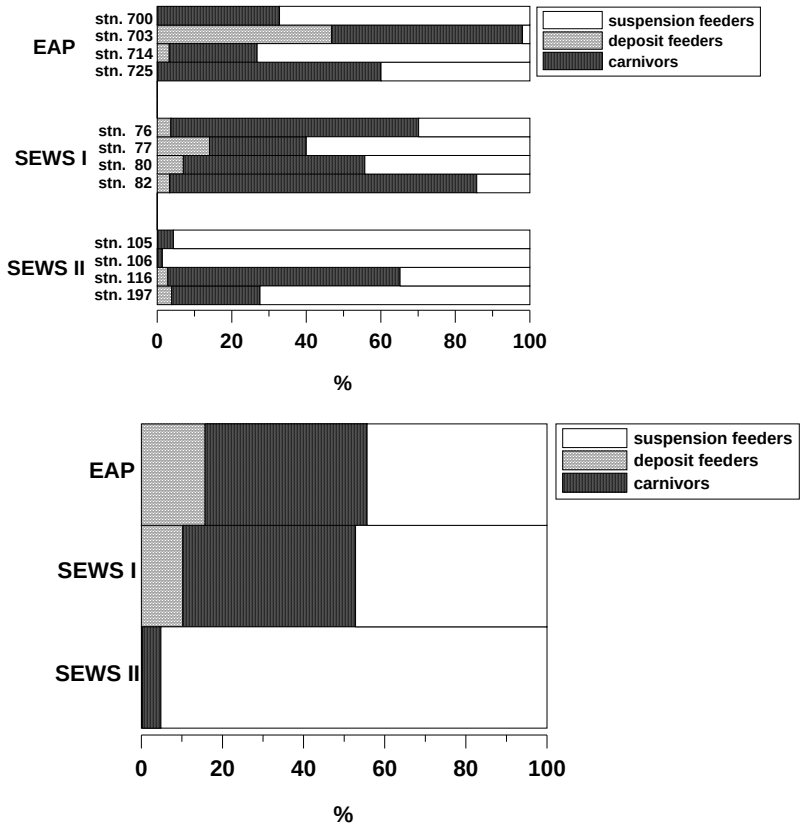

Fig. 3.3a Relative biomass of suspension feeders, deposit feeders and carnivors at stations 700, 703, 714, 725 (EAP), stations 76, 77, 80, 82 (SEWS I) and stations 105, 106, 116, 197 (SEWS II). **3.3b** Relative biomass of suspension feeders, deposit feeders and carnivors in EAP, SEWS I and SEWS II regions.

3.4.1.2 Sediment biochemistry differences between SEWS I and SEWS II

Different phytoplankton abundances have been observed in SEWS I and SEWS II water column (Michels, 2007). Chl*a* has been detected in the entire SEWS II water column while in SEWS I Chl*a* concentration was zero below ~100 m depth (Michels, 2007). Further, sediment trap studies confirmed higher flux of OM in SEWS II than in SEWS I (Isla et al., 2009). Within this flux, the higher faecal pellet input to the seafloor in SEWS II than in SEWS I (Isla et al., 2009) suggests differences in secondary production between the two regions. These differences can depend on the higher abundance of icebergs in SEWS I (D. Gerdes, personal observation) where they reduce available space and light penetration into the water column limiting primary production (Arrigo et al., 2002; Arrigo and van Dijken, 2003).

We observed a significant difference in LPD concentrations at SEWS I and SEWS II, with higher concentrations in SEWS I than in SEWS II (Tables 3.2 and 3.5). Apparently,

neither diatoms nor faecal pellets were responsible for the high LPD concentration in the SEWS I sediment the year of this study. Diatom flux was more intense in SEWS II than in SEWS I (Isla et al., 2009), thus the high LPD concentration in SEWS I sediment is not the result of the flux of diatom aggregates to the seafloor (Ramos et al., 2003). Faecal pellets (Schnack-Schiel and Isla, 2005) concentrate LPD (phytosterols) from algae (Mühlebach and Weber, 1998) but zooplankton grazing is also more intense in SEWS II than in SEWS I (Isla et al., 2009). The observed differences among SEWS I and SEWS II benthic communities, with distinct higher abundance and biomass values in SEWS II (Table 3.3), may explain the differences in the sediment biochemistry (Tables 3.2 and 3.5). The energy content per unit carbon of LPD is 1.4 times higher than that of CHO and 1.2 times higher than that of PRT (Salonen et al., 1976). The rich benthic SEWS II community consumes higher amounts of high energetic LPD than the impoverished SEWS I benthic community, thus delimiting the LPD concentration in the SEWS II area (Table 3.2).

Table 3.4 Simpson diversity index at stations 700, 703, 714 and 725 (EAP), stations 76, 77, 80, 82 (SEWS I) and stations 105, 106, 116, 197 (SEWS II).

Station	Simpson diversity index	Region	Simpson diversity index
700	0.35	EAP	0.34
703	0.37		
714	0.30		
725	0.33		
76	0.20	SEWS I	0.28
77	0.23		
80	0.32		
82	0.35		
105	0.31	SEWS II	0.62
106	0.33		
116	0.95		
197	0.91		

Table 3.5 ANOVA with Scheffé post-hoc tests to identify differences between EAP, SEWS I and SEWS II in CHO, PRT and LPD concentrations.

	df	ss	ms	F	p	
CHO	2	11.91	1.39	8.55	0.0083	SEWS II≠SEWS I, EAP
PRT	2	2.48	0.08	32.40	<0.0001	SEWS II≠SEWS I, EAP
LPD	2	6.63	1.24	5.36	0.0293	SEWS II≠SEWS I

Table 3.6 Results of SIMPER test on macrofauna biomass data among EAP, SEWS I and SEWS II regions.

SIMILARITY		EAP	SEWS I	SEWS II
		Average 72.41	**Average 74.72**	**Average 74.07**
		Polychaetes 21.67	Polychaetes 22.00	Sponges 31.98
		Echinoderms18.81	Echinoderms 17.13	Polychaetes 15.04
		Others 15.78	Crustaceans 15.10	Echinoderms 11.45
		Molluscs 10.31	Molluscs 13.01	Molluscs 10.86
		Bryozoans 9.49	Sponges 12.28	Crustaceans 10.82
		Sponges 9.12	Others 9.69	Bryozoans 9.95
		Crustaceans 7.38	Bryozoans 5.58	
DISSIMILARITY				
		EAP	SEWS I	SEWS II
	EAP	X	X	X
	SEWS I	**Average 23.19**	X	X
		Sponges 16.76		
		Cnidarians 15.47		
		Crustaceans 13.12		
		Others 11.37		
		Bryozoans 9.87		
		Tunicata 9.39		
		Echinoderms 9.30		
		Molluscs 8.30		
	SEWS II	**Average 30.59**	**Average 29.53**	X
		Sponges 19.34	Sponges 18.62	
		Others 13.96	Cnidarians 13.07	
		Echinoderms 12.66	Echinoderms 12.70	
		Cnidarians 11.36	Polychaetes 12.48	
		Polychaetes 11.03	Tunicata 9.12	
		Crustaceans 9.83	Crustaceans 9.09	
		Tunicata 8.47	Bryozoans 8.48	
		Bryozoans 7.01	Others 8.41	

3.4.1.3 Sediment biochemistry in a global context

Numerous studies on LPD, CHO and PRT concentrations in marine sediments have been carried out in different oceanographic settings and are particularly abundant in polar regions and in the Mediterranean Sea (Table 3.7). LPD concentrations in SEWS I were higher than elsewhere and comparable with values found in autumn in the same region (Isla et al., 2006) (Table 3.7). An exception was the case of the coastal South Pacific (Neira et al., 2001a) where post El Niño conditions in this productive upwelling region presented extremely high OM concentrations (Table 3.7). Regarding CHO, the range of variation in a global context is wide (from 0.07 mg g^{-1} to 70.5 mg g^{-1}) (Table 3.7) difficulting to establish a clear pattern to explain CHO distribution in sediments. CHO concentration was higher in SEWS II than in EAP and SEWS I sediments (Table 3.2). Among areas with higher CHO concentration than both EAP and SEWS I there were oligotrophic areas (Danovaro et al., 2000) and coastal environments with river discharges (Mazzolla et al., 1999). Among these data is remarkable the high concentration of CHO found in a coastal lagoon rich in detrital material (Pusceddu et al., 1999) (Table 3.7). PRT content in EAP and SEWS I was lower than in SEWS II (Table 3.2) and similar to samples collected in the Mediterranean and the Antarctic continental shelf (Fabiano and Danovaro, 1994, 1999; Danovaro et al., 2000; Pusceddu et al., 2000) (Table 3.7). These comparisons make clear the high LPD content in SEWS I and the high CHO and PRT content in SEWS II.

3.4.2 Macrofaunal community

3.4.2.1 Macrofaunal community differences between EAP and SEWS

The higher macrofauna abundance and biomass in SEWS than in EAP (Table 3.3) suggest that the development of the benthic community in EAP has been affected by ice coverage and the consequent limitation in food supply (Grebmeier and Barry, 1991; Thomas et al., 2008). While the 42-70% of SEWS bottom presented signs of iceberg disturbance (Gutt and Starmans, 2001), only the 7% of EAP seafloor showed iceberg scours (Gutt et al., submitted), suggesting that Larsen A and B were covered by floating ice shelves and thus that EAP benthic communities have not been affected by the grounding of icebergs.

The taxonomic group which mostly contributed to the different values of macrofauna biomass in EAP and SEWS was that of sponges that had a higher relative biomass in SEWS, in particular in SEWS II, than in EAP (Fig. 3.2). EAP communities still present early stage of development while in SEWS II, like in other undisturbed Antarctic shelves, slow growing sponges (Clarke, 1983; Brey and Clarke, 1993; Arntz et al., 1994) dominate the benthic fauna (Fig. 3.2).

In spite of the lower relative biomass of sponges in EAP than in SEWS, in EAP sponges had the highest relative biomass in comparison with other taxonomic groups (Fig. 3.2). The low growth rate of sponges (Dayton et al., 1974; Post et al., 2007) suggests that this group lived in EAP seafloor before Larsen ice shelves disintegration (Gutt et al., submitted), in agreement with the observed high relative biomass of suspension feeders under ice shelves (Riddle et al., 2007). Suspension feeders under ice shelves may be maintained by OM which is laterally advected from adjacent regions (Dayton and Oliver, 1977; Riddle et al., 2007). The high relative abundance of ascidians in EAP (Gutt et al., submitted) gives further evidence of the presence of suspension feeders in this region (Fig. 3.2). In EAP, suspension feeders coexisted with typical surface deposit feeders such as holothurians of the species *Scotoplanes globosa* and ophiuroids (personal observation), adapted to live in habitats with scarce food resources like under ice shelves (Thomas et al., 2008). As it occurs in benthic communities at the first stages of recovery, the relative biomass of polychaetes was high in EAP (Gutt et al., 1996; Teixidó et al., 2004) (Fig. 3.2). The relative biomass of echinoderms, also considered rapid immigrants after iceberg scouring events (Gutt et al., 1996), was higher in EAP than in SEWS II (Fig. 3.2).

The Simpson index is sensitive to the dominant groups (Whittaker, 1965; Mouillot and Leprêtre, 1999), where a high value of the index means dominance of one or only few groups. Thus, based on the Simpson index, diversity was higher in EAP than in SEWS II but lower in EAP than in SEWS I (Table 3.4). The presence of gigant glass sponges in SEWS II (Fig. 3.2) increases diversity through favouring the development of epiphitic communities (White, 1984; Gutt and Starmans, 1998), but also reduces biomass homogeneity among taxonomic groups, thus, yielding higher Simpson index values (Table 3.4). Furthermore, if we consider EAP communties as representative of an early state of the ecological succession towards the climax stadium represented by SEWS II

community, a higher diversity in EAP than in SEWS II had to be expected since pioneer species occurring at early stages of ecological succession increase diversity.

3.4.2.2 Macrofaunal community differences between SEWS I and SEWS II

42-70% of the South Eastern Weddell Sea (including SEWS I and SEWS II) bottom presents signs of iceberg disturbance (Gutt and Starmans, 2001). We suggest that iceberg scours disturbance is more intense in SEWS I than in SEWS II due to the higher abundance of icebergs observed off of Atka Bay than off of Austasen (D. Gerdes, personal observation). A more pronounced iceberg grounding in SEWS I than in SEWS II, together with the higher flux of primary and secondary production debris in SEWS II than in SEWS I (Michels, 2007; Isla et al., 2009), may determine the observed differences in macrofauna abundance, biomass and composition between SEWS I and SEWS II regions (Table 3.3 and Fig. 3.2).

Iceberg scouring represents a source of disturbance for SEWS I benthic community. Evident differences in the benthic community have been observed in the Antarctic continental shelf between areas affected iceberg scouring and undisturbed areas (Gerdes et al., 2003). SEWS I macrofauna appeared impoverished when compared to SEWS II macrofauna and the relative biomasses of the 8 taxonomic groups were more similar between SEWS I and EAP than between SEWS I and SEWS II regions (Table 3.3 and Fig. 3.2).

The recovery time for an Antarctic mature benthic community is comprised between 230 and 500 years (Gutt et al., 1996; Gutt and Starmans, 2001), with early recovery stages that may take up to 10 years (Teixidó et al., 2004). Benthic communities recovery after iceberg disturbance has been described in 3 stages of succession, the first dominated by deposit feeders, the second by polychaetes and the third by suspension feeders like sponges and bryozoans (Gutt and Pipepenburg, 2003). Deposit feeders and polychaetes showed a higher relative biomass in both EAP and SEWS I in comparison with SEWS II where suspension feeders and in particular sponges were predominant (Fig. 3.2 and 3.3). The relative biomass of echinoderms, rapid immigrants after iceberg scouring events (Gutt et al., 1996), was similar in EAP and in SEWS I. In both regions echinoderms relative biomass was higher than in SEWS II (Fig. 3.2).

The numerous iceberg scours in SEWS I (D. Gerdes personal observation), which can be from few metres to 50 m width or more (Gerdes et al., 2003), could enhance diversity in this region (Gutt et al., 1998; Peck et al., 1999; Gutt, 2001; Gutt and Piepenburg, 2003; Conlan and Kvitek, 2005), as demonstrated by the Simpson index (Table 3.4). These observations are in agreement with the patchy disequilibria theory (Grassle and Morse-Porteous, 1987) which suggests that moderate and regular disturbances (Pickett and White, 1985) can induce faunal assemblage patchiness incrementing diversity.

3.4.3 Sediment grain size

The 63 μm grain size limit is the physical threshold used to differentiate fine (silt and clay) and coarse (sand and gravel) sediment. Fine sediments are usually associated to high OM contents due to the high surface to volume ratio (Mayer, 1994), but our results showed a poor correlation between fine sediment and CHO, PRT and LPD concentrations. As exemplified by the dominance of suspension feeders and deposit feeders in sandy and fine sediments, respectively (Sanders, 1958), physical factors such as sediment grain size can influence benthic communities. Results on sediment grain size showed finer sediment in EAP than in SEWS I and SEWS II (Fig. 3.4) in accordance with a higher deposit feeder biomass in EAP and a higher suspension feeder biomass in SEWS, in particular in SEWS II (Fig. 3.3). Thus, sediment grain size in the study area cannot explain OM concentration in the sediment column but may favour the development of deposit feeders in EAP.

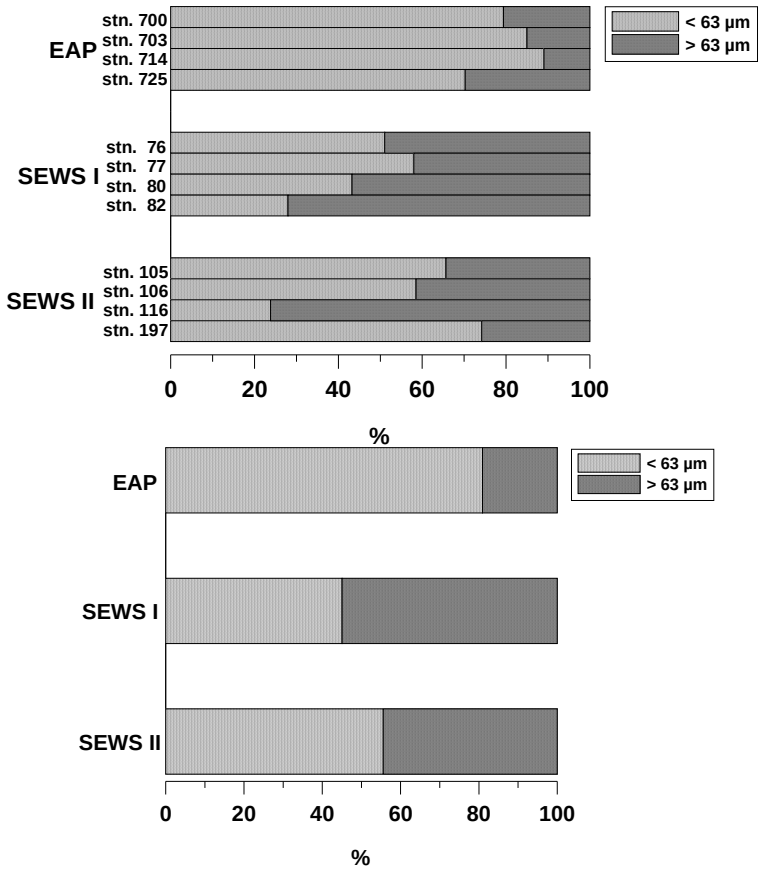

Fig. 3.4a Avergage % from 0 to 5 cm depth of sediment with grain size superior and inferior to 63 µm at stations 700, 703, 714, 725 (EAP), stations 76, 77, 80, 82 (SEWS I) and stations 105, 106, 116, 197 (SEWS II). **3.4b** Avergage % from 0 to 5 cm depth of sediment with grain size superior and inferior to 63 µm in EAP, SEWS I and SEWS II regions.

3.4.4 Summary

The low concentration of LPD and PRT in EAP sediment (Table 3.2) is related to the limited OM supply to the seafloor as a consequence of the only recent Larsen A and B ice shelf collapses. Before ice shelf disintegrations, ice coverage limited euphotic PP and permitted only the lateral arrival to the sediment column of refractory OM rich in CHO (Table 3.2). As a consequence of the reduced flux of fresh OM, EAP macrofauna has low abundance and biomass (Table 3.3). EAP communities present early stages of development in a changing environment and show a high relative biomass of sponges but also of polychaetes and echinoderms (Fig. 3.2). Furthermore, typical deep organisms adapted to live in habitats with scarse food resources, like holothurians of the species *Scotoplanes globosa* and iceberg scourings colonizers, like ascidians and

Table 3.7 CHO, PRT and LPD concentrations (mg g^{-1} DW) in a global context.

Reference	Location	Station depth (m)	core depth (cm)	CHO (mg g^{-1})	PRT (mg g^{-1})	LPD (mg g^{-1})
Pfannkuche and Thiel, 1987	Barents Sea (summer)	240	0-5	2.40	33.62	no data
Meyer-Reil, 1983	Baltic Sea (autumn-spring)	18	0-1	0.4-4.0	3.8-7.7	no data
Parrish, 1998	North Atlantic (spring)	59	0-2	no data	no data	1.8
Cividanes et al., 2002	Atlantic (autumn-spring)	intertidal flat	0-5	0.68 (summer)	3.44 (spring)	1.48 (autumn)
Pusceddu et al., 1999	Mediterranean (annual)	1	0-1	0.8-70.5	2.2-12.1	0.3-4.5
Danovaro et al., 1994	Mediterranean (autumn)	4	0-1	3.59	1.62	1.07
Fichez, 1991	Mediterranean	6-17	no data	3.2	1.6	0.23
Fabiano et al., 1995	Mediterranean (spring)	10	0-4	0.52	0.05	0.15
Mazzolla et al., 1999	Mediterranean (summer)	10	0-1	2.82	2.44	1.44
Buscail et al., 1995	Mediterranean (autumn)	26	0-1	1.55	no data	no data
Fabiano and Danovaro, 1994	Mediterranean (autumn)	50	0-10	1.03	0.88	0.012
Albertelli et al., 1999	Mediterranean (summer)	135	0-1	1.60	0.35	0.35
Danovaro et al., 2000	Mediterranean (summer)	200	0-10	2.66	0.53	0.24
Danovaro et al., 1993	Mediterranean (summer)	204	0-15	1.61	0.15	0.09
Grémare et al., 2002	Mediterranean (summer)	340	0-1	3.53	no data	0.16
Danovaro et al., 1993	Mediterranean (summer)	550	0-15	1.88	0.157	0.096
Relexans et al., 1996	Tropical Atlantic (winter)	3500	no data	0.07	0.7	0.19
Neira et al., 2001a	South Pacific (autumn)	27	0-1	5.8	5.75	7.2
Isla et al., 2006	Antarctica (autumn)	63-107	0-5	2.13	3.94	1.10
Pusceddu et al., 2000	Antarctica (summer)	127	0-2	0.09	0.66	0.42
Isla et al., 2006	Antarctica (autumn)	209-480	0-5	1.64	2.29	1.73
Isla et al., 2006	Antarctica (autumn)	295-421	0-5	2.25	4.81	2.99
Fabiano and Danovaro, 1999	Antarctica (summer)	436	0-2	0.29	0.51	0.054
This study EAP	**Antarctica (summer)**	**326**	**0-5**	**1.81**	**0.52**	**0.41**
This study SEWS I	**Antarctica (summer)**	**391**	**0-5**	**1.25**	**0.60**	**2.56**
This study SEWS II	**Antarctica (summer)**	**293**	**0-5**	**1.96**	**0.99**	**0.12**

ophiuroids, characteristic of the first stages of iceberg scours recovery, were abundant in EAP. In SEWS I sediments the concentration of OM, and in particular of LPD, is rather controlled by the benthic community than by the OM flux to the seafloor. We suggest that differences in LPD concentration between SEWS I and SEWS II (Tables 3.2 and 3.5) depend on differences between SEWS I and SEWS II benthic communities (Table 3.3). Apparently, iceberg grounding reduces macrofauna abundance and biomass in SEWS I (Table 3.3) and the smaller consumption enables a high concentration of LPD in the upper sediment column of this region (Table 3.2). On the contrary, SEWS II benthic community represents a climax stage of development. The high input of OM to the seafloor together with the reduced iceberg scouring disturbance enhanced the development in SEWS II seafloor of a rich macrofauna representative of the typical Weddell Sea benthic assemblages (Table 3.3 and Fig. 3.2). These assemblages consume high energetic OM mainly represented by LPD making the LPD concentration low in SEWS II region (Table 3.2).

Differences among regions in PRT, LPD and CHO concentrations in the sediment are not determined by sediment grain size, while benthic community abundance and biomass results suggest that the granulometry of the sediment benefits in EAP the establishment of deposit feeders and in SEWS II the establishment of suspension feeders.

Fatty acid composition and diatom valve distribution in sediments off the Northern Antarctic Peninsula and Larsen A and B bays.

Edited version of E. Sañé, E. Isla, A.M. Pruski, M.-A., Bárcena, G. Vétion. Fatty acid composition and diatom valve distribution in sediments off the Northern Antarctic Peninsula and Larsen A and B bays

Submitted to Continental Shelf Research (CSR1825)

4.1 Introduction

In the last 60 years atmospheric and oceanic temperatures have increased in Antarctica and world wide (Vaughan et al., 2001; Gille, 2002), leading to a faster retreat of the glaciers in the Antarctic Peninsula (Cook et al., 2005). In 1995, 4200 Km^2 of the Larsen A ice shelf collapsed, whereas 3200 Km^2 of the Larsen B ice shelf disintegrated in 33 days in 2002. These events drastically modified the local conditions relatively constant for hundreds of years (Domack et al., 2005a). The ice shelf collapses enabled primary production in the recently open space (Bertolin and Schloss, 2009) developing a flux of fresh organic debris to the seabed. Thus, studying the organic matter (OM) content in the sediment beneath extinct ice shelves may reveal how changes at the euphotic zone impact the benthic realm.

Fatty acids (FA), aliphatic hydrocarbon chains with a carboxylic group at one extremity, are synthesised in the cytosol. In marine organisms FA are predominantly found in energetic reserves which consist of triacylglycerols and wax esters, as well as in the phospholipids of the membrane lipid bilayer (Ding and Sun, 2005). A partial and selective degradation of FA occurs in the water column and in the sediment (Sun et al., 1997; Wakeham et al., 1997) and is particularly intense at the sediment-water interface (Laureillard et al., 1997). However, FA occurrence in the sediment column has been broadly studied (Canuel and Martens, 1996; Sun and Wakeham, 1994). Since different taxa of marine algae are characterized by different FA (Volkmann et al., 1989; Dunstan et al., 1992; Viso and Marty, 1993), these compounds can be used as trophic markers (Graeve et al. 1994; Cripps et al., 1999; Nelson et al., 2001; Auel et al., 2002). Furthermore, FA can also be used as indicators of the physiological state of the phytoplanktonic community (Hayakawa et al., 1996). The specificity of FA for particular marine algae taxa together with the different labilities of FA depending on their chemical structure (Haddad et al., 1992; Canuel and Martens, 1996; Sun and Wakeham, 1994; Camacho-Ibar et al., 2003b; Lü et al., 2010), make FA analysis a useful tool to investigate on OM sources and quality.

Sediment microscopical observations support the analysis of FA to have information about the origin of the OM which is in the sediment (Reuss and Poulsen, 2002).

Diatoms represent 40% of the total primary production in the Southern Ocean (Cortese and Gersonde, 2007) with high biomasses in Antarctic coastal regions (Wright and van den Enden, 2000; Beans et al., 2008). In the water column diatom valves are subjected to grazing (Crosta, 2009), advection and dissolution (Buffen et al., 2007), nevertheless

their frustules composed of hydrated silica are well-preserved in sediments and diatom microfossils are the predominant biogenic proxies preserved in the sediment column (Tsoy et al., 2009). Diatoms are sensitive to changes in salinity, temperature and nutrients, thus the abundance and composition of valves in the sedimentary record reflect the environmental conditions at the moment of their incorporation in the sediment column making diatoms a useful tool to reconstruct past environmental changes regarding for example currents, water temperatures, ice conditions and productivity (Sancetta, 1981, 1982; Zielinski and Gersonde, 1997; Armand et al., 2005; Tsoy et al., 2009). In this study, diatom valves of sea-ice related taxa, of the species *Fragilariopsis kerguelensis* and *Thalassiosira antarctica*, and resting spores (RS) of the genera *Chaetoceros* have been considered. Sea ice related species are those present within the Sea Ice Zone southward of the Polar Front that live within, on or under the sea ice (Armand et al., 2005). *Chaetoceros* RS abundance reflects episodes of high primary production (Donegan and Schrader, 1982; Leventer, 1991; Sancetta et al., 1992; Karpuz and Jansen, 1992), whereas *Fragilariopsis kerguelensis*, a cold open water species (Roberts et al., 2007), is the most abundant in Antarctic surface sediments (Cortese and Gersonde, 2007). *Thalassiosira antarctica* is a sea ice-related species (Garrison et al., 1987; Garrison, 1991) indicative of seasonally varying sea-ice conditions (Pike et al., 2008) which shows maximum abundance near the ice shelf edge, but requires cold open water to dwell (Pike et al., 2008).

Sediment FA composition analysis and microscopical counts of diatom valves have been carried out in the sedimentary record to identify relationships with the oceanographic conditions at Larsen A and B embayments, recently affected by ice shelf collapses, and off the Northern Antarctic Peninsula (NAP) seafloor, which has not been covered by ice shelf for at least 1 kyr.

4.2 Materials and methods

4.2.1 Sediment collection and preparation

Sediment samples were collected during the Antarctic expedition ANT-XXIII/8 off the Eastern coast of the Antarctic Peninsula (EAP) and at the North of the Antarctic Peninsula (NAP) (Fig. 4.1) using a multi-corer with polycarbonate core barrels of 10 cm of diameter (Barnett et al., 1984). In EAP, sediments were sampled at 5 stations, namely Larsen B South (LBS), Larsen B West (LBW), Larsen B Central (LBC), Larsen B North (LBN) and Larsen A (LA). Two other stations were sampled in NAP, Elephant Island (EI) and South Shetland Islands (SSI) (Fig. 4.1). After recovery, sediment cores

were sliced onboard in slices 0.5 cm thick from 0 to 10 cm depth and in slices 1 cm thick from 10 to 11 cm depth. Subsamples were immediately frozen at -20ºC. The sediment samples were freeze-dried (P=0.1 mbar and T=-80ºC) for 24 hours before laboratory analyses and microscopical observations. LA core was only 7.5 cm long while the other 6 cores were longer (EI=11 cm, SSI=19 cm, LBS=26 cm, LBW=34 cm, LBC=24 cm and LBN=24 cm). In order to make comparisons among cores only analyses that refer to the first 11 cm of sediment are reported.

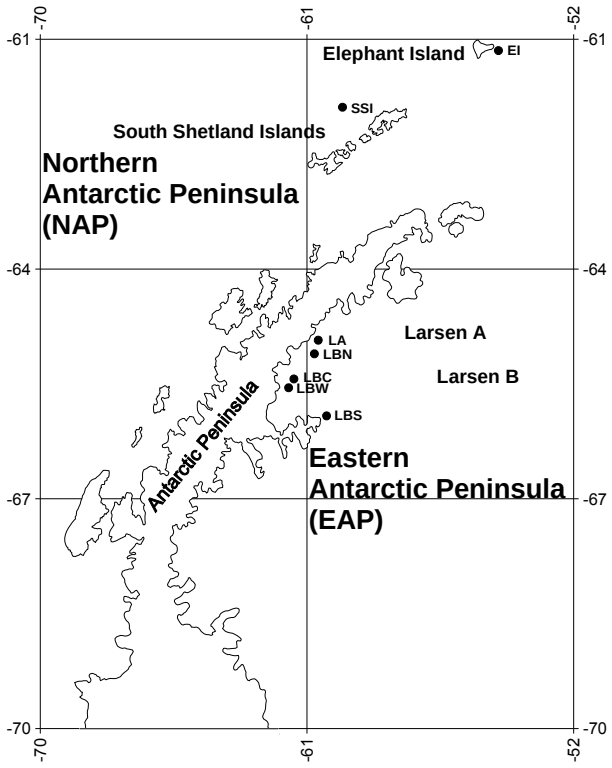

Fig. 4.1 Study area with the seven sampling stations.

4.2.2 Fatty acid extraction

Fatty acids were extracted trough a one step transesterification process adapted from Lewis et al., (2000) and Indarti et al. (2005) according to the recommendations of Christie (2003). The analytical protocol is detailed in Nahon et al (2010). Approximately 2 g of dried sediment were extracted in 8 ml of a cold solution of methanol, 98% sulfuric acid and chloroform in the presence of butyl hydroxytoluene (BHT), an antioxidant at a concentration of 50 mg l^{-1} (Christie, 2003). 20 µl of the internal standard C19:0 (nonadecanoic acid) (1mg ml^{-1}) were added and the samples were placed in a preheated oven at 90°C for 90 minutes. With this procedure lipids were extracted and the released fatty acids were directly methylated in fatty acid methyl esters (FAME). Ultra pure water (2 ml) was added to each sample to partition the extract in two phases. Following centrifugation (5 minutes at 1500 rpm and 4ºC), the inferior chloroform phase was recovered. A second extraction was made with a solution of hexane and chloroform (4:1 v/v) and after centrifugation (5 minutes at 1500 rpm and 4ºC) the superior phase was recovered and added to the first organic phase. This procedure was repeated twice. The organic phases were pooled and cleaned with a cold solution of potassium carbonate (2%) and after centrifugation (5 minutes at 1500 rpm and 4ºC) 6 to 9 ml of the organic phase were recovered and an aliquot was evaporated to dryness in a rotary evaporator (Savant Speed Vac system) at room temperature. FAME were recovered in 75 µl of pure hexane prior to analysis. Fatty acids as methyl esters were analysed using a Varian 3900 gas chromatograph (GC) coupled to a Saturn 2100T ion-trap mass spectrometer (MS). Identification and quantification were made with reference to known standards (Supelco 37, PUFA nº1 and nº3) allowing the analysis of 60 individual fatty acids.

In order to present the dataset in a comprehensible form, fatty acids were grouped according to their chemical structure:

(1) The mid chain fatty acids (MC-FA): chain length $\leq C_{20}$
(2) The long chain fatty acids (LC-FA): chain length C_{21}-C_{26}
(3) The monounsaturated fatty acids (MUFA): compounds with one unsaturation like 16:1(n-7), 18:1(n-9)cis, 20:1(n-9), 22:1(n-9) and 24:1(n-9)
(4) The polyunsaturated fatty acids (PUFA): compounds with two or more unsaturated bonds like 18:2(n-6)cis and 20:5(n-3)

PUFA were 18:2(n-6)cis and 20:5(n-3), MUFA 16:1(n-7), 18:1(n-9)cis, 20:1(n-9), 22:1(n-9) and 24:1(n-9), LC-FA were 21:0, 22:0, 24:0 and 26:0, and MC-FA were 8:0,10:0, 11:0, 12:0, 13:0, 14:0, 15:0, 16:0, 17:0, 18:0 and 20:0.

4.2.3 Diatom slides preparation and microscopical observation

Sediment samples were prepared according to the standard randomly distributed microfossils method. Due to the high abundance of diatom valves it was not necessary to disaggregate sediment with sodium pyrophosphate. Hydrochloric acid (HCl) and hydrogen peroxide (H_2O_2) were added to a known weight of dry sediment to attack carbonates and OM, respectively. Sediment was rinsed several times with bi-distilled water, slides were mounted and diatom valve counts were performed at 1000 magnification using a Leica DMLB with phase-contrast illumination. Counts were carried out on permanent slides of acid-cleaned material (Permount mounting medium). Schrader and Gersonde (1978) recommendations were followed for the counting of microfossil valves. Depending on the diatom abundance, several traverses across each cover slip were examined. A minimum of 350 valves were counted for each sample, when possible. Moreover, a counting of at least 100 valves of non-dominant taxa per sample was performed.

Valves of sea-ice taxa, *T. antarctica* and *F. kerguelensis* were identified together with *Chaetoceros* RS.

4.2.4 Statistics

A Principal Component Analysis (PCA) was carried out to test differences among PUFA, MUFA, LC-SAFA and MC-SAFA labilities. Prior to analysis, FA percentages were fourth root transformed to downweight the contributions of the quantitatively dominant FA. Data were statistically treated using PRIMER 6 software (Clarke and Gorley, 2006).

4.3 Results

4.3.1 Total fatty acid concentrations

The total FA concentration ranged from 36.74 μg g^{-1} dry weight (DW) (station LBS at 10 cm depth) to 441.41 μg g^{-1} DW (station LBN at 5.5 cm depth). The average total FA concentration from 0 to 11 cm depth was lowest at SSI (79.77±19.46 μg g^{-1} DW) and highest at LBN (236.70±113.90 μg g^{-1} DW) with a general trend for higher values in EAP (133.56±88.43 μg g^{-1} DW) than in NAP (93.35±35.46 μg g^{-1} DW) (Fig. 4.2 and Table 4.1).

Total FA concentrations were significantly correlated with depth only at stations LBS, LBC and LA (Fig. 4.3 and Table 4.2).

4.3.2 Fatty acid composition

Overall, a total of 22 individual FA were identified in EAP and NAP sediments. The dominant FA in all samples were: 12:0, 16:0, 18:0 and 18:1(n-9) (Table 4.1). In general, sediments in EAP were enriched in 8:0, 10:0, 11:0, 12:0, 13:0, 16:0, 18:0, 18:1(n-9), 20:0 and 20:1(n-9), while average concentrations in 14:0, 15:0, 16:1(n-7), 18:2(n-6), 22:0, 22:1(n-9) and 24:0 were higher in the cores from NAP. The contribution of certain FA was minor and restricted to some samples: for instance 17:0 was present only at LBN and LA, 20:5(n-3) at EI, 21:0 at LBS and LBN, 24:1(n-9) at EI and LBS and 26:0 at SSI and LBS (Table 4.1). High amounts of 22:1(n-9) were only found at EI (Table 4.1).

Among diatom indicators, 16:2(n-4) and 16:3(n-4) were absent in the seven stations and 20:5(n-3) was present only at station EI (Table 4.1). 14:0 and 16:1(n-7) were present in all the stations. The average relative abundance from 0 to 11 cm depth of 14:0 and 16:1(n-7) was higher in NAP (2.80±1.11 % for 14:0 and 2.16±0.87 % for 16:1(n-7)) than in EAP (1.83±0.95 % for 14:0 and 1.56±0.95 % for 16:1(n-7)). The average 16:1(n-7)/16:0 ratio was < 1 in all the stations but was higher in NAP (0.09 in EI and 0.11 in SSI) than in EAP (from 0.05 LBW to 0.08 in LBS and LBC). 20:5(n-3)/22:6(n-3), 16:1(n-7)/18:4(n-3) and 18:1(n-7)/18:1(n-9) ratios are also used as diatom indicators but were not calculated because 22:6(n-3), 18:4(n-3) and 18:1(n-7) were not detected in the analyses.

Table 4.1 Percentage (%) of the 22 FA analyzed and present in the study area, and total FA concentration (µg g^{-1} DW) from 0 to 11 cm depth.

	Source	Chemical structure	EI	SSI	LBS	LBW	LBC	LBN	LA
8:0		MC-FA	0.25±0.21	0.54±0.26	0.35±0.28	0.32±0.15	0.68±0.48	0.34±0.15	0.35±0.12
10:0		MC-FA	1.97±0.64	2.93±0.73	3.31±1.04	2.61±0.52	3.07±1.11	2.07±0.79	1.84±0.59
11:0	bacteria	MC-FA	0.05±0.03	0.04±0.03	0.07±0.05	0.03±0.03	0.13±0.06	0.04±0.02	0.07±0.02
12:0		MC-FA	16.03±6.00	15.37±3.05	14.83±6.88	23.29±7.18	25.73±8.07	11.08±6.29	20.43±7.92
13:0	bacteria	MC-FA	0.09±0.05	0.14±0.07	0.13±0.07	0.11±0.05	0.23±0.07	0.15±0.03	0.14±0.04
14:0	diatoms	MC-FA	2.03±0.97	3.45±0.73	1.87±1.45	1.57±0.74	2.14±0.73	1.73±0.55	1.72±0.86
15:0	bacteria	MC-FA	0.36±0.17	0.62±0.16	0.36±0.22	0.31±0.13	0.45±0.15	0.46±0.11	0.31±0.12
16:0	dinoflagellates	MC-FA	17.71±4.71	24.25±2.29	22.11±3.01	25.60±2.86	24.71±4.69	23.13±4.51	21.30±1.74
16:1(n-7)	diatoms	MUFA	1.64±0.67	2.61±0.76	1.71±1.18	1.18±0.40	1.90±1.20	1.35±0.79	1.52±0.73
17:0		MC-FA	Not found	Not found	Not found	Not found	Not found	0.37±0.10	0.30±0.08
18:0		MC-FA	14.10±3.74	17.87±2.63	17.84±2.43	19.86±2.74	20.43±4.92	20.85±3.52	18.12±1.60
18:1(n-9)	dinoflagellates	MUFA	12.87±4.81	23.75±6.95	27.96±5.61	19.65±7.36	15.40±9.80	29.27±8.43	26.52±6.28
18:2(n-6)		PUFA	1.49±0.58	1.87±1.02	1.19±0.38	0.83±0.37	0.89±0.75	0.90±0.37	0.93±0.24
20:0		MC-FA	0.23±0.20	0.74±0.25	1.03±0.51	0.84±0.33	1.03±0.35	1.30±0.45	1.00±0.32
20:1(n-9)	zooplankton	MUFA	0.96±0.99	3.15±0.82	4.33±1.71	2.23±1.46	1.62±1.40	4.39±1.66	3.55±1.95
20:5(n-3)		PUFA	0.03±0.06	Not found	Not found	Not found	Not found	Not found	Not found
21:0		LC-FA	Not found	Not found	0.02±0.02	Not found	Not found	0.01±0.02	Not found
22:0		LC-FA	0.85±0.29	0.43±0.13	0.34±0.22	0.26±0.16	0.45±0.12	0.45±0.15	0.32±0.08
22:1(n-9)	zooplankton	MUFA	28.27±16.93	0.96±0.39	2.26±1.40	1.25±0.92	0.89±0.77	1.95±0.84	1.49±1.05
24:0		LC-FA	0.40±0.0.13	0.62±0.23	0.18±0.11	0.05±0.07	0.23±0.06	0.12±0.08	0.10±0.05
24:1(n-9)		MUFA	0.67±0.33	Not found	0.04±0.07	Not found	Not found	Not found	Not found
26:0		LC-FA	Not found	0.66±0.26	0.09±0.15	Not found	Not found	Not found	Not found
Total (µg g-1 DW)			109.33±43.33	79.77±19.46	95.88±53.42	98.80±64.46	98.53±30.95	236.70±113.90	166.14±84.46

Dinoflagellate indicators 16:0, 18:1(n-9), 18:4(n-3) and 22:6(n-3) were analyzed. 18:4(n-3) and 22:6(n-3) were absent in the seven stations. 16:0 and 18:1(n-9) cis were present at the seven stations (Table 4.1). The average relative abundance from 0 to 11 cm depth of 16:0 and 18:1(n-9) cis was higher in EAP (23.41±3.83 % for 16:0 and 23.51±9.28 % for 18:1(n-9)cis) than in NAP (21.24±4.85 % for 16:0 and 18.75±8.13 % for 18:1(n-9)cis).

Among the zooplankton indicators, were analyzed 20:1(n-9), 22:1(n-9), 22:1(n-11) and 20:5(n-3). 22:1(n-11) was not detected in all the stations, 20:5(n-3) was present only in EI and 20:1(n-9) and 22:1(n-9) were present at all the stations (Table 4.1). The average relative abundance from 0 to 11 cm depth of 20:1(n-9) was higher in EAP (3.20±1.97 %) than in NAP (2.15±1.42 %). However, the average relative abundance in the sediment column of 22:1(n-9) was higher in NAP (13.51±17.83 %) than in EAP (1.57±1.14 %).

Odd bacterial FA 9:0, 11:0, 13:0, iso15:0, anteiso15:0, 15:0, 15:1(n-5), iso17:0, 17:0, 17:1(n-7), $17:0^{D}$, $19:0^{D}$, 21:0 and 23:0 were analyzed. 9:0, iso15:0, anteiso15:0, 15:1(n-5), iso17:0, 17:1(n-7), $17:0^{D}$, $19:0^{D}$ and 23:0 were not detected in the seven stations.

17:0 was present only in LBN (0.55%) and LA (0.51%) and 21:0 was present only in LBS (0.02%) and LBN (0.01%) (Table 4.1). 11:0, 13:0 and 15:0 were present in all the stations. The average relative abundance from 0 to 11 cm depth of 11:0 and 13:0 was higher in EAP (0.07±0.05 % for 11:0 and 0.15±0.07 % for 13:0) than in NAP (0.04±0.03 % for 11:0 and 0.11±0.07 % for 13:0). The average relative abundance in the sediment column of 15:0 was higher in NAP (0.50±0.21 %) than in EAP (0.38±0.17 %). Other bacterial FA, like the hydroxylated FA (2-OH-C10, 2-OH-C12, 3-OH-C12, 2-OH-14 and 3-OH-14), the iso and anteiso compounds (iso15:0, anteiso15:0, iso16:0 and iso17:0), the cyclic FA ($17:0^{D}$ and $19:0^{D}$) and the vaccinic acid 18:1(n-7), were not detected in all NAP and EAP stations.

Higher contributions of the MC-FA occurred in EAP (68.64±11.93%) than in NAP (59.91±11.67%). Among the LC-FA, 22:0 and 24:0 were the only compounds present at the seven stations. 21:0 only occurred at LBS and LBN and 26:0 at SSI and LBS.

A trend of higher values of LC-FA was observed in NAP (1.50±0.54%) than in EAP (0.54±0.29%). The average MUFA relative abundance from 0 to 11 cm depth was higher in NAP (36.88±12.08%) than in EAP (29.85±11.68%). Four MUFA, namely

16:1(n-7), 18:1(n-9)cis, 20:1(n-9) and 22:1(n-9), were found in the seven stations while 24:1(n-9) only occurred at EI and LBS. PUFA represented a small component of the FA pool (Table 4.1). As observed for the MUFA fraction, they were more abundant in NAP (1.71±0.86%) than in EAP (0.96±0.48%). Only two PUFA were found in the set of samples: 18:2(n-6) cis was present at the seven stations and 20:5(n-3) was only detected at EI.

4.3.3 Microscopical observation of diatoms valves

Total abundance of diatoms ranged from 0 (stations LBS from 4 to 4.5 and from 6.5 to 11 cm depth, LBW at 5.5 cm depth and from 8 to 10 cm depth, LBC at 4.5 cm depth and LBN from 3 to 5 and from 7 to 10 cm depth) to 2.86 x 10^7 valves g^{-1} of DW (station SSI at 11 cm depth). The average abundance from 0 to 11 cm depth was lowest at LBS ($0.3x10^6 \pm 0.5x10^6$ valves g^{-1} DW) and highest at SSI ($17.09x10^6 \pm 6.07x10^6$ valves DW) (Fig. 4.2 and Table 4.3). Based on the regional average, at all depths the total number of valves was higher in NAP than in EAP.

The total number of valves and the depth were significantly correlated at all stations except at LA (Fig. 4.4 and Table 4.4).

Valves of sea-ice taxa and *T. antarctica* together with *Chaetoceros* RS were found in all NAP and EAP stations. Valves of *F. kerguelensis* were found only in EI and SSI (Table 4.3). The average relative abundance of sea-ice taxa from 0 to 11 cm depth was higher in EAP (33.90±32.30%) than in NAP (13.32±5.13%). The average relative abundance of *Chaetoceros* RS from 0 to 11 cm depth was higher in NAP (41.44±9.92%) than in EAP (22.45±26.70%). The average relative abundance of *T. antarctica* from 0 to 11 cm depth was higher in NAP (4.96±1.83%) than in EAP (0.83±1.44%).

Table 4.2 Characteristics (R, P, intercept and slope) of the linear regressions of the total FA concentration versus depth in the seven stations.

	EI	SSI	LBS	LBW	LBC	LBN	LA
R	0.265	-0.319	-0.691	-0.193	-0.575	-0.389	0.599
P	0.304	0.171	0.001	0.491	0.013	0.170	0.030
Intercept	93.767	88.930	149.721	114.252	123.733	298.611	90.172
Slope	3.392	-1.673	-10.824	-3.738	-5.306	-12.746	21.468

Table 4.3 Percentage (%) of sea ice taxa, *Chaetoceros* RS, *F. kerguelensis*, *T. antarctica* and non dominant taxa in the seven stations, and total number of diatom valves (valves g^{-1} DW) from 0 to 11 cm depth.

	EI	SSI	LBS	LBW	LBC	LBN	LA
sea ice taxa	16.19±3.99	8.08±1.44	17.42±28.67	49.91±41.50	26.71±26.88	19.06±27.51	56.02±7.29
Chaetoceros RS	35.65±6.84	52.08±3.89	10.90±19.09	12.10±27.58	41.46±34.16	25.29±32.38	27.85±10.24
F. kerguelensis	13.15±3.33	10.85±1.81	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
T. antarctica	4.60±1.83	5.63±1.71	0.47±1.05	0.15±0.62	0.42±0.82	0.27±0.69	2.63±1.73
non dominant taxa	30.42±5.03	23.37±2.89	71.21±43.25	37.84±43.75	31.40±43.04	55.39±49.40	13.50±4.97
Total (valves g^{-1} DW)	$3.28x10^6$±$2.07x10^6$	$17.09x10^6$±$6.07x10^6$±	$0.3x10^6$±$0.5x10^6$±	$0.29x10^6$±$0.62x10^6$±	$2.43x10^6$±$5.05x10^6$±	$0.88x10^6$±$1.99x10^6$±	$2.80x10^6$±$1.33x10^6$±

Table 4.4 Characteristics (R, P, intercept and slope) of the linear regressions of the total number of diatom valves versus depth in the seven stations.

	EI	SSI	LBS	LBW	LBC	LBN	LA
R	0.656	0.696	-0.706	-0.592	-0.601	-0.560	-0.118
P	0.0009	0.0009	0.0002	0.012	0.018	0.030	0.629
Intercept	1.101E6	5.002E6	828522.0	815588.0	6.474E6	2.346E6	3.049E6
Slope	412914.0	2.208E6	-108229.0	-123342.0	-954672.0	-349913.0	-56109.1

4.3.4 Statistics

The first two axis of the PCA explained 65% of the total variance. Axis 1 accounted for 38% of the variance and had positive loadings for all MC-SAFA and negative loadings for all PUFA, MUFA and LC-SAFA. Axis 2 accounted for 27% of the variance and there was not a correspondence among positive or negative loadings and PUFA, MUFA, LC-SAFA and MC-SAFA.

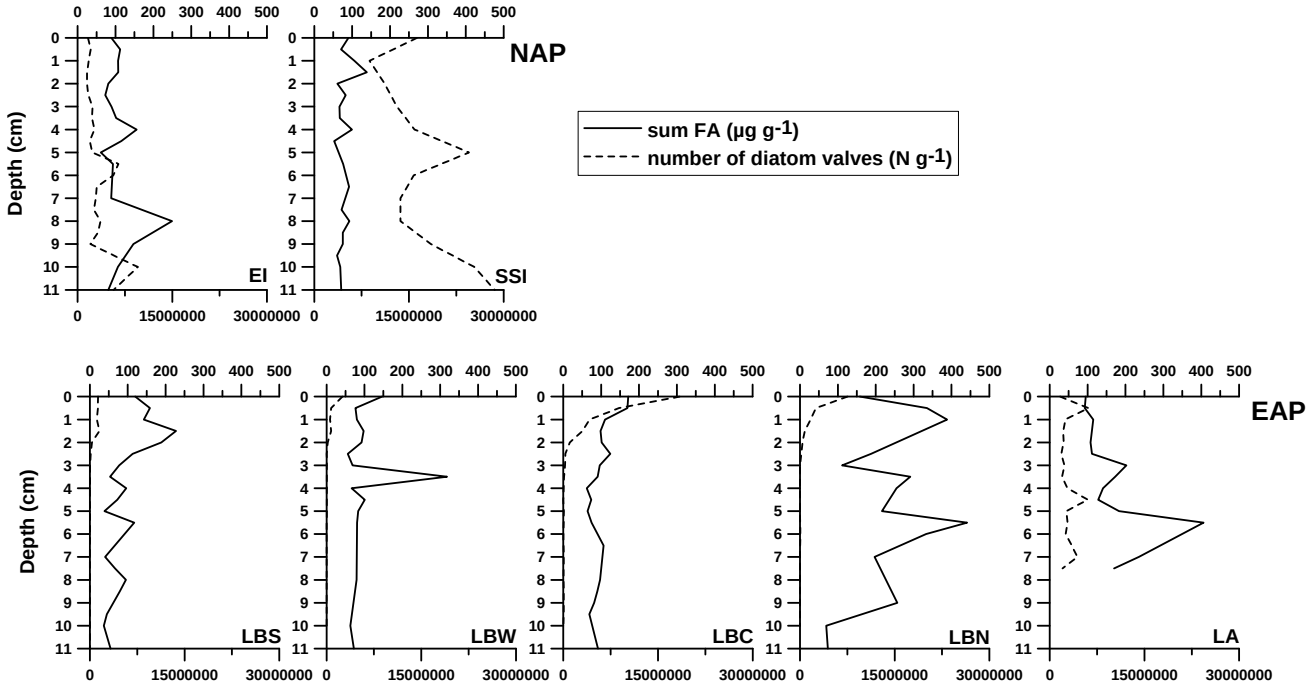

Fig. 4.2 Total FA concentration and number of diatom valves profiles in EI, SSI, LBS, LBW, LBC, LBN and LA.

4.4 Discussion

FA and diatom valves were assessed in the continental shelf of NAP and EAP to find out whether these biomarkers can reflect differences between regions derived from the presence and recent disintegration of the Larsen A and B ice shelves. Overall, there was an evident decrease in EAP in the number of diatom valves below 2 cm depth, whereas the valves distribution in NAP showed an increasing trend towards the base of the cores (Fig. 4.2). Thus, suggesting that the top 2 cm layer in EAP cores represent the material deposited after the ice shelf collapses. Therefore, this depth limit was chosen to make comparisons among the FA concentrations and the number of diatom valves.

This first section of the discussion which deals with sediment FA composition consists of three parts, the sediment FA composition in NAP and EAP to weigh principal

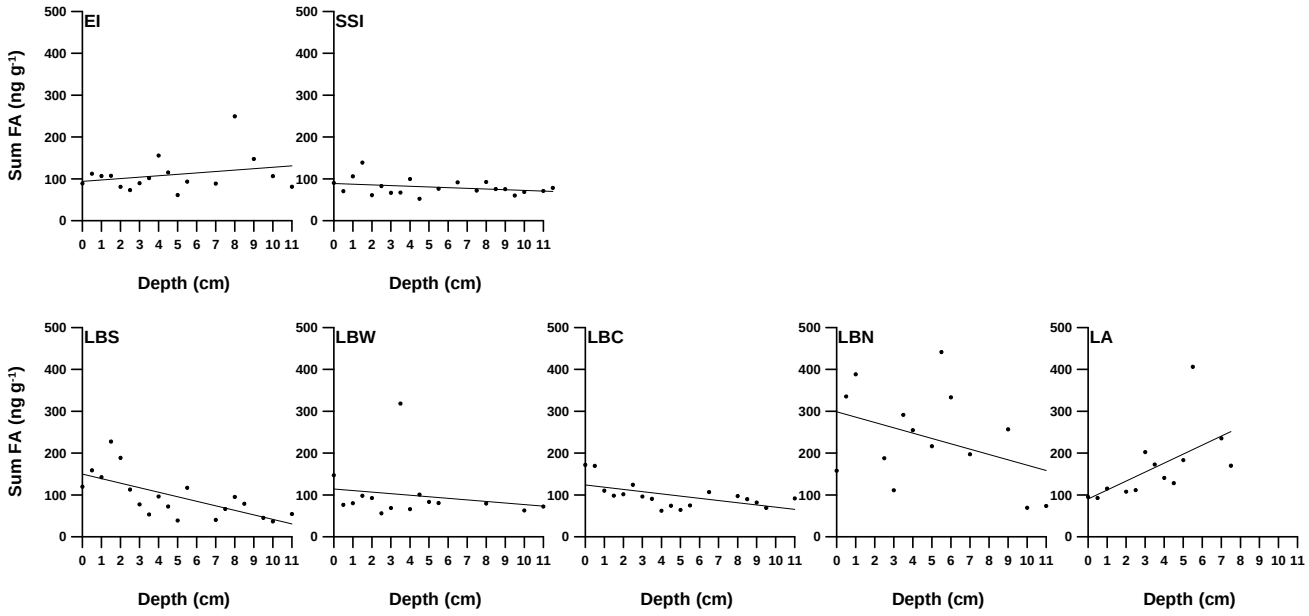

Fig. 4.3 Linear regressions of total FA concentration versus depth in NAP and EAP.

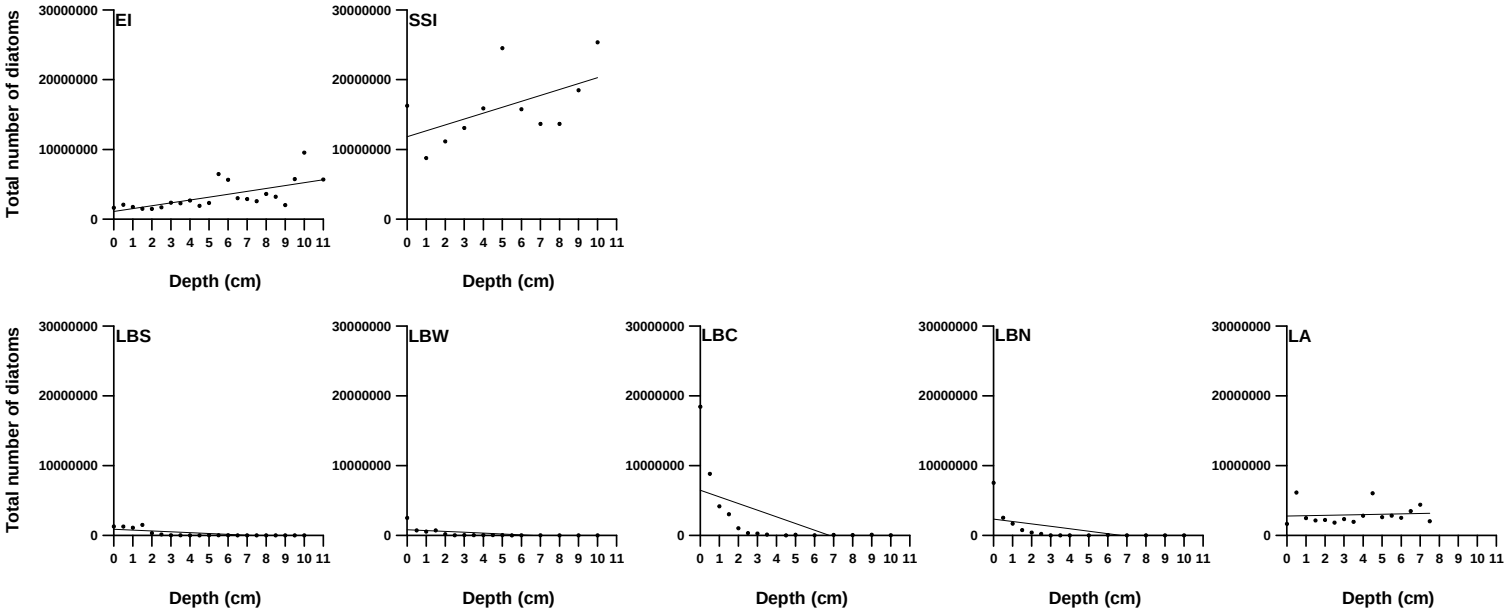

Fig. 4.4 Linear regressions of number of diatom valves versus depth in NAP and EAP.

differences among the two regions, the occurrence of FA to identify potential OM sources and the use of FA as OM indicators of lability.

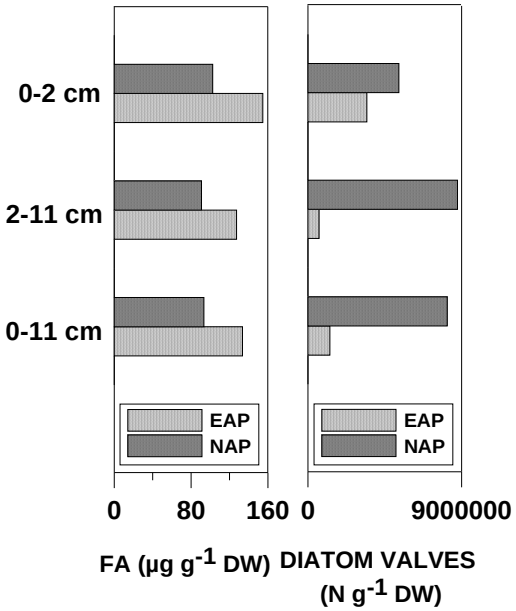

Fig. 4.5 Average total FA (ng g^{-1}DW) and total number of diatom valves (N g^{-1} DW) in NAP and EAP

The second section deals with the presence of diatom valves throughout the sediment cores to discuss the most recent distribution of valves and the present oceanographic conditions. As a corollary a summary is presented.

4.4.1.1 Sediment FA composition in NAP and EAP

FA total concentration in the study area was comparable to the total concentration found in sediments in a tropical intertidal environment (Volkman et al., 1980) and in the productive upwelling area of the southeastern Pacific (Niggemann and Schubert, 2006), but, as expected, lower than in Antarctic sea ice samples (Nichols et al., 1993) (Table 4.5).

The total FA concentration was high in NAP and EAP but in general the study area presented a low FA variety since only 22 individual components were detected. Commonly, more than 22 FA occur in a number of oceanographic settings from the tropic to the poles including the water and the sediment columns (Table 4.5). In general, most of the undetected FA in our study corresponded to PUFA related to diatoms (e.g., 16:2(n-4), 16:3(n-4), 20:4(n-6)), dinoflagellates (e.g., 18:4(n-3), 22:3(n-3)) and bacteria (e.g., iso15:0, anteiso15:0, iso16:0, iso17:0).

Table 4.5 Relative abundance (%) of FA absent in NAP and EAP, relative abundance of PUFA and total concentration of FA in Antarctic surface sediment sampled in austral spring and summer.

[a] Intertidal environment located at Old Yanakie Beach, Corner Inlet, Victoria (lat 38º49'S).

[b] FFA in sea ice algal samples during the spring bloom.

[c] Estimated fluxes of FFA (μg m^{-2} day^{-1}) in sinking material recovered from sediment traps.

[d] Sample sediments from the Chilean coastal upwelling region.

	iso15:0	anteiso15:0	iso16:0	iso17:0	anteiso17:0	16:2(n-4)	18:3(n-3)	18:4(n-3)	20:4(n-6)	22:4(n-6)	22:5(n-3)	22:6(n-3)	Total PUFA	Total FA
Volkman et al., 1980[a]	0.58	0.72	0.17	0.14	0.12	0.46	0.39	1.0	2.9	0.17	0.32	no data	14	93±5 μg g^{-1} DW
Venkatesan, 1988			0.4 μg g^{-1} DW			no data	no data	no data	no data	no data	no data	no data	no data	9.4 μg g^{-1} DW
Nichols et al., 1993	no data	no data	no data	no data	no data	absent	0.4	1.5	no data	no data	no data	absent	25.6	6.56 mg g^{-1} DW
Hayakawa et al., 1996	0.7	0.8	no data	1.7	1.8	1.0	2.1	0.6	no data	no data	no data	0.3	8.6	no data
Hayakawa et al., 1997	0.9	0.4	no data	2.5	1.4	1.3	1.1	0.2	no data	no data	no data	0.2	5.2	no data
Fileman et al., 1998	no data	no data	no data	no data	no data	no data	no data	0.8	no data	no data	no data	9.7	no data	no data
Cripps and Clarke, 1998[c]	no data	no data	no data	no data	no data	2.16	no data	5.10	no data	no data	no data	0.66	no data	32.08
Niggemann and Schubert, 2006[d]	no data	no data	no data	no data	no data	no data	no data	no data	no data	no data	no data	no data	no data	20-203 μg g^{-1} DW

Table 4.6 Relative abundance (%) of *Chaetoceros* spp., *Thalassiosira antarctica*, *Fragilariopsis kerguelensis* and sea ice taxa valves and total number of valves counted in Antarctic surface sediments.

LA: Larsen A

NAP: Northern Antarctic Peninsula

	Chaetoceros RS	*Thalassiosira antarctica*	*Fragilariopsis kerguelensis*	Sea ice taxa	Total number of valves (valves/g sediment) x 10^{-6}
Leventer, 1992	21.8	14.3	no data	no data	28.48
Taylor et al., 1997	8.30	0.01	0.96	no data	no data
Zielinski and Gersonde, 1997	92.6	32.7	92	no data	50-200
Armand et al., 2005[a]	91.8	31.8	no data	no data	no data
Mohan et al., 2006	no data	no data	>71	no data	no data
Buffen et al., 2007 (LA)	5	1.2 (T2), 0.2 (T1)	0.0	no data	6.65
Buffen et al., 2007 (NAP)	4.4	0.4 (T2), 1.6 (T1)	0.0	no data	33.41
Tsoy et al., 2009	no data	13.2-20.0	no data	no data	5.0-15.3

The presence of FA in Antarctic sediment has been ascribed to marine primary and secondary production due to the absence of terrestrial inputs (Venkatesan and Kaplan, 1987; Cripps, 1995; Cripps and Clarke, 1998). Thus, the high concentration of FA found in NAP and EAP should reflect a relatively high marine production in both regions. However, based on the total valve profiles is possible to assume that a larger primary production and for longer periods of time has been taking place in NAP. This assumption is supported not only by the larger absolute number of valves (Fig. 4.2) but also by the larger relative abundances of *F. Kerguelensis*, which represents open ocean conditions, especially related to the polar front (Table 4.3) (Crosta et al., 2005). The higher FA concentrations in EAP than in NAP (Fig. 4.5) and the fact that differences in FA concentrations between the two regions are enhanced in the superficial sediments (Fig. 4..5) (FA concentration in NAP is the 67% of FA concentration in EAP, whereas in the deeper part is 72%) suggest that benthic consumption is more intense in NAP. Furthermore, in NAP higher bioturbation and oxygen penetration could enhance the aerobic degradation of both membrane and intracellular FA in the sediment column (Ding and Sun, 2005). It should also be borne in mind that the higher concentration of FA in EAP was mainly due to the higher abundance of refractory FA, especially MC-SAFA (Fig. 4.7) presumably laterally transported.

4.4.1.2 Sediment organic matter sources

FA 14:0 and 16:0 have been associated to diatoms (Nichols et al., 1993; Dunstan et al., 1994) however these FA are not specific for this group of microalgae and were also found in dinoflagellates (Dalsgaard et al., 2003) and zooplankton (Pruski, unpublished results). FA 16:1(n-7) was found in diatoms, especially in spring bloom or isolation situations (Nichols et al., 1986; Nichols et al., 1993; Dunstan et al., 1994) and recently, it was found to be abundant in pelagic and ice-related diatoms from the Arctic Svalbard region and nearly absent in small flagellates and *Phaeocystis* detritus (Søreide et al., 2008). The higher concentrations of FA 16:1(n-7) point to a larger input of diatoms in NAP sediments (Table 4.1 and Fig. 4.6), which is also supported by the diatom valve differences found between regions (Fig. 4.5). In contrast, the higher concentration of 18:1(n-9) cis in EAP (Table 4.1) suggests a higher contribution of flagellates material (Søreide et al., 2008) in this region (Fig. 4.6). However, the low 16:1(n-7)/16:0 and 16:1(n-7)/C18:1(n-9) ratios (<1) found indicate a higher contribution of flagellates over

diatoms (Viso and Marty, 1993; Budge and Parrish, 1998; Reuss and Poulsen, 2002) to the sediments in both regions. 18:1(n-9)cis can also be associated to detrital material (Fahl and Kattner, 1993), thus, its presence as indicator of lateral transport of degraded OM cannot be discarded.

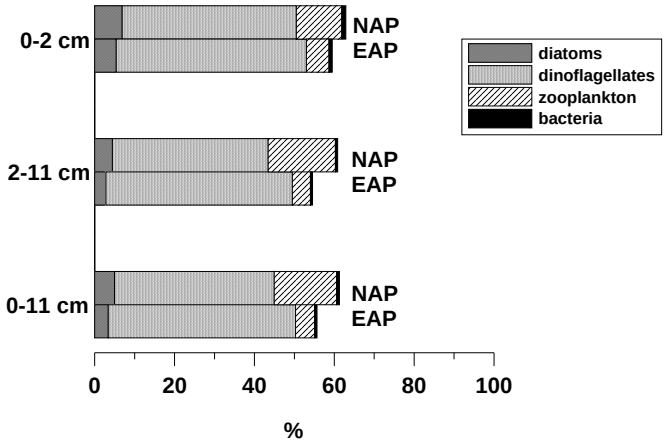

Fig. 4.6 Percentage (%) of diatom (14:0 and 16:1(n-7), dinoflagellate (16:0, 18:1(n-9)cis), zooplankton (20:1(n-9) and 22:1(n-9) and bacteria (11:0, 13:0 and 15:0) indicators in NAP and EAP, from 0 to 2, from 2 to 11 and from 0 to 11 cm depth.

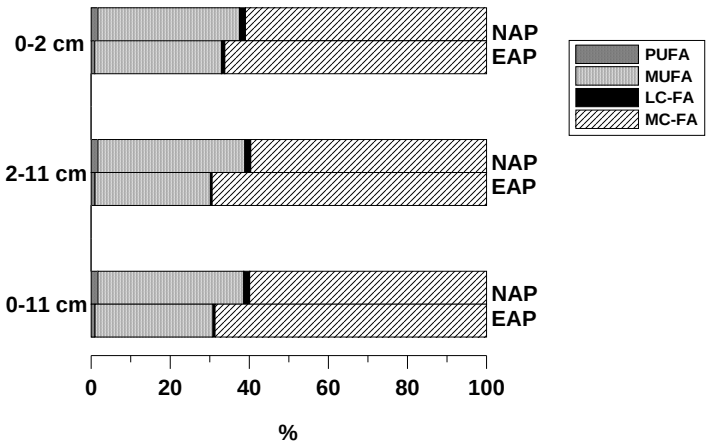

Fig. 4.7 Percentage (%) of PUFA, MUFA, LC-SAFA and MC-SAFA in NAP and EAP, from 0 to 2, from 2 to 11 and from 0 to 11 cm depth.

The absence of *iso*- and *anteiso*-FA (Parkers and Taylor, 1983; Kaneda, 1991), hydroxylated FA and 18:1(n-7) (Perry et al, 1979) and the absence of any clear trend in the distribution of FA with an odd number of carbon atoms (Lee, 1992; Dalsgaard et al., 2003 and references therein) showed the low content of bacterial material in both regions. Branched iso and anteiso FA are characteristic of bacteria and originate in the sediments from the bacterioplankton derived from the water column as well as from bacteria produced *in situ* in the sediments. Odd number saturated FA as well as hydroxylated FA are also abundant in bacteria although differences exist between strains. The contributions of bacterial FA were relatively small in the sediments of the study area suggesting a low microbial remineralization of the detrital material.

Regarding zooplankton, the clearest signal of its signature came from the presence of the FA 22:1(n-9) (Falk-Petersen et al., 1999). This FA was more abundant in EI with a relative concentration of 20%-30%, whereas in the rest of the cores it only accounted for less than 5% (Table 4.1). EI is the closest station to the polar front and the outer limit of the seasonal sea-ice where more krill is found (Nicol et al., 2000).

FA composition in the study area was diverse and showed no evident patterns to clearly differentiate single OM sources or a stronger contribution from any group to a particular region, with the only exception of the zooplanktonic biomarker 22:1(n-9) in EI (Fig. 4.6). However, the FA dataset provides important insights into potential differences in OM lability among regions.

4.4.1.3 FA and OM degradation

The confusing picture emerging from OM sources to NAP and EAP sediments through FA analyses may be determined by the different stabilities of the individual FA. Thus, chemical characteristics of sedimentary FA may better help distinguishing particular conditions of each region in the study area.

Based on their chemical structure FA were grouped into four classes, PUFA, MUFA, MC-FA and LC-FA. A PCA analysis considering the relative abundance of the 22 FA in the sediment column of the seven stations resulted in the separation of MC-FA from PUFA, MUFA and LC-FA (Fig. 4.8). Such a separation was previously found in the southeastern Pacific coastal upwelling region (Niggemann and Schubert, 2006). In the present study the principal axis 1 explained 38 % of the variability with the positive coefficient factors coinciding with MC-FA and the negative coefficient factors coinciding with LC-FA, MUFA and PUFA (Fig. 4.8). Based on PUFA, MUFA, LC-FA and MC-FA labilities and their distribution in the study area, NAP sediments presented a better

quality and less refractory OM (Fig. 4.7). Furthermore, the ratio of the labile OM (PUFA+MUFA+LC-FA) to refractory OM (MC-FA) was higher in NAP (0.67) than in EAP (0.46) for the whole core average.

Sediment samples in the present study were collected during the austral summer when the annual pulse of fresh OM to the seabed takes place. Our results showed the presence of a high number of diatom valves (Fig. 4.2 and 4.5) at the top of each core making clear the arrival of such seasonal pulse. However, PUFA are rapidly degraded in the water column and after deposition onto the seabed (Smith et al., 1983; Wakeham et al., 1997; Budge and Parrish, 1998; Hu et al., 2006); thus, the low proportion of PUFA and the absence of PUFA diatom indicators, such as 16:2(n-4), 16:3(n-4) and 16:4(n-l) (Volkman et al., 1989; Wakeham, 1995) in the study area may reflect a rapid FA degradation even in this polar environment. Macrobenthic studies in EAP (Sañé et al. *c.*-CAP3) showed low abundance and biomass in the EAP region suggesting that FA consumption takes place mainly in the water column.

Higher average relative concentrations of MUFA and LC-FA were found in NAP than in EAP, both in surface (from 0 to 2 cm depth) and in deeper sediments (from 2 to 11 cm depth) (Fig. 4.7). However, differences among regions were smaller at the surface layer suggesting that the differences in the 2 to 11 cm depth layer can be related to a longer period of fresh OM accumulation in NAP than in EAP as a consequence of ice shelves influence.

MUFA like PUFA are more labile than SAFA. The absence of double bonds or other functional groups in MC-FA make these FA chemically resistant. LC-SAFA of terrestrial origin are usually considered less subjected to degradation than planktonic FA and also more persistent in the sediment column (Meyers and Eadie, 1993; Canuel and Martens, 1996; Meyers, 1997; Camacho-Ibar et al., 2003a) due to the inorganic matrix which protects them (Haddad et al., 1992; Canuel and Martens, 1996). Nevertheless, the absence of terrestrial inputs in the study area makes evident that the LC-FA found in NAP and EAP have a marine origin and may be the result of a chain lengthening process of MUFA (Nichols et al., 1986).

The higher MC-FA average concentration in EAP than in NAP (Fig. 4.7) cannot be only attributed to a recent deposition of OM after ice shelf collapses because higher MC-FA concentrations have been found in the EAP sediment column at all depths and not only in the upper sediment column which chronologically corresponds to Larsen A and B ice shelf collapses and contents the consequent flux of fresh OM to the seafloor.

Therefore, the high MC-FA concentrations in EAP sediment column may be the result of the accumulation of refractory material that had been laterally advected.

4.4.2 The diatom record

The total number of diatom valves in NAP and EAP was comparable to the total number of diatom valves previously found in Larsen A embayment (Buffen et al., 2007) and lower than values from the Antarctic George V Coast (Leventer, 1992) and the Northern Antarctic Peninsula (Buffen et al., 2007) (Table 4.6).

The higher average total number of diatom valves in NAP than in EAP is due to the evident difference in the total concentration of valves below 2 cm depth (Fig. 4.2 and 4.5). These values may demonstrate the longer period of diatom accumulation in NAP than in EAP sediment providing further support to the hypothesis that is only after Larsen A and B ice shelf collapses that diatom debris is present in the EAP region, supporting previous observations (Buffen et al., 2007). Furthermore, the absence of diatom valves below the upper 3 cm layer in EAP sediment suggest that there is a vertical transport of the recently produced diatoms and that the lateral transport of diatom valves is negligible. Thus, diatom valve concentrations in sediment may reflect the local conditions at the euphotic zone and surface water productivity (Leventer, 1992; Scherer, 1994; Leventer et al., 1993, 1996, 2002; Sjunneskog and Taylor, 2002).

A relatively high number of total diatom abundance was found in LBC from 0 to 2 cm depth and in LA below 2 cm depth. In the case of LBC, diatom valve contents in the upper 2 cm layer may be linked to the particular bathymetric characteristics of this station, which lays at the axis of a glacial trough that acts as a sediment trap, while the high total number of diatoms in LA below 2 cm depth may be linked to the earlier ice shelf collapse in that area (1995) than in the Larsen B area (2002).

The higher abundances in NAP than in EAP below 2 cm depth of sea-ice taxa, *Chaetoceros* RS and *T. antarctica* (Fig. 4.9) are related to NAP open water conditions (Armand et al., 2005; Buffen et al., 2007), which are corroborated with the presence only in NAP samples of the cold open water species *F. kerguelensis* (Crosta et al., 2005; Roberts et al., 2007).

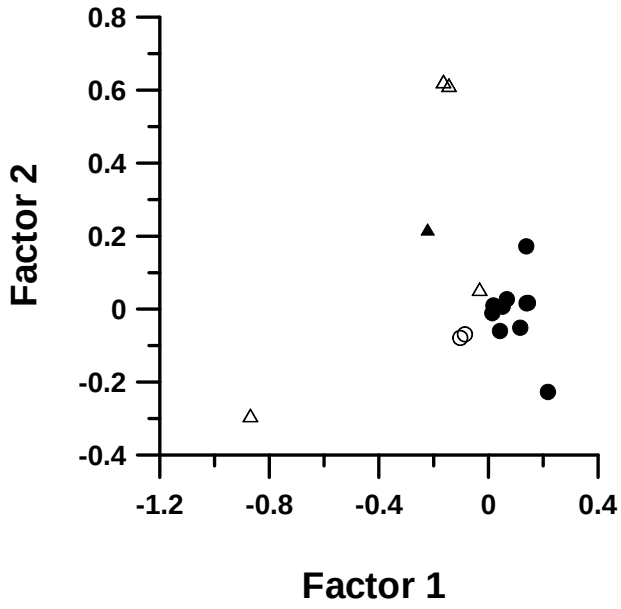

Fig. 4.8 Factors loadings of individual FA for the first two principal components identified by PCA. Black circles=MC-SAFA, open circles=LC-SAFA, open triangles=MUFA and black triangles=PUFA.

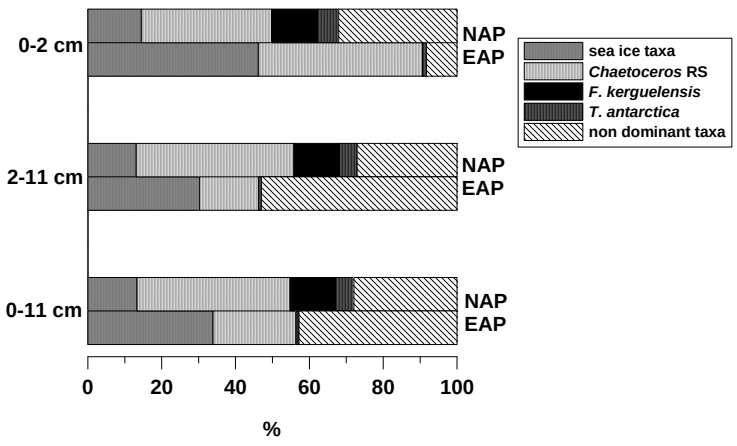

Fig. 4.9 Percentage (%) of sea ice taxa, *Chaetoceros* spp., *F. kerguelensis*, *T. antarctica* and non dominant taxa in NAP and EAP, from 0 to 2, from 2 to 11 and from 0 to 11 cm depth.

4.4.3 Summary

Based on our results, the different climatic histories of EAP and NAP regions are reflected in the observed sediment FA concentrations and diatom abundances. In both studied regions, FA and diatom valves showed different profiles throughout the sediment cores hampering the identification of common trends. However, each variable provided information that enabled interpreting differences between regions and their climatic histories. On the one hand, the presence of FA with refractory characteristics throughout the sediment cores in EAP seems to be the result of the lateral input of refractory OM (MC-FA). These patterns in parallel to the distribution of diatom valves also showed that unsaturated FA degrade rapidly in the study area and cannot be used as indicators of phytoplankton debris or fresh OM. On the other hand, the distribution of diatom valves showed an exponential decreasing pattern in EAP in contrast to the more constant distribution in NAP. This distribution was interpreted as the change after ice shelf collapses of the conditions which hampered in EAP the diatom valves supply to the seabed. Further, the proportion of diatom taxa related to open water conditions (e.g., Antarctic Circumpolar Current) such as *T. antarctica* and *F. kerguelensis* were higher in NAP or in the case of the latter just absent in EAP demonstrating oceanographic conditions imposed by the ice shelves.

Biogenic silica in sediments from the Eastern and the Northern Antarctic Peninsula

Edited version of E. Sañé, E. Isla, M.A. Bárcena. Biogenic silica in sediments from the Eastern and the Northern Antarctic Peninsula (Short Note)

5.1 Introduction

In the last 60 years atmospheric and oceanic temperatures increased in the Antarctic Peninsula above the world average (Vaughan et al., 2001; Gille, 2002). These increases caused the ice shelves to retreat (Vaughan et al., 2003; Cook et al., 2005) and in 1995 and 2002, 4200 Km^2 of the Larsen A and 3200 Km^2 of the Larsen B ice shelves, in the Eastern Antarctic Peninsula (EAP), collapsed and rapidly disintegrated (Rott et al., 1996; Skvarca et al 1999). After ice shelf collapses, the rather stable conditions for at least a thousand years (Domack et al., 2005a) drastically changed Primary production developed (Bertolin and Schloss, 2009) and consequently a flux of fresh organic matter to the seafloor. Diatoms, radiolaria, siliceous sponges, and silicoflagellates contribute with their siliceous skeleton to the biogenic silica flux to the seafloor and the accumulation of this biogenic constituent in the sediment column (Abelmann and Gersonde, 1991; DeMaster, 2002). From this pool, diatom valves and sponge spicules represent the principal sources of biogenic silica in sediments (Rützler and MacIntyre, 1978; Bavestrello et al., 1996). Diatoms occupy an important place in the production of biogenic silica in the upper ocean and its export to the sea floor (Ragueneau et al., 2000). In the Southern Ocean, diatoms represent 40% of the total primary production (Cortese and Gersonde, 2007) with high biomasses in Antarctic coastal regions (Wright and van den Enden, 2000; Arrigo et al., 2008; Beans et al., 2008). Siliceous diatom frustules are well preserved in the sediment column despite partial degradation by grazing (Crosta, 2009) and dissolution (Buffen et al., 2007) in the sediment column. Diatom valves represent the predominant biogenic proxies in sediments (Tsoy et al., 2009). Sponges are important components of Antarctic benthic communities (Gerdes et al., 2003; Teixidó et al., 2004). Most Demospongiae and Hexactinellida produce silica-made skeletons consisting of individualized elements (spicules) of lengths ranging from micrometers to centimeters (Uriz et al., 2003). Hexactinellids are one of the dominant groups of the Ross and Weddell seas benthic communities (Barthel and Gutt, 1992; Bullivant, 1967; Dayton et al., 1974) and are important in the formation of substrata by generation of spicule mats (Barthel et al., 1991; Barthel and Gutt, 1992; Kunzmann, 1996). Spicules are fragile and may occur fragmented in the sedimentary record thus disabling them as accurate oceanographic proxies. However, they could be important contributors to the biogenic silica contents in the sedimentary column as they are long living and their spicules dissolve slower than diatom frustules (Bavestrello et al., 1996; Maldonado et al., 2005). The Southern Ocean sediment contains more than 50% of the biogenic silica deposited in marine

environments world wide and most of this budget has been attributed to diatoms (Tréguer et al., 1995; DeMaster, 2002). The recent disintegration of the sections A and B of the Larsen ice shelf offers a unique opportunity to assess the relationship between biogenic silica concentration and the number of diatom valves found in the sediment column on the basis that the arrival of diatoms to the sedimentary record presumably took place after the ice shelf collapses.

5.2 Materials and Methods

5.2.1 Sediment collection and preparation

The Northern Antarctic Peninsula (NAP) and Larsen A and B bays, in the Eastern Antarctic Peninsula (EAP), were reached in austral summer 2006-2007 during ANT-XXIII/8 onboard *Polarstern*. Five sediment cores (10 cm in diameter) were taken in EAP, at stations Larsen B South (LBS), Larsen B West (LBW), Larsen B North (LBN), Larsen B Central (LBC) and Larsen A (LA) (Fig. 5.1). Four cores were 11 cm long (LBS, LBW, LBN and LBC) and one was 7.5 cm long. Two other cores were taken in NAP at stations Elephant Island (EI) and South Shetland Islands (SSI). Both had a diameter of 10 cm and were 11 cm long. Cores were subsampled onboard in slices 0.5 cm thick from 0 to 10 cm and 1 cm thick from 10 to 11 cm depth. Samples were stored onboard at -20ºC and freeze dried (P=0.1 mbar and T=-80ºC) during 24 hours before laboratory and microscope analyses.

5.2.2 Biogenic silica

Biogenic silica percentage in the sediment was measured following Mortlock and Froelich (1989) and DeMaster (1981) procedures. 5 ml of a solution of H_2O_2 (10%) were added to approximately 100-200 mg of dry sediment and after 30 min, 5 ml of HCl (10 %) were added to the sediment and the solution of H_2O_2 (10%). Samples were rinsed with bi-distilled water and after centrifugation (5 min at 5000 rpm) were dried in the oven before alkaline extraction. After sonication for 5 min within 40 ml of Na_2CO_3 2M samples were placed on a bath (T=85ºC) for 5 h. 5 ml of extract was taken two times, after two and five hours of extraction. The early extractions target biogenic silica while the later target the silica minerals that take a longer time to dissolve in the NaOH bath (Klein, 2008). After extraction, 17.5 ml of a solution of ammonium molybdate were added to every aliquot and after 20 min 7.5 ml of a reducing solution with sodium metol-sulfite, oxalic acid and sulphuric acid were added to produce the blue chromophore read in the spectrophotometer at 815 nm. The weight percent of biogenic

silica was mathematically derived from the concentration determined by the spectrophotometer. A linear regression was plotted running through the two values

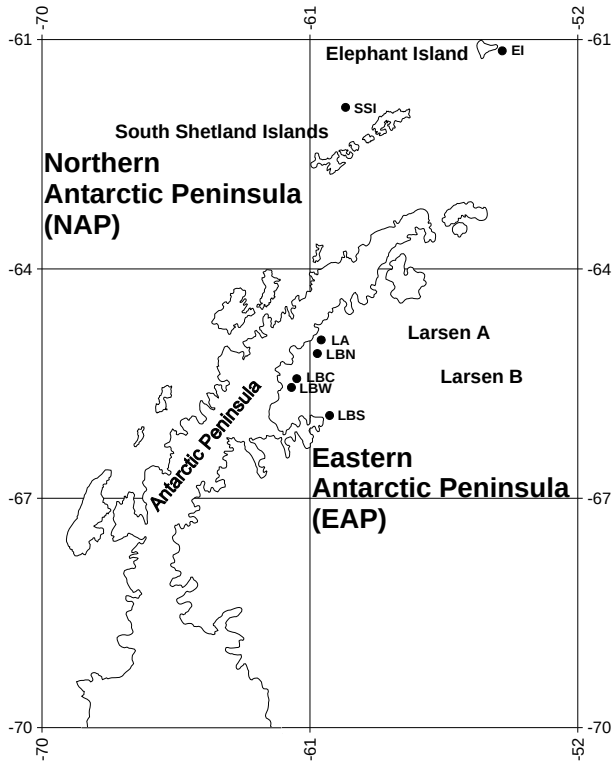

Fig. 5.1 Study area with the seven sampling stations.

corresponding to 2 and 5 hours of extraction. The y-intercept of regression line corresponded to the weight % of biogenic silica in the sample (DeMaster, 1981).

5.2.3 Diatom slides preparation and observations at the microscope

After the addition of HCl and H_2O_2 to a known weight of dry sediment, the sediment was rinsed several times with bi-distilled water until a pH~6 was reached. Slides were mounted and, according to the standard randomly distributed microfossils method, diatom valves were counted at 1000 magnification using a Leica DMLB with phase-contrast illumination. Counts were carried out on permanent slides of acid-cleaned material (Permount mounting medium). Schrader and Gersonde (1978) recommendations were followed for the counting of microfossil valves. Depending on the diatom abundance, several traverses across each cover slip were examined. A minimum of 350 valves were counted for each sample, when possible. Moreover, a counting of at least 100 valves of non-dominant taxa per sample was performed.

5.3 Results

5.3.1 Biogenic silica

The percentage of biogenic silica ranged from 0.07% (station EI at 4.5 cm depth) to 2.31% (station LBN at 2 cm depth) (Fig 5.2). Core average percentage from 0 to 11 cm depth was lowest at SSI (0.55% ± 0.69) and highest at LBN (1.45% ± 0.58) (Table 5.1). Based on the regional average, at all depth intervals the percentage of biogenic silica was higher in EAP than in NAP (Table 5.1).

5.3.2 Microscopical observation of diatoms valves

Total abundance of diatoms ranged from 2.86 x 10^7 valves g^{-1} of dry sediment (station SSI at 11 cm depth) to 0 valves g^{-1} of dry sediment (stations LBS from 4 to 4.5 and from 6.5 to 11 cm depth, LBW at 5.5 cm depth and from 8 to 10 cm depth, LBC at 4.5 cm depth and LBN from 3 to 5 and from 7 to 10 cm depth) (Fig. 5.2). Core average concentrations were lowest at LBS (~0.3x10^6±0.5x10^6 valves g^{-1} of dry sediment) and highest at SSI (~17.09x10^6 ± 6.07x10^6 valves g^{-1} of dry sediment) (Table 5.2). Based on the regional average, at all depth intervals the total number of valves was higher in NAP than in EAP (Table 5.2).

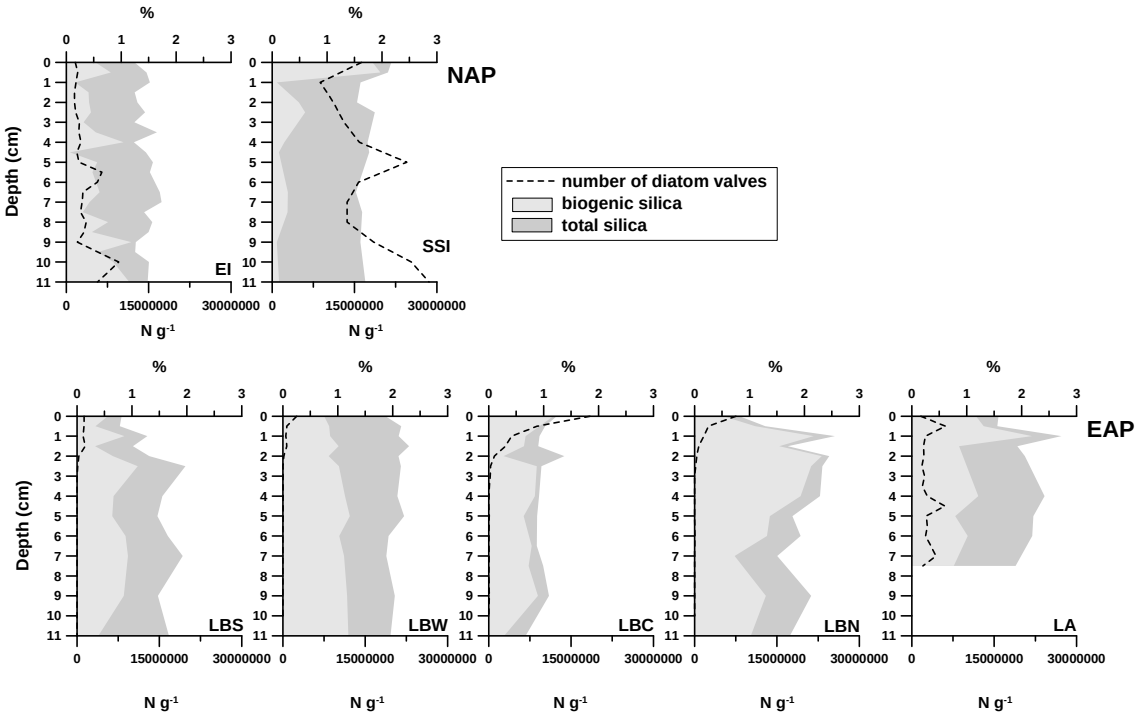

Fig. 5.2 Percentage of biogenic silica, percentage of total silica and number of diatom valves profiles in EI, SSI, LBS, LBW, LBC, LBN and LA.

Table 5.1 Average percentage of biogenic silica in the seven stations, EI, SSI, LBS, LBW, LBC, LBN and LA, and the two regions, NAP and EAP from 0 to 11 cm depth.

EI	SSI	LBS	LBW	LBC	LBN	LA	NAP	EAP
0.58±0.30	0.55±0.69	0.68±0.25	1.01±0.16	0.73±0.26	1.45±0.58	1.14±0.41	0.57±0.46	1.00±0.45

Table 5.2 Average total number of diatom valves in the seven stations, EI, SSI, LBS, LBW, LBC, LBN and LA, and the two regions, NAP and EAP from 0 to 11 cm depth.

EI	SSI	LBS	LBW	LBC	LBN	LA	NAP	EAP
$3.28x10^{6}$±$2.07x10^{6}$	$17.09x10^{6}$±$6.07x10^{6}$	$0.03x10^{6}$±$0.05x10^{6}$	$0.29x10^{6}$±$0.62x10^{6}$	$2.43x10^{6}$±$5.05x10^{6}$	$0.88x10^{6}$±$1.99x10^{6}$	$2.80x10^{6}$±$1.33x10^{6}$	$8.16x10^{6}$±$7.74x10^{6}$	$1.29x10^{6}$±$2.54x10^{6}$

5.4 Discussion

5.4.1 NAP: biogenic silica from diatom valves

The higher average total number of diatom valves in NAP than in EAP is due to the evident difference between the two regions in the total concentration of valves below 2 cm depth (Fig. 5.2 and Table 5.2). This clear difference suggest that the input of diatom valves to the sea floor in EAP started after Larsen A and B ice shelf collapses (in 1995 and 2002, respectively). Below the 2 to 3 cm depth horizon in EAP the number of diatoms valves dramatically reduced even reaching zero (Fig. 5.2). Overall the diatom valve profiles showed that the period of diatom accumulation has been longer in NAP than in EAP further supported by the diatom valve profiles in NAP that showed peaks as deep as 19 cm depth. Furthermore, the scarce diatom valves in the deep part (below 3 cm depth) of EAP sediment cores made evident that the lateral transport of diatom valves in the region is negligible, probably due to the great extent of the ice shelves (>1000 km^2), which hampered the input of valves from richer vicinities under open water conditions. The vertical transport of the recently produced OM in Larsen A and B bays reflects the ongoing primary production after ice shelf collapses (Bertolin and Schloss, 2009).

5.4.2 EAP: biogenic silica from sponge spicules

In the Antarctic continental shelf sponges show high abundances and biomasses (Gerdes et al., 1992; Barthel and Gutt, 1992; Sará et al., 1992; Teixidó et al., 2002) and the number of species, which varies between 300 and 352 (Sará et al., 1992; Arntz et al., 1997), is comparable with species richness in temperate, tropical and Arctic seas (van Soest, 1994). Eighty-one percent of Antarctic sponges belongs to the class Demospongiae (McClintock et al., 2005), which members have a well developed siliceous skeleton. The majority of Demospongiae species live in large depth intervals (McClintock et al., 2005) and the principal disturbance sources for this class are iceberg scouring (Gutt, 2001) and anchor ice (Dayton et al., 1969). Hexactinellida class has a lower species richness than Demospongiae class (Barthel and Tendal, 1994). Hexactinellida have siliceous spicules which form three-dimensional ‘‘spicule mats’’ (Koltun, 1968) providing refuge for a variety of marine invertebrates (Barthel and Gutt, 1992).Typical Antarctic large glass sponges pertain to this class (McClintock et al., 2005).

Siliceous sponges were present and had moderate biomasses in EAP (25% of the total) (Sañé et al., *c.*-CAP.3; personal observation). The presence of sponges was more evident in the station where the ice shelves disintegrate earlier (st. Larsen B South and Larsen A) (Sañé et al., *c.*-CAP.3). Their low growth rate (Dayton et al., 1974; McClintock et al., 2005; Post et al., 2007) suggests that these sponges lived in EAP seafloor before Larsen ice shelves disintegration (Gutt et al., submitted) and coincide with previous observations on the dominance of suspension-feeding organisms like sponges and bryozoans under ice shelves (Riddle et al., 2007). These evidences make the sponges strong candidates as suppliers of biogenic silica to the sediment column in EAP.

Based on our results, we suggest that the higher percentages of biogenic silica in EAP than in NAP sediment depend on the incorporation of sponge spicules of classes Demospongiae and Hexactinellida into the sediment column of EAP. The presence of biogenic silica from spicules is feasible taking into account that sponges are long living and their spicules dissolve slower than diatom frustules (Bavestrello et al., 1996; Maldonado et al., 2005). Our hypothesis confirms that sponges can have an important role as biogenic silica suppliers to the sediment column because they can reach high abundances in many areas of the ocean. The higher biogenic silica contents in EAP cores revealed that the supply of other sources of biogenic silica different to diatoms can play an important role in the silica accumulation in Southern Ocean sediments, at least on the continental shelf.

Utility of ^{210}Pb as a chronological tool for sediments off the eastern Antarctic Peninsula: the case of the continental shelf under the extinct Larsen A and B ice shelves.

Edited version of E. Isla and E. Sañé. Utility of ^{210}Pb as a chronological tool for sediments off the eastern Antarctic Peninsula: the case of the continental shelf under the extinct Larsen A and B ice shelves.

6.1. Introduction

Biogenic and lithogenic particulate matter settling onto the seabed undergoes biological, chemical and physical processes upon arrival before being buried for long-temporal scales (thousands to millions of years). Biological and physical processes such as bioturbation, winnowing and resuspension redistribute the particles in the upper sediment column hampering their preservation in an evident chronological order. To establish reliable chronologies of sedimentation events, radionuclides have been quite helpful because of their known radioactive decay constants. Naturally occurring ^{210}Pb has been extensively used to estimate sediment accumulation rates taking place in decadal time scales (i.e., sensibility of 4-5 times its 22.3 years half-life) (Nittrouer et al., 1983; DeMaster et al., 1985; Harden et al., 1992). ^{210}Pb has also a strong affinity to adsorb onto organic particles, which is ecologically meaningful to calculate organic matter diagenetic and sedimentary processes (Nittrouer et al., 1983; Furlong and Carpenter, 1988; Alperin et al., 2002; Smith and Rabouille, 2002). The main processes affecting the ^{210}Pb distribution in the sedimentary record include particle mixing (diffusion), sediment accumulation (advection) and radioactive decay. In consequence, assessing the depth profile of ^{210}Pb in the sediment column provide insights into the processes governing the organic matter sedimentary dynamics during the last century.

In 1995 and 2002 sections A and B of the Larsen ice shelf at the eastern Antarctic Peninsula collapsed and rapidly disintegrated uncovering thousands of square kilometers of continental shelf (Vaughan et al., 2001; Skvarca et al., 1993, 1998, 1999). These events were linked to anthropogenic global warming (Marshall et al., 2006), which causes the reduction of the ice shelf thickness and a retreat of the glacier front (Shepherd et al. 2003; Cook et al. 2005; Wingham et al., 2009). Primary production under ice shelves is negligible, thus the vertical flux of organic matter to the sea floor (Littlepage and Pearse, 1962). However, primary production in the Larsen A and B bays started developing after the ice shelf collapses, which liberated space for phytoplankton to bloom (Arrigo et al., 2002; Arrigo and van Dijken, 2003; Bertolin and Schloss, 2009). Such disintegrations gave access to the unique opportunity to investigate how those drastic changes at the sea surface may impact the benthic realm. Here, with the use of ^{210}Pb activity we attempt to establish an approximate base line to track organic matter sedimentary processes in a region where presumably the arrival of fresh organic matter to the seabed is taking place only during the last decade.

6.2 Materials and Methods

7 stations were occupied on the continental shelf during the expedition ANT-XXIII/8 in the austral summer of 2006-2007 (Fig. 6.1). Two stations were located at the North of the Antarctic Peninsula (NAP) and five off the eastern coast of the Antarctic Peninsula (EAP). NAP stations have been free of the influence of ice shelves at least for a thousand years (Ingolfsson et al., 1998; Anderson et al., 2002), whereas EAP stations were liberated from the ice shelves coverage 4 to 11 years ago (Table 6.1). Sediment cores were recovered within a depth range of 240 to 450 m depth, with the exception of station Larsen B central located in the axis of a glacial through at 850 m depth. Multi-core sampling ensured the recovery of the upper sediment column in almost undisturbed state (Barnett et al., 1984). Sediment cores were subsampled on board in 0.5 cm slices (upper 10 cm), 1 cm slices (from10 to 20 cm depth) and 2 cm slices (from 20 cm depth to the bottom of the core). The outer 0.5 cm ring was removed to avoid inter-layer contamination due to down core smearing during extraction. Each slice was frozen at -20ºC until treatment in the laboratory.

The ^{210}Pb activity was calculated by measuring the activity of its daughter ^{210}Po (DeMaster, 1985). Approximately 8-10 g of freeze-dried sediment were spiked with 1 ml of ^{209}Po and digested with HCl and HNO_3 to eliminate calcareous and organic matter. Two subsequent HCl digestions to a final dried sample were performed into centrifuged remains. The dried sample was picked up with 6 N HCl and the solution was diluted to 1.5 N HCl. Ascorbic acid was added to complex iron and remove it from the solution before submerging a 1 cm^2 silver plate for a 12-h period. The silver plates were placed in an Alpha spectrometer to measure the activity of spontaneously electrodeposited ^{209}Po during plating. Excess ^{210}Pb activity was calculated subtracting the background levels below the logarithmic decay layer, where ^{210}Pb activity showed nearly constant values. ^{210}Pb inventories were calculated by summing the product of excess ^{210}Pb activity, the depth interval (slice thickness) and the dry bulk density (results not shown) of each sub sample, whereas the supporting flux was calculated multiplying inventories by the ^{210}Pb radioactive decay constant 0.031.

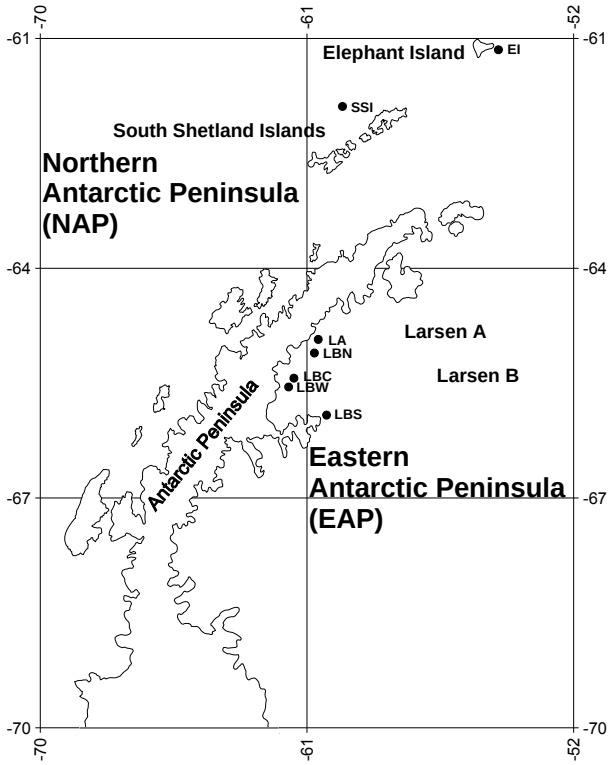

Fig. 6.1 Study area and station acronyms (see text for complete names).

Table 6.1 Station depth and time period after ice shelf disintegrations (YAISD).

Station	Depth (m)	YAISD (yr)
Elephant Island (EI)	404	>1000
South Shetland Islands (SSI)	358	>1000
Larsen B South (LBS)	446	>11
Larsen B West (LBW)	297	4
Larsen B Central (LBC)	849	4
Larsen B North (LBN)	322	4
Larsen A (LA)	239	11

6.3 Results

Total and excess ^{210}Pb activities throughout the sediment cores are shown in Fig. 6.2. NAP profiles showed the typical relatively uniform activity region or surface mixed layer (SML) with 7 cm (st. Elephant Island) and 9 cm (st. South Shetland Islands) thickness. In contrast, EAP profiles presented a logarithmic decay from the top to the bottom of the core and no evident SML. Total activity in the surface layer (upper 0.5 cm) varied between 14 dpm g^{-1} (st. Elephant Island) and 22 dpm g^{-1} (st. South Shetland Islands) in NAP and 8 dpm g^{-1} (st. Larsen B South) and 25 dpm g^{-1} (st. Larsen B Central) in EAP, whereas background levels of ^{210}Pb activity were approximately 0.9 dpm g^{-1} in NAP

and ranged from 1.4 dpm g^{-1} to 2.5 dpm g^{-1} in EAP. ^{210}Pb inventories (Table 6.2) were 81 dpm cm^{-3} and 102 dpm cm^{-3} for st. South Shetland Islands and st. Elephant Island, respectively, whereas in EAP ^{210}Pb inventories varied between 12 dpm cm^{-3} (st. Larsen A) and 21 dpm cm^{-3} (st. Larsen B Central).

Table 6.2 Excess ^{210}Pb activity inventories, associated fluxes, sediment accumulation rates (SAR) and mixing coefficient (Db). Surface ^{210}Pb excess activity values correspond to the upper 5 mm layer of the sediment column.

Station	^{210}Pb Surface excess activity (dpm g^{-1})	Inventory (dpm cm^{-2})	Supported flux (dpm cm^{-2} yr^{-1})	SAR (mm yr^{-1})	Db (cm^2 yr^{-1})
Elephant Island (EI)	13.31	113.12	3.51	3.02	0.58
South Shetland Islands (SSI)	20.66	89.90	2.79	1.90	0.43
Larsen B South (LBS)	6.19	14.84	0.46	0.43	0.04
Larsen B West (LBW)	8.23	16.61	0.52	0.27	0.02
Larsen B Central (LBC)	23.42	22.92	0.71	0.49	0.09
Larsen B North (LBN)	10.17	19.84	0.62	0.40	0.04
Larsen A (LA)	8.85	13.57	0.42	0.42	0.04

6.4 Discussion

6.4.1 Excess ^{210}Pb activity in marine sediments

Excess ^{210}Pb activity profiles in the sediment show several patterns which have been grouped in four representative types (Soetaert et al., 1996; Jaeger et al., 1998). Type I describes the typical steady-state accumulation, where a region in the upper sediment column presents a uniform excess ^{210}Pb activity distribution also known as the SML. At the base of it continues downcore a region of logarithmic decay that finds a relatively constant excess ^{210}Pb activity layer, known as background layer, where excess ^{210}Pb activity is supported by the *in situ* ^{226}Ra activity. Type II displays a similar pattern to Type I but a discontinuity in the logarithmic decay region where an event layer (non-local exchange) peaks the ^{210}Pb activity. At the base of this deeper peak the logarithmic decay continues. Type II represents an “event-layer” deposition pattern. Type III is composed by rather two layers, each showing distinct logarithmic slopes. This type pattern represents a change in the steady-state accumulation rate. Finally, Type IV presents a profile of excess ^{210}Pb activity without evident SML, which coexists with the occurrence of activity peaks at several depths. This profile shows a “varying-activity” pattern.

On the one hand, NAP cores clearly matched with Type I profile, as expected for sedimentary environments under steady-state conditions. NAP stations have been free of ice shelves for more than 1000 yr (Ingolfsson et al., 1998; Anderson et al., 2002) and

major primary production and current regimes have been relatively constant at least since the last glacial maximum (approximately 18000 yr) (Mackensen et al., 2004; Kohfeld et al., 2005). On the other hand, EAP cores showed an evident logarithmic decay profile from the sediment-water interface to the bottom of each core (Fig. 6.2). This distribution resembled the Type I profile without SML. Thus, suggesting that sediment accumulation in EAP is governed by advection rather than diffusion and/or non-local exchange processes. Benthic fauna, phytopigments and amino acids have also been studied in EAP (Sañé et al., *a.*-CAP.1; Sañé et al., *b.*-CAP.2; Sañé et al., *c.*-CAP.3). These studies have shown that the relative abundance of macrofauna in EAP was rather low, coincident with logarithmic decreasing trends in each of the organic variable profiles and the lack of any homogeneous layer such as the SML (Fig. 6.3). Based on those results is possible to assume that the scarce benthic fauna has got relatively little time to redistribute organic matter from the sediment surface, which presumably started settling in the EAP region after the ice shelf collapses (4 to 11 years ago).

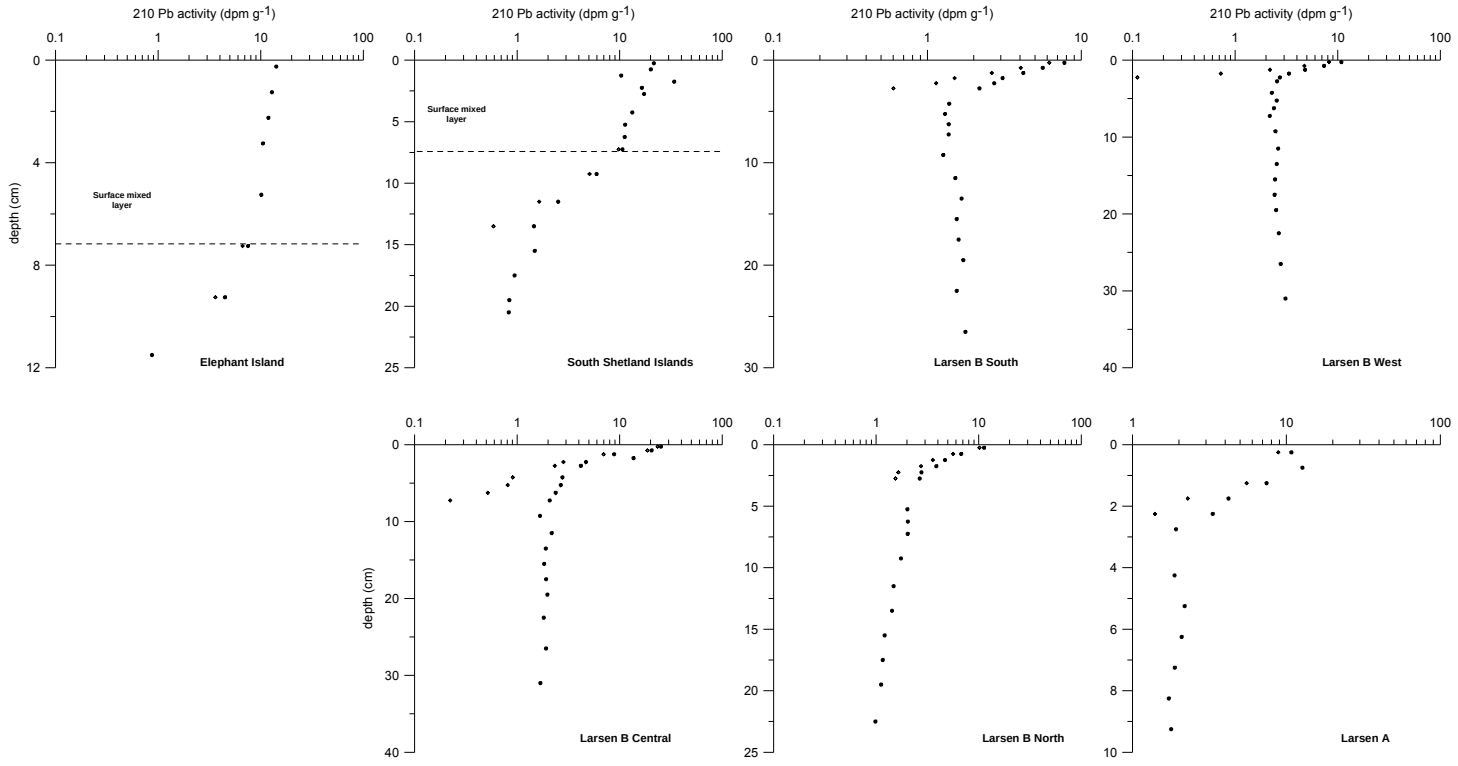

Fig. 6.2 Total (black dots) and excess (grey dots) ^{210}Pb activity profiles. Only shown the excess ^{210}Pb activity samples used to calculate the sediment accumulation rates.

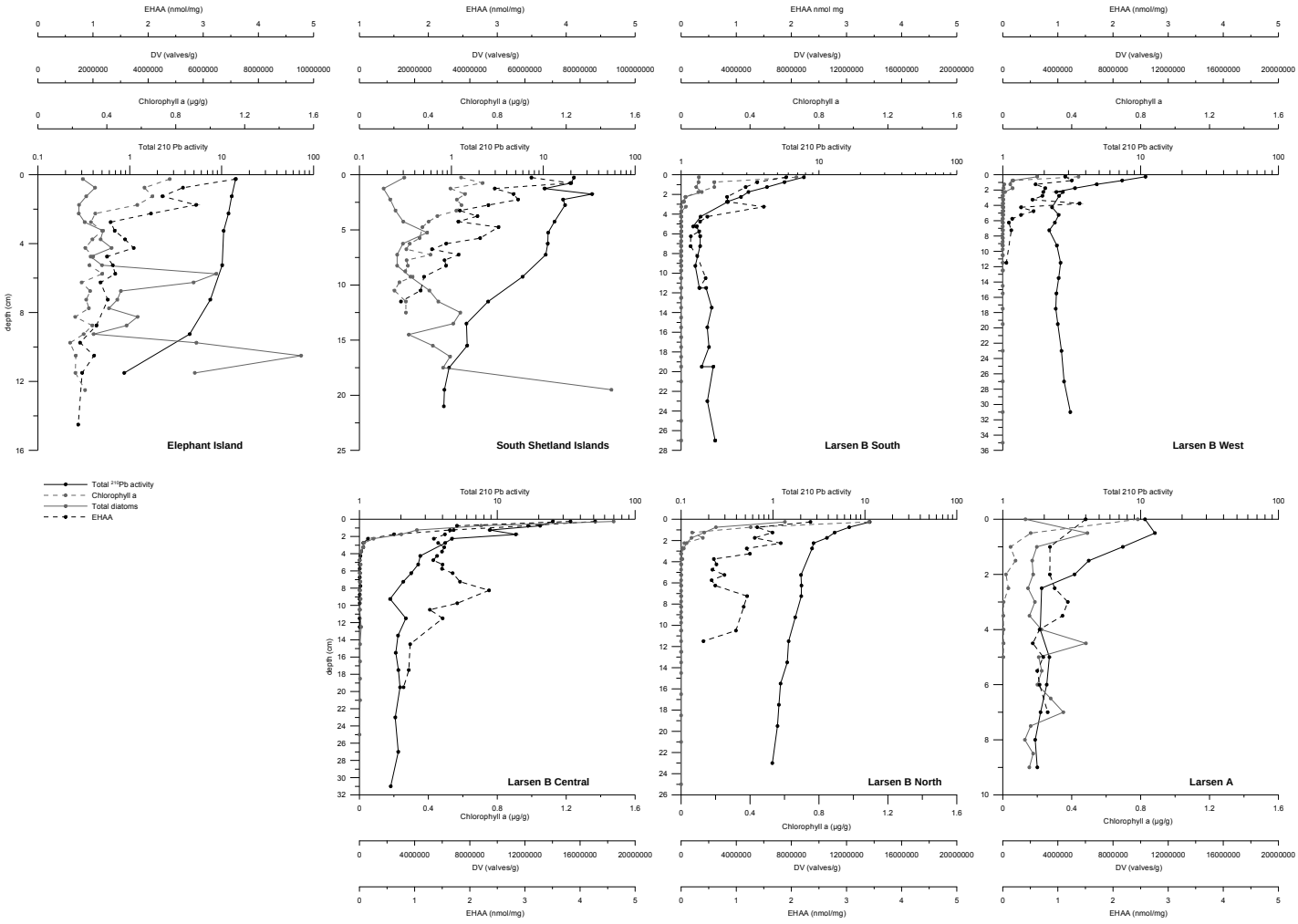

Fig. 6.3 Total ^{210}Pb activity, chlorophyll a (Chl*a*), enzymatically hydrolysable amino acid (EHAA) concentrations and total diatom valves (DV) profiles. Each station has different scale in the depth axis. Elephant Island and South Shetland Islands have different scale in the DV axis.

6.4.2 Steady or non-steady state conditions?

Given the relatively recent drastic change at the sea surface in EAP one would expect transient, non-steady state conditions determining the current sediment accumulation rates. Excess ^{210}Pb activity distribution under steady-state accumulation conditions develops a logarithmic profile in the region of radioactive decay (Nittrouer et al., 1979), whereas in non-steady regimes presents strong variability along the sediment column (Kuehl et al., 1986; Jaeger et al., 1998). NAP and EAP cores showed a logarithmic decreasing activity layer and stronger variability neither above nor below this layer. The low benthic abundances found in EAP and the negligible bioturbation associated to it explains the absence of deeper excess ^{210}Pb activity peaks produced by non-local exchange processes such as biologic “injection” of fresh organic matter below the sediment-water interface. The lack of a clear SML further supports the negligible bioturbation in EAP making evident that “conveyor belt” transport is not developing in contrast to the profiles observed in NAP.

Non-steady conditions have also been addressed in Antarctic sediment analyses (Rabouille et al., 1998). Antarctic sediment undergoes non-steady conditions as a consequence of the marked seasonality, which delivers a strong pulse of fresh organic matter only during the spring-summer season. However, seasonality can be masked when slow bioturbation occurs and no deep burial of fresh organic matter takes place implying that only low reactivity carbon can be found at depth (Rabouille et al., 1998). Effective mixing produced by intense bioturbation can also erase seasonal marks rapidly redistributing fresh organic matter from the sediment-water interface to deeper layers (Smith et al., 1993). To track the Antarctic seasonal variation seasonal sampling and pore water analyses are reliable approaches; however, the lack of such measurements in the present study hampers identifying seasonal non-steady state features. The greater deviation in applying a steady state model to profiles derived from non-steady state conditions is an underestimation of the true sediment accumulation rates (DeMaster et al., 1985). Thus, the sediment accumulation rates obtained from ^{210}Pb excess activity in the present study represent at least minimum values and are referred as apparent sediment accumulation rates. Another approach is to combine the sediment accumulation rates obtained from two different naturally occurring radionuclides (Harden et al., 1992). In Antarctic sediments the combination of ^{14}C (1000-yr time scales) and ^{210}Pb (100-yr time scales) has been use to accurately assess sediment mixing and sediment accumulation rates (Harden et al., 1992) due to their different temporal sensitivity. Mixing coefficients and sediment accumulation rates

obtained for each radionuclide present convergence values which satisfy the solution for each advection-diffusion equation at one single point. The convergent solution; thus, provides the more accurate value for both the mixing coefficient and the sediment accumulation rate at one station (Harden et al., 1992).

6.4.3 Sediment accumulation rates

To model excess ^{210}Pb activity distribution in the sediment column the advection-diffusion equation introduced by Goldberg and Koide (1962) has been successfully applied to a number of sediment cores from different environments (Nittrouer et al., 1983; DeMaster et al., 1985; Khuel et al., 1986; Harden et al., 1992) as following:

$$\frac{dA}{dt} = Db\,\rho\,\frac{\partial^2 A}{\partial z^2} - S\,\rho\,\frac{\partial A}{\partial z} - \lambda\,\rho\,A \qquad (1)$$

where A is the excess activity of ^{210}Pb (dpm g^{-1}), t is time (yr), Db is the particle mixing coefficient (cm^{-2} yr^{-1}), ρ is the dry bulk density of the sediment in the SML (g cm^{-3}), z is depth in the sediment column relative to the sediment-water interface (cm), S is sediment accumulation rate (cm yr^{-1}) and λ is the ^{210}Pb radioactive decay constant (0.031 yr^{-1}). This model assumes that the particle mixing occurs in a diffusive mode, meaning a large number of small random events. Within the mixed layer Db, ρ and S are constant. Below the SML the decrease in the nuclide activity is controlled by sediment accumulation, dissolution, radioactive decay and in situ production. If the mixing term is negligible, S can be calculated as follows under steady state conditions, dA/dT=0:

$$S = \frac{z\,\lambda}{\ln [A_0/A(z)]} \qquad (2)$$

where A_0 is the activity at z=0.

On the same basis of steady state conditions, the mixing coefficient can be calculated from equation 1 as follows:

$$Db = \frac{z^2\lambda}{\ln [A_0/A(z)]^2} \qquad (3)$$

Sediment accumulation rates and mixing coefficients for NAP and EAP cores are listed in Table 6.2.

6.4.4 Excess ^{210}Pb activity in sediment under the extinct Larsen A and B ice shelves

Sediment accumulation rates (SAR) showed low values (<1mm yr^{-1}) in the EAP stations whereas NAP stations presented SAR one order of magnitude higher (Table 6.2). This difference was expected in the comparison between contrasting environments such as NAP and EAP based on the assumption that the ice shelves hampered primary production and the consequent vertical flux of particulate matter to the sea floor. These numbers also suggest that the lateral transport of particles to EAP has been rather weak. This hypothesis is further supported by the fact that the ^{210}Pb inventories in NAP are one order of magnitude higher than in EAP, whereas the surface (upper 5 mm layer) ^{210}Pb excess activity is similar in both regions (Table 6.2). This imply that the most recent supply of ^{210}Pb to the seabed is of similar magnitude in both regions, whereas the accumulated supply of the tracer over a longer period of ice shelf free conditions (1000 yr) developed larger ^{210}Pb inventories in NAP. Among EAP cores, SAR and the ^{210}Pb inventories also made evident that station Larsen B central is acting as a sediment deposition spot. This is in accordance with stations located at the base of submarine canyons or in this case, a glacial through, which may act sediment traps that concentrate sediment from adjacent areas (Gardner, W.D., 1989; Kudrass et al., 1998; Vetter and Dayton, 1998; Duineveld et al., 2001).

The rather low SAR and mixing rates in the study area were similar to those found in deep-sea environments (Table 6.5 in DeMaster and Cochran, 1982; Radakovitch and Heussner, 1999); however, they varied one order of magnitude between EAP and NAP (Table 6.2). These numbers reflect the weak bioturbation activity in the EAP region (macrofaunal benthic biomass were two orders of magnitude lower than in the southeastern Weddell Sea (Sañé et al., *c.*-CAP.3) expressed also in the absence of SML.

6.4.5 ^{210}Pb and biogenic constituents: further evidence of the vertical flux of organic matter only after ice shelves disintegrations.

A set of biogenic variables has been assessed for the study area (Sañé et al., *a.*-CAP.1; Sañé et al., *b.*-CAP.2; Sañé et al., *d.*-CAP.4), among them chlorophyll-*a* (Chl*a*), enzymatically hydrolysable amino acid (EHAA) concentrations and total diatom valves (DV) were related to excess ^{210}Pb activities (Table 6.3). Linear regression analyses

showed that excess ^{210}Pb activities were highly correlated to these biogenic variables in EAP, especially Chl*a* and DV, with the exception of LA. These analyses strongly suggest that in EAP the transport of ^{210}Pb is mostly related to biogenic particles; more than 70% of ^{210}Pb variability was explained by the occurrence of these variables (Table 6.3). Figure 6.3 shows that their occurrence in the sedimentary record is restricted to the upper 2.5 cm of the sediment column. Chl*a* and DV profiles clearly matched the logarithmic decreasing pattern of total ^{210}Pb setting solid basis to assume that these three variables have been incorporated in the sediment only recently, presumably after the ice shelf disintegrations. However, estimated SAR indicated that the layer of sediment correspondent to the deposition after the disintegrations would be 0.4 to 4 mm thick depending on the station (c.f. Tables 6.2 and 6.3). The mismatch between the set of results lead to two solutions; on the one hand, calculated SAR underestimated the true SAR because the sedimentary dynamics in EAP undergo non-steady state conditions and SAR values were calculated with a steady state model (DeMaster et al., 1985), on the other hand, biogenic variables started accumulating in the sediment

Table 6.3 Statistical output of the linear regression analyses between excess ^{210}Pb activity and chlorophyll a (Chl*a*), enzymatically hydrolysable amino acid (EHAA) concentrations and total diatom valves (DV) in NAP and EAP sediment cores.

Variable	station	n	R^2	p	Intercept	slope
Excess ^{210}Pb vs. Chl*a*	EI	8	0.57	0.0308	1.44	16.86
	SSI	11	0.59	0.0057	-7.10	43.98
	LBS	12	0.87	<0.0001	0.54	10.00
	LBW	12	0.80	0.0001	0.87	18.81
	LBC	12	0.90	<0.0001	1.53	16.57
	LBN	12	0.92	<0.0001	1.34	8.69
	LA			>0.05 ns		
Excess ^{210}Pb vs. EHAA	EI	7	0.63	0.0342	1.92	3.80
	SSI	11	0.50	0.0082	-10.48	8.79
	LBS	10	0.92	<0.0001	-1.12	3.69
	LBW	11	0.55	0.0055	-1.17	5.27
	LBC	13	0.54	0.0027	-7.85	8.15
	LBN	10	0.57	0.0072	-2.24	4.09
	LA	8	0.70	0.0095	-6.96	10.38
Excess ^{210}Pb vs. DV	EI	8	0.67	0.0133	15.00	<0.0001
	SSI			>0.05 ns		
	LBS	17	0.71	<0.0001	0.30	<0.0001
	LBW	17	0.89	<0.0001	0.36	<0.0001
	LBC	10	0.88	0.0001	2.08	<0.0001
	LBN	10	0.97	<0.0001	1.36	<0.0001
	LA			>0.05 ns		

ns stands for non-significant relationship

column before the ice shelves disintegrated. The later solution is unlikely given the drastic decrease of DV below the upper 2 cm of the profile even reaching the absence of valves, in comparison to the rather high numbers found throughout the sediment cores from NAP and the subsurface peaks down to 19 cm depth. SAR Values represent the apparent accumulation rates and should be considered minimum values that should be validated under the light of a non-steady state model despite several characteristics suggested steady state conditions. Namely, absence of SML and rather weak bioturbation, logarithmic decreasing trend in the measured variables and the absence of any truncation in such profile, the absence of conveyor belt and non local exchange transports.

Excess ^{210}Pb activity inventories demonstrated that there is a one order of magnitude difference between NAP and EAP; thus, in the supply and incorporation of particles in the sediment deposits. The presence of the Larsen ice shelves strongly limited such supply in EAP. In this region, ^{210}Pb was significantly associated to biogenic particles implying that in EAP ^{210}Pb is associated to the quality of the settling particles. Further, the ^{210}Pb activity profiles in EAP suggest that its distribution is only influenced by the sedimentation rate, radioactive decay and supported activity.

Samples from the Eastern Antarctic Peninsula (EAP), the Northern Antarctic Peninsula (NAP) and the South Eastern Weddell Sea (SEWS) were obtained during the austral summer; therefore, differences in the OM content in the sediment linked to the marked Antarctic seasonality at the sea surface should be negligible. The main difference between the three regions regarding the OM supply to the seabed is that EAP has been free of ice shelf influence only since a decade, whereas NAP and SEWS regions for at least a thousand years. Except for Larsen B Central, all samples were collected on the continental shelf (250 to 450 m water depth). Thus, OM degradation in the water column, assuming that the transport to the seabed had a larger vertical than lateral component, should have been similar among stations.

EAP

Recently deposited OM was found just in the upper 10 mm of the sediment column. Older and more refractory OM was found below this layer throughout the entire sediment column. The presence of labile OM in the superficial sediment was evidenced by the relatively high Chl*a* concentrations, Chl*a* to Pheo*a* ratio and EHAA to THAA ratio. The concentration of labile OM compounds such as pigments or amino acids sharply decreased in the sediment column below 1 cm depth, however, the concentrations of Chl*a* and EHAA in the upper layer were similar to NAP. Refractory FA like mid-chain fatty acids and presumably structural refractory CHO were found throughout the sediment cores, implying an accumulation in the sediment column during years of ice coverage and lack of fresh OM supply. The significant relationship between excess ^{210}Pb activity and Chl*a* (r^2> 0.80, p=0.0001), EHAA (r^2> 0.54, p=0.0027) and diatom valves (r^2> 0.71, p=0.0001) throughout the sediment column corroborated the arrival of fresh biogenic material.

The total number of diatom valves was high in the superficial sediment and decreased below 2 cm depth. The similarity between the diatom valve abundance and the pigments (r^2> 0.89, p<0.0001) and amino acids (r^2> 0.58, p<0.0014) concentrations in the sediment column indicated that the recently deposited OM constituents mainly originate from diatoms. Furthermore, the absence of diatom valves below the upper 3 cm of sediment implies that diatoms arrived mainly through vertical transport and that the lateral transport from adjacent regions brought into the region refractory material from other sources, presumably from secondary production. Thus, refractory

carbohydrates and fatty acids found in EAP accumulated in the sediment column mainly via lateral advection and not as the result of OM deposition after Larsen A and B ice shelf collapses. The absence of Chl*b* confirmed the lack of terrestrial inputs of OM from the Antarctic continent. Further, the absence of *iso*- and *anteiso*-FA, hydroxylated FA and 18:1(n-7) indicated the lack of OM of bacterial origin.

Sponges, polychaetes and echinoderms represented the taxonomic groups with the highest relative biomass. The low growth rate of sponges suggested that this group lived in EAP seafloor before Larsen ice shelves disintegration. Previous research on benthos below ice shelves suggested that laterally advected OM can maintain suspension feeders under ice shelves. Further, the high relative abundance of ascidians confirmed the presence of a rich suspension feeders community in this region, which represented 50% of the total biomass. Suspension feeders coexisted with typical surface deposit feeders such as holothurians of the species *Scotoplanes globosa* and ophiuroids, adapted to live in habitats with scarce food resources like under ice shelves. Like in other benthic communities at the first stages of recovery, polychaetes and echinoderms had a high relative biomass. The presence of these typical pioneer species which occur at the early stages of the ecological succession enhanced the diversity of the macrobenthic community. EAP communities presented early stages of development.

The profiles of biogenic silica percentage were not significantly correlated to those of diatom valves ($p>0.05$) and pigments ($p>0.05$). Based on the presence and biomass of sponges found in the region (25% of the total biomass), in particular of Demospongiae and Hexactinellida, we suggested that this group of organisms contributed with their spicules to the observed percentages of biogenic silica in the sediment column. Thus, the accumulation of biogenic silica in the sediment column was not linked to ice shelf collapses.

NAP

Chl*a* and Chl*c*, and THAA and EHAA concentrations were relatively high in the superficial sediment (upper 2 cm) and their vertical profiles showed a slight decline with depth. In comparison to EAP, the vertical distribution of pigments and amino acids suggested a higher input of labile OM to the seafloor and a longer period of accumulation of labile OM together with the action of biological mixing that redistributed

the material throughout the sediment core. The low Chl*a* to Pheo*a* and Chl*c* to Pheo*c* ratios indicated higher OM degradation than in EAP. Bioturbation enhanced degradation of OM and increased sediment mixing. On the contrary, THAA and EHAA data did not make clear differences in the lability of the OM between the two regions. The EHAA:THAA ratio indicated that amino acids undergo similar degradation in NAP and EAP sediments and comparisons with other geographical regions indicated that in a global context OM quality is relatively high (high lability) in NAP and EAP sediments. The different information from pigment and amino acid data on the quality of the OM depended on the different lability of these two OM constituents. Pigments degrade faster than amino acids, thus pigment distribution throughout the sediment cores evidenced better than amino acid the recent deposition of OM.

Based on the lability index values obtained with the amino acid concentrations there is evidence to support the fact that fresh OM material reaches the seabed in NAP suggesting an efficient vertical transport from the euphotic zone. Furthermore, the high relative abundance of amino acids associated with biogenic opal like Gly, Ser and Thr indicated that diatoms contributed to the OM found in the sediment, in agreement with the high abundance of diatom valves observed in the sediment column. The high Chl*a* to Chl*c* ratio also indicated the high contribution of diatoms to the pigment concentrations found in the sediment but the contribution from dinoflagellates, and crysophytes should not be discarded.

In Elephant Island a particularly high relative abundance of FA 22:1(n-9) evidenced an important contribution from zooplankton to the FA found in this station coincident to the proximity to the Polar Front, which is an area of high salps and krill development.

As well as in EAP, the absence of Chl*b* confirmed the lack of terrestrial inputs of OM from the Antarctic continent to the sediment column, whereas the absence of *iso*- and *anteiso*-FA, hydroxylated FA and 18:1(n-7) evidenced the lack of OM of bacterial origin.

The vertical distribution of biogenic silica concentrations correlated neither to that of diatom valves ($p<0.0001$) nor to any of the Chlorophylls ($p<0.0001$), indicating that the supply of this biogenic variable to the region has other sources in addition to diatoms.

SEWS

A high LPD concentration was found off SEWS I, whereas off SEWS II high PRT and CHO concentrations were found. The high LPD contents were attributed to a high input of diatom aggregates, which commonly develop from retreating sea ice and in the intense seasonal bloom forming green mats after deposition onto the seabed. Off SEWS II, where the benthic communities represent the typical epiphytic three-dimensional assemblage of the southeastern Weddell Sea, benthic biomass and abundance were larger than in SEWS I and EAP suggesting that a more intense preferential consumption diminished the LPD concentration in the sediment. CHO concentration in the sediment has stimulated discussion about their potential sources, advocating for a wide spectra of potential inputs varying from refractory structural CHO to reservoir CHO contained in diatoms. This is because total CHO analysis does not distinguish between structural or reservoir material; thus, total CHO concentration cannot provide information on the lability of the OM. We suggested that CHO found in SEWS I and SEWS II did not represented refractory OM and originated from fresh diatom storage compounds in accordance to the strong seasonal primary production pulse.

Overall, macrofauna in SEWS I presented lower biomass and abundance values than SEWS II. Deposit feeders and polychaetes showed a higher relative biomass in both EAP and SEWS I in comparison to SEWS II where suspension feeders and in particular sponges were predominant. The relative biomass of echinoderms, rapid immigrants after iceberg scouring events, was similar in EAP and SEWS I and higher than in SEWS II. Diversity was higher in SEWS I than in SEWS II, in agreement with the patchy disequilibria theory which suggests that moderate and regular disturbances can induce faunal assemblages patchiness incrementing diversity. The presence of giant glass sponges in SEWS II reduced biomass homogeneity among taxonomic groups, thus yielding higher Simpson index values. To explain these differences we proposed that the higher abundance of icebergs observed off SEWS I than off SEWS II exerted more intense scouring in the former region than in the latter. However, iceberg scouring cannot explain these differences alone. The different oceanographic conditions (e.g, currents regime, sediment grain size and primary production) of both areas despite its vicinity (41 nm) were also a factor determining the biochemical variable concentration and the macrobenthic community characteristics.

Relationship between organic matter concentration and sediment grain size

Our results showed a lack of any clear relationship between sediment grain size and pigment, amino acid, carbohydrate, protein or lipid concentrations. On the contrary, sediment grain size was correlated with the macrofauna and in particular with the relative abundance of the three feeding groups, suspension feeders, deposit feeders and carnivores. The finer sediment in EAP than in SEWS II coexisted with a higher deposit feeder biomass in the former and a higher suspension feeder biomass in the latter.

Principal conclusions of this work

1. Deposition of recently produced OM in EAP superficial sediment

After Larsen A and B ice shelf collapses, PP in EAP water column started developing and consequently the phytoplankton detritus flux to the seafloor. Although the ice shelf collapse opened space at the EAP sea surface enabling phytoplankton blooms, the large amount of icebergs that calved from the ice shelves greatly reduced the available ice-free areas drastically limiting primary production.

Recently deposited OM was found in the upper millimetres of the seabed in EAP. In NAP, pigment and amino acid concentrations were higher than in EAP throughout the sediment cores. Diatom valves, ^{210}Pb activity, pigment and amino acid vertical distributions indicated a lower input of labile OM to the seafloor and a shorter period of accumulation in EAP than in NAP. CHO and MC-FA represented the refractory organic matter found in the entire sediment column of EAP.

2. Diatoms are the main source of OM to the seabed in EAP

Recently deposited OM constituents originated from diatoms in both EAP and NAP. In EAP sediment, labile OM originated from primary production was mainly vertically transported from the euphotic zone, while refractory CHO and MC-FA probably accumulated by lateral advection during years of ice coverage and lack of fresh OM supply. In the study area the absence of Chl*b* confirmed the lack of terrestrial inputs of OM from the Antarctic continent and the absence of *iso*- and *anteiso*-FA, hydroxylated FA and 18:1(n-7) evidenced the lack of OM of bacterial origin.

3. Different preservation of OM constituents in the sediment

Pigments revealed as the best markers of the deposition of OM after Larsen A and B ice shelf collapses in EAP. However, amino acids provided useful information as well. The very low proportion of PUFA and the absence of diatom PUFA, in both EAP and NAP reflected a rapid PUFA degradation even in this polar environment and suggested that, in the case of the present study, PUFA cannot be used as indicators of phytoplankton debris or fresh OM in a mid-term (years). Total CHO, PRT and LPD and biogenic silica are not good indicators to track recent changes in the water column because they are not specific to any source of material. The use of pigments, amino acids and fatty acids is more adequate to investigate on the lability and the sources of the OM.

4. Ice shelves impede the vertical input of OM

Overall, the quantity and chemical quality of the biogenic variables throughout the sediment column demonstrated that the presence of ice shelves effectively hamper the vertical input of labile OM to the seabed. Diatom valves and pigment profiles strongly suggest that this is mainly the consequence of rather limited primary production.

5. Abundance and biomass of macrofauna in EAP indicated early stages of colonization

Benthic macrofauna in EAP presented relatively low abundance and biomass. Sponges, polychaetes and echinoderms were the taxonomic groups with the highest relative biomass. Typical pioneer species increased diversity. Pigment, diatom valves and ^{210}Pb activity profiles demonstrated that the benthic assemblage of EAP did not produce important bioturbation in subsurface sediment.

6. No correlation between sediment grain size and OM concentration

Differences among regions in the concentration of any measured constituent of OM in the sediment were not determined by sediment grain size.

7. Establishment of a base line for future work

The results of the present work in relation to EAP represent a reliable and broad pool of data to track environmental changes in this transforming environment.

Future research

Based on the information generated during the PhD period a postdoctoral research plan has been designed supported on the following hypothesis:

1. How rapid is the ecosystem changing?

With Antarctic expedition ANT-XXIII/8 we had the opportunity to reach Larsen A and B and to sample sediment after ice shelf collapses (11 years after in the case of Larsen A and 4 years after in the case of Larsen B). This PhD work, based on the high resolution chemical analysis of the sediment columns produced a series of OM profiles that showed how Larsen ecosystems changed after ice shelf collapses. With the opportunity to revisit the area in a near future and the possibility to recover sediment from the same stations it will be possible to analyze how OM has been degrading and penetrating into the sediment column in relation to the changes in the pelagic and benthic communities under a precise temporal frame.

2. How rapid is the transport of OM from the euphotic zone to the continental shelf?

Assessment of ^{210}Pb profiles with non-steady state models and more radionuclides such as ^{14}C to validate the sediment accumulation rates obtained in the present study.

3. Development of models to describe OM diagenesis in the sediment column of different environmental characteristics

Incorporation of analyses of dissolved oxygen and nutrients in the pore water in sediment cores to track diagenetic changes.

4. How are changes in OM input to the seafloor related to the benthos?

Benthic communities in steady state (SEWS) and recolonization stages (EAP) presumably, will show changes in their structure (if any in the case of the southeastern Weddell Sea community), reinforcing the necessity to revisit the stations in the near future, principally in EAP. Will recolonization communities in EAP present changes towards the steady state communities found in SEWS? Will changes in the OM characteristics in the sediment support benthic community changes?

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