Diatom valve distribution and sedimentary fatty acid composition in Larsen Bay, Eastern Antarctica Peninsula

E. Sañé, E. Isla, Audrey M Pruski, M. A. Bárcena, G. Vétion, D. J. Demaster

To cite this version:

E. Sañé, E. Isla, Audrey M Pruski, M. A. Bárcena, G. Vétion, et al.. Diatom valve distribution and sedimentary fatty acid composition in Larsen Bay, Eastern Antarctica Peninsula. Continental Shelf Research, 2011, 31 (11), pp.1161-1168. 10.1016/j.csr.2011.04.002 . hal-02908657

HAL Id: hal-02908657
https://hal.sorbonne-universite.fr/hal-02908657v1
Submitted on 29 Jul 2020

www.elsevier.com/locate/csr

Diatom valve distribution and sedimentary fatty acid composition in the Larsen A and B bays, Eastern Antarctica Peninsula

E. Sañé, E. Isla, A.M. Pruski, M.A. Bárcena, G. Vétion, D. DeMaster

PII: S0278-4343(11)00129-4
DOI: doi:10.1016/j.csr.2011.04.002
Reference: CSR 2360

To appear in: *Continental Shelf Research*

Received date: 18 March 2010
Revised date: 10 March 2011
Accepted date: 5 April 2011

Cite this article as: E. Sañé, E. Isla, A.M. Pruski, M.A. Bárcena, G. Vétion and D. DeMaster, Diatom valve distribution and sedimentary fatty acid composition in the Larsen A and B bays, Eastern Antarctica Peninsula, *Continental Shelf Research*, doi:10.1016/j.csr.2011.04.002

Diatom valve distribution and sedimentary fatty acid composition in the Larsen A and B bays, Eastern Antarctica Peninsula.

[1]Sañé, E., [1]Isla, E., [2,3]Pruski, A.M., [4]Bárcena, M.A., [2,3]Vétion, G., [5]DeMaster, D.

[1]Institut de Ciències del Mar-CSIC, Passeig Maritim de la Barceloneta 37-49, Barcelona E-08039, Spain
[2] UPMC Univ Paris 06, FRE 3350, LECOB, Observatoire Océanologique, F-66651 Banyuls/mer, France
[3] CNRS, FRE 3350, LECOB, Observatoire Océanologique, F-66651, Banyuls/mer, France
[3]Depto. de Geología y Paleontología, Facultad de Ciencias, Universidad de Salamanca 37008 Salamanca, Spain
[5]Department of Marine, Earth and Atmospheric Sciences, North Carolina State University, Raleigh, NC 27695-8208, U.S.A.

Abstract

During austral summer 2006-2007, five sediment cores were recovered from the Eastern Antarctic Peninsula (EAP) continental shelf. Microscopic observations and sediment fatty acid (FA) composition analyses were carried out to investigate whether the drastic changes at the sea surface in EAP may be reflected in the sedimentary record. A sharp decrease in the number of diatom valves was observed below 2 cm depth. This evident difference between the upper 2 cm of sediment and the deeper part of the sediment column was attributed to the drastic change in the upper water column conditions after the ice shelf collapses, which allowed the arrival of phytoplankton debris and fresh organic matter to the seafloor in EAP. The presence of bacterial-, zooplankton- and detrital-related FA throughout EAP cores suggests that there has been an input of older, more refractory organic matter into the region, presumably by lateral transport, before Larsen ice shelves disintegration.

1. Introduction

In the last 60 years atmospheric and oceanic temperatures have risen (Vaughan et al., 2001; Gille, 2002), leading to an increase of glacier retreat 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 (Rott et al., 1996; Domack et al., 2005). These events drastically modified the local conditions at the sea surface, relatively constant for hundreds of years (Domack et al., 2005). The ice shelf collapses enabled primary production in the recently open space (Bertolin and Schloss, 2009) to develop a flux of fresh organic debris to the seabed. Thus, studying the sediments organic matter (OM) content beneath extinct ice shelves may reveal how changes at the euphotic zone impact the benthic realm.

Sediment microscopic observations of phytoplankton provide information about the origin of the OM present in the sediment (Reuss and Poulsen, 2002). Diatoms, radiolaria, siliceous sponges, and silicoflagellates contribute with their siliceous skeleton to the biogenic silica flux to the seafloor and the consequent accumulation of this biogenic constituent in the sediment column (Abelmann and Gersonde, 1991; DeMaster, 2002). Diatom valves and sponge spicules represent the principal sources of biogenic silica in sediments (Rützler and MacIntyre, 1978; Bavestrello et al., 1996) and, 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). In the water column, diatom valves are subjected to grazing (Crosta, 2009), advection and dissolution (Buffen et al., 2007), nevertheless their frustules are well-preserved in sediments (Tsoy et al., 2009). *Fragilariopsis kerguelensis* is the most abundant diatom species in Antarctic surface sediments (Cortese and Gersonde, 2007) and in this study has been considered as an indicator of open-water conditions (Crosta et al., 2005; Roberts et al., 2007). The diatom valves of sea-ice related taxa (*Fragilariopsis curta, F. cylindrus, F. obliquecostata* and *F. sublinearis*), auxospores of *Thalassiosira antarctica*, as well as the resting spores (RS) of genus *Chaetoceros* have been treated as sea-ice related species (Armand et al., 2005). These sea-ice related taxa are present within the Sea Ice Zone southward of the Polar Front, living within, on or under the sea ice (Armand et al., 2005). *Thalassiosira antarctica* is a sea-ice related species (Garrison et al., 1987; Garrison, 1991) indicative of seasonally varying sea-ice conditions, which shows maximum abundance near the ice shelf edge, but requires cold open water to dwell (Pike et al., 2008) and *Chaetoceros* RS abundance reflects episodes of high primary production (Donegan and Schrader, 1982; Leventer, 1991; Sancetta et al., 1992; Karpuz and Jansen, 1992).

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 (Farrington and Quinn, 1973; Perry et al., 1979; Volkman et al., 1980; Venkatesan, 1988; Canuel and Martens, 1996; Sun and Wakeham, 1994; Cripps and Clarke, 1998). The presence of FA in Antarctic sediments 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). Diatoms, dinoflagellates, bacteria and zooplankton organisms are characterized by different FA and through their signature is possible to obtain information about the potential sources of the sedimentary organic matter found in the sea floor (Budge and Parrish, 1998; Camacho-Ibar et al., 2003). The specificity of FA for particular organisms 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., 2003; Lü et al., 2010), make FA analysis a useful tool to investigate on OM sources and quality.

Microscopic counts of diatom valves and sediment FA composition analysis have been carried out in the sedimentary record to verify the presence of temporal changes in the FA and diatom valve signatures related to Larsen A and B ice shelves collapse.

2. Methods

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) (Fig. 1) using a multi-corer with polycarbonate core barrels of 10 cm of diameter (Barnett et al., 1984). 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) (Fig.1). After recovery, sediment cores were sliced onboard in slices 0.5 cm thick from 0 to 9 cm depth. LA core was only 7.5 cm long. Subsamples were immediately frozen at -20ºC. Sediment samples were freeze-dried (P=0.1 mbar and T=-80ºC) for 24 hours before laboratory analyses and microscopic observations.

2.2 Diatom slides preparation and microscopic 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. 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 diatoms 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 and *F. kerguelensis*, auxospores of *T. antarctica* were identified together with *Chaetoceros* RS.

Diatom valve inventories were calculated by summing the product of the number of diatom valves, the depth interval (slice thickness) and the wet bulk density of each sub sample. Inventories are expressed in number of diatom valves per square centimeter (valves cm^{-2}). Diatom valve fluxes were calculated from diatom valve inventories and expressed in number of diatom valves per square centimeter per year (valves cm^{-2} yr^{-1}). Fluxes were calculated by dividing diatom valve inventories by the number of years of deposition, assuming no differences in the flux of diatoms to the seabed among years.

2.3 Fatty acid extraction

Fatty acids were extracted through 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% sulphuric acid and chloroform in the presence of butyl hydroxytoluene (BHT), an antioxidant at a concentration of 50 mg l^{-1} (Christie, 2003) The ratio of methanol to chloroform to sulphuric acid in the solvent extraction was 1.7:2:0.3 v/v/v. 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). A Varian Factor Four capillary column WAX-ms was used. The column had a length of 30 m and an internal diameter of 0.25 mm; film thickness was 0.25 µm. The flow was constant with a velocity of 1 ml/min. The column oven stabilization time was 0.30 min, the injector temperature was 260°C and the volume injected was 1 µl. The use of known standards as reference (Supelco 37, PUFA nº1 and nº3) allowed the identification of 22 individual fatty acids.

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

(1) Polyunsaturated fatty acids (PUFA): compounds with two or more unsaturated bonds.

(2) Monounsaturated fatty acids (MUFA): compounds with one unsaturation.

(3) Mid chain fatty acids (MC-FA): chain length $\leq C_{20}$.

(4) Long chain fatty acids (LC-FA): chain length C_{21}-C_{26}.

3. Results

3.1 Microscopic observation of diatom valves

The total abundance of diatom valves in the upper 0.5 cm of sediment ranged from ~1.3x10^6 valves g^{-1}(station LBS) to ~18.4x10^6 valves g^{-1} (station LBC) (Fig. 2). Diatom valve abundances decreased with depth and, in the four Larsen B cores, they were negligible below 2 cm depth (Fig. 2).

Diatom valve inventories varied between ~4.7x10^6 valves cm^{-2} (station LBW) and ~35.3 x10^6 valves cm^{-2} (station LBC), whereas diatom valve fluxes varied between ~9.4 x10^5 valves cm^{-2} yr^{-1} (station LBW) and ~70.5 x10^5 valves cm^{-2} yr^{-1} (station LBC) (Table 1).

As regards diatoms composition, valves of sea-ice taxa, auxospores of *T. antarctica* and *Chaetoceros* RS were found in all stations. Mean relative abundances of sea-ice taxa and *Chaetoceros* RS in the upper 0.5 cm of sediment of the five EAP cores were ~40% and ~52%, respectively, and decreased with depth (Fig. 3). The mean relative abundance of the auxospores of *T. antarctica* was ~1% and didn't change with depth (Fig. 3).

3.2 Fatty acid composition

Diatom indicators 14:0 and 16:1(n-7) (Nichols et al., 1986; Nichols et al., 1993; Dunstan et al., 1994) were present in all the stations (Fig. 4). In the superficial sediment (upper 0.5 cm), the concentration of FA 14:0 varied between ~4 µg g^{-1} (LBA) and ~8 µg g^{-1} (LBS), whereas that of FA 16:1(n-7) varied between ~3 µg g^{-1} (LBA) and ~9 µg g^{-1} (LBC). A decrease in the concentration of diatom indicators with depth was evident in cores LBS, LBC and LBN (Fig. 4). Dinoflagellate indicators 16:0 and 18:1(n-9) cis (Dalsgaard et al., 2003; Søreide et al., 2008) and zooplankton indicators 20:1(n-9) and 22:1(n-9) (Falk-Petersen et al., 1999) were present at the five stations (Fig. 4). The superficial concentration of dinoflagellate indicator FA 16:0 varied between ~23 µg g^{-1} (LBA) and ~42 µg g^{-1} (LBN), whereas that of dinoflagellate indicator FA 18:1(n-9) cis varied between ~18 µg g^{-1} (LBA) and ~52 µg g^{-1} (LBC). As regards zooplankton indicators, the superficial concentration of 20:1(n-9) varied between ~2 µg g^{-1} (LBA) and ~4 µg g^{-1} (LBC and LBN), and that of FA 22:1(n-9) between ~3 µg g^{-1} (LBA) and ~6 µg g^{-1} (LBS). Odd bacterial FA 11:0, 13:0 and 15:0 (Lee, 1992; Dalsgaard et al., 2003 and references therein) were present in all the stations (Fig. 4). In the superficial sediment, the concentration of FA 11:0 was ~0.1-0.2 μg g^{-1}, that of FA 13:0 was ~0.2-0.4 μg g^{-1} and that of FA 15:0 was ~0.6-1.1 μg g^{-1}.

PUFA represented a small component of the total FA pool. Only one PUFA was present at the five stations, 18:2(n-6) cis. The concentration of 18:2(n-6) cis in the superficial sediment varied between ~1 μg g^{-1} (LA) and ~2 μg g^{-1} (LBC) (Fig. 5). 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 five stations, whereas 24:1(n-9) only occurred at LBS. The total concentration of MUFA in the superficial sediment varied between ~26 μg g^{-1} (LA) ~70 μg g^{-1} (LBC) (Fig. 5). MC-FA 8:0, 10:0, 11:0, 12:0, 13:0, 14:0, 15:0, 16:0, 18:0 and 20:0 were present in the five cores. In the superficial sediment, the total concentration of MC-FA varied between ~68 μg g^{-1} (LA) ~101 μg g^{-1} (LBW) (Fig. 5). Among the LC-FA, 22:0 and 24:0 were the only compounds present at the five stations. 21:0 only occurred at LBS and LBN and 26:0 at LBS. The total concentration of LC-FA in the superficial sediment varied between ~0.5 μg g^{-1} (LA) and ~1.4 μg g^{-1} (LBC) (Fig. 5).

4. Discussion

FA and diatom valves were assessed in the continental shelf of EAP to find whether these indicators can reflect changes in the sediment column derived from the presence and recent disintegration of the Larsen A and B ice shelves.

Radionuclides (^{210}Pb and ^{14}C) data were used to establish sediment chronologies and determine which layer in the EAP sediment column could correspond to the time when Larsen ice shelf collapses occurred (Isla et al., unpublished results). Sediment cores were obtained only a decade after Larsen A and B ice shelf collapsed and, given the ^{210}Pb half life (22.3 y), steady state conditions were not yet attained in this region. The analysis of ^{14}C in sediment core LBW showed that the SAR was on the order of 0.04 cm y^{-1} (Isla et al., unpublished results). This low sedimentation rate suggested that in EAP, accumulation (advection) is still negligible and diffusion is the main responsible for particle motion in the sediment cores of this region. The rather low sediment accumulation in EAP led us to argue that the layer which corresponds to the time period after the ice shelf collapses in Larsen A and Larsen B is, at most, only few millimetres thick. These low accumulation rates hamper distinguishing differences between Larsen A and B profiles (Fig. 2, 4 and 5), despite the 7-year difference in the respective ice shelf collapses in the two bays. The significant correlation between the excess ^{210}Pb activity, diatom valves abundance and pigment concentration profiles (Fig. 6, see also Sañé et al., 2011) provided evidence to suggest that pigments and diatom valves were deposited in EAP only after the ice shelves collapsed and primary production started developing (Bertolin and Schloss, 2009; Isla et al., unpublished results). Then, the biogenic material from the upper millimetres has been redistributed along the upper 2 cm layer during the last decade (Fig. 6) and we assume that all the organic matter present below 2 cm depth reached EAP region though lateral transport before the collapse of Larsen ice shelves.

Based on the fact that primary production started in the Larsen bays only ~10 years ago, after ice shelves collapsed (Bertolin and Schloss, 2009), we hypothesized that higher diatom valve abundances and FA concentrations should be found at the top of the sediment cores than below 2 cm depth. Furthermore, we also hypothesised that differences in FA concentrations related to organic matter lability would be found between the upper 2 cm of sediment (more labile), where the biogenic matter deposited after ice shelf collapses (Isla et al., unpublished results; Sañé et al., 2011) and the deeper part of the sediment cores (more refractory).

4.1 Diatom signature

Our results on diatom valves abundance (Fig. 2) confirm that primary production and the vertical flux of organic matter to the sea floor are negligible under ice shelves (Littlepage and Pearse, 1962) and that diatom valve abundances augmented after Larsen ice shelf collapses (Buffen et al., 2007). Furthermore, the absence of diatom valves below the upper 2 cm layer in EAP sediment suggests that the lateral transport of diatom valves into the region is negligible. The diatom valves present in the upper 2 cm of sediment have been recently produced and vertically transported through the water column. Given the relatively short period of accumulation of diatom valves in EAP it is rather unlikely that diatom valves in EAP had undergone vigorous dissolution up to the degree that they are not visible towards the base of the core. Thus, valve profiles corroborate that diatoms arrived to EAP sea floor only after Larsen A and B ice shelf collapses.

No significant differences in diatom valve fluxes were found between EAP region and two stations off the Northern Antarctic Peninsula which have not been covered by ice shelf for at least 1 kyr (Ingólfsson et al., 1998). In the case of Larsen B cores, diatom valve fluxes were calculated dividing diatom valve inventories from 0 to 5 cm depth by 5 years, which is the time span between the ice shelf collapse and the sampling expedition. Based on the excess ^{210}Pb activity and the pigment profiles (Fig. 6 and Sañé et al., 2011), diatom fluxes for EAP were calculated using diatom valve inventories from 0 to 5 cm depth to assure including diatom valves deposited after the ice shelf collapse. In the case of the two stations off the Northern Antarctic Peninsula, the diatom valves inventory of the 11 cm long sediment core corresponding to the Elephant Island station was divided by 36 years (based on a sediment accumulation rate of 3.02 mm y^{-1}; Isla et al., unpublished results), whereas the diatom valves inventory of the 11 cm long sediment core corresponding to the South Shetland Island station was divided by 58 years (based on a sediment accumulation rate of 1.90 mm y^{-1}; Isla et al., unpublished results). The presence of icebergs in EAP region, related to the recent Larsen A and B ice shelf collapses, should reduce the available area for phytoplankton blooms to develop, and, consequently, primary production in this region (Arrigo et al., 2002; Arrigo and van Dijken, 2003). Nevertheless, similarities in diatom valve fluxes between EAP region and the two stations off the Northern Antarctic Peninsula may be related to the rather moderate to low primary production off the South Shetland and Elephant Islands (Bodungen et al., 1986; Holm-Hansen and Mitchell, 1991; Holm-Hansen et al., 1997).

The absence of *Fragilariopsis kerguelensis* in EAP is consistent with the absence of open water conditions (Crosta et al., 2005) until 1995 and 2002 in Larsen A and B, respectively, whereas the high percentage of sea-ice related taxa implies that this region is not experiencing true seasonal open-water conditions yet (Fig. 3).

4.2 Fatty acid signature

Changes in the FA profiles between the parts of the sediment column corresponding to the pre- and the post- ice shelves collapse were less evident than those observed for the diatom valves signature (Fig. 4, 5), probably due to FA lability. FA are characterized by different labilities depending on their chemical structure. FA with a high number of unsaturations or polyunsaturated FA (PUFA) represent the most labile group of FA (Haddad et al., 1992; Sun and Wakeham, 1994). The low concentration of PUFA (Fig. 5) and the absence of PUFA diatom indicators, such as 16:2(n-4) and 16:3(n-4) (Volkman et al., 1989; Wakeham, 1995), even in the upper 2 cm of the sediment column where high abundances of diatom valves were found, suggests that PUFA were previously degraded in the water column or/and after deposition onto the seabed (Smith et al., 1983; Wakeham et al., 1997; Budge and Parrish, 1998; Grossi et al., 2003; Hu et al., 2006). Differently from PUFA diatom indicators, MUFA and MC-FA diatom indicators, like FA 16:1(n-7) and FA 14:0, were found in EAP and their concentrations decreased with depth in the five cores (Fig. 4), reflecting changes in the water column related to Larsen ice shelves disintegration. Differences between FA profiles may be related to the lower lability of MUFA and MC-FA in relation to PUFA (Haddad et al., 1992). The low concentration of FA 14:0 and FA 16:1(n-7) below 2 cm depth (Fig. 4) suggested that these fatty acids which originate from diatoms did not accumulate in EAP sediment column by lateral transport before the collapse of Larsen ice shelves.

On the contrary, no temporal changes were observed in the profiles of dinoflagellate indicators MUFA 18:1(n-9) cis and MC-FA 16:0, and in the profiles of zooplankton indicators, MUFA 20:1(n-9) and 22:1(n-9) (Fig. 4). MUFA 18:1(n-9) cis has not only been associated to flagellate-derived material (Søreide et al., 2008), but also to detrital material (Fahl and Kattner, 1993). Its presence throughout EAP cores, like the presence of zooplankton indicators MUFA 20:1(n-9) and 22:1(n-9), could suggest the input of older more refractory OM into the region presumably by lateral transport before ice shelves collapses. Dinoflagellate indicators FA 18:1(n-9) cis and FA 16:0 and zooplankton indicators FA 20:1(n-9) and FA 22:1(n-9) have similar labilities to diatom indicators FA 14:0 and FA 16:1(n-7). Therefore, the low concentration of FA 14:0 and FA 16:1(n-7) below 2 cm depth (Fig. 4) is independent from the lability of these two fatty acids and suggested that they did not reach Larsen region before ice shelf collapses through lateral transport.

The absence of bacterial indicators like hydroxylated FA and 18:1(n-7) (Perry et al, 1979) or like *iso*- and *anteiso*-FA (Parkers and Taylor, 1983; Kaneda, 1991) suggests a low bacterial activity; the only bacterial indicators present in EAP, MC-FA with an odd number of carbon atoms (Lee, 1992; Dalsgaard et al., 2003 and references therein), may also have accumulated in this region before ice shelf collapses by lateral transport. The idea that MUFA and MC-FA could have been laterally transported to EAP is supported by previous studies on benthos under ice shelves. Even if primary production below ice shelves is negligible (Littlepage and Pearse, 1962), the few studies on benthos below ice shelves revealed that a lateral flux of organic matter maintained benthic assemblages of suspension feeders at different distances from the ice shelf edge (Dayton and Oliver, 1977; Lipps et al.,1979; Riddle et al., 2007).

Long-chain saturated FA, LC-FA, are mainly of terrestrial origin and usually considered more resistant to degradation than planktonic FA (Canuel and Martens, 1996; Camacho-Ibar et al., 2003). Due to their low lability (Haddad et al., 1992; Sun and Wakeham, 1994), we expected to find evidence of the lateral transport in the study area also of this group of FA. Terrestrial inputs are absent in the study area, therefore, in spite of their low lability, only a low concentration of LC-FA was found in our sediment samples (Fig. 5) and the LC-FA found in EAP may be the result of MUFA chain lengthening (Nichols et al., 1986).

4.3 Summary

Diatom valve abundance in sediment cores collected from the continental shelf of the Larsen A and B bays provided evidence to suggest that diatom valves were deposited only after Larsen ice shelves collapse. Temporal changes in the FA signature were less evident than those observed for the diatom valves signature. In spite of the presence of diatom valves in the upper 2 cm of sediment, some diatom indicators like unsaturated FA 16:2(n-4) and 16:3(n-4) were not found in EAP cores, probably due to their high lability. The presence of some bacterial- and zooplankton- related MUFA and MC-FA suggests that there has been an input of refractory organic matter into the region, presumably by lateral transport, before Larsen ice shelves collapse.

5. References

Abelmann, A., and Gersonde, R., 1991, Biosiliceous particle flux in the Southern Ocean: Marine Chemistry 35, 503-536.

Arrigo, K.R., van Dijken, G.L., Ainley, D.G., Fahnestock, M.A., Markus, T., 2002. Ecological impact of a large Antarctic iceberg. Geophys. Res. Lett. 29, 1-4.

Arrigo, K.R. and van Dijken, G.L., 2003. Impact of iceberg C-19 on Ross Sea primary production. Geophys. Res. Lett. 30, 1-4.

Arrigo, K.R., van Dijken, G.L., Bushinsky, E., 2008. Primary production in the Southern Ocean, 1997–2006. Journal of Geophysical Research 113, C08004.

Armand, L., Crosta, X., Romero, O., Pichon, J.J., 2005. The biogeography of major diatom taxa in Southern Ocean sediments. 1. Sea ice related species. Palaeogeography, Palaeoclimatology, Palaeoecology 223, 93-126.

Barnett, P.R.O., Watson, J., Connelly, D., 1984. A multiple corer for taking virtually undisturbed samples from shelf, bathyal and abyssal sediments. Oceanol. Acta 7, 399-408.

Bavestrello, G., Cattaneo-Vietti, R., Cerrano, C., Cerutti, S., Sará, M., 1996. Contribution of Sponge Spicules to the Composition of Biogenic Silica in the Ligurian Sea. Mar. Ecol. 17, 41-50.

Beans, C., Hecq,J.H., Koubbi, P.,Vallet, C.,Wright, S., Goffart, A., 2008. A study of the diatom-dominated microplankton summer assemblages in coastal waters from Terre Adélie to the Mertz Glacier, East Antarctica (1391E–1451E). Polar Biol. 31, 1101-1117.

Bertolin, M.L. and Schloss, I.R., 2009. Phytoplankton production after the collapse of the Larsen A Ice Shelf, Antarctica. Polar Biol. 32, 1435-1446.

Bodungen, B.V., Smetacek, V.S., Tilzer, M.M., Zeitzschel, B., 1986. Primary production and sedimentation during spring in the Antarctic Peninsula region. Deep-Sea Res. 33, 177-194.

Budge, S.M. and Parrish, C.C., 1998. Lipid biogeochemistry of plankton, settling matter and sediments in Trinity Bay, Newfoundland. II. Fatty acids. Org. Geochem. 29, 1547–1559.

Buffen, A., Leventer, A., Rubin, A., Hutchins, T., 2007. Diatom assemblages in surface sediments of the northwestern Weddell Sea, Antarctic Peninsula. Mar. Micropal. 62, 7-30.

Camacho-Ibar, V.F., Aveytua-Alcázar, L., Carriquiry, J.D., 2003. Fatty acid reactivities in sediment cores from the northern Gulf of California. Organic Geochemistry 34, 425-439.

Canuel, E.A. and Martens, C.S., 1996. Reactivity of recently deposited organic matter: degradation of lipid compounds near the sediment-water interface. Geochim. Cosmochim. Acta 60, 1793-1806.

Christie, W.W. Lipid Analysis: Isolation, Separation, Identification and Structural Analysis of Lipids, 3rd Oily Press, Bridgwater, UK (2003) 207 pp.

Cook, A.J., Fox, A.J., Vaughan, D.G., Ferrigno, J.G., 2005. Retreating Glacier Fronts on the Antarctic Peninsula over the Past Half-Century. Science 308, 541-544.

Cortese, G. and Gersonde, R. 2007. Morphometric variability in the diatom *Fragilariopsis kerguelensis* : implications for Southern Ocean paleoceanography. Earth and Planetary Science Letters 257, 526-544.

Cripps, G.C., 1995. The occurrence of monounsaturated n-C_{21} and polyunsaturated C_{25} sedimentary hydrocarbons in the lipids of Antarctic marine organisms. Polar Biol. 15, 253-259.

Cripps, G.C. and Clarke, A., 1998. Seasonal variation in the biochemical composition of the particulate material collected by sediment traps at Signy Island, Antarctica. Polar Biol. 20, 414-423.

Crosta, X., 2009. Holocene size variations in two diatoms species, East Antarctica: productivity vs environmental conditions. Deep Sea Res. I 56, 1983-1993.

Crosta, X., Romero, O., Armand, L.K., Pichon, J.J., 2005. The biogeography of major diatom taxa in Southern Ocean sediments: 2. Open ocean related species Palaeogeography, Palaeoclimatology, Palaeoecology 223, 66-92.

Dalsgaard, J., St. John, M., Kattner, G., Muller-Navarra, D., Hagen, W., 2003. Fatty acid and trophic markers in the pelagic marine environment. Advances in Marine Biology 46, 225-340.

Dayton, P.K. and Oliver, J.S., 1977. Antarctic Soft-Bottom Benthos in Oligotrophic and Eutrophic Environments. Science 197, 55-58.

DeMaster D. J., 2002. The accumulation and cycling of biogenic silica in the Southern Ocean: revisiting the marine silica cycle. Deep-Sea Res. II 49, 3155-3167.

Ding, H. and Sun, M.-Y., 2005. Biochemical degradation of algal fatty acids in oxic and anoxic sediment-seawater interface systems: effects of structural association and relative roles of aerobic and anaerobic bacteria. Mar. Chem. 93, 1-19.

Domack, E., Duran, D., Leventer, A., Ishman, S., Doane, S., McCallum, S., Amblas, D., Ring, J., Gilbert, R., Prentice, M., 2005. Stability of the Larsen B ice shelf on the Antarctic Peninsula during the Holocene epoch. Nature 436, 681-685.

Donegan, D. and Schrader, H., 1982. Biogenic and abiogenic components of laminated hemipelagic sediments in the central Gulf of California. Mar. Geol. 48, 215-237.

Dunstan, G.A., Volkman, J.K., Barrett, S.M., Leroi, J-M, Jeffrey, S.W., 1994. Essential polyunsaturated fatty acids from 14 species of diatom (Bacillariophyceae). Phytochemistry 35, 155-161.

Fahl, K. and Kattner, G., 1993. Lipid content and fatty acid composition of algal communities in sea-ice and water from Weddell Sea (Antarctica). Polar Biol. 13, 405-409.

Falk-Petersen, S., Sargent, J.R, Lonne, O.J., Timofeev, S., 1999. Functional biodiversity in lipids of Antarctic zooplankton: *Calanoides acutus*, *Calanus propinquus*, *Thysanoessa macrura* and *Euphasia crystallorophias*. Polar Biol. 21, 37-47.

Farrington, J.W. and Quinn, J.G., 1973. Biogeochemistry of fatty acids in recent sediments from Narragansett Bay, Rhode Island. Geochim. Cosmochim. Acta 37, 259-268.

Garrison, D.L., 1991. Antarctic sea ice biota. American Zoologist 31, 17-33.

Garrison, D.L., Buck, K.R., Fryxell, G.A., 1987. Algal assemblages in Antarctic pack ice and in ice-edge plankton. J. Phycol. 23, 564-572.

Gille, S.T., 2002. Warming of the Southern Ocean Since the 1950s. Science 295, 1275-1277.

Grossi, V., Caradec, S., Gilbert, F., 2003. Burial and reactivity of sedimentary microalgal lipids in bioturbated Mediterranean coastal sediments. Mar. Chem. 81, 57-69.

Haddad, R.I., Martens, C.S., Farrington, J.W., 1992. Quantifying early diagenesis of fatty acids in a rapidly accumulating coastal marine sediment. Org. Geochem. 19, 205-216.

Holm-Hansen, O. and Mitchell, B.G., 1991. Spatial and temporal distribution of phytoplankton and primary production in the western Bransfield Strait region. Deep-Sea Res. 38, 961-980.

Holm-Hansen, O., Hewes, C.D., Villafañe, V.E., Helbling, E.W., Silva, N., Amos, T., 1997. Distribution of phytoplankton and nutrients in relation to different water masses in the area around Elephant Island, Antarctica. Polar Biol. 18, 145-153.

Hu, J., Zhang, H., Peng, P., 2006. Fatty acid composition of surface sediments in the subtropical Pearl River estuary and adjacent shelf, Southern China. Estuarine, Coastal and Shelf Science 66, 346-356.

Indarti, E., Abdul Majid, M.I., Hashim, R., Chong, A., 2005. Direct FAME synthesis for rapid total lipid analysis from fish oil and cod liver oil. Journal of food composition and analysis 18, 161-170.

Ingólfsson, Ó., Hjort, C., Berkman, P., Björck, S., Colhoun, E., Goodwin, I.D., Hall, B., Hirakawa, K., Melles, M., Möller, P., Prentice, M., 1998. Antarctic glacial history since the Last Glacial Maximum: an overview of the record on land. Ant. Sci. 10, 326-344.

Isla, E., Sañé, E., DeMaster, D.J. 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. Unpublished results.

Kaneda, T., 1991. Iso- and anteiso-fatty acids in bacteria: biosynthesis, function and taxonomic significance. Microbiological Reviews 55, 288-302.

Karpuz, N.K. and Jansen, E., 1992. A high-resolution diatom record of the last deglaciation from the SE Norvegian Sea: documentation of rapid climatic changes. Paleoceanography 7, 499-520.

Laureillard, J.,Pinturier, L., Fillaux, J., Saliot, A., 1997. Organic geochemistry of marine sediments of the Subantarctic Indian Ocean sector: Lipid classes-sources and fate Deep Sea Res. II 44, 1085-1108.

Lee, C., 1992. Controls on organic carbon preservation: The use of stratified water bodies to compare intrinsic rates of decomposition in oxic and anoxic systems. Geochim. Cosmochim. Acta 56, 3323-3335.

Leventer, A., 1991. Sediment trap diatom assemblages from the northern Antarctic Peninsula region. Deep-Sea Res. 38, 1127-1143.

Lewis, T., Nichols, P.D., McMeekin, T.A., 2000. Evaluation of extraction method for recovery of fatty acids from lipid-producing microheterotrops. Journal of Microbiological Methods 43, 107-116.

Lipps, J.H., Ronan, T.E., DeLaca, T.E., 1979. Life below the Ross Ice Shelf, Antarctica. Science 203, 447-449.

Littlepage, J.L. and Pearse, J.S., 1962. Biological and oceanographic observations under an Antarctic ice shelf. Science 137, 679-681.

Lü, D., Song, Q., Wang, X., 2010. Decomposition of algal lipids in clay-enriched marine sediment under oxic and anoxic conditions Chinese Journal of Oceanology and Limnology 28, 131-143.

Nahon, S., Charles, F., Lantoine, F., Vétion, G., Escoubeyrou, K., Desmalades, M., Pruski, A.M., 2010. Ultraviolet radiation negatively affects growth and food quality of the pelagic diatom *Skeletonema costatum*. J. Exp. Mar. Biol. Ecol. 383, 164-170.

Nichols, P.D., Palmisano, A.C., Smith, G.A., White, D.C., 1986. Lipids of the Antarctic sea ice diatom *Nitzschia cylindrus*. Phytochemistry 25, 1649-1653.

Nichols, D.S., Nichols, P.D., Sullivan, C.W., 1993. Fatty acid, sterol and hydrocarbon composition of Antarctic sea ice diatom communities during the spring bloom in McMurdo Sound. Antarctic Science 5, 271-278.

Parkes, R.J. and Taylor, J., 1983. The relationship between fatty acid distributions and bacterial respiratory types in contemporary marine sediments. Estuar. Coast. Shelf Sc. 16, 173-189.

Perry, G.J., Volkman, J.M., Johns, R.B., Bavor, H.J., 1979. Fatty acids of bacterial origin in contemporary marine sediments. Gechim. Cosmochim. Acta 43, 1715-1725.

Pike, J., Allen, C.S., Leventer, A., Stickley, C.E., Pudsey, C.J., 2008. Comparison of contemporary and fossil diatom assemblages from the western Antarctic Peninsula shelf. Mar. Micropal. 67, 274-287.

Reuss, N. and Poulsen, L., 2002. Evaluation of fatty acids as biomarkers for a natural bloom community. A field study of a spring bloom and a post-bloom period off West Greenland. Mar. Biol. 141, 423-434.

Riddle, M.J., Craven, M., Goldsworthy, P.M., Carsey, F., 2007. A diverse benthic assemblage 100 km from open water under the Amery Ice Shelf, Paleoceanography, 22. PA1204, doi:10.1029/2006PA001327.

Roberts, D., Craven, M., Minghong, C., Allison, I., Nash, G., 2007. Protists in the marine ice of the Amery Ice Shelf, East Antarctica. Polar Biol. 30, 143-153.

Rott, H., Skvarca, P., Nagler, T., 1996. Rapid collapse of northern Larsen Ice Shelf, Antarctica. Science 271.

Rützler, K. and Macintyre, I.G., 1978. Siliceous sponge spicules in coral reef sediments. Mar. Biol. 49, 147-159.

Sancetta, C., Heusser, L., Hall, M.A., 1992. Late Pliocene climate in the Southeast Atlantic: preliminary results from a multidisciplinary study of DSDP Site 532. Mar. Micropal. 20, 59-75.

Schrader, H.J., and Gersonde, R., 1978. Diatoms and silicoflagellates. *In* Zachariasse, W.J., et al. (Eds.), *Micropaleontological Counting Methods and Techniques: An Exercise of an Eight Metres Section of the Lower Pliocene of Cap Rossello, Sicily.* Utrecht Micropaleontol. Bull. 17, 129-176.

Smith, D.J., Eglinton, G., Morris, R.J., 1983. The lipid chemistry of an interfacial sediment from the Peru Continental Shelf: Fatty acids, alcohols, aliphatic ketones and hydrocarbons. Geochim. Cosmochim. Acta 47, 2225-2232.

Sañé, E., Isla, E., Grémare, A., Gutt, J., Vetion, G., DeMaster, D.J., 2011. Pigments in sediments beneath a recently collapsed ice shelves: the case of Larsen A and B shelves, Antarctic Peninsula. Journal of Sea Research, 65, 94-102.

Søreide, J.E, Falk-Petersen, Nøst Hegseth, E., Hop, H., Carroll, M.L., Hobson, K.A., Blachowiak-Samolyk, K., 2008. Seasonal feedingstrategies of *Calanus* in thehigh Arctic Svalbard region. Deep-Sea Res. II 55, 2225–2244.

Sun, M.-Y. and Wakeham, S.G., 1994. Molecular evidence for degradation and preservation of organic matter in the anoxic Black Sea Basin. Geochim Cosmochim. Acta 58, 3395-3406.

Sun, M.-Y., Wakeham, S.G.,Lee, C., 1997. Rates and mechanisms of fatty acid degradation in oxic and anoxic coastal marine sediments of Long Island Sound, New York, USA. Geochim Cosmochim. Acta 61, 341-355.

Tsoy, I.B., Obrezkova, M.S., Artemova, A.V., 2009. Diatoms in Surface Sediments of the Sea of Okhotsk and the Northwest Pacific Ocean. Oceanology 49, 130-139.

Vaughan, D.G., Marshall, G.J., Connolley, W.M., King, J.C., Mulvaney, R., 2001. Devil in the Detail. Science 293, 1777-1779.

Venkatesan, M.I., 1988. Organic geochemistry of marine sediments in Antarctic region: marine lipids in McMurdo Sound. Org. Geochem. 12, 13-27.

Venkatesan, M. and Kaplan, I., 1987. The lipid geochemistry of Antarctic marine sediments: Bransfield Strait. Mar. Chem. 21, 347-375.

Volkman, J.K., Johns, R.B., Gillan, F.T., Perry, G.J., 1980. Microbial lipids of an intertidal sediment-I. Fatty acids and hydrocarbons. Geochim. Cosmochim. Acta 44, 1133-1143.

Volkman, J.K., Jeffrey, S.W., Nichols, P.D., Rogers, G.I., Garland, C.D., 1989. Fatty acid and lipid composition of 10 species of microalgae used in mariculture. J. Exp. Mar. Biol. Ecol. 128, 219-240.

Wakeham, S.G., 1995. Lipid biomarkers for heterotrophic alteration of suspended particulate organic matter in oxygenated and anoxic water columns of the ocean. Deep-Sea Res. I 42, 1749-1771.

Wakeham, S.G., Hedges, J.I., Lee, C., Peterson, M.L., Hernes, P.J., 1997. Compositions and transport of lipid biomarkers through the water column and surficial sediments of the equatorial Pacific Ocean. Deep-sea Res. II 44, 2131-2162.

Wright, S.W. and van den Enden, R.L., 2000. Phytoplankton community structure and stocks in the East Antarctic Marginal ice zone (BROKE survey, January-March 1996) determined by CHEMTAX analysis of HPLC pigment signatures. Deep-Sea Res. II 47, 2363-2400.

Table 1. Inventories and fluxes of diatom valves.

Core station	Diatom valves inventory (Diatoms cm^{-2})	Diatom valves flux (Diatoms cm^{-2} yr^{-1})
LBS	4765774	9353155
LBW	4700737	940147
LBC	35260876	7052175
LBN	13045842	2609168
LA	25056923	5011385

>Sediments were studied to see if changes in the water column reflect in sediments.>Sediments off the Northern and the Eastern Antarctic Peninsula were compared.>2 ice shelf collapses in 1995 and 2002 affected the Eastern Antarctic Peninsula.>The lability of the organic matter was higher in the Northern than in the Eastern Antarctic Peninsula.>Diatom valves were deposited only after the ice shelves collapses.

Figure caps

Figure 1: Study area with the five sampling stations.

Figure 2: Diatom valves profiles in LBS, LBW, LBC, LBN and LA.

Figure 3: Sea ice taxa, *Chaetoceros* spp., *F. kerguelensis*, *T. antarctica* and non dominant taxa in EAP.

Figure 4: 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) FA indicators in EAP.

Figure 5: PUFA, MUFA, LC-FA and MC-FA in EAP.

Figure 6: Chl*a* concentration, diatom valves abundance and excess ^{210}Pb activity in the EAP region.

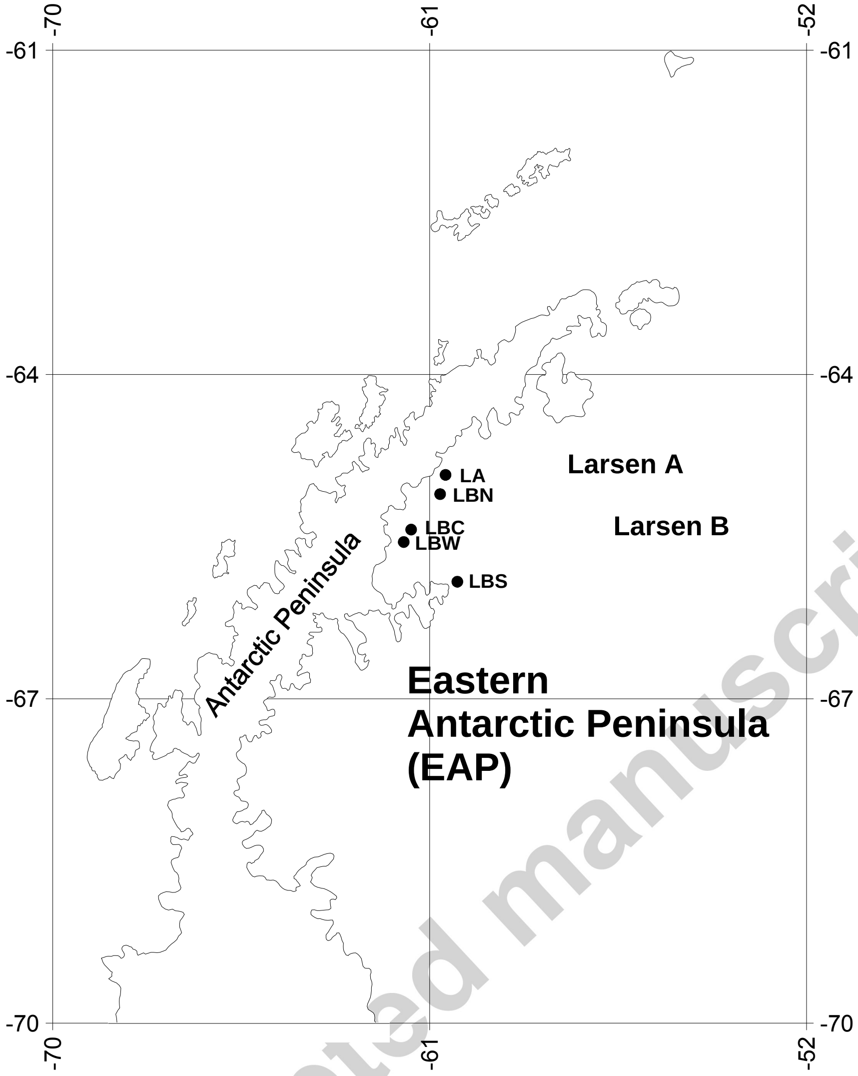

-70
-61
-52
-61
-64
-67
-70
LA
LBN
LBC
LBW
LBS
Larsen A
Larsen B
Antarctic Peninsula
Eastern Antarctic Peninsula (EAP)

Fig. 1

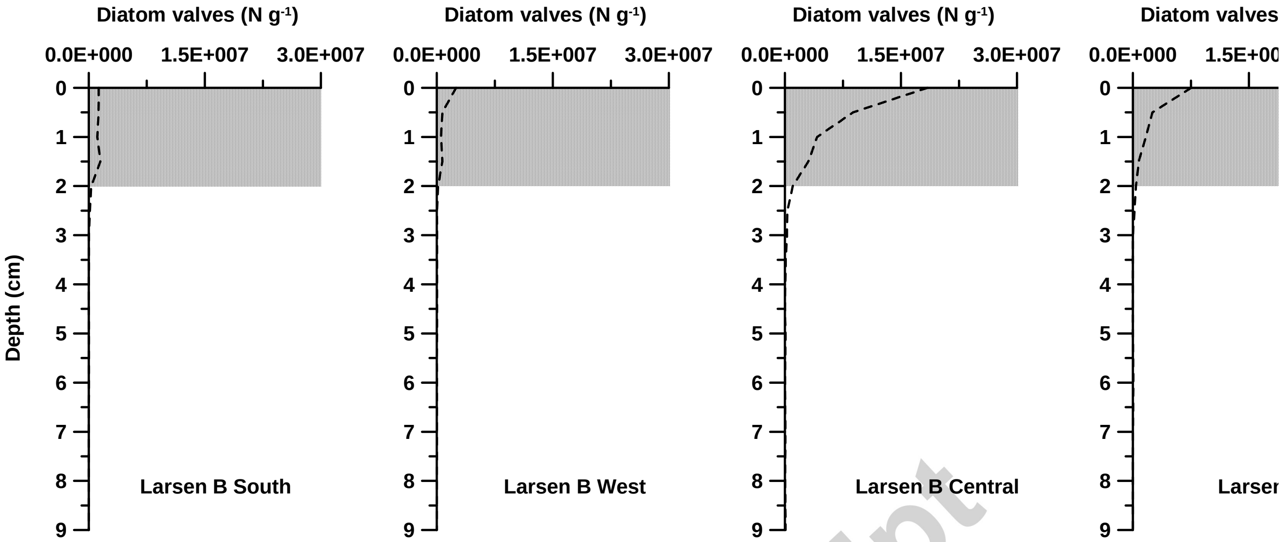

Diatom valves (N g-1)
0.0E+000
1.5E+007
3.0E+007
Depth (cm)
0
1
2
3
4
5
6
7
8
9
Larsen B South
Larsen B West
Larsen B Central
Larser

Fig. 2

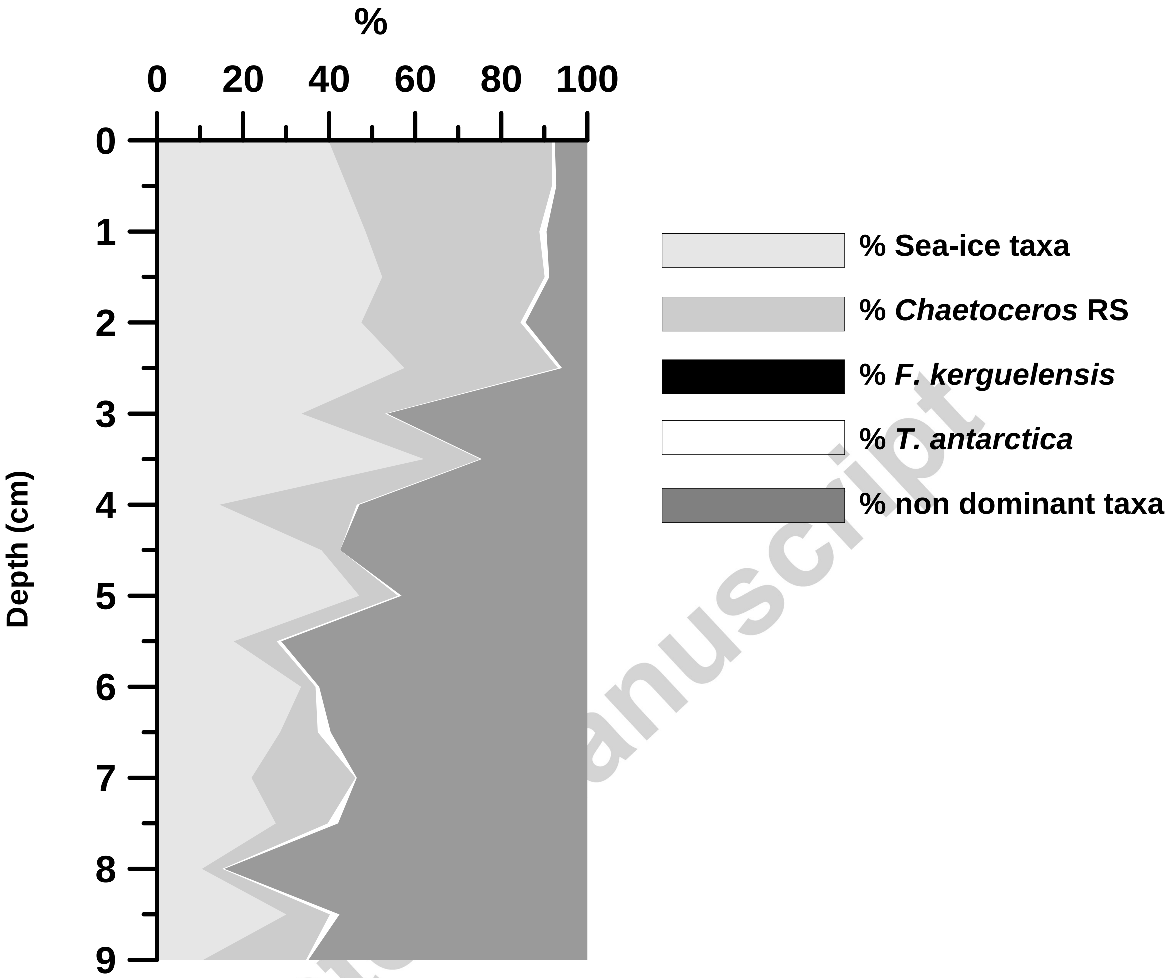

%
0
20
40
60
80
100
0
1
2
3
4
5
6
7
8
9
Depth (cm)
% Sea-ice taxa
% *Chaetoceros* RS
% *F. kerguelensis*
% *T. antarctica*
% non dominant taxa

Fig. 3

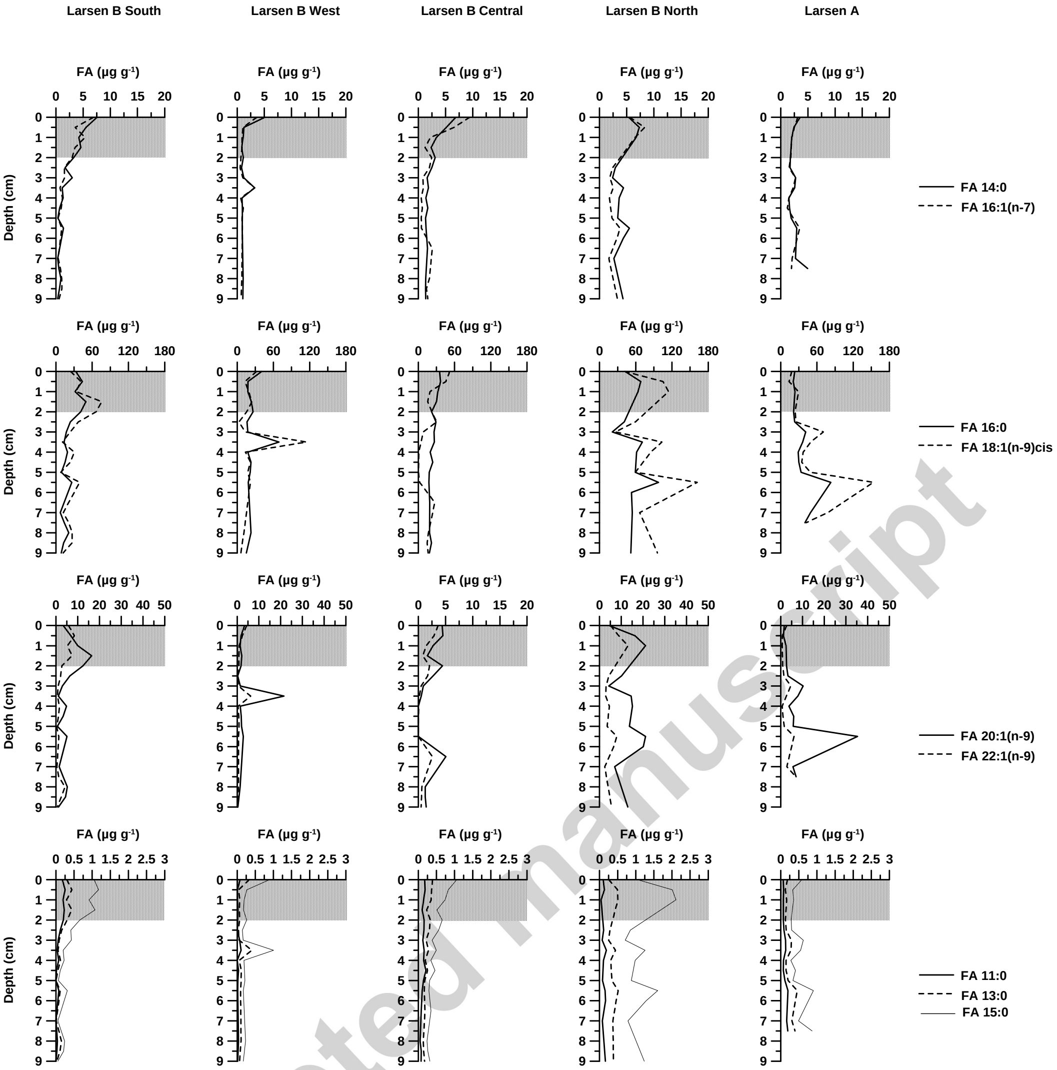

Larsen B South
Larsen B West
Larsen B Central
Larsen B North
Larsen A
FA (μg g-1)
Depth (cm)
0 5 10 15 20
0 60 120 180
0 10 20 30 40 50
0 0.5 1 1.5 2 2.5 3
0 1 2 3 4 5 6 7 8 9
FA 14:0
FA 16:1(n-7)
FA 16:0
FA 18:1(n-9)cis
FA 20:1(n-9)
FA 22:1(n-9)
FA 11:0
FA 13:0
FA 15:0

Fig. 4

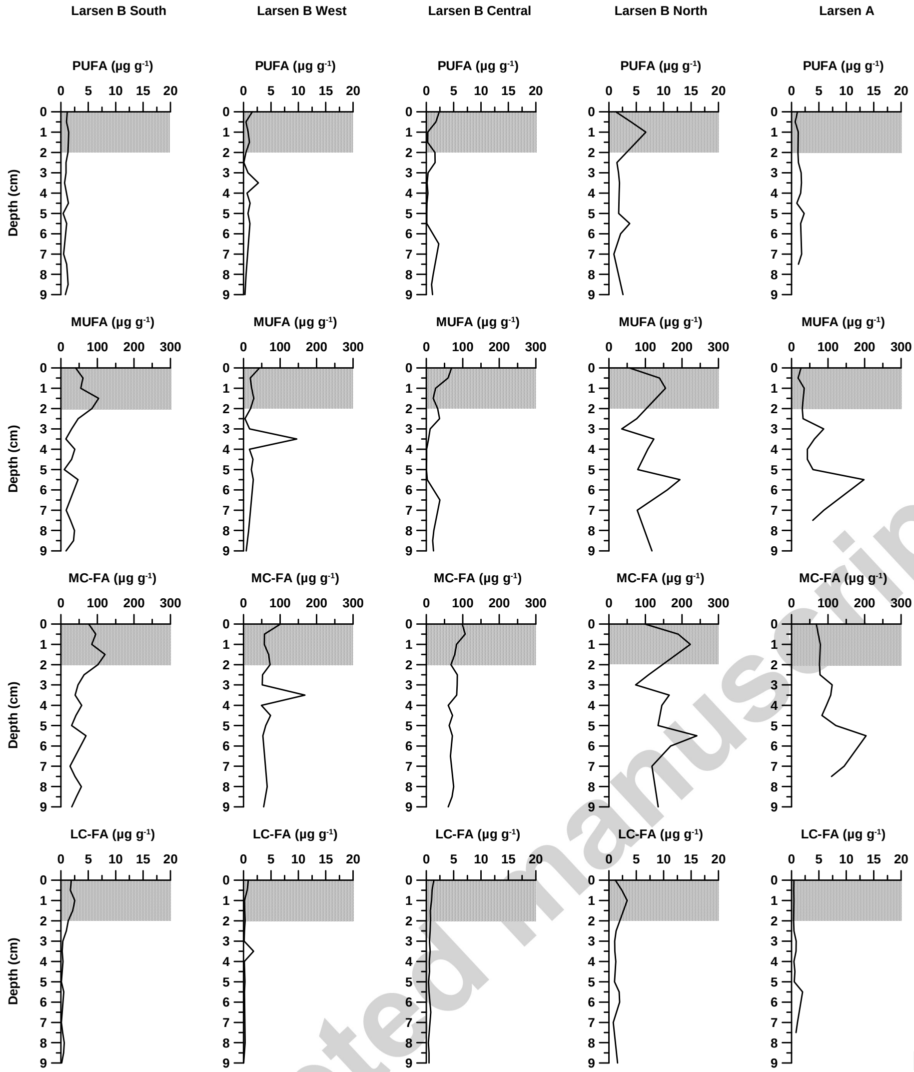
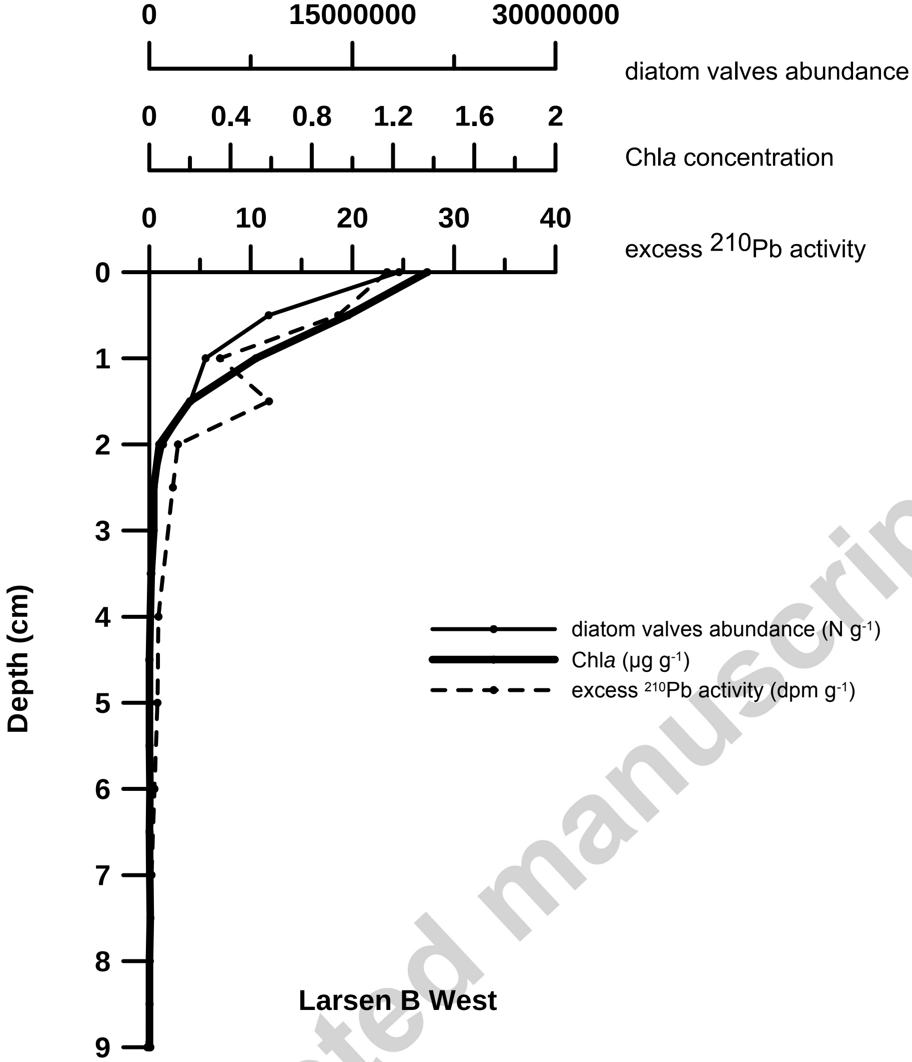

Larsen B South
Larsen B West
Larsen B Central
Larsen B North
Larsen A
PUFA (µg g-1)
0 5 10 15 20
MUFA (µg g-1)
0 100 200 300
MC-FA (µg g-1)
0 100 200 300
LC-FA (µg g-1)
0 5 10 15 20
Depth (cm)
0 1 2 3 4 5 6 7 8 9

Fig.5



0
15000000
30000000
diatom valves abundance
0
0.4
0.8
1.2
1.6
2
Chl*a* concentration
0
10
20
30
40
excess ^{210}Pb activity
0
1
2
3
4
5
6
7
8
9
Depth (cm)
diatom valves abundance (N g^{-1})
Chl*a* (µg g^{-1})
excess ^{210}Pb activity (dpm g^{-1})
Larsen B West

Fig.6