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

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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 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 collapse of the ice shelves, which allowed the arrival of phytoplankton debris and fresh organic matter to the sea floor in EAP. The presence of bacterial-, zooplankton- and detrital-related FA throughout EAP cores suggests that there has been an input of older and more refractory organic matter into the region, presumably by lateral transport before the 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 on the Antarctic Peninsula (Cook et al., 2005). In 1995, 4200 Km² of the Larsen A ice shelf collapsed, whereas 3200 Km² 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, which have been relatively constant for hundreds of years (Domack et al., 2005). The collapse of the ice shelves has enabled primary production in the area and increased new production (Arrigo et al., 2008; beans et al., 2008). 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 (Crost, 2009), advection and dissolution (Buffen et al., 2007), nevertheless their frustules are well-preserved in sediments (Tsai et al., 2009). Fragilariopsis kerguelensis is the most abundant diatom species in Antarctic surface sediments (Cortese and Gersonde, 2007) and in this study it has been considered as an indicator of open-water conditions (Crost et al., 2005; Roberts et al., 2007). The diatom valves of sea-ice related taxa (Fragilariopsis corta, 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 thrive (Pike et al., 2008) and Chaetoceros RS abundance reflects episodes of high primary production (Donegan and Schrader, 1982; Leveter, 1991; Sancetta et al., 1992; Karpuz and Jansen, 1992).
Fatty acids (FA), aliphatic hydrocarbon chains with a carboxylic group extremity, are synthesized 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 signatures it 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; Liu et al., 2010), make FA analysis a useful tool to investigate OM sources and OM quality.

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

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 10 cm in 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 subsampled onboard in slices of 0.5 cm thick from 0 to 9 cm depth, except LA core that was only 7.5 cm long. Subsamples were immediately frozen at −70 °C for 24 h before laboratory analyses and microscopic observations.

2.2. Diatom slides preparation and microscopic observation

Diatom 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 the sediment with sodium pyrophosphate. Hydrochloric acid (HCl) and hydrogen peroxide (H2O2) 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 valves 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 during counting of the 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, F. kerguelensis and 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 as number of diatom valves per square centimeter per year (valves cm−2 y−1). Fluxes were calculated by dividing diatom valve inventories by the number of years of deposition, assuming there are 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 by 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) and 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; 1 mg ml−1) were added and the samples were placed in a preheated oven at 90 °C for 90 min. With this procedure, lipids were extracted and the released fatty acids were directly methylated into fatty acid methyl esters (FAME). Ultra pure water (2 ml) was added to each sample to partition the extract into two phases. Following centrifugation (5 min at 1500 rpm and 4 °C), the inferior chloroform phase was recovered. A second extraction was carried out with a solution of hexane and chloroform (4:1 v/v) and after centrifugation (5 min at 1500 rpm and 4 °C), the superior phase was recovered and added.
to the first organic phase. This procedure was repeated twice. The organic phases were pooled and cleaned using a cold solution of potassium carbonate (2%), and after centrifugation (5 min at 1500 rpm and 4°C), 6–9 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 analyzed 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 injector temperature was 260°C and the volume injected was 1 µl. The use of known standards as reference (Supelco 37, PUFA no. 1 and no. 3) 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 as follows.

1. Poly-unsaturated fatty acids (PUFA): compounds with two or more unsaturated bonds.
2. Mono-unsaturated fatty acids (MUFA): compounds with one unsaturated bond.
3. Mid chain fatty acids (MC-FA): chain length ≤ 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 ~1.3 × 10^6 (station LBS) to ~18.4 × 10^6 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 ~4.7 × 10^6 (station LBW) and ~35.3 × 10^6 valves cm^{-2} (station LBC), whereas diatom valve fluxes varied between ~9.4 × 10^3 (station LBW) and ~7.05 × 10^3 valves cm^{-2} y^{-1} (station LBC) (Table 1).

With regard to diatom 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 did not change with depth (Fig. 3).

#### 3.2. Fatty acid composition

Diatom indicators 14:0 and 16:1(n-7) (Nichols et al., 1986, 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 (LBA) and ~8 µg g^{-1} (LBS), whereas that of FA 16:1(n-7) varied between ~3 (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

<table>
<thead>
<tr>
<th>Core station</th>
<th>Diatom valves inventory (diatoms cm^{-2})</th>
<th>Diatom valves flux (diatoms cm^{-2} y^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>LBS</td>
<td>4765774</td>
<td>9351155</td>
</tr>
<tr>
<td>LBW</td>
<td>4700737</td>
<td>940147</td>
</tr>
<tr>
<td>LBC</td>
<td>35260876</td>
<td>7052175</td>
</tr>
<tr>
<td>LBN</td>
<td>13045842</td>
<td>2690168</td>
</tr>
<tr>
<td>LA</td>
<td>25056923</td>
<td>5011385</td>
</tr>
</tbody>
</table>

![Fig. 2. Diatom valves profiles at LBS, LBW, LBC, LBN and LA.](image2.png)

![Fig. 3. Sea-ice taxa, Chaetoceros spp., F. kerguelensis, T. antarctica and non-dominant taxa in EAP.](image3.png)
(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 \(~23\) (LBA) and \(~42\ \mu g \text{ g}^{-1}\) (LBN), whereas that of dinoflagellate indicator FA 18:1(n-9) cis varied between \(~18\) (LBA) and \(~52\ \mu g \text{ g}^{-1}\) (LBC). With regard to zooplankton indicators, the superficial concentration of 20:1(n-9) varied between \(~2\) (LBA) and \(~4\ \mu g \text{ g}^{-1}\) (LBC and LBN) and that of FA 22:1(n-9) between \(~3\) (LBA) and \(~6\ \mu g \text{ g}^{-1}\) (LBS). Odd bacterial FA 11:0, 13:0 and 15:0 (Lee, 1992; Dalsgaard et al., 2003 and references therein) were present at all the stations (Fig. 4). In the superficial sediment, the concentration of FA 11:0 was \(~0.1–0.2\ \mu g \text{ g}^{-1}\), that of FA 13:0 was \(~0.2–0.4\ \mu g \text{ g}^{-1}\) and that of FA 15:0 was \(~0.6–1.1\ \mu g \text{ g}^{-1}\).

PUFA represented a small component of the total FA pool. Only one PUFA was present at the five stations, 18:2(n-6) cis.

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**Fig. 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.
The concentration of 18:2(n-6)cis in the superficial sediment varied between ~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) occurred only at LBS.

The total concentration of MUFA in the superficial sediment varied between ~26 (LA) and ~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

Fig. 5. PUFA, MUFA, LC-FA and MC-FA in EAP.
concentration of MC-FA varied between ~68 (LA) and ~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 occurred only at LBS and LBN and 26:0 at LBS. The total concentration of LC-FA in the superficial sediment varied between ~0.5 (LA) and ~1.4 µg g⁻¹ (LBC) (Fig. 5).

4. Discussion

FA and diatom valves were assessed on the continental shelf of EAP to determine whether these indicators reflect changes in sedimentation during the presence and recent disintegration of the Larsen A and B ice shelves.

Radionuclides (²¹⁰Pb and ¹⁴C) data were used to establish sediment chronologies and determine which horizon in the EAP sediment column corresponds to the time when the Larsen ice shelf collapsed (Isla et al., unpublished results). Sediment cores were obtained only a decade after the Larsen A and Larsen B ice shelves collapsed and, given the ²¹⁰Pb half life (22.3 y), steady state conditions have not been attained in this region. The analysis of ¹⁴C in sediment core LBW showed that the long-term sediment accumulation rate (SAR) was in the order of 0.04 cm y⁻¹ (Isla et al., unpublished results). This low sedimentation rate suggested that under the former Larsen ice shelves, sediment accumulation (advection) is probably negligible and bio-diffusion is mainly responsible for particle transport in the sediment column of this region. The rather low sediment accumulation under the Larsen ice shelves led us to argue that the thickness of the sediment layer which corresponds to the time period after the ice shelf collapsed in Larsen A and Larsen B is at most, only a few millimeters thick. Furthermore, this low accumulation rate hampers distinguishing differences between the Larsen A and B profiles (Figs. 2, 4 and 5), despite the 7-year difference in the respective ice shelf collapse. The significant correlation between the excess ²¹⁰Pb activity, diatom valves abundance and pigment concentration profiles (Fig. 6, see also Sañé et al., 2011) provides evidence to suggest that the pigments and diatom valves have been deposited in EAP only after the ice shelves collapsed and primary production started developing (Bertolin and Schloss, 2009; Isla et al., unpublished results). Consequently, the biogenic material from the upper millimeters 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 the Larsen ice shelves.

Based on the fact that primary production started in the Larsen bays only 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 rather than below 2 cm depth. Furthermore, we also hypothesized 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 was deposited after the collapse of the ice shelves (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 the primary production and the vertical flux of organic matter to the sea floor are negligible under ice shelves (Littlepage and Pearse, 1962) and also that the diatom valve abundances augmented after the collapse of the Larsen ice shelves (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. During the relatively short period of accumulation of diatom valves in EAP it is rather unlikely that the diatom valves have undergone vigorous dissolution up to the extent that they are not visible towards the base of the core. Thus, valve profiles corroborate that diatoms arrived to EAP sea floor only after the Larsen A and B ice shelves collapsed.

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 thousand years (Ingolfsson et al., 1998). In the case of the Larsen B cores, diatom valve fluxes were calculated by 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 ²¹⁰Pb 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 inclusion of diatom valves deposited after the ice shelf collapse. In the case of the two stations off the Northern Antarctic Peninsula, the diatom valve 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 the EAP region, related to the recent collapse of the Larsen A and B ice shelves, should reduce the available area for the development of phytoplankton blooms and, consequently, limit 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 on the Northern Antarctic Peninsula may be related to the rather moderate to low primary production off the South Shetland and Elephant Islands (Rodungen et al., 1986; Holm-Hansen and Mitchell, 1991; Holm-Hansen et al., 1997).

The absence of Fragilariaopsis 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 valve signatures (Figs. 4 and 5), probably due to FA lability. FA are characterized by different labilities depending on their chemical structure. FA with a high number of unsaturated bonds 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, suggest 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, MUFAs 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 the Larsen ice shelves disintegration. Differences between FA profiles may be related to the lower lability of MUFAs 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 the Larsen ice shelves.

On the contrary, no temporal changes were observed in the profiles of dinoflagellate indicators MUFAs 18:1(n-9)cis and MC-FA 16:0 and in the profiles of zooplankton indicators MUFAs 20:1(n-9) and 22:1(n-9) (Fig. 4). MUFAs 18:1(n-9)cis has not only been associated with flagellate-derived material (Sareide et al., 2008), but also with 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 associated with flagellate-derived material (Søreide et al., 2008), but also with detrital material (Fahl and Kattner, 1993). Its presence throughout 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 the Larsen ice shelves collapsed.

4.3. Summary

Diatom valve abundance in sediment cores collected from the continental shelf beneath the former Larsen Bay A and B ice shelves provided evidence to suggest that diatom valves were deposited only after the Larsen ice shelves collapsed. 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 MUFAs and MC-FA suggests that there has been an input of refractory organic matter into the region, presumably by lateral transport before the Larsen ice shelves collapsed.

References


