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# Diatom valve distribution and sedimentary fatty acid composition in the Larsen A and B bays, 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 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<sup>2</sup> of the Larsen A ice shelf collapsed, whereas 3200 Km<sup>2</sup> 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

48 column, diatom valves are subjected to grazing (Crosta, 2009), advection and  
49 dissolution (Buffen et al., 2007), nevertheless their frustules are well-preserved in  
50 sediments (Tsoy et al., 2009). *Fragilariopsis kerguelensis* is the most abundant diatom  
51 species in Antarctic surface sediments (Cortese and Gersonde, 2007) and in this study  
52 has been considered as an indicator of open-water conditions (Crosta et al., 2005;  
53 Roberts et al., 2007). The diatom valves of sea-ice related taxa (*Fragilariopsis curta*, *F.*  
54 *cylindrus*, *F. obliquecostata* and *F. sublinearis*), auxospores of *Thalassiosira antarctica*,  
55 as well as the resting spores (RS) of genus *Chaetoceros* have been treated as sea-ice  
56 related species (Armand et al., 2005). These sea-ice related taxa are present within the  
57 Sea Ice Zone southward of the Polar Front, living within, on or under the sea ice  
58 (Armand et al., 2005). *Thalassiosira antarctica* is a sea-ice related species (Garrison et  
59 al., 1987; Garrison, 1991) indicative of seasonally varying sea-ice conditions, which  
60 shows maximum abundance near the ice shelf edge, but requires cold open water to  
61 dwell (Pike et al., 2008) and *Chaetoceros* RS abundance reflects episodes of high  
62 primary production (Donegan and Schrader, 1982; Leventer, 1991; Sancetta et al.,  
63 1992; Karpuz and Jansen, 1992).

64 Fatty acids (FA), aliphatic hydrocarbon chains with a carboxylic group at one extremity,  
65 are synthesised in the cytosol. In marine organisms FA are predominantly found in  
66 energetic reserves which consist of triacylglycerols and wax esters, as well as in the  
67 phospholipids of the membrane lipid bilayer (Ding and Sun, 2005). A partial and  
68 selective degradation of FA occurs in the water column and in the sediment (Sun et al.,  
69 1997; Wakeham et al., 1997) and is particularly intense at the sediment-water interface  
70 (Laureillard et al., 1997). However, FA occurrence in the sediment column has been  
71 broadly studied (Farrington and Quinn, 1973; Perry et al., 1979; Volkman et al., 1980;  
72 Venkatesan, 1988; Canuel and Martens, 1996; Sun and Wakeham, 1994; Cripps and  
73 Clarke, 1998). The presence of FA in Antarctic sediments has been ascribed to marine  
74 primary and secondary production due to the absence of terrestrial inputs (Venkatesan  
75 and Kaplan, 1987; Cripps, 1995; Cripps and Clarke, 1998). Diatoms, dinoflagellates,  
76 bacteria and zooplankton organisms are characterized by different FA and through  
77 their signature is possible to obtain information about the potential sources of the  
78 sedimentary organic matter found in the sea floor (Budge and Parrish, 1998; Camacho-  
79 Ibar et al., 2003). The specificity of FA for particular organisms together with the  
80 different labilities of FA depending on their chemical structure (Haddad et al., 1992;  
81 Canuel and Martens, 1996; Sun and Wakeham, 1994; Camacho-Ibar et al., 2003; Lü et  
82 al., 2010), make FA analysis a useful tool to investigate on OM sources and quality.

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

86

## 87 **2. Methods**

### 88 *2.1 Sediment collection and preparation*

89 Sediment samples were collected during the Antarctic expedition ANT-XXIII/8 off the  
90 Eastern coast of the Antarctic Peninsula (EAP) (Fig. 1) using a multi-corer with  
91 polycarbonate core barrels of 10 cm of diameter (Barnett et al., 1984). Sediments were  
92 sampled at 5 stations, namely Larsen B South (LBS), Larsen B West (LBW), Larsen B  
93 Central (LBC), Larsen B North (LBN) and Larsen A (LA) (Fig.1). After recovery,  
94 sediment cores were sliced onboard in slices 0.5 cm thick from 0 to 9 cm depth. LA  
95 core was only 7.5 cm long. Subsamples were immediately frozen at -20°C. Sediment  
96 samples were freeze-dried (P=0.1 mbar and T=-80°C) for 24 hours before laboratory  
97 analyses and microscopic observations.

98

### 99 *2.2 Diatom slides preparation and microscopic observation*

100 Sediment samples were prepared according to the standard randomly distributed  
101 microfossils method. Due to the high abundance of diatom valves, it was not necessary  
102 to disaggregate sediment with sodium pyrophosphate. Hydrochloric acid (HCl) and  
103 hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) were added to a known weight of dry sediment to attack  
104 carbonates and OM. Sediment was rinsed several times with bi-distilled water, slides  
105 were mounted and diatom valve counts were performed at 1000 magnification using a  
106 Leica DMLB with phase-contrast illumination. Counts were carried out on permanent  
107 slides of acid-cleaned material (Permount mounting medium). Schrader and Gersonde  
108 (1978) recommendations were followed for the counting of microfossil valves.  
109 Depending on diatoms abundance, several traverses across each cover slip were  
110 examined. A minimum of 350 valves were counted for each sample, when possible.  
111 Moreover, a counting of at least 100 valves of non-dominant taxa per sample was  
112 performed. Valves of sea-ice taxa and *F. kerguelensis*, auxospores of *T. antarctica*  
113 were identified together with *Chaetoceros* RS.

114 Diatom valve inventories were calculated by summing the product of the number of  
115 diatom valves, the depth interval (slice thickness) and the wet bulk density of each sub  
116 sample. Inventories are expressed in number of diatom valves per square centimeter  
117 (valves cm<sup>-2</sup>). Diatom valve fluxes were calculated from diatom valve inventories and  
118 expressed in number of diatom valves per square centimeter per year (valves cm<sup>-2</sup> yr<sup>-1</sup>).  
119 Fluxes were calculated by dividing diatom valve inventories by the number of years

120 of deposition, assuming no differences in the flux of diatoms to the seabed among  
121 years.

122

### 123 *2.3 Fatty acid extraction*

124 Fatty acids were extracted through a one step transesterification process adapted from  
125 Lewis et al., (2000) and Indarti et al. (2005) according to the recommendations of  
126 Christie (2003). The analytical protocol is detailed in Nahon et al (2010). Approximately  
127 2 g of dried sediment were extracted in 8 ml of a cold solution of methanol, 98%  
128 sulphuric acid and chloroform in the presence of butyl hydroxytoluene (BHT), an  
129 antioxidant at a concentration of 50 mg l<sup>-1</sup> (Christie, 2003) The ratio of methanol to  
130 chloroform to sulphuric acid in the solvent extraction was 1.7:2:0.3 v/v/v. 20 µl of the  
131 internal standard C19:0 (nonadecanoic acid) (1mg ml<sup>-1</sup>) were added and the samples  
132 were placed in a preheated oven at 90°C for 90 minutes. With this procedure lipids  
133 were extracted and the released fatty acids were directly methylated in fatty acid  
134 methyl esters (FAME). Ultra pure water (2 ml) was added to each sample to partition  
135 the extract in two phases. Following centrifugation (5 minutes at 1500 rpm and 4°C),  
136 the inferior chloroform phase was recovered. A second extraction was made with a  
137 solution of hexane and chloroform (4:1 v/v) and, after centrifugation (5 minutes at 1500  
138 rpm and 4°C), the superior phase was recovered and added to the first organic phase.  
139 This procedure was repeated twice. The organic phases were pooled and cleaned with  
140 a cold solution of potassium carbonate (2%) and after centrifugation (5 minutes at 1500  
141 rpm and 4°C) 6 to 9 ml of the organic phase were recovered and an aliquot was  
142 evaporated to dryness in a rotary evaporator (Savant Speed Vac system) at room  
143 temperature. FAME were recovered in 75 µl of pure hexane prior to analysis. Fatty  
144 acids as methyl esters were analysed using a Varian 3900 gas chromatograph (GC)  
145 coupled to a Saturn 2100T ion-trap mass spectrometer (MS). A Varian Factor Four  
146 capillary column WAX-ms was used. The column had a length of 30 m and an internal  
147 diameter of 0.25 mm; film thickness was 0.25 µm. The flow was constant with a velocity  
148 of 1 ml/min. The column oven stabilization time was 0.30 min, the injector temperature  
149 was 260°C and the volume injected was 1 µl. The use of known standards as  
150 reference (Supelco 37, PUFA n°1 and n°3) allowed the identification of 22 individual  
151 fatty acids.

152

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

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

- 157 (2) Monounsaturated fatty acids (MUFA): compounds with one unsaturation.  
158 (3) Mid chain fatty acids (MC-FA): chain length  $\leq C_{20}$ .  
159 (4) Long chain fatty acids (LC-FA): chain length  $C_{21}-C_{26}$ .

160

### 161 3. Results

162

#### 163 3.1 Microscopic observation of diatom valves

164 The total abundance of diatom valves in the upper 0.5 cm of sediment ranged from  
165  $\sim 1.3 \times 10^6$  valves  $g^{-1}$  (station LBS) to  $\sim 18.4 \times 10^6$  valves  $g^{-1}$  (station LBC) (Fig. 2). Diatom  
166 valve abundances decreased with depth and, in the four Larsen B cores, they were  
167 negligible below 2 cm depth (Fig. 2).

168 Diatom valve inventories varied between  $\sim 4.7 \times 10^6$  valves  $cm^{-2}$  (station LBW) and  $\sim 35.3$   
169  $\times 10^6$  valves  $cm^{-2}$  (station LBC), whereas diatom valve fluxes varied between  $\sim 9.4 \times 10^5$   
170 valves  $cm^{-2} yr^{-1}$  (station LBW) and  $\sim 70.5 \times 10^5$  valves  $cm^{-2} yr^{-1}$  (station LBC) (Table 1).

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

177

#### 178 3.2 Fatty acid composition

179 Diatom indicators 14:0 and 16:1(n-7) (Nichols et al., 1986; Nichols et al., 1993;  
180 Dunstan et al., 1994) were present in all the stations (Fig. 4). In the superficial  
181 sediment (upper 0.5 cm), the concentration of FA 14:0 varied between  $\sim 4 \mu g g^{-1}$  (LBA)  
182 and  $\sim 8 \mu g g^{-1}$  (LBS), whereas that of FA 16:1(n-7) varied between  $\sim 3 \mu g g^{-1}$  (LBA) and  
183  $\sim 9 \mu g g^{-1}$  (LBC). A decrease in the concentration of diatom indicators with depth was  
184 evident in cores LBS, LBC and LBN (Fig. 4). Dinoflagellate indicators 16:0 and 18:1(n-  
185 9) cis (Dalsgaard et al., 2003; Søreide et al., 2008) and zooplankton indicators 20:1(n-  
186 9) and 22:1(n-9) (Falk-Petersen et al., 1999) were present at the five stations (Fig. 4).  
187 The superficial concentration of dinoflagellate indicator FA 16:0 varied between  $\sim 23 \mu g$   
188  $g^{-1}$  (LBA) and  $\sim 42 \mu g g^{-1}$  (LBN), whereas that of dinoflagellate indicator FA 18:1(n-9) cis  
189 varied between  $\sim 18 \mu g g^{-1}$  (LBA) and  $\sim 52 \mu g g^{-1}$  (LBC). As regards zooplankton  
190 indicators, the superficial concentration of 20:1(n-9) varied between  $\sim 2 \mu g g^{-1}$  (LBA)  
191 and  $\sim 4 \mu g g^{-1}$  (LBC and LBN), and that of FA 22:1(n-9) between  $\sim 3 \mu g g^{-1}$  (LBA) and  $\sim 6$   
192  $\mu g g^{-1}$  (LBS). Odd bacterial FA 11:0, 13:0 and 15:0 (Lee, 1992; Dalsgaard et al., 2003  
193 and references therein) were present in all the stations (Fig. 4). In the superficial

194 sediment, the concentration of FA 11:0 was  $\sim 0.1\text{-}0.2 \mu\text{g g}^{-1}$ , that of FA 13:0 was  $\sim 0.2\text{-}$   
195  $0.4 \mu\text{g g}^{-1}$  and that of FA 15:0 was  $\sim 0.6\text{-}1.1 \mu\text{g g}^{-1}$ .

196 PUFA represented a small component of the total FA pool. Only one PUFA was  
197 present at the five stations, 18:2(n-6) cis. The concentration of 18:2(n-6) cis in the  
198 superficial sediment varied between  $\sim 1 \mu\text{g g}^{-1}$  (LA) and  $\sim 2 \mu\text{g g}^{-1}$  (LBC) (Fig. 5). Four  
199 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  
200 stations, whereas 24:1(n-9) only occurred at LBS. The total concentration of MUFA in  
201 the superficial sediment varied between  $\sim 26 \mu\text{g g}^{-1}$  (LA)  $\sim 70 \mu\text{g g}^{-1}$  (LBC) (Fig. 5). MC-  
202 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  
203 cores. In the superficial sediment, the total concentration of MC-FA varied between  $\sim 68$   
204  $\mu\text{g g}^{-1}$  (LA)  $\sim 101 \mu\text{g g}^{-1}$  (LBW) (Fig. 5). Among the LC-FA, 22:0 and 24:0 were the only  
205 compounds present at the five stations. 21:0 only occurred at LBS and LBN and 26:0 at  
206 LBS. The total concentration of LC-FA in the superficial sediment varied between  $\sim 0.5$   
207  $\mu\text{g g}^{-1}$  (LA) and  $\sim 1.4 \mu\text{g g}^{-1}$  (LBC) (Fig. 5).

208

#### 209 4. Discussion

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

213 Radionuclides ( $^{210}\text{Pb}$  and  $^{14}\text{C}$ ) data were used to establish sediment chronologies and  
214 determine which layer in the EAP sediment column could correspond to the time when  
215 Larsen ice shelf collapses occurred (Isla et al., unpublished results). Sediment cores  
216 were obtained only a decade after Larsen A and B ice shelf collapsed and, given the  
217  $^{210}\text{Pb}$  half life (22.3 y), steady state conditions were not yet attained in this region. The  
218 analysis of  $^{14}\text{C}$  in sediment core LBW showed that the SAR was on the order of  $0.04$   
219  $\text{cm y}^{-1}$  (Isla et al., unpublished results). This low sedimentation rate suggested that in  
220 EAP, accumulation (advection) is still negligible and diffusion is the main responsible  
221 for particle motion in the sediment cores of this region. The rather low sediment  
222 accumulation in EAP led us to argue that the layer which corresponds to the time  
223 period after the ice shelf collapses in Larsen A and Larsen B is, at most, only few  
224 millimetres thick. These low accumulation rates hamper distinguishing differences  
225 between Larsen A and B profiles (Fig. 2, 4 and 5), despite the 7-year difference in the  
226 respective ice shelf collapses in the two bays. The significant correlation between the  
227 excess  $^{210}\text{Pb}$  activity, diatom valves abundance and pigment concentration profiles  
228 (Fig. 6, see also Sañé et al., 2011) provided evidence to suggest that pigments and  
229 diatom valves were deposited in EAP only after the ice shelves collapsed and primary  
230 production started developing (Bertolin and Schloss, 2009; Isla et al., unpublished



231 results). Then, the biogenic material from the upper millimetres has been redistributed  
232 along the upper 2 cm layer during the last decade (Fig. 6) and we assume that all the  
233 organic matter present below 2 cm depth reached EAP region though lateral transport  
234 before the collapse of Larsen ice shelves.

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

243

#### 244 *4.1 Diatom signature*

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

257 No significant differences in diatom valve fluxes were found between EAP region and  
258 two stations off the Northern Antarctic Peninsula which have not been covered by ice  
259 shelf for at least 1 kyr (Ingólfsson et al., 1998). In the case of Larsen B cores, diatom  
260 valve fluxes were calculated dividing diatom valve inventories from 0 to 5 cm depth by  
261 5 years, which is the time span between the ice shelf collapse and the sampling  
262 expedition. Based on the excess  $^{210}\text{Pb}$  activity and the pigment profiles (Fig. 6 and  
263 Sañé et al., 2011), diatom fluxes for EAP were calculated using diatom valve  
264 inventories from 0 to 5 cm depth to assure including diatom valves deposited after the  
265 ice shelf collapse. In the case of the two stations off the Northern Antarctic Peninsula,  
266 the diatom valves inventory of the 11 cm long sediment core corresponding to the  
267 Elephant Island station was divided by 36 years (based on a sediment accumulation

268 rate of  $3.02 \text{ mm y}^{-1}$ ; Isla et al., unpublished results), whereas the diatom valves  
269 inventory of the 11 cm long sediment core corresponding to the South Shetland Island  
270 station was divided by 58 years (based on a sediment accumulation rate of  $1.90 \text{ mm y}^{-1}$ ;  
271 Isla et al., unpublished results). The presence of icebergs in EAP region, related to  
272 the recent Larsen A and B ice shelf collapses, should reduce the available area for  
273 phytoplankton blooms to develop, and, consequently, primary production in this region  
274 (Arrigo et al., 2002; Arrigo and van Dijken, 2003). Nevertheless, similarities in diatom  
275 valve fluxes between EAP region and the two stations off the Northern Antarctic  
276 Peninsula may be related to the rather moderate to low primary production off the  
277 South Shetland and Elephant Islands (Bodungen et al., 1986; Holm-Hansen and  
278 Mitchell, 1991; Holm-Hansen et al., 1997).  
279 The absence of *Fragilariopsis kerguelensis* in EAP is consistent with the absence of  
280 open water conditions (Crosta et al., 2005) until 1995 and 2002 in Larsen A and B,  
281 respectively, whereas the high percentage of sea-ice related taxa implies that this  
282 region is not experiencing true seasonal open-water conditions yet (Fig. 3).

283

#### 284 4.2 Fatty acid signature

285 Changes in the FA profiles between the parts of the sediment column corresponding to  
286 the pre- and the post- ice shelves collapse were less evident than those observed for  
287 the diatom valves signature (Fig. 4, 5), probably due to FA lability. FA are characterized  
288 by different labilities depending on their chemical structure. FA with a high number of  
289 unsaturations or polyunsaturated FA (PUFA) represent the most labile group of FA  
290 (Haddad et al., 1992; Sun and Wakeham, 1994). The low concentration of PUFA (Fig.  
291 5) and the absence of PUFA diatom indicators, such as 16:2(n-4) and 16:3(n-4)  
292 (Volkman et al., 1989; Wakeham, 1995), even in the upper 2 cm of the sediment  
293 column where high abundances of diatom valves were found, suggests that PUFA  
294 were previously degraded in the water column or/and after deposition onto the seabed  
295 (Smith et al., 1983; Wakeham et al., 1997; Budge and Parrish, 1998; Grossi et al.,  
296 2003; Hu et al., 2006). Differently from PUFA diatom indicators, MUFA and MC-FA  
297 diatom indicators, like FA 16:1(n-7) and FA 14:0, were found in EAP and their  
298 concentrations decreased with depth in the five cores (Fig. 4), reflecting changes in the  
299 water column related to Larsen ice shelves disintegration. Differences between FA  
300 profiles may be related to the lower lability of MUFA and MC-FA in relation to PUFA  
301 (Haddad et al., 1992). The low concentration of FA 14:0 and FA 16:1(n-7) below 2 cm  
302 depth (Fig. 4) suggested that these fatty acids which originate from diatoms did not  
303 accumulate in EAP sediment column by lateral transport before the collapse of Larsen  
304 ice shelves.

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

318 The absence of bacterial indicators like hydroxylated FA and 18:1(n-7) (Perry et al,  
319 1979) or like *iso*- and *anteiso*-FA (Parkers and Taylor, 1983; Kaneda, 1991) suggests a  
320 low bacterial activity; the only bacterial indicators present in EAP, MC-FA with an odd  
321 number of carbon atoms (Lee, 1992; Dalsgaard et al., 2003 and references therein),  
322 may also have accumulated in this region before ice shelf collapses by lateral  
323 transport. The idea that MUFA and MC-FA could have been laterally transported to  
324 EAP is supported by previous studies on benthos under ice shelves. Even if primary  
325 production below ice shelves is negligible (Littlepage and Pearse, 1962), the few  
326 studies on benthos below ice shelves revealed that a lateral flux of organic matter  
327 maintained benthic assemblages of suspension feeders at different distances from the  
328 ice shelf edge (Dayton and Oliver, 1977; Lipps et al., 1979; Riddle et al., 2007).

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

337

### 338 **4.3 Summary**

339 Diatom valve abundance in sediment cores collected from the continental shelf of the  
340 Larsen A and B bays provided evidence to suggest that diatom valves were deposited  
341 only after Larsen ice shelves collapse. Temporal changes in the FA signature were less

342 evident than those observed for the diatom valves signature. In spite of the presence of  
343 diatom valves in the upper 2 cm of sediment, some diatom indicators like unsaturated  
344 FA 16:2(n-4) and 16:3(n-4) were not found in EAP cores, probably due to their high  
345 lability. The presence of some bacterial- and zooplankton- related MUFA and MC-FA  
346 suggests that there has been an input of refractory organic matter into the region,  
347 presumably by lateral transport, before Larsen ice shelves collapse.

348

## 349 5. References

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608



609 **Table 1.** Inventories and fluxes of diatom valves.  
610

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

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614 >Sediments were studied to see if changes in the water column reflect in  
615 sediments.>Sediments off the Northern and the Eastern Antarctic Peninsula were  
616 compared.>2 ice shelf collapses in 1995 and 2002 affected the Eastern Antarctic  
617 Peninsula.>The lability of the organic matter was higher in the Northern than in the  
618 Eastern Antarctic Peninsula.>Diatom valves were deposited only after the ice shelves  
619 collapses.  
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- 622 Figure caps
- 623 Figure 1: Study area with the five sampling stations.
- 624 Figure 2: Diatom valves profiles in LBS, LBW, LBC, LBN and LA.
- 625 Figure 3: Sea ice taxa, *Chaetoceros* spp., *F. kerguelensis*, *T. antarctica* and non
- 626 dominant taxa in EAP.
- 627 Figure 4: Diatom (14:0 and 16:1(n-7), dinoflagellate (16:0, 18:1(n-9)cis), zooplankton
- 628 (20:1(n-9) and 22:1(n-9) and bacteria (11:0, 13:0 and 15:0) FA indicators in EAP.
- 629 Figure 5: PUFA, MUFA, LC-FA and MC-FA in EAP.
- 630 Figure 6: Chla concentration, diatom valves abundance and excess  $^{210}\text{Pb}$  activity in the
- 631 EAP region.
- 632
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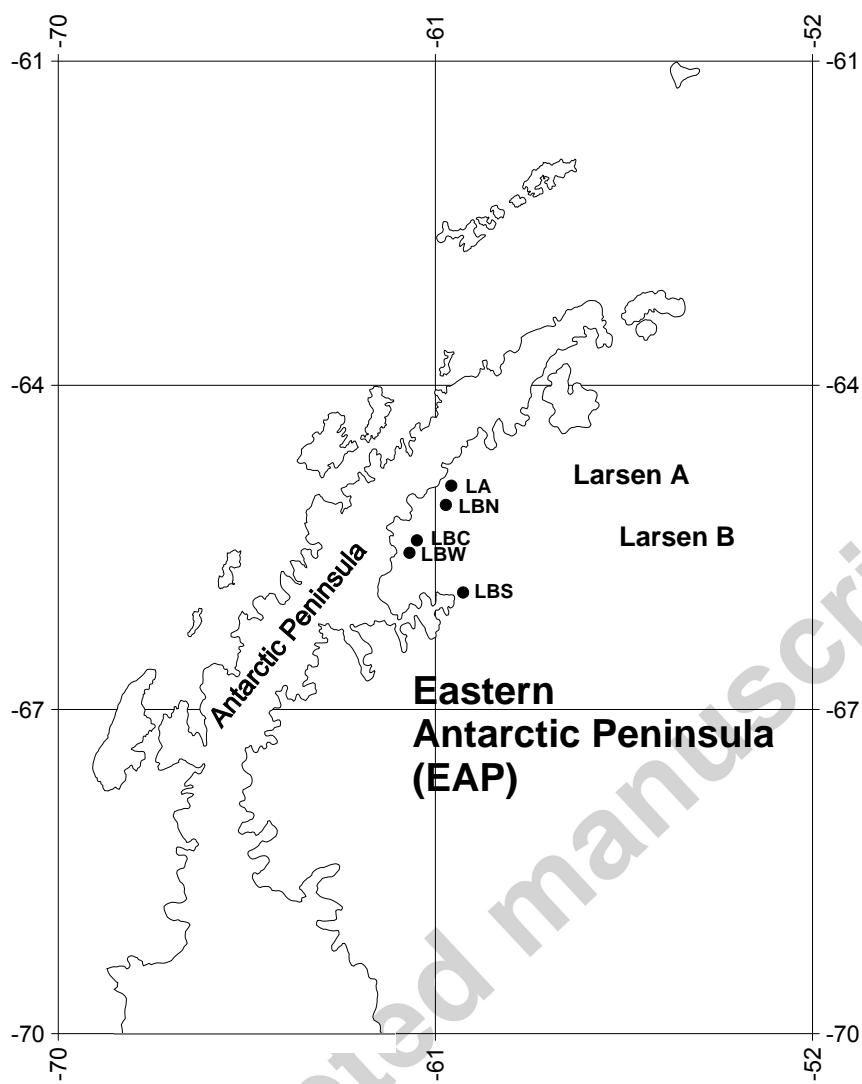
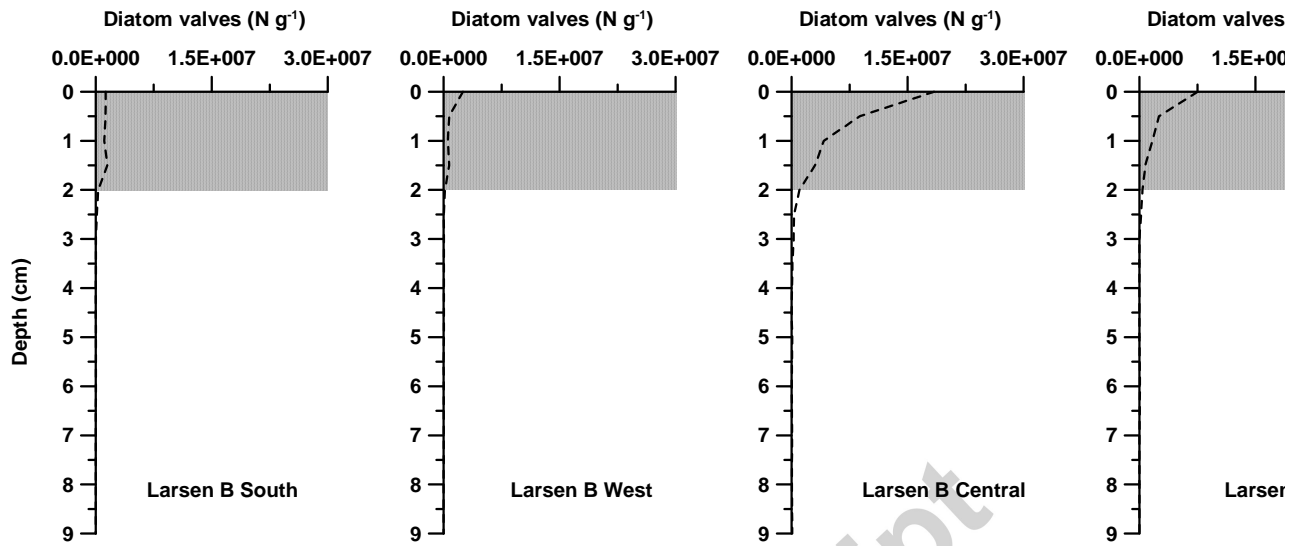


Fig. 1

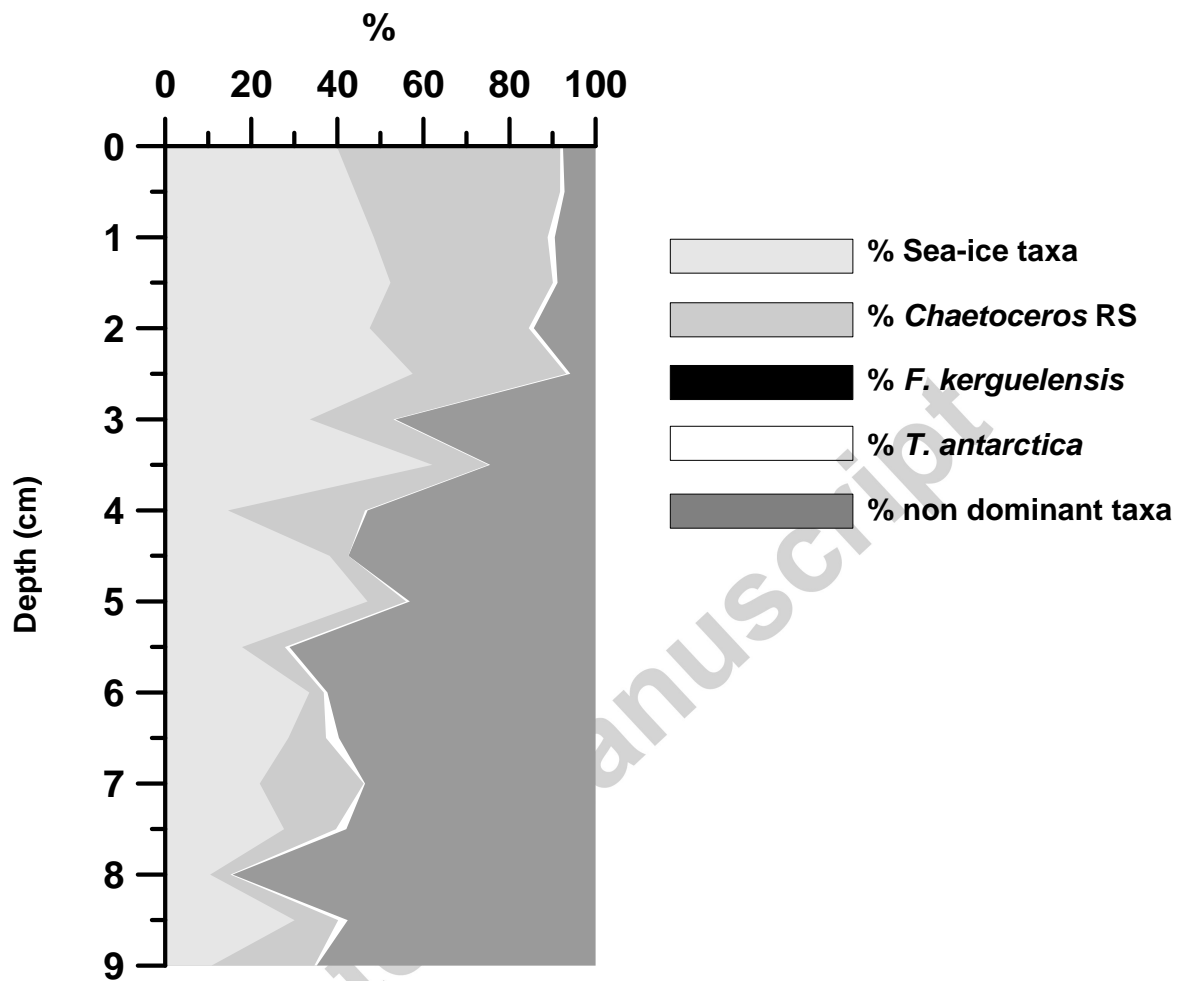
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Fig. 2

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Fig. 3

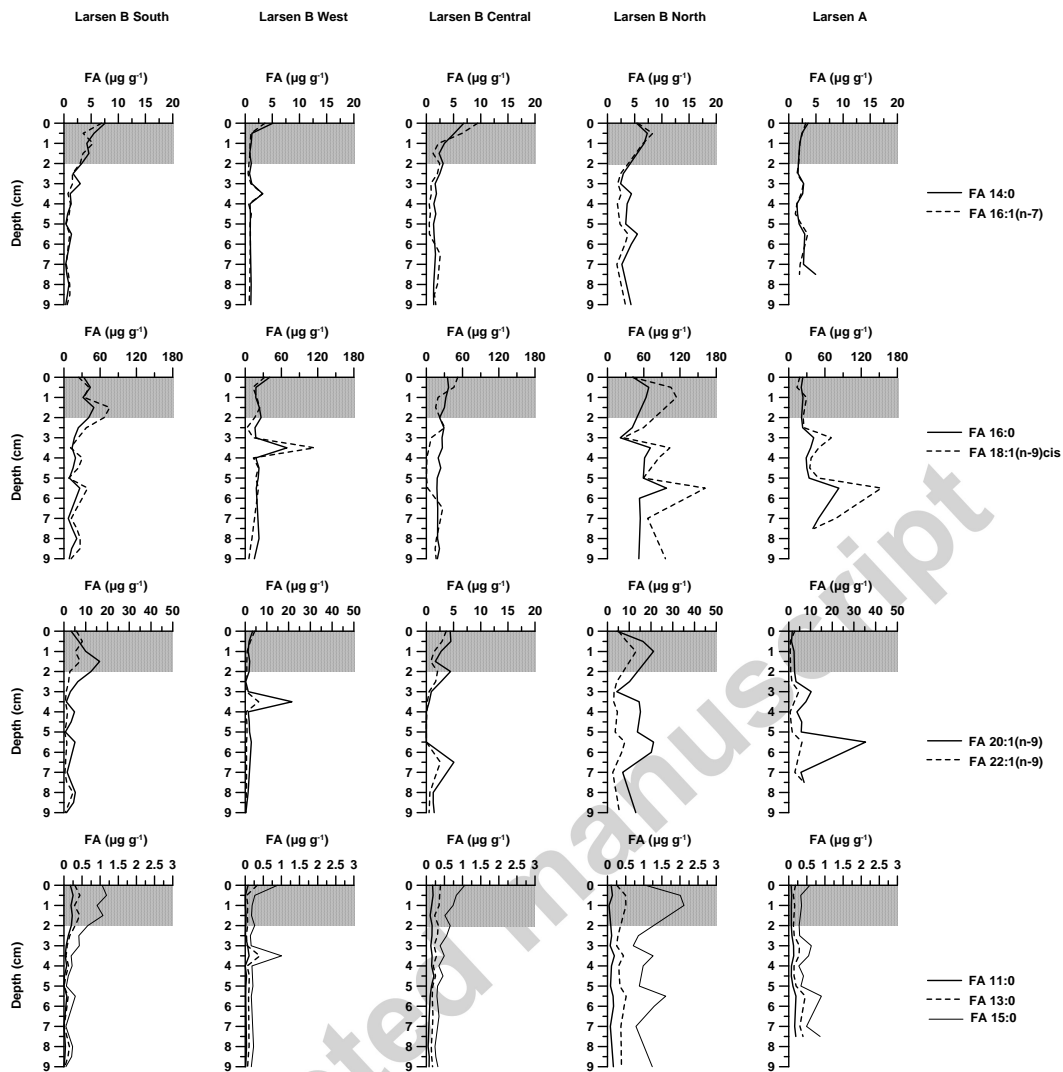
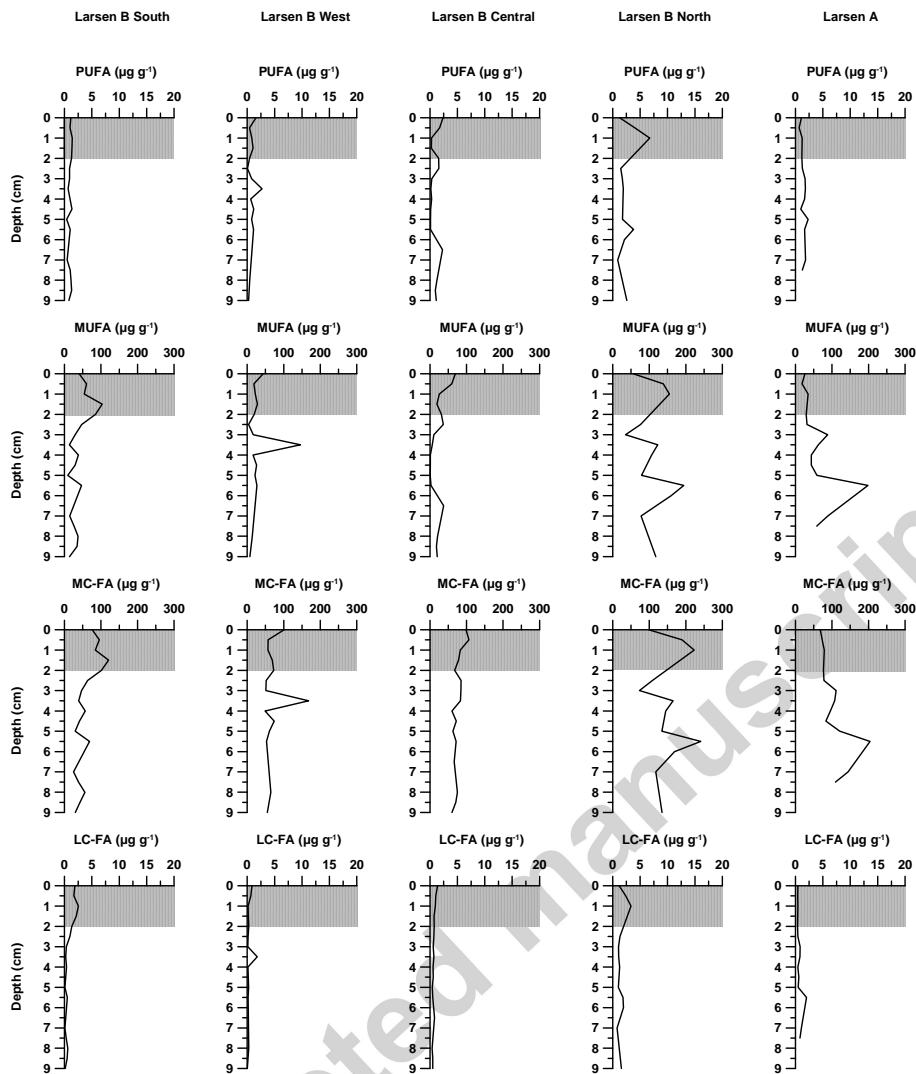
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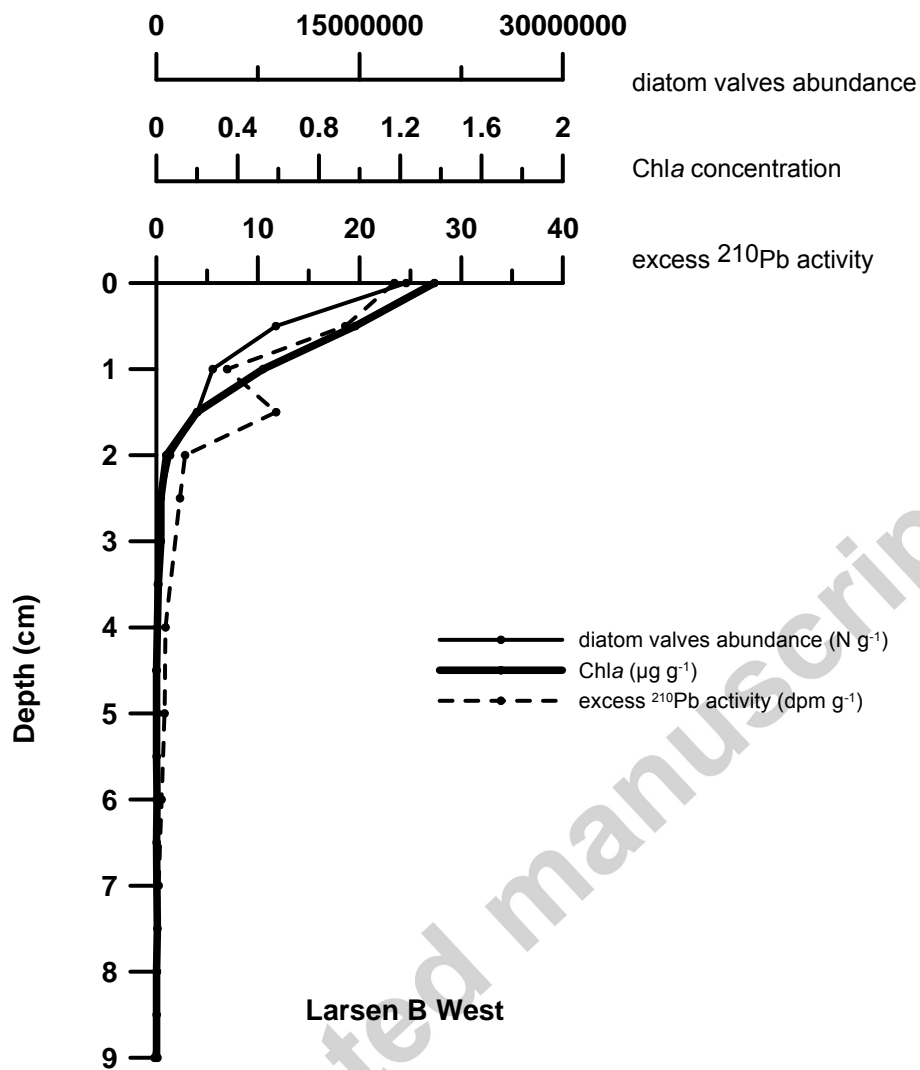
Fig. 4



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Fig.5





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Fig.6