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# Bioaccumulation record and paleoclimatic significance in the Western Bransfield Strait. The last 2000 years

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#### Abstract

Two gravity cores, A-3 and A-6, from the western basin of the Bransfield Strait, Antarctica, were recovered during the BIO Hespérides expedition FRUELA 96. Both cores consist mainly of hemipelagic and laminated muds with black layers rich in sand-sized volcanic ash. Geochemical analyses (TOC and opal), radiometric dating techniques (AMS <sup>14</sup>C and <sup>210</sup>Pb), and micropaleontological analyses (diatoms) were performed on both cores. AMS analyses on TOC yielded <sup>14</sup>C ages older than expected:  $3960 \pm 50$  yr BP for the core top of A-3, and  $3410 \pm 50$  yr BP for A-6. <sup>210</sup>Pb analyses revealed that core top age for both gravity cores could be estimated to be about  $100 \pm 15$  yr BP The results of diatom analyses were related to the sequence of neoglacial events that have occurred over the last two millennia. The abundance patterns of *Chaetoceros* RS, the biogenic silica content, and the abundance of diatom valves agree with the high productivity values previously reported for the Bransfield Strait waters. The significant recent reduction in resting spores of the diatom *Chaetoceros* suggests as a reduction in surface productivity. Trend differences between *Chaetoceros* resting-spore abundance and TOC contents are explained in terms of organic matter preservation. Diatom communities from the Bransfield Strait did not play an important role in the global CO<sub>2</sub> cycle during cold periods. Bio- and geochemical changes have an overprinted high-frequency cyclicity at about 200–300 yr, which might be related to the 200-yr solar cycle. © 2001 Elsevier Science Ltd. All rights reserved.

#### 1. Introduction

Coastal waters near the Antarctic Peninsula support highly productive ecosystems where large phytoplankton blooms develop throughout the austral spring and summer. These areas therefore may represent key sites where the *biological pump* transports organic carbon below the mixed layer and consequently sequesters atmospheric  $CO_2$ (Sarnthein et al., 1987; Broecker, 1981, 1982a, b). Between 10% and 50% of photosynthetically fixed carbon may be released by respiratory processes (Aristegui et al., 1996), and respiration rates vary with water temperature, phytoplankton populations and oceanographic fronts and currents (Aristegui and Montero, 1995).

The sedimentary record affords long-term information about all these processes occurring in the water column. Siliceous microfossil

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assemblages, together with carbon and opal stored in the sediments, may offer an efficient tool for identifying paleoclimatic and paleoceanographic changes.

The Holocene is characterised by alternating periods of neoglacial expansions and subsequent retreats. Evidence for these events, among others, has been found in Antarctic marine sediments by Leventer and Dunbar (1988), Leventer et al. (1996), and Bárcena et al. (1998). The Bransfield Strait is unusually sensitive to fine-scale climatic and oceanographic changes, as well as to changes in local tidewater glaciers. Previous studies have shown that the general trend for the last several thousand years is a recent reduction in primary productivity (Bárcena et al., 1998). Overprinted on this trend is a high-frequency oscillation in diatom abundance, which correlates with an approximately 250-year cyclicity recognised in the magnetic susceptibility, organic carbon, and siliceous microfossil data (Leventer et al., 1996; Bárcena et al., 1998). These changes in primary productivity over time are mainly controlled by sea-ice conditions and surface water stability and stratification. Since vertical fluxes are restricted to a short period, the austral summer (Wefer et al., 1988), paleoclimatic evolution may help to study and better understand the biogenic cycles involved.

The present work addresses the sedimentary record during the last 2000 years and its relationship with paleoceanographic evolution, such as changes in primary production, fluctuations in the sea-ice cover, and surface hydrodynamics. This evolution is studied on the basis of the diatom assemblages preserved in the sedimentary column and biogenic silica and organic carbon stored in the sediments. The relatively high accumulation rates found in this area, estimated as higher than  $1.1 \,\mathrm{cm}\,\mathrm{yr}^{-1}$ , afford sufficient resolution to study the effects of climatic changes over the last two millennia. Study of the changes that took place in the past may help to understand better the carbon cycle and to evaluate the possible causes of present climatic-oceanographic changes. The distinction between the anthropogenic action and natural mechanisms should be studied and verified over longer periods of time.

### 2. Physical environment

The Bransfield Strait is a semi-enclosed basin limited to the south by the Antarctic Peninsula and the South Shetland Islands to the north. The Bransfield Basin is composed of three separate subbasins that are separated from one another by sills about 500 m deep. The western subbasin is relatively shallow (1000 m) and irregularly shaped, and lies south and west of Livingston and Deception Islands. The central subbasin is located south of Robert, Nelson and King George Islands, is deeper (2000 m), and has a more regular shape than the others. The eastern subbasin extends north-eastward, is narrower than the central subbasin, and reaches a depth of 2500 m (Fig. 1).

Surface circulation in the Bransfield Strait has two primary sources, the Bellingshausen and Weddell Sea waters (Fig. 1). Waters coming from the Bellingshausen Sea are warm and relatively fresh, while waters from the Weddell Sea are colder and denser (García et al., 2002). The circulation patterns of both water currents have been described in detail by Gordon and Nowlin (1978) and Gomis et al. (2002). These currents meet in the vicinity of Trinity Island and form a front of biological significance (Amos, 1987). Advection of circumpolar deep water (CDW) into the Strait from the Drake Passage is prevented by the presence of shallow sills. Gordon and Nowlin (1978) suggested in situ deep and bottom water formation through the sinking of surface waters of the Bransfield Strait. These waters are characterised by having lower temperatures and salinity, higher oxygen and lower nutrient concentrations (García et al., 2002) in comparison with deep waters outside the basin. Additionally, the vertical distribution of these parameters also indicates that there are significant differences within each subbasin (Gordon and Nowlin, 1978).

Seasonal sea-ice distribution in the Bransfield Strait is complex. The information concerning annual sea-ice coverage points to a winter maximal extent of  $57^{\circ}$ S off the Antarctic Peninsula, but in summer the Bransfield Strait is a completely icefree area (N.O.C., 1985). Surface productivity, and hence the settling of biogenic particles into sediments, is restricted to periods in which the



Fig. 1. A-3 and A-6 core locations in the Bransfield Basin (closed circles). Open circles indicate locations for Gebra-1 and Gebra-2, cores previously studied by Bárcena et al. (1998).

area is ice-free, reaching one of the highest rates in the entire Southern Ocean (Wefer et al., 1988; Abelmann and Gersonde, 1991; Varela et al., 2002). Since surface productivity is linked to seaice coverage, biogenic particle sedimentation, especially that of diatoms and radiolarians, is also directly related to seasonal variations in the sea-ice extension. Using time-series sediment traps, Abelmann and Gersonde (1991) showed that particleflux peaks occur during periods with open-water conditions, whereas during sea-ice coverage the vertical flux of siliceous organisms from the surface waters is extremely low.

The sediment distribution in the Bransfield Strait is related to the morphology of the sea floor. Jeffers and Anderson (1990) reported that the characteristic sediments of the deepest basin consists of three main components. In order of abundance, these are: biosiliceous material, mostly diatoms; terrigenous silt-sized quartz; and volcanic ash.

The sedimentary basins in the Bransfield Strait act as a giant sediment trap as they collect large amounts of resuspended material, resulting in high sedimentation rates for the basin sediments (Abelmann and Gersonde, 1991). Comparison of these high sedimentation rates with those estimated from surface production indicates that the accumulation rate of opal in the Bransfield Strait accounts for only about half of the surface production (DeMaster et al., 1987). Alteration of the assemblages of siliceous organisms during vertical transport through the water column is due to mechanical breakdown by grazing zooplankton and to dissolution (Gersonde and Wefer, 1987). Another factor responsible for the composition of the biosiliceous signal in the sediment record is the input of laterally transported material (Abelmann and Gersonde, 1991).

#### 3. Material and methods

Gravity cores A-3 and A-6 were recovered during the RV *Hespérides* cruise FRUELA 96 in the Bransfield Basin at 63°10.06′S/59°18.13′W and 62°54.71′S/59°58.21′W, respectively (Fig. 1). Water depths at the core locations are 810 m (A-3) and 1066 m (A-6). Samples were taken every 5 cm for total organic carbon (TOC) and opal analyses. For micropaleontological studies, core A-3 was sampled every 10 cm and A-6 every 5 cm. Gravity cores are composed of "basin floor sediments", following the terminology of Jeffers and Anderson (1990), with biosiliceous material as the main component.

TOC was determined by sediment dried at  $40^{\circ}$ C until constant weight, homogenised in an agate grinder, and analysed on a LECO CN-2000 resistance furnace at 1050°C. All the C was converted into CO<sub>2</sub> and passed through an IR cell, converted to voltage, and transformed into carbon concentration (LECO CN-2000 instruction manual, 1994).

Opal was determined using the alkaline extraction method of Mortlock and Froelich (1989) (extraction of silica in 2 M Na<sub>2</sub>CO<sub>3</sub> at 85°C for 5 h) and measured by molibdate-blue spectrometry. Opal percentages were calculated as the percentages of Si extracted into the solution multiplied by 2.4, which includes the average water content of diatomaceous silica (about 10% water =SiO<sub>2</sub>  $\times$  0.4 H<sub>2</sub>O). The contribution of silica from coexisting clay minerals was evaluated by the double leaching method (Eggimann et al., 1980). The relative precision of this technique is 5% and was estimated including sediment inhomogenities and analytical errors. Opal percentages were computed on a dry weight basis without corrections for dry sea-salt contents.

Cleaning of the sediment samples and preparation of permanent mounts for light microscopy were accomplished according to the randomly distributed microfossils method outlined in Bárcena and Abrantes (1998). Absolute diatom numbers were determined from microscope slides with randomly distributed microfossils. Using a Leica DMLB microscope at 1000X magnification. A counting of at least 100 valves of non-dominant taxa per sample was performed using the method of Schrader and Gersonde (1978). In general, more than 600 valves per sample were considered (Tables 2 and 3). The preservation status of the fossil assemblage was estimated by visual examination.

## 3.1. Chronological assessment

Two different radiometric dating techniques, <sup>14</sup>C AMS and excess <sup>210</sup>Pb, were used to determine the age of the sediments. The <sup>14</sup>C AMS technique on TOC was carried out to estimate sedimentation rates as well as the age of the cores investigated. The conventional radiocarbon ages of three stratigraphic levels in core A-3 and two in core A-6 were analysed (Table 1, Fig. 2).

The <sup>14</sup>C AMS methodology yielded <sup>14</sup>C ages older than expected:  $3960 \pm 50$  yr BP for the top of core A-3, and  $3410 \pm 50$  yr BP for the top of core A-6 (Table 1). Despite this, the ages indicate a sedimentation rate of  $208 \text{ cm kyr}^{-1}$  for A-3 and  $80.7 \text{ cm kyr}^{-1}$  for A-6, in agreement with the accumulation rates given in the literature, which range between 60 and 490 cm kyr<sup>-1</sup> (DeMaster et al., 1987; Enst Van, 1987; Laban and De Groot,

Table 1

<sup>14</sup>C conventional ages of the three sections of each core analysed

Core	Section (cm)	<sup>14</sup> C Conventional age (yr)				
A-3	0 300 437	$3960 \pm 50$ $5090 \pm 50$ $5990 \pm 50$				
A-6	0 134	$\begin{array}{c} 3410 \pm 50 \\ 5070 \pm 50 \end{array}$				



Fig. 2. Age-depth curve for cores A-3 and A-6. See also Table 1.

1986; Venkatesan and Kaplan, 1987; Harder et al., 1992; Domack et al., 1993; Scherer and Leventer, 1995; Leventer et al., 1996; Bárcena et al., 1998) (Fig. 2). These values also agree with the expected high accumulation rate in the area, which receives sediment inputs from the Antarctic Peninsula and is under the influence of the highly productive oceanic front between the cold Weddell Sea water and the warmer water from Gerlache and Bellingshausen areas.

The <sup>14</sup>C core top ages of  $3960 \pm 50$  yr BP for the top of core A-3 and  $3410 \pm 50$  yr BP for the top of core A-6 are in the same order as those obtained by Harden et al. (1992), Domack et al. (1993), Leventer et al. (1996) and Bárcena et al. (1998) in the Antarctic Peninsula area. Radiocarbon dating of Antarctic sea water samples and marine organisms has yielded anomalously old ages of up to 2860 yr (Stuiver et al., 1981). Two main factors have been considered to explain the old age of the sediments: the large and regionally variable

reservoir effect of 1200–1400 yr (Stuiver et al., 1981; Berkman et al., 1998; Ingólfsson et al., 1998) and possible inputs of older eroded sediment, transported by currents or by ice rafting. Nevertheless, the input of terrestrial organic matter can be considered insignificant since most of the organic matter present in the sediments is derived from primary local producers (Venkatesan and Kaplan, 1987).

Due to its half-life (22.3 yr), <sup>210</sup>Pb can thus be used to determine the age of the care surface (Goldberg and Koide, 1962; Nozaki et al., 1977). <sup>210</sup>Pb concentrations were determined at each cmdepth along the top 20 cm of gravity cores A-3 and A-6, following the methodology described in Sánchez-Cabeza et al. (1998). Excess <sup>210</sup>Pb (taken as the difference between total <sup>210</sup>Pb and supported <sup>210</sup>Pb) in core A-3 was detected on the top 3 cm, while in core A-6 it was only present in the first section (0–1 cm). Surface excess <sup>210</sup>Pb concentrations were  $26\pm 6$  and  $31\pm 4$  Bq kg<sup>-1</sup> for

cores A-3 and A-6, respectively. The fact that excess <sup>210</sup>Pb was still detectable indicates that the tops of both gravity cores are not older than approximately 100 yr.<sup>210</sup>Pb data from the gravity cores was also compared to the <sup>210</sup>Pb profiles obtained from multicore samples collected at stations A-3 and A-6 and described in a companion paper by Masqué et al. (2002), in which <sup>210</sup>Pb is used to determine recent mixing and sediment accumulation rates in the area. It is concluded that in both cases the top 20-22 cm of gravity cores A-3 and A-6 were lost during collection of the samples. Therefore, by using the mean sediment accumulation rates derived from the multicores, the age of the surface of both gravity cores can be estimated to be about 100 + 15 yr.

The chronological criteria used in this work allowed us to determine the age of the sediments recorded in the A-3 and A-6 gravity cores. We constructed an age model based on a combination of <sup>210</sup>Pb determination, radiocarbon ages for the evaluation of sedimentation rates, and biogenic evidence. Thus, we considered that the core tops of both cores could have an age of around  $100 \pm 15$  yr BP The base of cores A-3 and A-6, as extrapolated from linear sedimentation rates (208 cm kyr<sup>-1</sup> and 80.7 cm kyr<sup>-1</sup>, respectively), were estimated at 2050 and 1760 yr BP, respectively.

Furthermore, the regional reservoir effect, as well as local processes, has a strong influence on stratigraphic control. Fine-scale differences in sedimentation rates cannot be determined owing to limitations in radiocarbon dating and may undergo some variations. Assuming this, we tentatively link the variations in the organic components of the sediments as well as the siliceous microfossil abundance patterns of A-3 and A-6 to climatic changes (Fig. 5). Based on glacial advances and retreats, <sup>14</sup>C anomalies in tree-rings, and in marine sediments from the Antarctic Peninsula region, four cold episodes have been recognised in the last two millennia (Wigley and Kelly, 1990; Leventer et al., 1996; Bárcena et al., 1998). Following the terminology and discussion employed by Bárcena et al. (1998), we have recognised the last four neoglacial episodes recorded for the last 2000 years (neoglacial stages 4, 3, 2 and 1).

# 4. Results

# 4.1. Diatoms

A large number of diatom valves per gram of dry sediment was observed in both cores, ranging between  $2 \times 10^7$  and  $14.7 \times 10^8$  (Fig. 3a and d). The diatoms are in general well preserved. The diatom assemblages are dominated by Chaetoceros resting spores (RS) (73-89% of the total) (Tables 2 and 3). The sea-ice taxa, grouping species such as Fragilariopsis curta (V. Heurck) Hasle, F. cylindrus (Grun.) and F. vanheurckii Hasle, are also frequent (up to 9.48% of the total) (Tables 2 and 3). These species are commonly found in the sea-ice, and are dominant in the ice-edge blooms as well as in the marginal ice zone (Gersonde, 1986; Leventer et al., 1996). Thalassiosira antarctica Comber/T. scotia Fryxell and Hoban in the spore stage (RS), is another component of the assemblage. This species group has been related to oceanic conditions from the Weddell and Scotia Sea (Klöser, 1990; Abelmann and Gersonde, 1991; Bárcena and Flores, 1991; Bárcena and Francés, 1998). Species such as F. kerguelensis (O'Meara) Hasle, Rhizosolenia spp., Proboscia alata (Brightwell) Sundstrom, Thalassiosira gracilis (Karsten) Hustedt, T. gravida Cleve, T. oliverana (O'Meara) Sournia, T. trifulta Fryxell and T. tumida (Jan.) Hasle are also common components of the fossil diatom assemblage.

The species distributions in both cores as well as their relative abundance are in agreement with the values compiled from the literature for the Bransfield Strait area (Gersonde and Wefer, 1987; Wefer et al., 1988, 1990; Abelmann and Gersonde, 1991; Leventer, 1991; Zielinski, 1993; Zielinski and Gersonde, 1997; Bárcena et al., 1998; Varela et al., 2002).

For core A-3, the total abundance of diatom valves/g of dry sediment tends to decrease towards the top. Maximum values are recorded between a core depth of 370–320 cm and between 220 and 180 cm, while minima are recorded in the uppermost 50 cm (Fig. 3a). The abundance pattern of *Chaetoceros* RS follows a similar trend to that observed for total diatom valve abundance. The most striking features are three minima recorded



Fig. 3. Diatom abundance (% of assemblage) in cores A-3 and A-6. Thicker line indicates a three-point smoothing.

at the base, between 265 and 215 cm, and in the uppermost 100 cm. These minima are bounded by strongly marked maxima (Fig. 3b). The abundance pattern of the sea-ice taxa group follows the opposite behaviour to that observed for *Chaetoceros* RS. Maximum values in *Chaetoceros* RS correspond to minima in sea-ice taxa (Fig. 3b and c).

The diatom patterns of cores A-3 and A-6 are remarkably similar given the missing core top for A-6 as well as differences in sedimentation rates. In core A-6 two maxima in *Chaetoceros* RS coincide with minima in sea-ice taxa (Fig. 3e and f).

# 4.2. Total organic carbon and biogenic opal

The mean values in TOC contents are 1.03% for A-3 (Fig. 4a) and 0.47% for A-6 (Fig. 4c). These values are not high for marine sediments, but are typical of siliceous muds in the Bransfield Strait area (De Master et al., 1987; Yoon et al., 1994; Leventer et al., 1996; Fabrés et al., 1997; Bárcena et al. (1998)). The mean biogenic opal content is higher in A-3 (21.66%) (Fig. 4b) than in A-6 (13.2%) (Fig. 4d).

The TOC record of A-3 shows three clear minimum values: at 35, 230 and 405 cm. The

Table 2					
Abundance of the most s	significant diatom	groups and	geochemical	data in	core A-3

Diatoms			Geochemic						
Sample (cm)	Valves/g $(\times 10^8)$	Chaetoceros RS (%)	Sea-ice taxa (%)	Sample (cm)	TOC (%)	Biogenic silica (%)	Sample (cm)	TOC (%)	Biogenic silica (%)
0	1.74	78.52	6.93	0	1.05	17.69	215	1.04	23.53
10	1.04	80.15	3.83	5	1.12	21.57	220	1.09	22.32
20	1.06	76.92	7.12	10	1.15	21.59	225	1.06	21.58
30	1.03	73.54	7.52	15	1.18	20.94	230	0.87	19.9
40	1.15	69.28	9.01	20	0.99	19.86	235	0.94	18.94
50	0.21	68.63	6.75	25	0.92	18.89	240	1.03	19.24
60	1.24	76.78	8.45	30	1.02	19.8	245	1.08	21.29
70	2.07	80.00	8.33	35	0.93	17.32	250	1.05	20.59
80	1.75	77.02	5.11	40	0.99	19.13	255	1.01	23.83
100	1.53	78.63	7.44	45	1.01	20.13	260	1.00	20.52
110	1.99	85.91	5.64	50	1.03	19.39	265	1.01	22.57
120	1.22	75.54	7.58	55	1.09	19.22	270	1.00	20.36
130	1.75	82.02	4.53	60	1.08	21.5	275	1.15	20.76
140	2.15	84.94	5.29	65	1.01	22.81	280	1.04	24.1
150	1.49	81.58	6.30	70	1.12	24.73	285	1.07	25.32
160	1.25	82.28	5.04	75	1.01	24.46	290	1.05	22.86
170	1.66	81.08	4.28	80	1.00	22.66	295	1.06	23.38
180	3.42	81.63	4.71	85	1.09	22.39	300	1.00	19.75
190	4.00	84.39	3.83	90	1.06	19.7	305	0.95	20.45
200	3.18	84.75	5.65	95	1.06	20.13	310	1.04	21.32
210	3.74	88.24	5.19	100	1.08	23.23	315	1.03	22.82
220	2.99	81.92	5.60	105	1.09	21.21	320	1.07	23.95
230	1.99	81.38	4.84	110	1.04	21.53	325	1.00	21.73
250	1.35	76.79	7.14	115	1.09	19.63	330	1.05	
260	1.72	76.90	6.55	120	1.07	18.33	335	0.91	23.44
270	2.17	82.08	7.20	125	1.21	21.74	340	1.03	22.46
280	4.35	82.90	5.10	130	1.16	21.92	345	1.00	22.71
290	3.66	82.90	6.63	135	1.19	21.97	350	1.00	24.64
300	3.06	80.00	8.50	140	1.10		355	1.00	22.45
310	2.72	81.39	4.62	145	1.14	22.94	360	0.94	22.71
320	4.07	86.22	5.41	150	1.09	22.63	365	1.01	22.21
330	3.55	86.51	3.31	155	1.03	20.73	370	1.01	23.89
340	6.36	85.47	5.62	160	0.96	18.17	375	1.01	24.14
350	2.85	83.53	2.83	165	1.11	22.22	380	0.95	23.23
360	3.73	80.52	6.76	170	1.08		385	0.95	21.22
370	7.02	88.86	4.08	175	1.08	21.15	390	0.95	20.95
380	3.43	83.90	5.71	180	1.06	22.85	395	0.98	25.49
390	4.16	87.05	3.39	185	1.09	24.22	400	0.94	21.97
400	3.43	89.51	4.81	190	1.06	22	405	0.62	
410	1.70	77.12	6.17	195	1.04	23.13	410	0.93	19.54
420	3.51	85.52	5.39	200	0.97	20.55	415	1.04	21.21
430	1.50	73.44	8.48	105	1.07	21.55	420	1.01	19.95
437	4.02	87.19	5.47	210	1.14	25.41	425	1.00	20.96
	=						430	0.96	21.13
							435	0.99	23.37
								-	

Diatoms		GEOCHEMIC				
Sample (cm)	valves/g ( $\times 10^8)$	Chaetoceros RS (%)	Sea-ice taxa (%)	TOC (%)	Biogenic silica (%)	
0	2.16	79.16	6.62	0.43	9.59	
5	1.08	76.95	2.6	0.29	9.24	
10	2.95	75.36	9.48	0.56	13.01	
15	4.34	83.86	3.44	0.66	14.64	
20	2.51	81.2	6.96	0.61	13.75	
25	2.92	86.79	5.68	0.26	9.54	
30	0.54	83.55	5.81	0.19	7.85	
35	4.66	89.19	3.01	0.53	15.33	
40	5.30	86.44	5.27	0.49	14.33	
45	7.01	85.81	3.02	0.8	14.26	
50	6.08	85.3	5.86	0.6	14.68	
55	6.40	87.68	3.24	0.62	14.73	
60	3.50	83.13	6.79	0.54	14.43	
65	14.7	88.43	4.48	0.48	13.29	
70	4.23	81.68	6.77	0.47	13.75	
75	9.93	87.12	3.11	0.56	13.9	
80	3.93	79.93	7.99	0.47	13.23	
85	2.76	87.24	4.25	0.48	13.08	
90	4.76	87.97	4.77	0.39	13.03	
95	4.63	87.55	4.29	0.44	12.73	
100	1.79	82.68	3.89	0.37	12.07	
105	6.28	87.14	3.83	0.34	11.12	
110	10.8	90.78	3.06	0.53	13.64	
115	2.70	85.71	4.19	0.43	12.36	
120	4.06	84.22	6.16	0.45	12.79	
125	2.61	83.33	4.9	0.35	12.03	
130	4.72	84.18	5.32	0.48	15.07	
133	6.95	85.43	5.26			

 Table 3

 Abundance of the most significant diatom groups and geochemical data in core A-6

lowest values of biogenic silica are seen at almost the same depths: 35, 235 and 410 cm. Whereas the biogenic silica minimum follow a decreasing trend, the TOC minimum increases (Fig. 4). Both variables follow the same trend in core A-6, with TOC peaks at 15 and 45 cm. The maximum in biogenic silica is recorded at 35 cm, just below a minimum at 30 cm.

The overall patterns of the organic components are well-correlated, and the most striking features are seen for all three components: TOC, biogenic opal content, and absolute abundance of diatom valves (Tables 2 and 3, Figs. 3 and 4). Biogenic opal contents and diatom valve abundances tend to decrease towards the core top, while TOC mainly increases upwards. Despite the foregoing, sequences can be identified in the organic components along both cores. In the 360–230 cm and 210–40 sections of core A-3, two main sequences, increasing for TOC and decreasing for biogenic opal, can be identified. These two sequences are bounded by a strongly marked minimum. The concentrations point to a series of more or less symmetric cycles, with thicknesses between 25 and 50 cm. This cyclicity also can be observed in core A-6 (Fig. 4).

# 5. Discussion

Three well-documented maxima in sea-ice taxa seem to be quite closely related to the neoglacial



Fig. 4. Total organic carbon and biogenic silica values obtained from cores A-3 and A-6. Thicker line indicates a three-point smoothing.

events described for the Holocene, such as those observed by Bárcena et al. (1998). Gersonde (1986) related the presence of sea-ice taxa in surface sediments to areas strongly influenced by sea-ice, and Gersonde et al. (1990) used this group as a tracer of the sea-ice extent. Zielinski and Gersonde (1997) and Bárcena and Francés (1998) report a coincidence between the winter sea-ice extent in the Weddell and Scotia Seas and the northern boundary of significant occurrences of sea-ice taxa in surface sediments. Abelmann and Gersonde (1991) observed that during periods of sea-ice coverage the vertical flux of biosiliceous particles decreases significantly, both for sea-ice taxa and for the rest of the planktonic communities, and that maximum values of sea-ice taxa are reached during and after ice retreat. Thus, we interpret that the higher values of sea-ice taxa in cores A-3 and A-6 may be related to a more extensive sea-ice cover, both spatially and seasonally. Furthermore, maxima of sea-ice taxa are related to lower values for *Chaetoceros* RS, indicating a reduced, but not arrested, interannual diatom production.

We therefore considered that sea-ice taxa can be used as a good indicator of colder atmospheric conditions involving sea-ice advances and greater sea-ice coverage. Warmer interneoglacial periods are characterised by increases in *Chaetoceros* RS and by decreases in sea-ice taxa. Warmer temperatures and shorter sea-ice coverage periods would have been re-established in the Bransfield Basin during interneoglacial stages, and the paleoceanographic regime might have been similar to that observed today.

The abundance patterns of *Chaetoceros* RS in cores A-3 and A-6 agree with the high productivity values reported for the Bransfield Strait waters

(Varela et al., 2002). In general, high concentrations in Chaetoceros RS in the fossil record have been interpreted as indicating very high primary productivity, and this notion is supported by experimental and field data (Leventer et al., 1996). Sedimentologically, a massive sedimentation of Chaetoceros RS may have had a determinant effect on the high accumulation rates biogenic silica in Antarctic sediments of (DeMaster et al., 1987; Bareille et al., 1991). From our data, it seems reasonable to speculate that during the time period recorded in A-3 and A-6 surface productivity in the Bransfield Basin was higher than today (Fig. 5). A similar pattern in Chaetoceros RS abundance has been observed by Scherer and Leventer (1995), Leventer et al. (1996) and Bárcena et al. (1998), who reported a reduction in primary siliceous productivity over the last 2000 years. In this sense, Leventer et al. (1996) linked enhanced productivity to warmer atmospheric conditions,



Fig. 5. Diatom and geochemical data in cores A-3 and A-6 and their relationships to Holocene neoglacial episodes. The neoglacial events recognised have been labelled with numbers (1–4) after Bárcena et al. (1998). Maximum values in paleoproductivity are recorded during the warmest periods. Comparison of sedimentological data with the  $CO_2$  curve produced by Barnola et al. (1995) for the last millennium. Minimum  $CO_2$  atmospheric values are related to minima in TOC, biogenic silica, diatoms, and *Chaetoceros* RS.

upper water-column stratification, and nutrient depletion. The inferred reduction in paleoproductivity towards the present, together with a progressive increase in sea-ice taxa, seems to indicate a cooling trend (Bárcena et al., 1998).

Additionally, the abundance of Chaetoceros RS along the core runs parallel to the biogenic silica content and the number of diatom valves per gram of dry sediment, indicating a reduction in paleoproductivity (Fig. 5). Nevertheless, TOC tends to increase towards the present. TOC decays towards the top of neoglacial periods (Fig. 5), where seasurface paleoproductivity is expected to have been minimum. Also, at the base of the neoglacial events TOC shows slight increases, probably due to preservational factors. Trend differences between Chaetoceros RS abundance and TOC content could be explained in terms of organic matter preservation and/or in terms of the resuspension of sediments from the continental shelf into the Bransfield Basin, as observed by Bárcena et al. (1998) and discussed by Fabrés et al. (2000). As reported by Bárcena et al. (1998), higher TOC contents during cold periods could be in response to preservation rather than to production. Jordan and Pudsey (1992) and Leventer et al. (1996) postulated that a high planktonic cell density occurs close to receding ice edges as a result of the sea-ice melting and increased upper water-column stratification. This large amount of biogenic material will flocculate and descend rapidly as aggregates to the sea floor, preventing organic matter remineralization. Moreover. Broecker and Peng (1989) considered that during cold periods the nutrient content of Antarctic surface waters could have been similar or even higher than today. Because the extent of nutrient utilisation is larger, the O<sub>2</sub> content of deep Antarctic waters would have been two times lower (Broecker and Peng, 1989). If this scenario is true, oxidation of the organic matter would have been lower. During neoglacial events, a similar situation would have occurred over a short time: a large amount of biogenic particles produced and precipitated during sea-ice melting would have preserved the organic matter on the sea floor. Although during warmer episodes surface productivity is higher, the settling of biogenic particles might have been less concentrated and hence more exposed to oxidation.

During the Holocene there have been several globally quasi-synchronous neoglacial periods lasting for centuries and followed by warmer periods. The most recent neoglacial period was the Little Ice Age (Lamb, 1965). On a 1000-year time scale, climatic changes are associated with Milankovitch orbital effects. However, during the Holocene a century time scale has been imposed on neoglacial events. The world-wide occurrence of neoglacial events has meant that a primary astronomical forcing has been invoked to account for climate changes. Several studies have proposed a solar forcing with a 200 y rhythm, related to sunspot activity (Wigley and Kelly, 1990; Leventer et al., 1996). The changes have been well correlated with <sup>14</sup>C anomalies (<sup>14</sup>C maxima correspond to temperature minima) (Wigley and Kelly, 1990). This 200-yr periodicity also has been observed in marine sediments around the Antarctic peninsula area by Domack et al. (1993). Scherer and Leventer (1995), Leventer et al. (1996), and Bárcena et al. (1998). Although the cores of the study area do not allow precise correction for the <sup>14</sup>C ages, the three data points do allow the evaluation of the cyclicity record. The assumption of a constant sedimentation rate between each age control-point and application of Blackman-Tuckey spectral analysis routines (Analyses series 1.1, Paillard et al., 1996) on different records (diatom, TOC, and biogenic silica) result in a period of 200-300 yr, using a Barllett Window type, a confidence interval of 80%, and a band width of 0.002 (Fig. 6). Cross spectral analyses of the valves per gram of dry sediment, the sea-ice taxa and biogenic silica content demonstrate their spectral density coherence at the 80 and 90% levels, respectively, at 250 yr. Also, a cross spectral analysis of the biogenic silica content and sea-ice taxa and TOC contents shows their coherence at the 89 and 80% level, respectively, at 250 yr.

This period is in concordance with those observed by Domack et al. (1993), Scherer and Leventer (1995), Leventer et al. (1996), and Bárcena et al. (1998). Such periodicity could be related to the effect of the 200-yr solar cycle on the oceanic system. Little is known about solar



Fig. 6. Spectral analysis of Biogenic silica content and TOC content calculated for core A-3. The signal has a statistically significant (80% level) concentration of variance in approximately a  $\approx 250$  yr periodicity. The *x*-axis shows periodicity in years. The *y*-axis shows spectral density (logarithmic scale). Blackman–Tuckey spectral analysis routines were done according to Analyses series 1.1 routines (Paillard et al., 1996).

influence on these restricted oceanic areas from the Antarctic Continent, but the observed variations in planktonic communities, organic matter and biogenic silica in the same time range as solar cycles do suggest a possible influence.

# 5.1. Atmospheric CO<sub>2</sub> versus Bransfield Strait paleoproductivity

Changes in atmospheric  $pCO_2$  represent an important factor inducing changes in global climate and ice-volumes. Atmospheric pCO2 fluctuations are largely controlled by the exchange rates of  $CO_2$  between the atmosphere and ocean reservoirs, an exchange jsut depends strongly upon the primary productivity of plankton in oceanic upwelling regions, where the carbon/carbonate ratio is high (Sarnthein et al., 1987). Additionally, variations in the efficiency with which nutrients are used by marine biota could provide the necessary link between high-latitude insolation and CO<sub>2</sub>. If all the nutrients in surface waters were used by biota, the marine biological pump would operate at maximum efficiency, drawing carbon from the atmosphere to the deep ocean and lowering the level of atmospheric CO<sub>2</sub> (Broecker, 1981, 1982a, b). However, in coastal Antarctic waters, Estrada et al. (1992) and Aristegui et al. (1996) considered that the respiratory processes of phytoplankton communities could be responsible for the loss of more than 50% of photosynthetically fixed carbon. These authors also considered that microbial respiration and air-breathing top predators may return high amounts of photosynthetically fixed carbon to the atmosphere, causing these coastal Antarctic ecosystems to be inefficient as a carbon sink.

The ice core data suggest that  $CO_2$  levels rose significantly during previous warm periods. On a 100-yr time scale, Barnola et al. (1995) recorded pre-industrial fluctuations in atmospheric CO<sub>2</sub> over the last millennium. Numerous data point to an intensification in upwelling and therefore enhanced paleoproductivity during glacial periods (Sarnthein et al., 1987, 1988; Abrantes, 1991a, b). However, there is also evidence of low paleoproductivity during glacial periods in areas such as the North Atlantic and Catalonian-Balearic Seas (Villanueva, 1996; Flores et al., 1997). Villanueva (1996) addressed the possibility of low sea-surface paleoproductivity as a consequence of sea-ice coverage, which prevents the normal growth of planktonic communities. For the Bransfield Strait area there is also evidence of lower paleoproductivity during Holocene neoglacial periods (Bárcena et al., 1998). During today's winters, sea-ice coverage restricts surface productivity (Wefer et al., 1988; Abelmann and Gersonde, 1991), which is directly related to seasonal variations in sea-ice extents.

As revealed by the data obtained in cores A-3 and A-6 (TOC, biogenic silica content and the diatom assemblage), maximum values in paleoproductivity are recorded during the warmest periods. On comparing our data to the  $CO_2$  curve described by Barnola et al. (1995) for the last millennium (Fig. 5), minimum  $CO_2$  atmospheric values are seen to be related to minimum in TOC, biogenic silica, diatoms and *Chaetoceros* RS.

From a global point of view, glacial periods and enhanced paleoproductivity in upwelling regions may leads the drawdown of total  $CO_2$  by photosynthesis (Sarnthein et al., 1987). Nevertheless, for specific areas, such as the Bransfield Strait, diatom communities do not play an important role in the global  $CO_2$  cycle during cold periods. In this sense, Broecker and Peng (1989) proposed that decreased  $CO_2$  occurring during glacial times is a consequence of increased alkalinity of Antarctic surface waters. They argued that this change is not only due to biologic pump efficiency, but is also a natural consequence of the glacial demise of the Atlantic's conveyor (North Atlantic Deep Water).

# 6. Conclusions

<sup>14</sup>C AMS chronology yielded an older age than expected for cores A-3 and A-6:  $3960 \pm 50$  yr BP and 3410 + 50 yr BP, respectively. The <sup>14</sup>C AMS ages of both cores display a downcore pattern that indicates a linear sedimentation rate of  $208 \text{ cm kyr}^{-1}$  for A-3, and  $80.7 \text{ cm kyr}^{-1}$  for A-6. The last two millennia have been recorded in core A-3 (2050 yr), while in core A-6 the last 1760 years are documented, in agreement with the accumulation rates given in the literature. The <sup>210</sup>Pb profiles obtained from the uppermost 20 cm of cores A-3 and A-6 permit the conclusion that in both cases the top 20-22 cm were lost during the coring process. Therefore, both core top ages can be estimated to be about  $100 \pm 15$  yr.

The variations in the diatom fossil assemblages recorded in cores A-3 and A-6 respond to known neoglacial events for the Holocene. Changes in species composition reflect changes in environmental conditions, including water masses and seaice coverage.

The abundance patterns of *Chaetoceros* RS, biogenic silica contents, and the number of diatom valves per gram of dry sediment are consistent with the high productivity values reported for the Bransfield Strait waters. The general trend indicates a reduction in surface productivity.

Trend differences between *Chaetoceros* RS abundance and TOC contents may be explained in terms of organic matter preservation into the Bransfield Strait.

Bio and geochemical changes have an overprinted high-frequency cyclicity at about 200– 300 yr, possibly related to the 200-yr solar cycle.

Diatom assemblages from the Bransfield Strait did not play an important role in the global  $CO_2$  cycle during cold periods.

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