

## Article

## Origins and Paleoceanographic Significance of Layered Diatom Ooze from Bransfield Strait in the Northern Antarctic Peninsula around 2.5 kyrs BP

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**Abstract :** We used diatom and porewater data of two piston cores from the central subbasin and one from the western subbasin in the Bransfield Strait in the northern Antarctic Peninsula to elucidate the depositional mechanism of the layered diatom ooze. The layered diatom ooze is characterized by an abundance of organic carbon, biogenic silica, sulfide sulfur, and lower porewater sulfate concentration. This lack of porewater sulfate concentration in the diatom ooze interval may reflect development of reducing micro-environment in which bacterially mediated sulfate reduction occurred. The negative relationship between the total organic carbon and sulfate contents, however, indicates that sulfate reduction was partly taking place but does not control organic carbon preservation in this unit. Rather, well-preserved *Chaetoceros* resting spores in the layered diatom ooze indicate a rapid sedimentation of the diatom as a result of repetitive ice-edge blooms on the Bransfield shelf during the cold period (around 2500 yrs BP) when the permanent sea-ice existed on the shelf. During this period, it is expected that the downslope-flowing cold and dense water was also formed on the Bransfield shelf as a result of sea ice formation, playing an important role for the formation of layered diatom ooze in the Bransfield subbasins.

**Key words :** layered diatom ooze, *Chaetoceros* resting spore, Bransfield Strait, Antarctic Peninsula.

### 1. Introduction

As a major zone for the oceanic front in the Antarctic, the northern Antarctic Peninsula (Fig. 1) is one of particular interesting region for the studies of biological and modern geological processes as well as hydrological processes (Wefer *et al.* 1988; Dunbar 1985; Dunbar *et al.* 1985). In particular, the Bransfield Strait, which lies between the Antarctic Peninsula and the South Shetland Islands, is the region where oceanic (Circumpolar Deep Water) and the Antarctic continental shelf waters (Ice Shelf Water) meet (Whitworth III *et al.* 1994; Amos and Lavender 1992; Figueiras *et al.* 1998). Thus the mixture of these two water masses are weakly stratified and quite homogeneous in the vertical, with temperature and salinities lower, and oxygen concentrations higher than those in the adjacent

waters to the north and south (Whitworth III *et al.* 1994; Patterson and Sievers 1980). During austral summer the Bransfield Strait not only lacks fluvial discharge systems but also receives only minor amounts of terrigenous sediments except for ice-rafting and ice marginal dumping. Modern sedimentation under such regime is therefore dominantly biogenic. Sediment trap and biological oceanographic studies reveal that the flux of biogenic components into the Bransfield basin is highly episodic and is tightly coupled to surface-ocean processes of primary production (Wefer *et al.* 1988).

A recent study on three piston cores from the western and central subbasins in the Bransfield Strait reported the remarkably well-layered siliceous sediment intervals in the cores, containing relatively high concentration of organic matter (more than 1.5% organic carbon) (Yoon *et al.* 1994). This type of siliceous sediments are often generally described as 'laminated diatom ooze' in the

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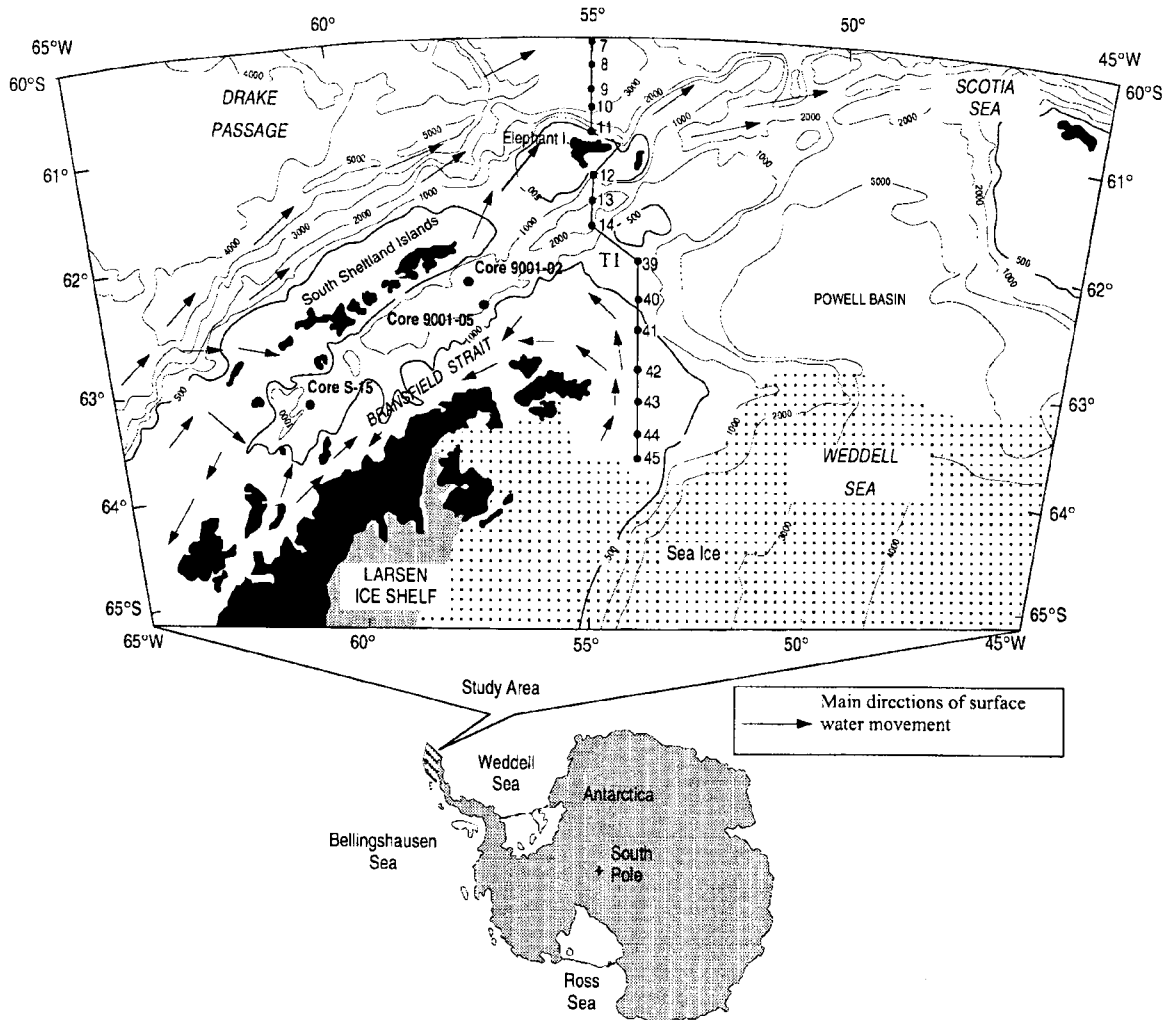


Fig. 1. Bathymetry, core locations and CTD with water sampling stations in the Bransfield Strait. Contours in meters. Station locations during the 1995 KARP cruise, which were occupied from 4 to 14 January 1995. Inferred surface water flows are shown by arrow (after Hofmann *et al.* 1992).

Antarctic ocean, and have been undauntedly interpreted as having been deposited by vertical sedimentation and/or lateral transportation of diatom blooms from the surface ocean (Jordan *et al.* 1991; Leventer *et al.* 1993). However, the formation of the diatom ooze layer from other places may commonly be ascribed to the inhibition of benthic community by low concentration of dissolved oxygen either in anoxic silled basins or beneath zones of strong upwelling, where an oxygen minimum layer intersects the shelf or slope (Schulz *et al.* 1996; Bull and Kemp 1996; Schimmelmann and Lange 1996). Therefore, it is essential that porewater chemistry for the diatom ooze interval is fully discussed to identify the bottom water condition during the formation of layered diatom ooze before we

accept enhanced production and flux for the origin of layered ooze interval. In this study, we examine porewater chemistry, sedimentology and micropaleontology to provide an outline of the main mode of preserving layered diatom ooze from the Bransfield Strait, which undergoes a seasonal sea-ice fluctuation, and suggest a process for the deposition of the layered diatom ooze.

#### Climate and Glacier

The Bransfield Strait is a region that experiences the strongest climatic gradients in Antarctica. The  $-3^{\circ}\text{C}$  mean annual isotherm penetrates through the Bransfield Strait, separating the warmer South Shetland Islands to the north from the colder peninsula to the south (Reynolds 1981).

The weather of the strait is affected predominantly by the passage of cyclonic storms that provide ample amounts of moisture for precipitation (Deacon 1984). In the northern half of the Bransfield Strait, valley and piedmont glaciers of the South Shetland Islands generally terminate on land as a result of the relatively warm climate and high levels of precipitation (Griffith and Anderson 1989). On the other hand, the Gerlache Strait region in the southern half is heavily glaciated and most glaciers are grounded below sea level (Griffith and Anderson 1989).

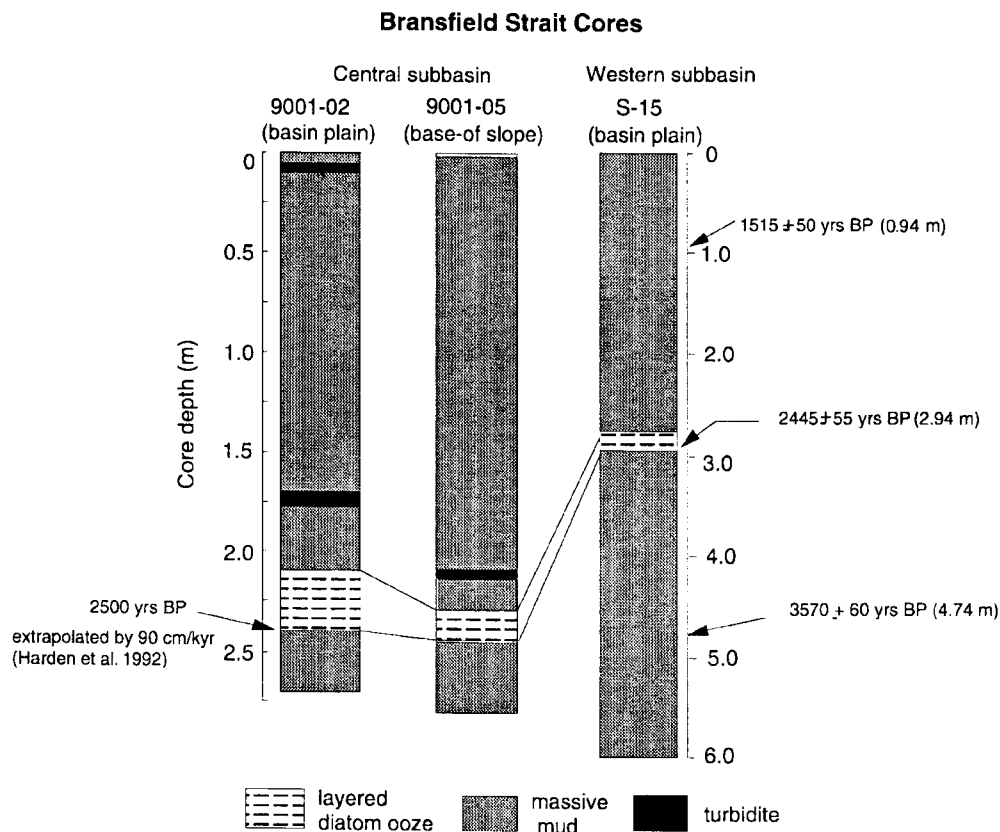
### Sea ice

The annual fluctuation of sea-ice coverage affects the ice-ocean-atmosphere dynamics in the Bransfield Strait by modifying the flux of heat, salt, and momentum between the ocean and atmosphere. Brine rejection associated with ice formation during oceanic cooling causes higher density of surface water, resulting in convective overturning which

leads to enhanced mixing and development of deep mixed layers. In some cases, the combination of brine rejection and cooling is sufficient to form deep-water masses, such as Antarctic Bottom Water, as observed in the Weddell Sea. The modern Bransfield Strait, however, is not known as a region of deep-water formation. In the austral spring, as the sea ice melts, meltwater lens is produced which stabilizes the upper water column and thereby restricts mixing and allows local heating to occur (Deacon 1984). This change in surface buoyancy when coupled with warming from increased solar irradiance causes a shallow seasonal pycnocline, resulting in diatom blooms on the surface ocean.

## 2. Methods

In order to understand the origins of layered diatom ooze in the Bransfield Strait sediments, two piston cores



**Fig. 2.** Lithological logs of the cores 9001-02 and -05 from the central subbasin, and the core S-15 from the western subbasin in the Bransfield Strait. Note the base of the layered diatom ooze of core S-15 has an AMS C-14 age of about 2500 years when a 1300-year reservoir correction was applied. Extrapolating the accumulation rate of 90 cm/kyr obtained by Harden *et al.* (1992) from the central subbasin in the Bransfield Strait, it is inferred that the base of the layered diatom ooze of the core 9001-02 is equivalent to 2500 yrs BP.

(7 cm in diameter) were obtained from the central subbasin and one was from the western subbasin of the Bransfield Strait (Fig. 1). The cores were splitted for X-radiography and were subsampled on board at 5-cm intervals. The subsamples were analyzed for grain size, total organic carbon, biogenic silica, sulfide sulfur, and pore water sulfate. Scanning Electron Microscope (SEM) and smear slides were used for lithologic descriptions and for identification of diatom species. For quantitative analysis of diatoms, slides were prepared using a settling technique described by Scherer (1995) and successfully utilized with other Antarctic marine sediments (Leventer *et al.* 1993). This technique helps diatom valves to be evenly distributed with minimal clumping, and produces absolute diatom concentrations per gram of sediment.

Total carbon and carbonate carbon were determined using a Carlo Erba NA-1500 Elemental Analyzer by measuring the CO<sub>2</sub> formed by combustion at 1100°C, and by treating with hot 10% HCl, respectively. Organic carbon was obtained by difference. For the cores from central basin, total reduced sulfur concentration was determined by treating the dried sediment with aqua and by precipitating and weighing the resulting sulfate. Interstitial water samples for sulfate analysis were first retrieved by centrifugation, and then sulfate was determined by precipitation and weighing of BaSO<sub>4</sub> using standard seawater as a reference (Howarth 1978). Biogenic silica (bioSi) was determined by the sequential leaching method of DeMaster (1981). Sulfide sulfur was measured by precipitating sulfur as barium sulfate (Vogel 1975).

### Lithology

Sediment cores from the Bransfield Strait consist of two lithologies; layered diatom ooze in 220-240 cm for 9001-02, 238-244 cm for 9001-05 and 290-294 cm for S-15, and homogeneous mud with interbedded turbidite layers in the rest of the core (Fig. 2).

The layered diatom ooze is sometimes visible in split core, but is always much better defined by density difference observed in X-radiographs (Fig. 3a). The most diagnostic criterion is the presence of well-developed parallel (<5-10 mm) layer. Most layers are varve-like because they consist of alternating millimeter to centimeter scale of dark and light colored layers (Fig. 3a). The light layer mostly comprises well-preserved monospecific diatom assemblage such as *Chaetoceros* resting spore (90%) (Fig. 3c) with 14% of *Fragilariopsis curta* and 8% of *Fragilariopsis cylindrus*, while the dark layer contains mixed diatom assemblage such as 50% of *Chaetoceros*

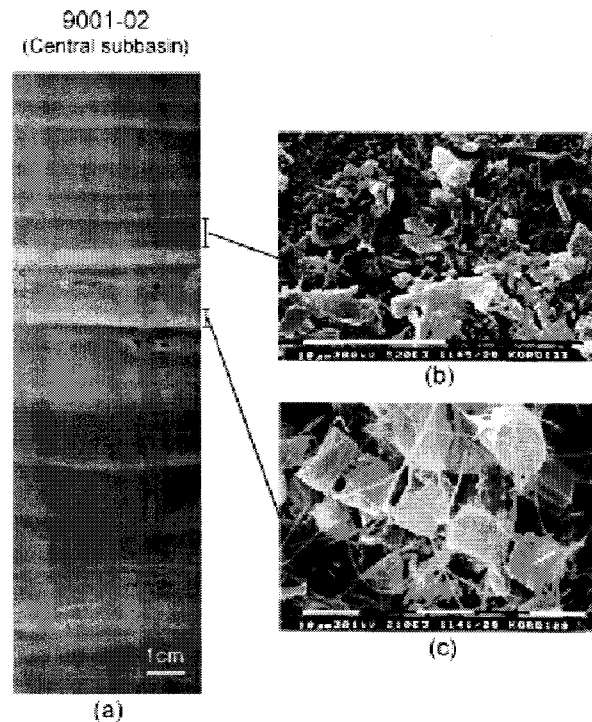


Fig. 3. (a) X-radiographs of core 9001-02 representing layered diatom ooze interval, showing well-layered diatom ooze (light band) alternating with clayey silt (dark band) (core 9001-02, 210-225 cm); (b) SEM micrograph of fragmented diatoms and debris in the dark band; (c) SEM micrograph of well-preserved *Chaetoceros* resting spore in the light band.

resting spores, 8% of *F. curta*, 0.5% *F. cylindrus*, and minor amount of *Rhizosolenia* and *Corethron* (Fig 4). Diatom valves in the dark layer have fragmented and undergone silica dissolution (Fig. 3b). Similar diatom floras were previously identified in the layered diatom ooze intervals from the central Bransfield Strait (Yoon *et al.* 1994).

### Organic carbon, sulfide sulfur and sulfate

Profiles of bioSi, organic carbon, sulfide sulfur and porewater sulfate contents in two cores (9001-02 and 9001-05) from the central subbasin are shown in Figs. 5 and 6. BioSi, organic carbon and sulfate sulfur contents are highest in the layered diatom ooze interval, moderate in homogeneous mud and lowest in turbidite.

Organic carbon content in core 9001-02 varies between 0.11% and 0.86% down to 200 cm and then increases sharply from 1.14% to 1.98% within the base 60 cm of sediments (Fig. 5). Similarly, bioSi content varies between

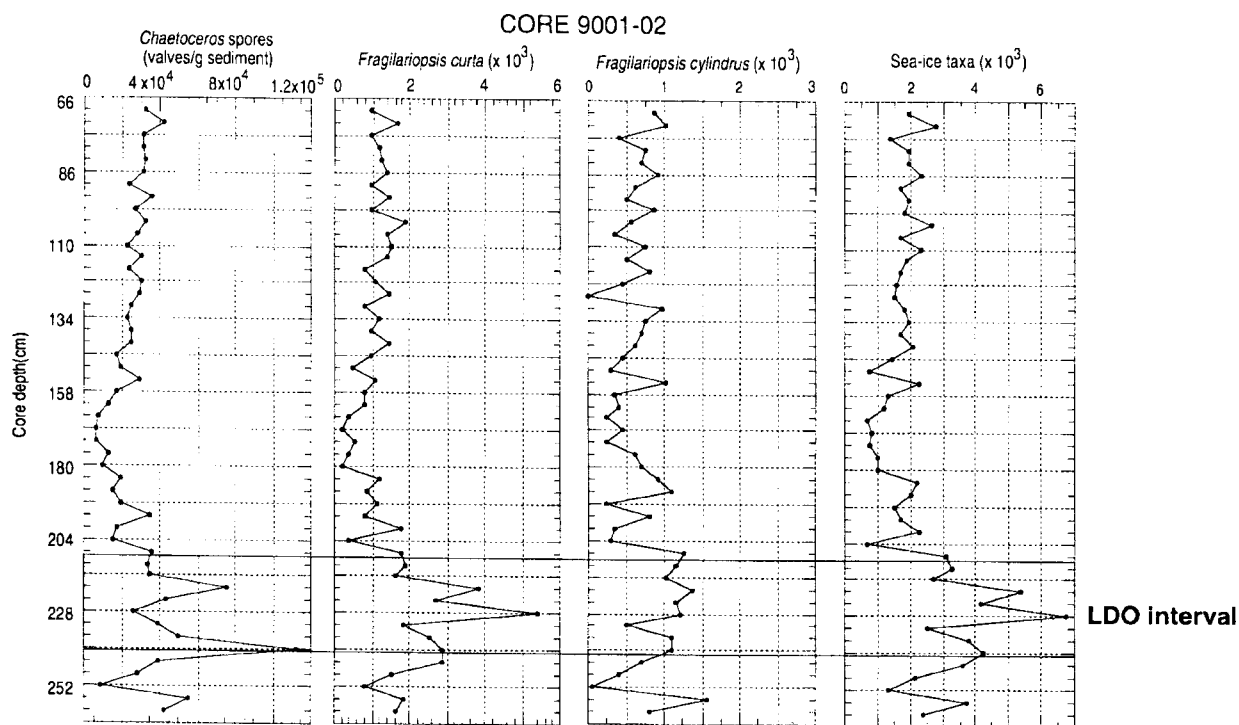


Fig. 4. Diatom analysis for core 9001-02. Note that an increase in number of diatom valves/grams of sediment in layered diatom ooze interval.

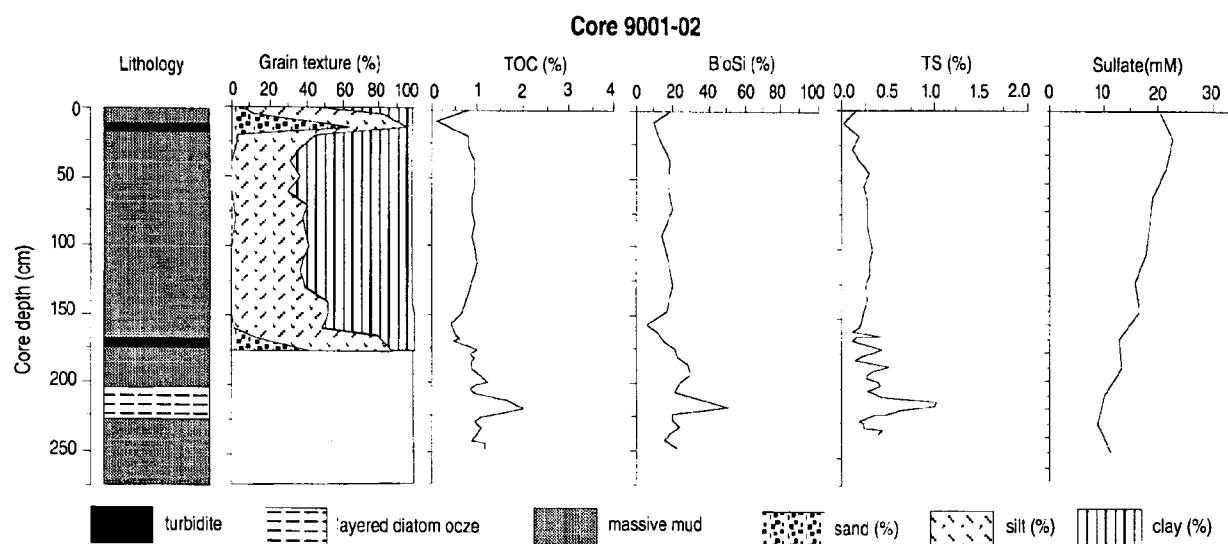


Fig. 5. Downcore variations in lithology, grain texture, total organic carbon (TOC), biogenic silica (BioSi), total sulfide sulfur (TS) and sulfate ( $\text{SO}_4$ ) for core 9001-02. Note that all TOC, bioSi profiles vary with sediment types, showing all their values being the highest in the layered diatom ooze. Negative relationship of the organic carbon and porewater sulfate content is shown.

9.6% and 30% down to 200 cm, below this level it increases sharply from 15% to 51% to the middle of the layered diatom ooze (Fig. 5). Porewater sulfate decreases

gradually from 23.2 m moles/kg at the sediment surface to 15.8 m moles/kg at the bottom, whereas sulfide sulfur content shows a minor fluctuation around 0.3% down to

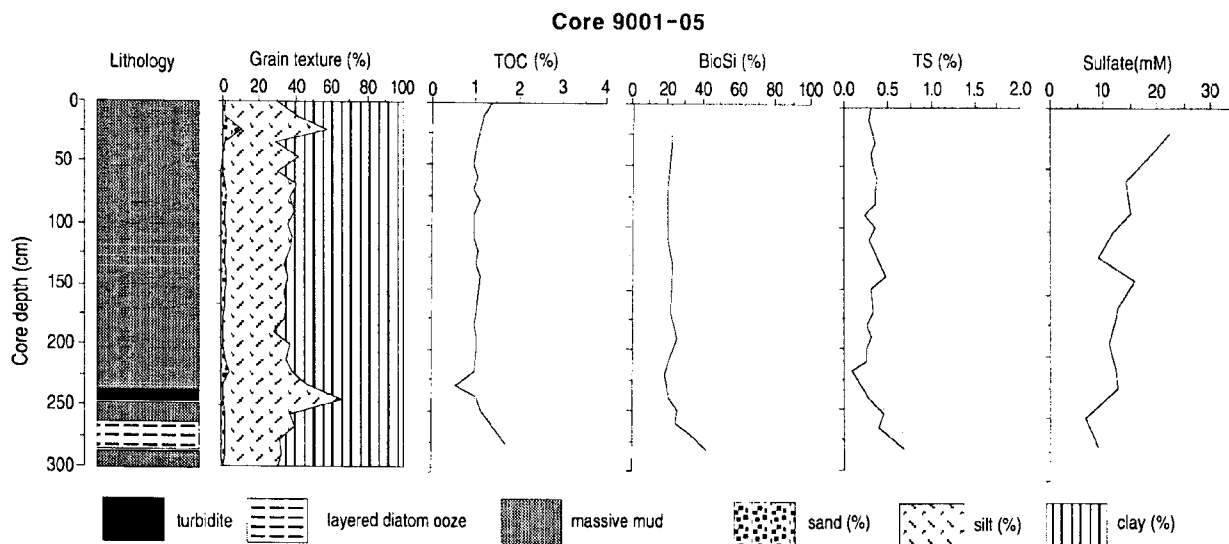


Fig. 6. Downcore variations in lithology, grain texture, total organic carbon (TOC), biogenic silica (bioSi), total sulfide sulfur (TS) and sulfate ( $\text{SO}_4$ ) for core 9001-05. Note that all TOC, bioSi profiles vary with sediment types, showing all their values being the highest in the layered diatom ooze. Negative relationship of the organic carbon and sulfate content is shown.

200 cm, below which there is a conspicuously sharp increase up to 1.2% near the bottom.

Total organic carbon content for core 9001-05 is constant with depth down to 250 cm, ranging from 0.96% to 1.07%, below this level it increases slightly with a maximum value of 1.30% in the layered diatom ooze (Fig. 6). BioSi content shows minor fluctuations down to 250 cm, ranging from 21% to 24%. Below this depth, bioSi content sharply increases with a maximum value of 33% at the bottom of the core. Sulfide sulfur content varies between 0.10% and 0.50% down to 250 cm and increases up to 0.75% at the bottom of the core, whereas porewater sulfate content decreases gradually, ranging from 22.0 to 5.00 m moles/kg (Fig. 6).

#### Origin of layered diatom ooze

The layered diatom ooze in the sediment cores from the Bransfield Strait are characterized by an abundance of organic carbon, biogenic silica as well as considerable preservation of sulfide sulfur, which can be accounted for by a relatively small sulfate reduction (Figs. 5 and 6). In contrast, the lack of porewater sulfate concentration in the diatom ooze interval may reflect development of reducing micro-environment in which bacterially mediated sulfate reduction occurred, which would result in a decrease in the organic carbon and porewater sulfate contents and an increase in sulfide sulfur. The negative relationship between

the total organic carbon and sulfate contents (Figs. 5 and 6), however, seems to be in contradiction to the general result of the bacterial sulfate reduction that shows a positive trend between organic carbon and porewater sulfate contents. This indicates that sulfate reduction is partly taking place but does not control organic carbon preservation in this interval. How can this increased organic component in the diatom ooze where bacterial sulfate reduction occurs be explained? Two possibilities can be considered; (1) increased flux of biogenic opal to the seafloor, and (2) lowering of oxygen minimum zone.

The first option requires increasing diatom productivity. Normally increased diatom productivity in the overlying waters would increase both the biogenic silica and organic carbon contents in marine sediment (Goll and Bjorklund 1974; Maynard 1976; Diester-Haass 1978), and their positive relationship would indicate a marine source of organic carbon (Figs. 5 and 6). Moreover, the most common diatom in the layered diatom ooze, *Chaetoceros* resting spore is generally known as the dominant species at the termination of bloom event under the condition of nitrogen deficiency in Antarctic waters (Davis *et al.* 1980; French and Hargraves 1980). In particular, excellent preservation of delicate surface ornament and setae (Fig. 3c) indicates that these cells did not experience either the fragmentation or abrasion by heterotrophic grazing or dissolution by corrosive water column (Grimm 1992;

Sancetta 1989). Rather, the intact nature of many of the diatom attests to rapid flocculation and consequent mass sinking at the termination of bloom events which are well known process, both from water-column observation (Alldredge and Gotschalk 1989), experimental study (Passow *et al.* 1994), and from BSEI studies of monospecific diatom laminae (Grimm *et al.* 1997). We may suppose, therefore, that the layered diatom ooze represents the mass sinking of diatoms from very high

primary productivity, which in the Antarctic depends on increased stratification of upper water column and the presence of a shallow mixed layer (Mitchell *et al.* 1991), as a function of both the proximity to low salinity meltwater and protection from intense Antarctic storm activity. This situation was observed in the northern Gerlache Strait, Antarctic Peninsula where *Chaetoceros* resting spores dominate sediment trap and surface sediment diatom assemblages (Leventer 1991). The surface water

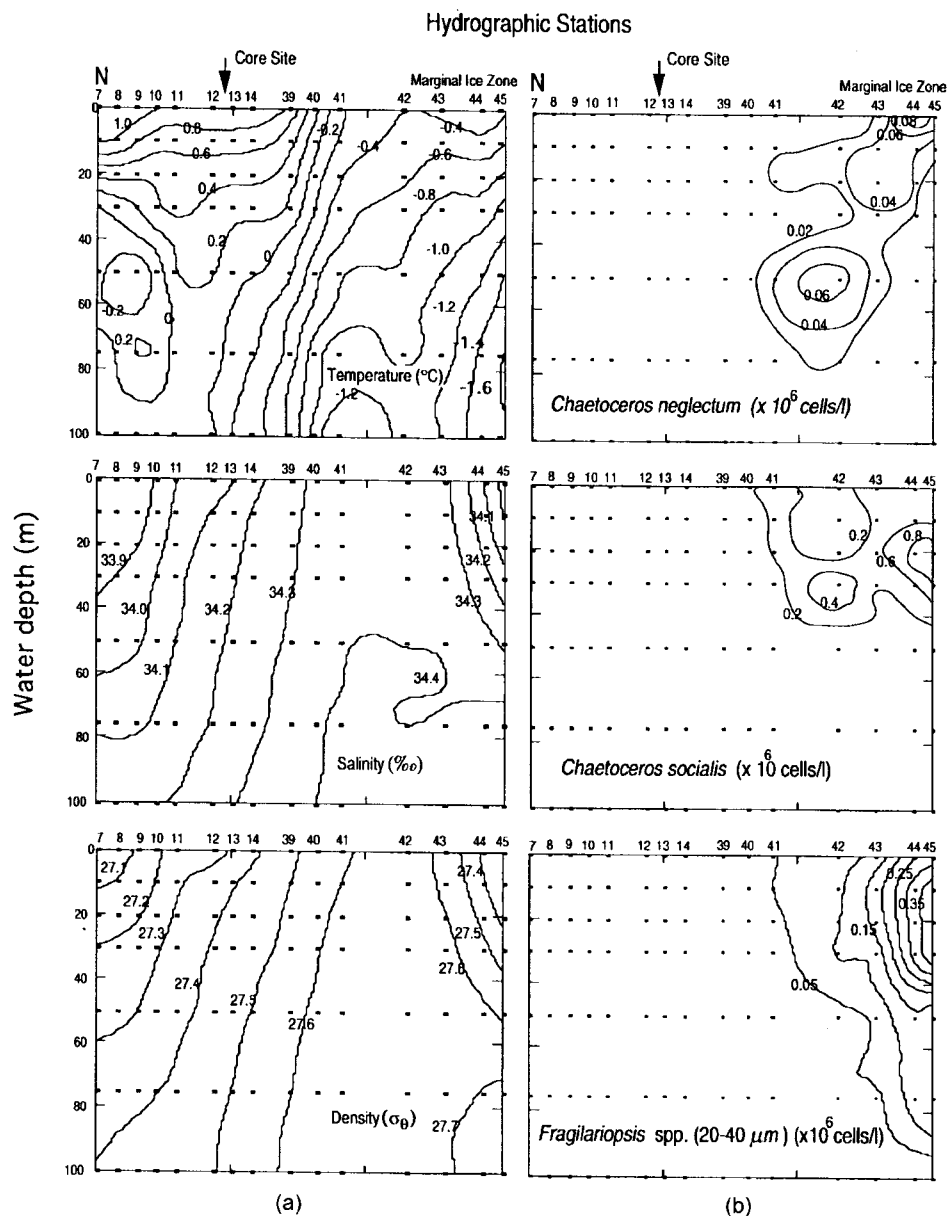


Fig. 7. Hydrography and phytoplankton assemblages between the marginal ice zone (MIZ) of the northwestern Weddell Sea and open water of the eastern Bransfield Strait (Modified from Fig. 7 in Kang *et al.* 2001).

of the Gerlache Strait experiences seasonal CO<sub>2</sub>, nitrogen and phosphorus depletion, indicating enhanced primary production and resultant high biogenic fluxes (Karl *et al.* 1991). Given their characteristic high primary productivity in summer stratified surface water of the modern Gerlache Strait, why do not these diatoms become concentrated to form layered diatom ooze even in the surface layer of the box core sediment from the Gerlache Strait? Rather, layered diatom ooze can be seen from the surface layer of sediment cores obtained from the open water of the eastern subbasin of the Bransfield Strait, where *Chaetoceros* diatoms typically occur in low abundance during the months of summer stratification (Kang and Lee 1995). Given this characteristic low abundance in the Bransfield open water, how then does this diatom become concentrated to form layered diatom ooze representing mass sinking in the eastern Bransfield Strait?

An alternative mechanism for the mass sinking that does not require vertical flux of diatom blooms from the upper water column may be surmised from a recent synthesis of the hydrography and phytoplankton assemblages between the marginal ice zone (MIZ) of the northwestern Weddell Sea and open water of the eastern Bransfield Strait (Modified from Figs. 1 and 7 in Kang *et al.* 2001). The hydrography in the Bransfield area shows a warm and less saline open water with temperature >0°C and salinity 33.8-34.2 p.s.u., while that in the MIZ where the sea ice was retreating southwards, shows a cold and saline Weddell Ice Shelf Water with temperature >0°C and salinity 34.3-34.4 p.s.u., causing a sharp thermal gradient (Fig. 7a). The diatom assemblage in the MIZ also shows a marked contrast with that in the Bransfield open waters. The Weddell Sea MIZ is characterized by chain-forming diatoms such as *Chaetoceros* spp., *Fragilariopsis* spp. accounts for 70% of the total phytoplankton, while the Bransfield open waters were depleted in sea ice-related diatoms (Fig. 7b), indicating that *C.* resting spores originated from ice-edge bloom at the northwestern Weddell Sea, and were then possibly transported laterally to the core site when plankton-rich, Weddell surface layer meets and mixes with circumpolar deep water. The lateral transport of diatom flocs is evidenced by recent sediment trap data from the eastern Bransfield Strait, which shows the higher flux values for diatoms and total particles in the lower than in the upper trap (Kim *et al.* 2000), suggesting a lateral influx of *C.* resting spore from the Weddell Sea MIZ by downslope bottom currents.

On the basis of the evidences presented above, it is not likely that the deposition of the layered diatom ooze from

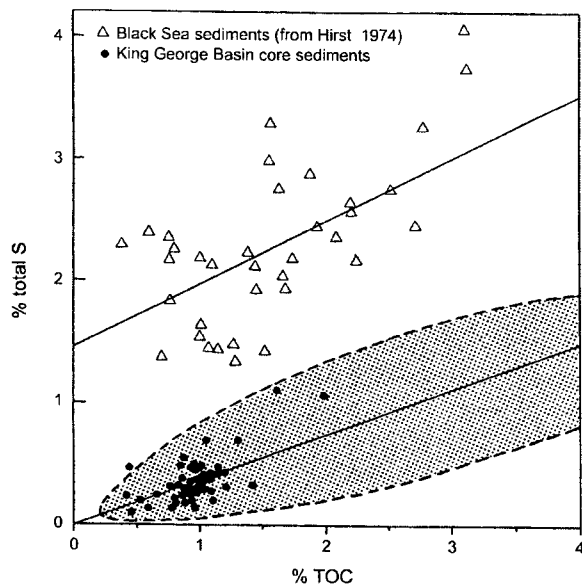
the central and western Bransfield Strait had resulted from the vertical sinking of diatoms from the productive upper ocean by increased productivity during the warmer period when the Bransfield Strait was completely ice-free, and meltwater lens was produced. Rather, the deposition of this unit requires stabilization of perennial sea-ice on the Bransfield shelf during the colder period when the sea-ice margin existed on the shelf even in the austral summer. During the cold phase, it is expected that ice-edge blooms had repeated over a longer period of time on the shelf, and the cold and dense water was also formed on the Bransfield shelf as a result of sea ice formation, whereas the modern Bransfield Strait is not known as a region of deep-water formation. Newly formed dense water on the glacial Bransfield shelf sank down the continental slope drawing diatom blooms down to the lower slope, forming a diatom-enriched underflow (i.e., bottom current). Diatom transport to the lower slope by bottom currents was maintained where the currents probably met equally dense water, forming an interflow. Layered diatom ooze was probably deposited from the bottom current driven water masses heavily laden with diatom valves. Relatively well preserved layers and no bioturbation suggest a rapid sedimentation of diatom ooze unit. Recent hydrographic study and paleoclimatic analysis of core sediment from the eastern Bransfield Strait demonstrates the existence of intermittent downslope currents coupled with deep-water convection and its possible role for the formation of layered diatom ooze during the colder period when the current activity was much more strengthened (Yih *et al.* 1998; Yoon *et al.* 2002).

Alternatively, it may be suggested that the expansion of the oxygen minimum zone and a weakening bottom-water circulation during deposition, as opposed to the enhanced diatom productivity, would lead to the observed high organic carbon preservation in the layered diatom ooze. However, the Bransfield Strait waters appear to have been rather well oxygenated. A hydrographic survey (Gordon and Nowlin 1978) revealed an oxygenation of the basinal waters of the central subbasin due to the local convection by the sinking of the winter surface water indicating deposition of the diatom ooze under oxidizing environment. Such oxygenation of bottom water is also reflected in the C-S (organic carbon *versus* sulfide sulfur) chart where our all data points fall near the normal marine sediments under oxidizing environment (Fig. 8).

#### **Wider implications**

The sedimentation rate in the present central subbasin





**Fig. 8.** Correlation between total organic carbon (TOC) and sulfide sulfur (Total S) in sediment. The data from Black Sea cores are plotted to show them to be representative for anoxic sediments having an excess amount of sulfide sulfur as evidenced by the positive intercept of the regression line onto the axis of the sulfur content. The stippled area on the diagram represents a domain for the present-day normal oxic marine sediments (after Leventhal 1983). The plot of our data inside the lobe strongly suggests that anoxic bottom water conditions had not prevailed during accumulation of the King George Basin (central subbasin) sediments.

of the Bransfield Strait is reported to be up to 90 cm/ kyr obtained by an AMS C-14 method (Harden *et al.* 1992). Based on this accumulation rate, it is inferred that the 250-cm levels of cores 9001-02 and -05 from the central subbasin is equivalent to about 2500 yrs BP. The date of the layered diatom ooze (280 cm in core depth) in core S-15 from the western subbasin also agrees with the 2500 yr BP date obtained from the central subbasin sediments, if we use a reservoir correction of 1300 years (as proposed for the Antarctic Peninsula). Paleoclimate study for the lake sediments in Livingston Island revealed that the areas adjacent to the central subbasin might have experienced more continental conditions with colder and drier climate at 2500 yrs BP than today (Bjorck *et al.* 1991). This climatic decline is supported by the paleoclimate studies for fjord sediments from Antarctic Peninsula (Shevenell *et al.* 1996; Leventer *et al.* 1996) in which they reveal a decrease in TOC and diatom abundance around 2700 yrs

BP, reflecting the formation of more extensive and seasonally persistent sea ice. The formation of persistent sea ice around 2500 yr BP corresponds to a global "T-Event" (3000-2000 yr BP), recently documented in the GISP2 ice core (O'Brien *et al.* 1995). Climatic cooling around 2500 yr BP would lead the existence of permanent sea ice on the Bransfield shelf. Summer melting of the sea ice during the colder period therefore would not only generate water column stability but also cause ice-edge bloom. During this cold phase, cold and dense waters were formed on the Bransfield shelf as a result of sea-ice formation. This dense water was concentrated with diatom blooms and flowed down the Bransfield slope, drawing diatoms down to the continental slope, forming an interflow by which layered diatom ooze was deposited.

### 3. Conclusion

To elucidate the depositional mechanism of the layered diatom ooze we used diatom and porewater data of two piston cores from the central subbasin and one from the western subbasin in the Bransfield Strait in the northern Antarctic Peninsula. The layered diatom ooze is characterized by an abundance of organic carbon, biogenic silica, sulfide sulfur, and lower porewater sulfate concentration. This lack of porewater sulfate concentration in the diatom ooze interval may reflect development of reducing micro-environment in which bacterially mediated sulfate reduction occurred. The negative relationship between the total organic carbon and sulfate contents, however, indicates that sulfate reduction is partly taking place but does not control organic carbon preservation in this unit. Rather, well-preserved diatom frustules in the layered diatom interval indicate a mass sedimentation of spring diatom bloom. Especially, given their characteristic high abundance in the sea ice margin, the condensation of *Chaetoceros* resting spores in the layered diatom ooze from the Bransfield Strait requires rapid sinking of diatom as a result of repetitive ice-edge blooms and their lateral influx by downslope currents at around 2500 yrs BP when the cold and dense water was formed on the Bransfield shelf as a result of the formation of persistent sea ice. The possibility of sea-ice formation in the Bransfield Strait around 2500 yrs BP may be deduced from a cold T-event documented in the Greenland ice core during the similar period, and a decrease in TOC and diatom abundance in Antarctic Peninsula fjord sediments around 2700 yrs BP, which reflects the formation of more extensive sea ice.

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