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Particle export and the biological pump in the Southern Ocean

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Abstract: The organic carbon particle export to the interior layers in the Southern Ocean in the New Zealand–Tasmania Sector was approximately 170 mmolC m^{-2} yr^{-1}. The export of particulate inorganic carbon in $CaCO_3$ was 110 mmolC m^{-2} yr^{-1} and was contributed mostly by pteropods shells in the Antarctic Zones. The Si flux from biogenic opal at the sub-Antarctic Zone was 67 mmolSi m^{-2} yr^{-1} and rapidly increased to the south up to nearly 1 molSi m^{-2} yr^{-1} in the Antarctic Zone. The Antarctic Polar Front clearly demarcated the area where the biological pump was driven by $CaCO_3$ to the north and biogenic SiO_2 particle export to the south. Summer stratification caused by the sub-zero winter water layer in the Seasonal Ice Zone (SIZ) curtails the zooplankton community and hinders the replenishment of Fe. This hypothesis explains the large organic carbon export with large *f*- and export ratios at the SIZ and extremely large opal production at the Antarctic Circumpolar Zone. Estimated regeneration rate of CO_2 from the export production and settling particulate fluxes of organic carbon in the water column between 100 m to 1 km was about 13 mmolC m^{-2} d^{-1} in the Antarctic Zone and Polar Frontal Zone.

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Key words: Antarctica, biogenic silica, export fluxes, particulate organic carbon, sediment trap

Introduction

Due to low water temperature, sea ice coverage and a deficiency of critical micro-nutrients (such as dissolved Fe), the array of biogeochemical processes known as the 'biological pump', that brings atmospheric CO_2 to the ocean interior and sea floor sink does not work to its full extent in the Southern Ocean. Only about a half of the nutrients are therefore utilized on an annual basis. However, the pronounced biological pump that is driven by large phytoplankton blooms could bring down a significant amount of atmospheric CO_2 as organic carbon to the oceanic interior in this relatively large area, and so the carbon cycle in the Southern Ocean plays a critical role in global climatic change.

The efficient removal of CO_2 in the Southern Ocean can be achieved by relatively large export fluxes of organic carbon that are associated with extensive diatom exports. In addition, a unique ecological setting provides the Southern Ocean with a significant capacity to absorb atmospheric CO_2 by maintaining alkalinity in the surface layers. In the lower latitude ocean, surface alkalinity is readily removed by the export of biogenic calcite particles, mainly coccoliths and planktonic foraminifera tests. The export of calcite particles abruptly ceases at the Antarctic Polar Front (APF, Fig. 1) and diatoms with silica frustules, that do not affect the surface alkalinity, dominate in the Antarctic Circumpolar Current (ACC, Fig. 1) and the oceanic zones to the south. APF, a boundary characterized by the marked changes in water temperature and salinity, is also a biogeochemical front system that separates the areas dominated by organisms with carbonate and siliceous hard-tissues. However, pteropods with aragonite shells dissolve faster in the water column and at the sea floor than calcite particles exported to the interior to the south of the APF, adding complexity to the surface CO_2 chemistry of the Southern Ocean. These intricacies in the Southern Ocean biological pump strongly support the argument calling for more in-depth investigation of the region.

The biological pump can be assessed by the quantity and quality of vertically settling particles that are intercepted at an interior depth. Deploying sediment traps in the oceanic interior is one direct method of measuring the biological pump. The majority of the sediment traps deployed since the mid 1980s in many parts of the world ocean are capable of collecting samples in time series the details of which are programmed into the device. This technology is advantageous in understanding the seasonal and annual variability of export fluxes, particularly in remote regions such as the Southern Ocean, which is often covered by sea ice. The major source of this study is the export flux data obtained from the AESOPS (1996–98; Smith *et al*. 2000) deep ocean sediment trap program deployed along the 170°W transect (Honjo *et al*. 2000, Collier *et al*. 2000, Ingalls *et al*. 2003) and from the Antarctic CRC Program (participated in by WHOI; Trull *et al*. 2001) on the sub-Antarctic Zone (SAZ) along the 142°E transect (Bray *et al*. 2000), both in New Zealand–Tasmania (NZT) Sector (Fig. 1).

The fluxes of particulate organic carbon at the boundary zone between the euphotic and mesopelagic layers (export production) were estimated from ^{234}Th disequilibria (Buesseler *et al*. 1998). This method was successively

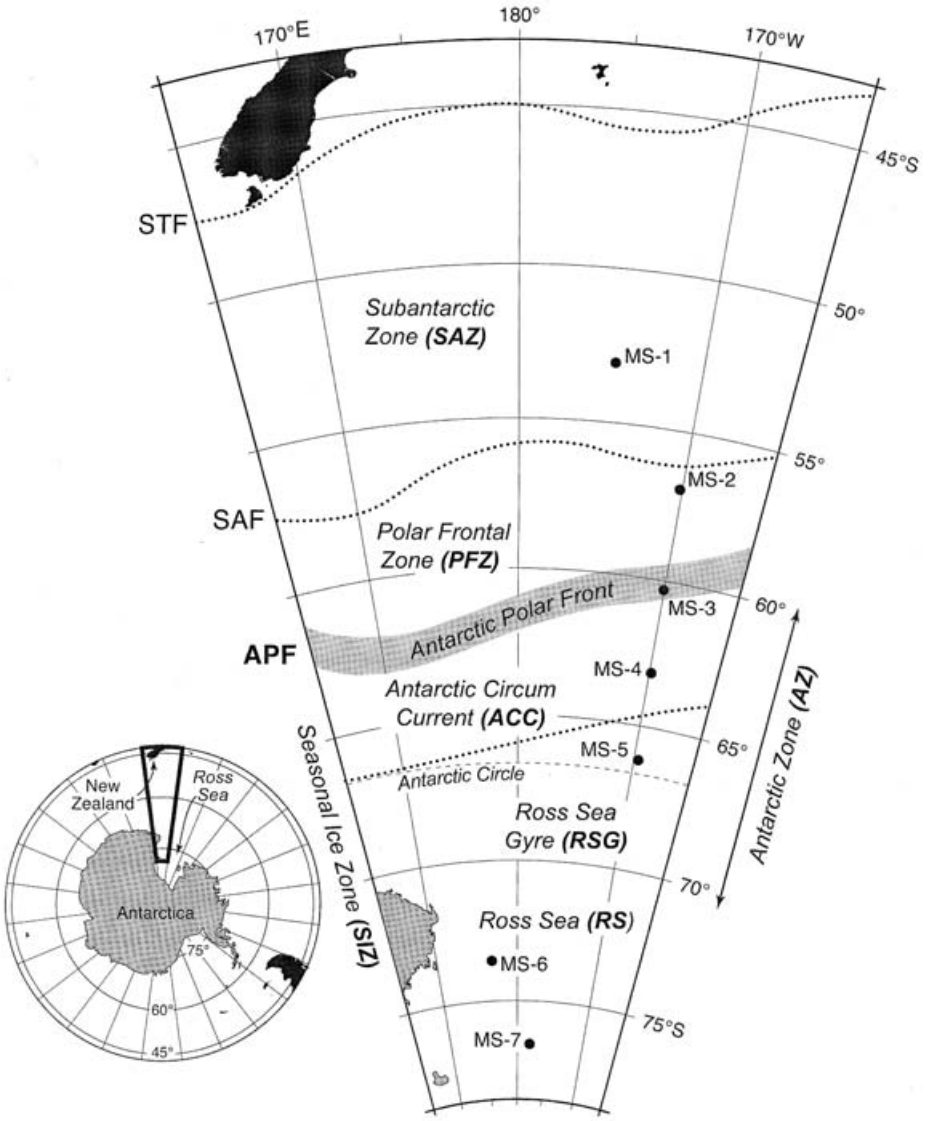

Fig. 1. The oceanic zones and the Polar Front in the New Zealand–Tasmania (NZT) Sector based on Tréguer & Jacques 1992, Moore *et al*. 2000. Along the left edge of the figure the approximate positions of STF (Subtropical Front), SAF (sub-Antarctic Front), APF (Antarctic Polar Front) and SACCF (Southern Antarctic Circumpolar Current Front) are indicated.

applied to access the export production along the above-mentioned 170°W transect. In this article the scheme of carbon cycle at each oceanographic zone of the southern Ocean is estimated by comparing mainly published AESOPS data including the

1) primary production (Hiscock *et al*. 2003),

2) inventory of dissolved Fe (Measures & Vink 2000,

3) the export production estimated from ^{234}Th disequilibria at 100 m (Buesseler *et al*. 2001, Buesseler *et al*. 2003) with

4) the settling fluxes of POC in the interior induced by sediment traps (Honjo *et al*. 2000, Collier *et al*. 2000, Bray *et al*. 2000).

Ingalls *et al*. (2003) published details of amino acids and organic compounds in the exported POC along the 170° transect.

JGOFS-AESOPS provided a great opportunity to measure many critical characteristics of the biogeochemical cycles in the Southern Ocean along a longitudinal transect, 170°W. However, the critical components of observation, measurement of primary production, export production, pCO_2 and the upper water concentration of dissolved Fe, were conducted in the summer of 1998 (partly in late 1997) while time-series measurements of the settling fluxes (export fluxes) were obtained during the period from late 1996 to mid-1998 with only a small period of overlap. This offset often limited further interpretation though all above-mentioned data sets are independently useful. Geographical coverage of settling particle study must be improved although international efforts including Fischer *et al*. 2002 (South Atlantic sector), Pondaven *et al*. 2000 and Pilskaln *et al*. 2004 (Indian Ocean sector) have just started to reveal circum-Southern Ocean links related to the biological pump. Future research should strive for more rigid synchronization among all time-series observations in order to understand better the spatial temporal relationship of the

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workings of biological pump and its physical characteristics.

Settling particles: the driver of the biological pump

The theory of settling particles as applied to the Southern Ocean

A settling particle is roughly 0.5 mm in size while settling in the lower mesopelagic and bathypelagic layers. However, it can be as large as centimetres in the upper layers under certain conditions. (at a rate of 100 to 200 m day^{-1}). A sediment trap intercepts and collects particles settling via gravitational velocity (*settling particles*) (Honjo 1996). Thus vertical mass flux can be measured when the duration of exposure is known. On the other hand, the vertical velocity of *suspended particles* is negligible and these particles are not able to be intercepted by sediment traps.

Settling and suspended particles have a reciprocal relationship: a settling particle is an aggregate of suspended particles. A suspended particle is suspended in water more often as an *individual particle* (independent coccoliths, clay particles etc.) that sloughed off from a sinking settling particle. A suspended particle is captured by a settling particle with overwhelming size and faster descending speed after a period of suspension. This cycle is continued throughout the water column. Thus all particles produced or added to the euphotic layer are either removed, metabolized or dissolved within a relatively short time in order to maintain a steady state. Settling particles, amorphous aggregates, are highly fragile (except for some faecal pellets). They disintegrate into smaller aggregates or individual particles while settling and their original configurations are rarely preserved when recovered by a sediment trap. The chemical constituents of settling and suspended particles in the same water column are identical.

The individual particles have diverse origin. They can be classified into two major categories: biogenic particles (including coccoliths, diatom frustules, cell materials and fragments of indigested organs, moulted fragments of crustaceans) and lithogenic aerosol particles (clay and crustal mineral particles). Customarily, the chemical characteristics of trap-collected particulate matter are analysed in the solids that pass through a 1 mm wet-sieving mesh and are retained on a membrane filter with a nominal pore size of 0.45 μm. In the open ocean, including the Southern Ocean, over 95% of the mass flux of particles pass through a 1 mm mesh during water sieving. The water sieving process disintegrates amorphous aggregates except copepod faecal pellets that are usually < 1 mm. The combined analytical errors exceed 5% thereby the particles that pass through 1 mm mesh are used for mass and component export particle fluxes. In general, a swimmer, (an accidental catch of a living organism in the water column), is rare at 1 km or deeper in the Southern Ocean particularly to the south of the Polar Front (with the exception of "Pteropod Raids" at the Ross Sea Shelf; Collier *et al*. 2000).

Settling fluxes of organic carbon and the role of ballast particles in the biological pump

The annual settling fluxes of organic carbon (fC_{org}) in the pelagic Southern Ocean along the 170°W transect at 1 km was *c.* 170 mmolC m^{-2} yr^{-1} (2 g m^{-2} yr^{-1}) and somewhat larger than the estimated average of organic carbon flux measured at the global mesopelagic zone (Honjo *et al*. 2004 (abstract)). The differences between fluxes among the Southern Ocean zones were relatively small. fC_{org} at 1km of the APF and ACC station was 195 and 183 mmolC m^{-2} yr^{-1}, respectively. fC_{org} was smaller at the PFZ and SAZ; 139 and 152 mmolC m^{-2} yr^{-1} (142°E transect station), respectively. All other biogenic constituents of particle fluxes were smaller at the RSG station than those found at the stations located in the south, but the fC_{org} was comparable to these station at 162 mmolC m^{-2} yr^{-1}.

Assessing quantity of POC export to the oceanic interior is crucial in order to understand the workings of the biological pump. POC, particularly cell materials, is hydrated in the ambient ocean so that its specific gravity is about equal to or, in the case of fatty and waxy material, lighter than seawater. The gluing materials generated by microbes and phytoplankton exo-ploysaccharides are also highly hydrated. Organic detritus is a major food source for the upper ocean ecosystem. All POC suspended in the upper ocean is ready to be remineralized and recycled to the atmosphere as CO_2 unless removed within a short time to the oceanic interior. The removal of POC from the upper ocean is the principal process by which the biological pump is set into action.

The biological pump only functions when the ocean ecosystem provides a means for POC to be aggregated to ballasting material (e.g. Honjo 1996, Armstrong *et al*. 2000, Francois *et al*. 2002). These ballasts available in the upper ocean are bio-mineralized particles such as coccoliths ($CaCO_3$) and diatom frustules (opal, $SiO_2 \cdot 0.4\ H_2O$). *Faecal pellets* produced by mesozooplankton including calanoid copepods are representative organic aggregates. A variety of amorphous aggregates, generally called *marine snow*, are also abundant settling particles. Thus the removal of particulate organic carbon is the result of an interplay in which all biogenic particles in the water column participate resulting in larger and heavier "settling particles."

Recent statistical analysis performed by Francois *et al*. (2002), indicated that the fraction of organic carbon exported from surface waters that reaches the bathypelagic zone is significantly higher in regions dominated by carbonate, as opposed to biogenic opal. This observation suggests that $CaCO_3$ particles, particularly coccoliths, may provide an efficient ballast that increases the efficiency of

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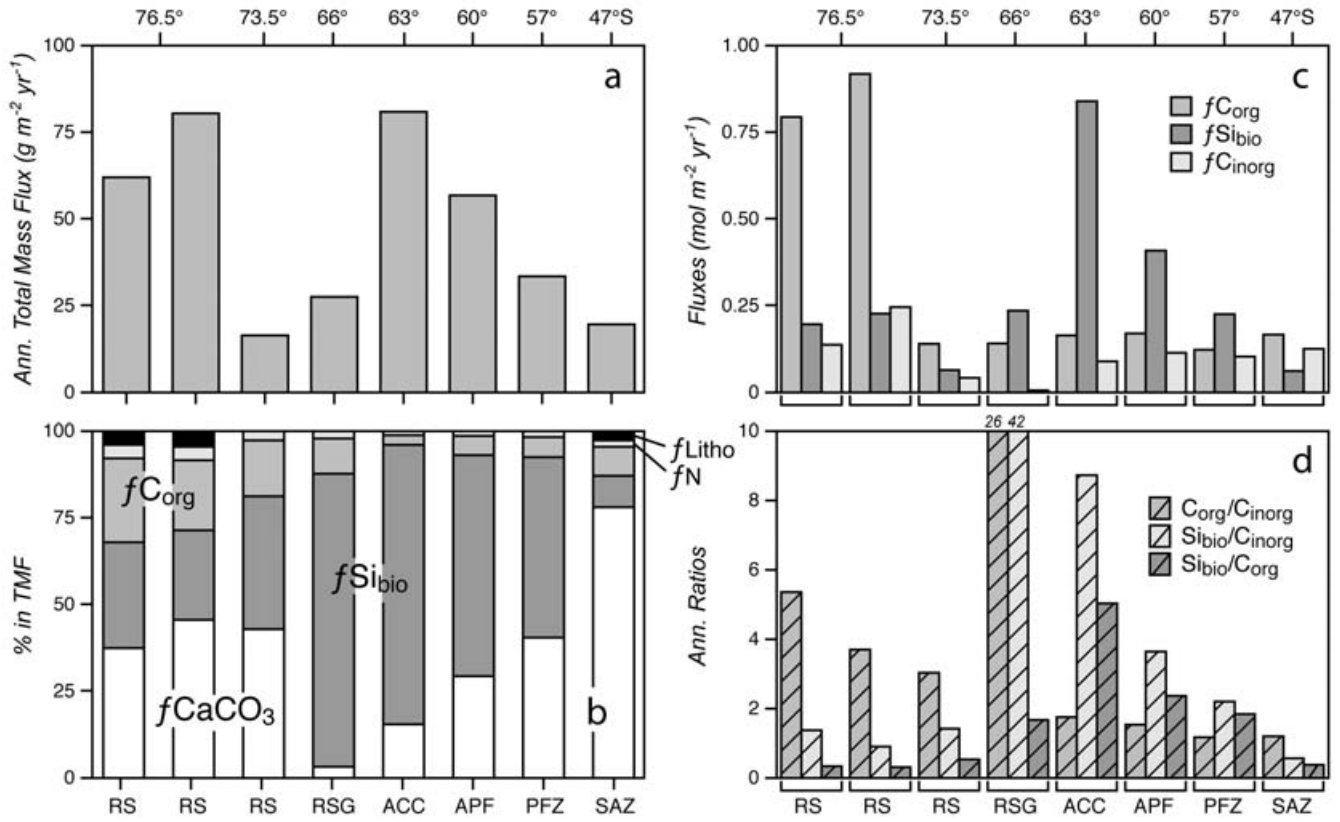

Fig. 2. Annual fluxes and their ratios at each zone represented by AESOPS stations at 1 km along 170°W transect from 1996–98 (Honjo *et al*. 2000). The longitudes where time-series traps were deployed along the 170°W AESOPS transect are indicated along the upper edge of panels **a.** and **c.** The station numbers in Honjo *et al.* 2000 are indicated along the upper edge of panel **a**. Southern Ocean zones that correspond to AESOPS stations are indicated along the horizontal axis at the bottom of panels **b.** and **d.** The SAZ data were cited from the data set obtained from 47°S station at 1 km along 142°E transect (south of Tasmania) from 1997–98, Antarctic CRC Program (Bray *et al*. 2000; see the caption of Table I). **a.** Annual total mass fluxes of particles. **b.** Weight-percentage of the major biogeochemical components. **c.** $f\mathrm{C}_{org}$, $f\mathrm{C}_{inorg}$ and $f\mathrm{Si}_{bio}$ in mol m^{-2} yr^{-1}. **d.** Biogeochemical ratios in mole.

transfer of particulate organic carbon to the oceanic interior and bottom. However, coccolithophorids that supply calcified coccoliths do not inhabit the Southern Ocean south of the APF. The relatively large $CaCO_3$ flux is due to an abundance of large pteropod shells as discussed below. Considering the difference of mass between an adult pteropod shell (the majority of pteropods were *Lamacina helicina* (0.7–0.8 mm diameter and 0.5–0.6 mm high) that settles at high speed and fragile organic detritus, empty pteropods play essentially no ballasting role. In the Southern Ocean diatoms play the major role in bringing POC to the ocean interior.

Carbonate fluxes

Judging from the exported particles that were intercepted at 1 km, the carbonate flux to the south of the APF is unique in the global sense because the pteropods are the major source of the carbonate export to the ocean interior whilst the export of coccoliths and foraminifera tests dominate in the SAZ at 170°W and 142°E stations. Planktonic foraminifera tests were minor carbonate constituents in the PFZ and ACC compared to pteropod shells. Our preliminary observations indicated that there were several species of normally-grown planktonic foraminifera tests in addition to *Neogloboquadrina pachyderma*, the dominant high latitude species, at these stations. In contrast, foraminifera test fluxes in the Seasonal Ice Zone (SIZ), south of the Southern Antarctic Circumpolar Current Front (Fig. 1, SACCF), were found only in trace amounts and were less calcified.

The annual carbonate flux was surprisingly invariant among the stations north of the SACCF. In the NZT Sector inorganic carbon in carbonate export ($f\mathrm{C}_{inorg}$) was 118 mmolC m^{-2} yr^{-1} in the PFZ, 128 mmolC m^{-2} yr^{-1} at the APF, and 107 mmol m^{-2} yr^{-1} in the ACC, and dramatically dropped to 6 mmolC m^{-2} yr^{-1} in the Ross Sea Gyre (RSG, Fig, 1). The northward increase in $\%CaCO_3$ is primarily due to a decrease of opal flux (Fig. 2). These carbonate fluxes are comparable to those measured in the Equatorial Pacific (Honjo *et al*. 1995) and the mid-latitude North Atlantic

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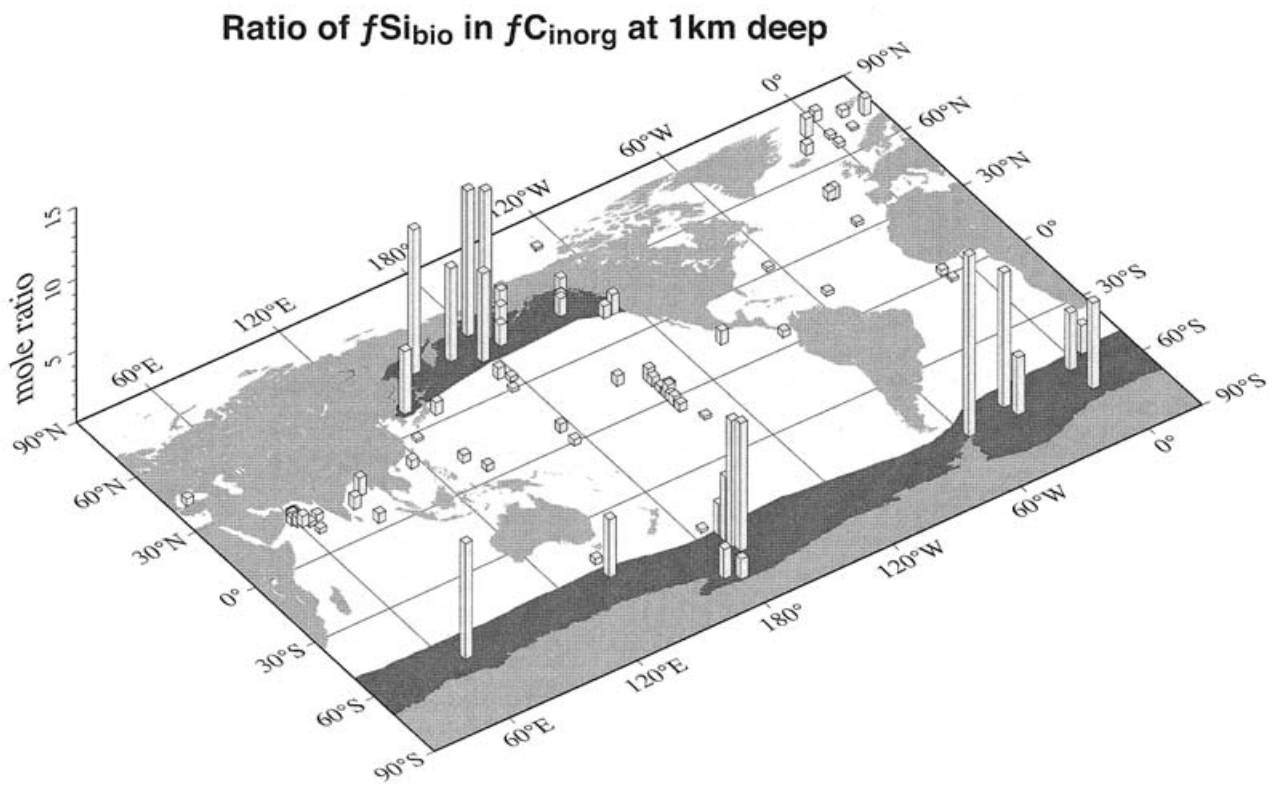

Fig. 3. Global distribution of $f\mathrm{Si}_{bio}$ in $f\mathrm{C}_{inorg}$ ratios at 1 km deep. The area of silica ocean where the $\mathrm{Si}_{bio}/\mathrm{C}_{inorg}$ is > 1 is limited to the south of the APF in the Southern Ocean and to the north of the sub-Arctic Front in the North-western Pacific. Data from SAZ was obtained from AESOPS 1981 m deep trap.

Ocean (Honjo & Manganini 1993, Newton *et al*. 1994) although pteropods are distributed, albeit sporadically, throughout all oceans (e.g. Betzer *et al*. 1984). Large export of their aragonite shells was found in the high latitudes of oceans such as Norwegian Sea (Meinecke & Wefer 1990). At the termination of a pteropod's life, its aragonite shell is gravitationally exported together with equivalent alkalinity. The rate of removal of alkalinity in the Southern Ocean to the north of the ACC may therefore be comparable to that of the North Atlantic and the Equatorial Pacific.

Although calcite (coccoliths and planktonic foraminifera tests) is generally believed to be unaffected by dissolution while sinking to the seafloor (Honjo & Weller 1998), there is evidence for significant carbonate dissolution in the water column above the calcite saturation horizon (Dymond & Lyle 1985, Nozaki & Oba 1995, Archer 1996, Milliman *et al*. 1999). This could occur more readily to the south of the PFZ, where a major fraction of the carbonate export consists of the more soluble aragonitic pteropod shells. Exported pteropod shells trapped at 1 km and deeper to the south of the PFZ, particularly smaller pteropod shells, showed signs of pitting and partial dissolution. In addition, larger specimens that settled independently with greater speed had a "frosted" appearance, indicating partial dissolution, that contrasted with the transparency of the shells of living pteropods captured by net tows (Berner 1977). Since the cups were sealed from ambient water after their respective collection interval, any carbonate dissolution that proceeded in the cup after collection would rapidly saturate the enclosed seawater, stopping further dissolution (Honjo & Manganini 1993). Such dissolution is unlikely to have occurred in the sampling cups during deployment. Dissolution due to CO_2 production from decay of organic matter can be discounted since the pH in the cups after recovery of the traps was invariably > 8.1 (Honjo *et al*. 2000).

Microscopic examination and biomarker analysis on the living phytoplankton samples (Wakeham, personal communication 2000) showed that coccolithophorids *Emiliania huxleyi* were abundant in the SAZ and APF, disappeared abruptly at the APF and living (or calcified) *E. huxleyi* were totally absent in the ACC and zones in the south. However, diversified Haptophyceae species, including *Wigwanmma* spp., which were poorly calcified and fragile were discovered in the Weddell Sea ice edge at 66°S to the south of the SIZ (Thomsen *et al*. 1988). Such extremely cold temperature adapted and poorly calcified coccolithophorids (Manton & Oates 1975) may live more ubiquitously to the south of the APF but their contribution to the export of calcite is likely to be negligible, though the effect of the cold-water adapted coccolithophorids on the biomarker distribution in the Southern Ocean is unknown.

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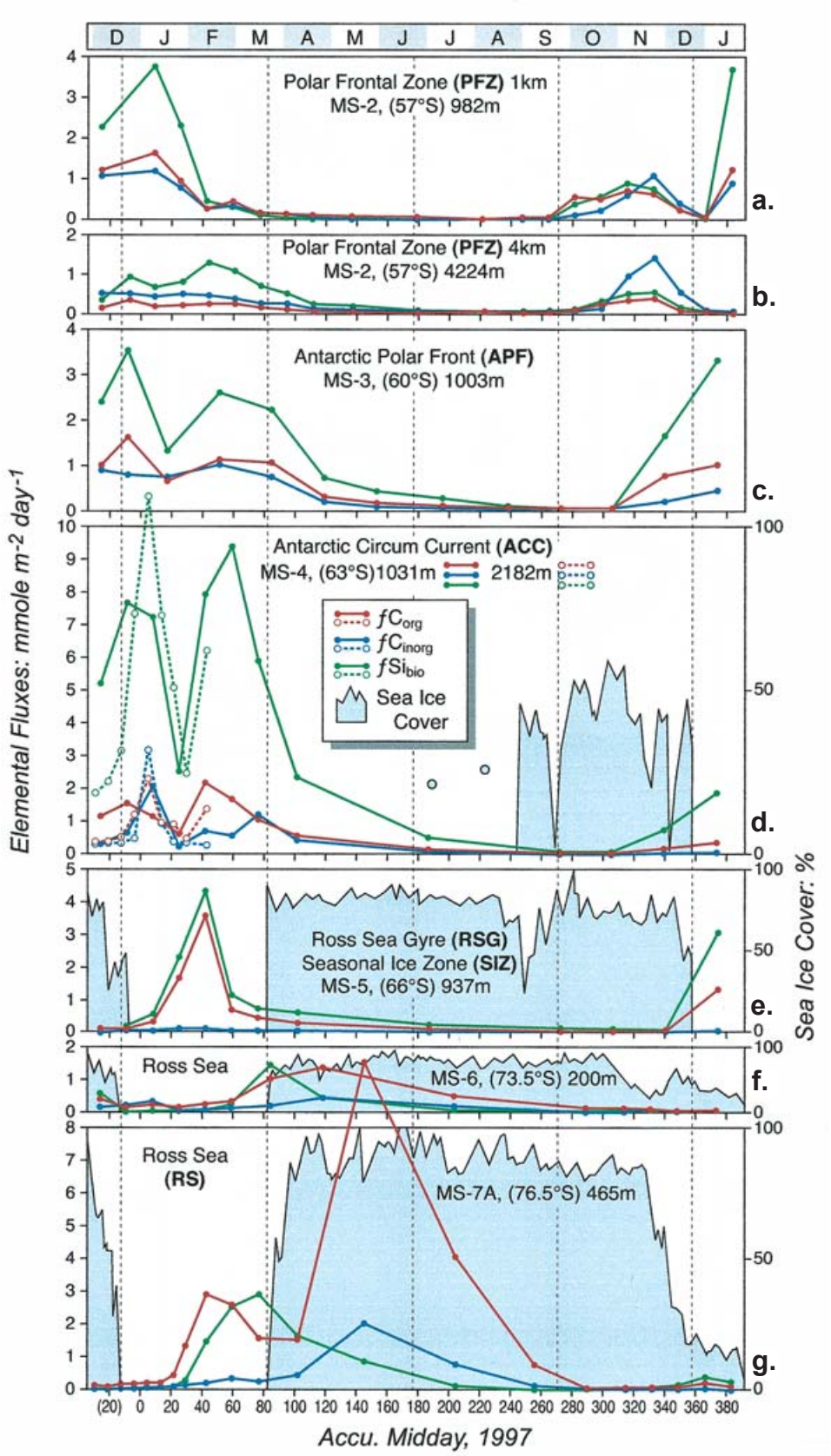

Fig. 4. Time-series of fC_{org}, fC_{inorg} and fSi_{bio} in mmol m^{-2} d^{-1} at 1 km depth at each zone to the south of the sub-Antarctic Front [4.2 km depth at PFZ(d) (Station MS-2; Honjo *et al*. 2000) is added]. The summer export fluxes at 2 km at the ACC are displayed with those at 1 km. Settling fluxes of three components measured in 1 km (solid lines) and 2 km (summer period only, broken lines) trap samples were compared in the ACC panel (**d.**). Comparison of the two plots indicates that the offset of arrival time at the deeper trap was only a week (as shown in fSi_{bio} plots at 1 and 2 km). The depletion of mass flux was small to unrecognizable while the biogenic mass settled from 1 to 2 km zone during the early part of the summer maximum flux period at this station. Large blue circles in the ACC panel (**d**) indicate short-life sea ice sightings. The extent of winter sea ice (**d.–g.**) was estimated from the DMSP F13 Special Sensor Microwave/Imager information distributed by the University of Colorado at Boulder.

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Biogenic silica fluxes

Arguably, the largest annual biogenic silicon export (fSi_{bio}) in opal known so far was found in the ACC at 1 km deep in the NZT Sector; 926 mmolSi m^{-2} yr^{-1} (57 g m^{-2} yr^{-1} of dehydrated opal flux) making the annual total mass flux as large as 81 g m^{-2} yr^{-1} (Honjo *et al*. 2000, Nelson *et al*. 2002) that was equivalent to the upwelling area of the Arabian Sea (Honjo *et al*. 1999). At the same station the flux during the peak bloom period, 21 January to 10 March 1997, fSi_{bio} was as high as 9.4 mmolSi m^{-2} day^{-1} (Fig. 4). South of the APF the annual mole ratio of biogenic Si export to the export of C in $CaCO_3$ (Si_{bio}/C_{inorg}) was as high as 9 in the ACC and 42 in the RSG section of the SIZ. In contrast, this ratio was about one or less to the north of the APF (Figs 2 & 3).

Because the AZ was generally considered to be a low productivity region, the occurrence of very high sedimentary opal accumulation rates on the seabed to the south of the APF was considered puzzling (e.g. Nelson *et al*. 1995). Enhanced opal preservation in the water column has been invoked to mitigate this apparent paradox, but no clear mechanisms that could explain higher opal preservation in this region have been put forth. This sediment trap data adds important constraints to this debate. The opal flux measured at 1 km depth at the ACC station (*c*. 0.9 molSi m^{-2} yr^{-1}) is equivalent to the upper limit of the annual opal production rate proposed by Nelson *et al*. (1995), based on measurements from the Weddell Sea (0.4–1.0 molSi m^{-2} yr^{-1}; Leynaert *et al*. 1993). Considering that 20 to 60% of the opal produced dissolves in the upper water column (Nelson *et al*. 1995), sustaining a flux of 1 molSi m^{-2} yr^{-1} at 1 km would require opal production rates 2–5 times higher. This calculation suggests that opal productivity in the AZ has been significantly underestimated.

In extreme silica ocean conditions, (defined as the open ocean area where the fSi_{bio}/fC_{inorg} is > 1 (Honjo 1997)), like those found in the AZ, organic carbon flux must depend on diatom frustules since there are no coccoliths. The new sediment in the AZ, either observed in sediment trap sampling bottles or at the seabed-water interface (Ingalls *et al*. 2003), formed a "diatom mat" (Kemp *et al*. 1999) or highly concentrated "green detritus flocks" or "fluff" often found on the deep ocean floor (Lampitt 1985). The mat looked like industrial "rock wool" (Honjo *et al*. 2000). A laboratory settling tube experiment showed that both fluff collected from the seabed surface and diatom matting collected by AZ traps (Honjo *et al*. 2000) descended at least an order of magnitude faster than normal amorphous aggregates of about 0.5 mm in low latitude oceans. A large mat is formed and removed from the mixed layer at a very high settling speed in the AZ where the grazing efficiency and the production rate of frustules are uncoupled.

Lithogenic flux and the biological pump

Lithogenic particles are supplied to the geographically isolated Southern Ocean via several pathways. At margin environments sea ice, rafting on icebergs, coastal erosion and resuspension from the shallow sea floor overwhelms aerosol supply. Pelagic lithogenic fluxes maintain a close positive relationship with biogenic particle export. Mesozooplankton's non-discriminative grazing habits and scavenging of large amorphous organic particles while settling through the water column can explain this. Lithogenic aerosol is therefore, in some areas, a part of the biological pump performing a ballasting role, which removes light organic carbon particles to the oceanic interior (e.g. Ittekkot 1993, Fischer *et al*. 2003). However, so few lithogenic particles are supplied to the pelagic Southern Ocean that their effect on settling efficiency is almost negligible in the open ocean (Francois *et al*. 2002).

Lithogenic fluxes measured at 2 km traps were larger to the north of the APF. The annual lithogenic Al flux in the SAZ was 2.2 mmolAl m^{-2} yr^{-1} (estimated lithogenic particle flux; 0.73 g m^{-2} yr^{-1}) at the 170°W station. Lithogenic particle fluxes decline an order of magnitude down to 0.37–0.38 mmolAl m^{-2} yr^{-1} (0.1 g m^{-2} yr^{-1} of the estimated lithogenic flux) in the PFZ, APF and ACC stations in the zones south of the SAF. This flux was an order of magnitude smaller compared to the SAZ station and lower latitude Pacific and North Atlantic statioFns. Further south in the RSG, Al flux was as small as 0.15 mmolAl m^{-2} yr^{-1} (0.05 g m^{-2} yr^{-1} of the lithogenic flux) comparable to the smallest aerosol lithogenic flux observed at an EqPac station 12°S, 135°W (0.07 g m^{-2} yr^{-1}) (Honjo *et al*. 1995) in one of the world's most land-based aerosol-free oceans (Duce *et al*. 1991). This may be an indication that the aerosol supply process south of the PFZ is isolated in its circulation in RSG. The lithogenic flux at 1.4 km at the off shore Prydz Bay station in the East Antarctica (62.5°S, 73°E) measured in 1999 was 0.22 g m^{-2} yr^{-1} (Pilskaln *et al*. 2004) four times larger than the deposition at RSG but still one of the smallest lithogenic aerosol fluxes know to us. Aerosol lithogenic particles are likely not be a significant source of dissolved Fe but also play no role of ballast in the south of PFZ in the Southern Ocean where the vigorous biological pump was operating by diatoms.

The residence time of a lithogenic particle in the euphotic layer during the productive season in the pelagic Southern Ocean is hours since they are incorporated into large biogenic aggregates that leave the upper ocean rather rapidly. Under the ice-covered period in the ACC and the RSG the lithogenic particle fluxes were almost below our analytical detection limit at this time (0.1 μmol Al m^{-2} dy^{-1}). At both the ACC and the RSG stations Al increased by an order of magnitude as soon as the bloom began but went down to a lower flux before the export peak arrived. The Al/C_{org} ratio was only high at the beginning of the bloom. This

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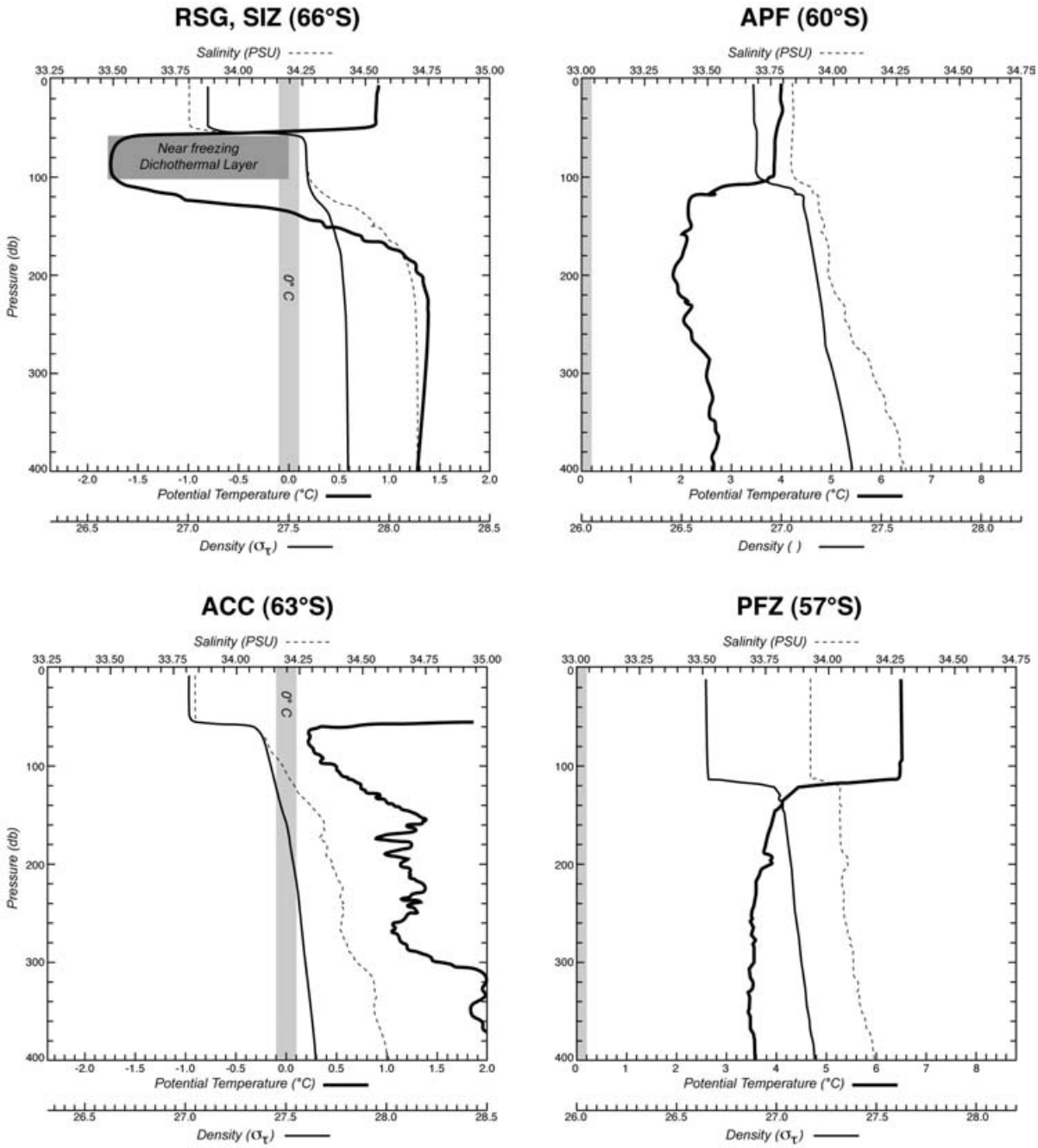

Fig. 5. Hydrographic profiles of the upper 400 m at each ocean zone from south to north. The temperature minimum zones of the APF, ACC and PFZ are illustrated as well as the sub-zero dichothermal layer at the RSG. Data from RV *N.B. Palmer* cruise NBP-02-98.

can be explained as the lithogenic aerosol particles that are deposited and retained in surface of ice were released to the water and incorporated with the onset of summer productivity. The biological pump exhausted the accumulated lithogenic particles from the surface layers in a short time. Wu *et al*. (2001) observed that "dissolved" Fe in the oligotrophic (subtropical gyres) surface layers is likely to have originated from aerosol lithogenic particles. However, dissolved Fe in the open deep ocean contains more colloidal Fe that is less bioavailable for phytoplankton compared to the soluble Fe. They also suggested that colloidal Fe is more readily scavenged by settling particles and thus quickly removed from the euphotic layer. Although speculative, a significant source of dissolved Fe may be the deep water brought to the mixed layer by upwelling in the NZT Sector. The axis of the upwelling is estimated to be approximately at the SACCF along 170°W. Hiscock *et al*. (2003), suggested the upwelling of Upper Circumpolar Deep Water as a source to replenish Fe to the mixed layer of the AZ.

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The export of lithogenic particles in the marginal and shelf areas that are caught in sediment traps are often dominated by ice-rafted and resuspended particles. The lithogenic fluxes are generally very large but highly inconsistent by trap location even though they may be located within a short distance of one another (Collier *et al*. 2000). The combination of ice-rafted and resuspended particle flux constitutes the majority of lithogenic export in the margin area. For example, Wefer *et al.* (1982), reported that lithogenic particles occupied 65% of the total mass flux in a near coast station at Bransfield Strait. These lithogenic particle fluxes do not show clear relationships with the biogenic particle fluxes but appear to be positively related with the distance from the shelf floor (Collier *et al*. 2000). This observation suggests that lithogenic particles play a negligible role in the biological pump in near-shelf environments.

Unique characteristics of the biological pump in the Southern Ocean

The carbonate/silica biogeochemical ocean front

The settling material collected in coccolith-dominated, low productivity regions has low Si_{bio}/C_{inorg} and C_{org}/C_{inorg} mole ratios that are smaller than 1. In more productive, diatom-dominated regions Si_{bio}/C_{inorg} and C_{org}/C_{inorg} mole ratios are greater than 1. The former region can be called a carbonate ocean and the latter a silica ocean (Honjo 1997) (Fig. 3). A biogeochemical front demarcating the carbonate and silica oceans in the north and south is developed between the SAZ and the ACC, which overlap at the PFZ. In theory, by removing ecosystem-produced carbonate particles in the carbonate ocean from the surface to the interior also depletes alkalinity at the surface to the ocean, which impedes the absorption of atmospheric CO_2. Alternately, in the silica ocean removal of silicate particles does not affect surface ocean alkalinity but CO_2 is removed as POC to the interior.

In the SAZ stations, the annual Si_{bio}/C_{inorg} was less than 1 and Si_{bio}/C_{org} was about 1. At the northern edge of the PFZ, a few degrees south of the SAZ, the Si_{bio}/C_{inorg} was 2.2. At a station on the APF, where Si_{bio}/C_{inorg} was 3.6 and reached up to 8.7 at the ACC with a Si_{bio}/C_{org} that was 1.5 and 1.7. The Si_{bio}/C_{inorg} and C_{org}/C_{inorg} were as large as 42 and 26 respectively in the Ross Sea Gyre (Fig. 2). The flux of carbonate in the SAZ was dominated by coccoliths, as in other low-latitude ocean with low-productivity areas such as the Subtropical Gyres. The northern PFZ was perhaps a transitory station with characteristics from both oceanic provinces.

It has been suggested that the Southern Ocean Zones are formed in a concentric manner around the Antarctic continent (e.g. Orsi *et al*. 1995, Belkin & Gorden 1996). Each zone maintains its unique physical properties. Is this also true for biogeochemical criteria? The silica/carbonate ocean boundary is robust. A few examples include the very high Si_{bio}/C_{inorg} in the ACC observed during a recent summer deployment in the Indian Ocean Sector (P. Tréguer, personal communication 2003) as well as the time-series observation conducted nearly two decades ago (Noriki *et al*. 1985). On the other hand, biogeochemical observations of the SIZ seem to be too scarce to be applied to a general Southern Ocean carbon cycle model.

The biological pump in the Seasonal Ice Zone (SIZ)

The efficiency of the biological pump (Francois *et al*. 2002) to the south of the APF is strongly linked to the upper ocean stratification caused by sea ice and supports the hypothesis that a stronger ocean stratification in the Southern Ocean contributes to the formulation of LGM climate (Francois *et al*. 1997). The RSG was covered extensively (> 80% of the sea surface) by seasonal sea ice for most of the year (Fig. 4) inducing the development of characteristic underwater stratification. The SIZ (*sensu* Tréguer & Jacques 1992) is characterized by the presence of the dichothermal layer that underlies the thin mixed layer (Toole 1981, Craig *et al*. 1981, Gordon *et al*. 1981). Rigid thermocline caused by the suspended layer of sub-zero (lower than 0°C) "winter water" generates a strong pycnocline that substantially reduces vertical mixing (Yang & Honjo 1996). The RSG was characterized by being underlain by a robust dichothermal layer at 60–100 m deep. (Honjo *et al*. 2000). The winter water is also formed under the ACC at about 60 m with a sharp temperature minimum (t-min) that does not reach below 0°C nor is a distinct "layer" configuration as at RGS station (Fig. 5).

The presence of a prominent sub-zero dichothermal layer just below the mixed layer may strongly affect the zooplankton community. We had no direct observation of the living community, but examination of exported particles suggested that the grazing zooplankton community was very small and possibly under stress conditions at the RSG station compared to the northern zones. Sediment traps deployed at 1 km and deeper at this station collected a far smaller number of zooplankton faecal pellets, foraminifera tests and pteropod shells compared to the northern stations (Honjo *et al*. 2000). Organic detritus in 1–5 mm range, mostly composed of fragmental crustacean moult, were only 0.2% of the total mass flux while such particles composed 3 to 4% of the total mass flux in the ACC and all northern pelagic stations. Furthermore, C/N in exported samples was significantly higher in the RSG sample. Such poor development of a zooplankton community might be linked with the strong dichothermal layer that severely limits their vertical movement. As a result, pteropod shells and the scarcity of foraminifera at the RSG station are reflected in the very small annual C_{inorg} export flux at 0.6 g m^{-2} yr^{-1}, which was only 6% of that at the ACC station

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(Fig. 2).

It seems that the Antarctic sub-zero water temperature itself does not affect the vertical distribution of the pteropod community. Pteropods densely populated the several hundred-metre water column of the Ross Sea Shelf (Collier *et al*. 2000) where the potential temperatures were often close to -2.05°C (Gordon *et al*. 2000), while no dichothermal layer developed in this area. AESOP traps deployed in the Ross Sea Shelf at a variety of locations and depths trapped abundant pteropod shells throughout the year. However, no consistency in fluxes in regard to the depth or distance from the shelf break was found. Since many of the shells preserved intact internal organs, some of them were alive when trapped (Collier *et al*. 2000).

Dissociation of organic carbon and opal in the AZ indicated by the Si_{bio}/C_{org} in the RSG station (1.7) was only a third of that at the ACC (5.1). This observation can also be explained by the inefficiency of grazing at the RSG station. fC_{org} measured at the former and the latter stations was comparable, 162 and 183 mmolC m^{-2} yr^{-1}, whereas fSi_{bio} was different, 267 and 926 mmolSi m^{-2} yr^{-1}, respectively (Fig. 2). Weak grazing activity at the RSG station remineralized the primary production in the mixed layer to a lesser extent than in the ACC and the northern stations. Thus a greater portion of the primary production at the RSG station was directly exported to the ocean interior, often in the form of "frustules matting", without being metabolized and mineralized in the mixed layer. Multicore surveys indicated that the floor of the RSG station was covered by diatom matting (Sayle *et al*. 2001, Ingalls *et al*. 2003). This hypothesis also explains the extremely high Si_{bio}/C_{inorg} at the RSG which was 42, compared to the ACC station where it was 9. Prydz Bay stations in the East Antarctica, 62–63°S, 73–76°E, occupied from late 1998 to early 2001 (Pilskaln *et al*. 2004), were under the SIZ of Antarctic Zone (Tréguer & Jacques 1992). The settling fluxes and their biogeochemical ratios were similar to the RSG station. In the PZB-1 1400 m trap, from which more complete time-series analytical data were published, fSi_{bio} and fN_{org} were similar, fC_{inorg} was approximately 30% larger than at the RSG station reflecting more but an order of magnitude smaller than those from the zones to the north of the SACCF along the 170°W AESOPS transect (Fig. 1). Thus C_{inorg}/Si_{bio} and C_{org}/C_{inorg} were extremely high, as high as 45 and 12, respectively (Pilskaln *et al*. 2004, table 2, p. 319). Functions of the biological pump similar to those found at the RSG station may be responsible for these unique settling fluxes. However, no upper ocean profiling to show the development of the sub-zero dichothermal layer is yet available.

Why is the export of biogenic silica at the interior of the ACC so large?

The fundamental cause of the unique and massive export of opal in the ACC is not yet well understood. However, involvement of dissolved Fe that brings a large primary production of diatom opal into the mixed zone of the ACC (e.g. Brzezinski *et al*. 2001) could be a direct cause. To address this, the following hypothesis posits that the relatively abundant dissolved Fe is supplied to the mixed layer of the ACC during the productive summer season enhancing the primary production. The source of the space-temporal variability of dissolved Fe concentration in the upper ocean layers along 170°W were Measures & Vink (2001). In early March 1997, dissolved Fe to the south of the SACCF was depleted to around 0.1 nmol and the exports of C_{org} and Si_{bio} started to cease. In the north the mixed layer of the ACC deepened to 100 m and was depleted of Fe to >0.2 nmol whilst vigorous export of Si_{bio} continued and C_{org} reached its peak of export at the ACC station. About two weeks later the export declined rapidly. In March Fe was depleted in the mixed layer of all zones to the south of the APF. In this period biogenic particle export at the RSG almost ceased. One speculative explanation for the large export of diatoms in the ACC is the timely supply of dissolved Fe carried by the topography controlled upwelling. The sub-zero dichothermal layer separated the upwelling, dissolved Fe from the mixed layer, and made it advect toward the ACC, thus enhancing primary production.

Si_{bio}/C_{org} in the ACC could reflect a higher Si_{bio}/C_{org} of diatoms growing in this region (Fig. 2). Laboratory cultures suggest that Fe-limitation can induce a two-fold increase in the Si_{bio}/C_{org} of diatoms (Takeda 1998, Hutchins & Bruland 1998). Dissolved iron limitation also produces thicker diatom frustules that sink faster (Muggli *et al*. 1996, Hutchins & Bruland 1998). The three-fold difference in Si_{bio}/C_{org} between these two zones would thus require Fe limitation in the AZ north of the SACCF, and Fe-replete conditions south of the SACCF. However, Fe concentration in the mixed layer at both areas was very low and comparable (0.10 to 0.15 nmolFe) (Measures & Vink 2001). It seems unlikely that differences in Fe limitation can explain the difference in the Si_{bio}/C_{org} of the particle flux in these two regions.

The five years of settling flux data reported from the Atlantic Southern Ocean ACC (Bouvet Island (BO) station, 50.09°S, 5.50°E, Fischer *et al*. 2002) was a third of the AESOPS data in regards to the TMF. The average fSi_{bio} in 450 to 515 m deep was 270 mmolSi m^{-2} yr^{-1} showing a very high interannual fluctuation compared to 926 mmolSi m^{-2} yr^{-1} at 170°W ACC. This station was characterized by a high lithogenic flux in the shallow layers (4.2 g m^{-2} yr^{-1} compared to only 0.12 g m^{-2} yr^{-1} at 170°W ACC station) suggesting an island effect. The C_{org}/C_{inorg}, Si_{bio}/C_{inorg} mole ratios observed at 170°W ACC were comparable to the ratio at the BO station.

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Seasonal procession of the settling flux

Seasonality of the settling fluxes in the Southern Ocean is strongly characterized by the intense contrast of a short and vigorous summer transport and a long empty period that lasts for the remainder of the year. This general pattern of settling flux by the zones in time-series was similar to the variability of primary production along the 170°E AESOPS transect (Buesseler *et al*. 2003, Hiscock *et al*. 2003; both data from 1997 and 1998). Another feature of the export is that the winter settling flux remains in trace amounts up until just before the summer begins. In the north of the ACC, the summer settling flux maximum consisted of two peaks; the mass flux temporally declined in December at SAZ and PFZ and January at APF and ACC.

Although the summer maximum season was as short as three months at the ACC, the settling flux was clearly separated into two peaks in respect of all components (Fig. 4d). Similar double peaks were also observed at the APF station. This double peak feature of settling flux during the maximum export period, which is often observed in lower latitude oceans, may be caused by a break in the primary production bloom due to a temporary depletion of nutrients or critical micronutrients. At the ACC, where the largest biogenic mass flux was observed, it took only approximately six weeks to reproduce the second and the most significant maximum (mid February). This came after the deep depletion of settling flux (late January) following the first maximum (early January), indicating that the replenishment of depleted nutrients took a relatively short time. Time series data by Fischer *et al*. (2002) at the APF station in the South Atlantic sector also showed a double peak feature (their fig. 4, p.1739, included no data from their ACC station).

An exception was the southernmost pelagic zone, the RSG, where the maximum settling flux had a single peak (Fig. 4e). There were 4–6 weeks free of sea ice cover after the plunge of settling flux at the RSG station. Therefore, the arrival of sea-ice cover in this area could not be the reason for the early truncation of settling flux. At the Prydz Bay station, the summer maximum flux of diatom frustules and planktonic foraminifera tests were represented by single peaks as at RSG station. An abrupt decline of biogenic particles started about eight weeks prior to the sea ice coverage at the PZB-1 station in 1999 (Pilskaln *et al*. 2004, fig. 5, p. 315). A similar process associated with strong stratification of the winter water, as observed at the RSG zone, may have caused an early truncation of settling flux at this station.

As observed at the ACC and RGS, the initiation of the vigorous summer settling of biogenic particles is related to the disappearance of sea ice coverage (Fig. 4d & e). It was observed at the RSG and ACC stations that smaller but significant levels of particle flux continued for many months until it virtually ceased at the end of winter, regardless of the sea ice cover (Fig. 4d & e). In the Ross Sea stations (Fig. 4g), highly erratic and very large organic and inorganic carbon was trapped under sea ice during mid winter (up to 10 mmolC m^{-2} yr^{-1} and 2 mmolC m^{-2} yr^{-1}, respectively by a 465 m trap (Collier *et al*. 2000)). However, when pteropod components were subtracted, opal fluxes decreased along with sea ice cover in a similar manner to what was observed in the pelagic zones.

Table I. Relation among primary production (PP), export production (EP) and settling fluxes (SF) at 1 km in the Southern Ocean Zones along the 170°W AESOPS transect.

Zone	Station for EF	PP	EP	SF	EP/PP	SF/EP	SF/PP	PP-EP	EP-SF
		mmolC $m^{-2}d^{-1}$			%			mmolC $m^{-2}d^{-1}$	
RSG	66°S	19.3	12.3	0.44	64	3.6	2.3	7.0	12.0
ACC	63°S	38.5	13.9	0.50	36	3.6	1.3	24.8	13.4
APF	60°S	36.4	13.7	0.53	38	3.9	1.6	22.7	13.2
PFZ	57°S	30.2	8.1	0.30	27	4.7	1.3	22.1	7.7
SAZ	47°S*	42.8	6.8	0.42*	16	5.9	1.0	36.0	6.4

RSG = Ross Sea Gyre, ACC = Antarctic Circumpolar Current, APF = Antarctic Polar Front, PFZ = Polar Frontal Zone, SAZ = Sub-Antarctic Zone, PP = ^{14}C-incubation based primary productivity (Hiscock *et al*. 2003, Buesseler *et al*. 2003), EP = ^{234}Th based export productivity estimate at 100 m. PR and EP measurement from 7 October 1997 to 8 May 1998 along AESOPS 170°W transect (Buesseler *et al*. 2003). SF = Settling flux of organic carbon at 1 km along the same 170°W transect measured from 28 November 1996 to 23 January 1998 by time series sediment traps (Honjo *et al*. 2000). *SF data from SAZ was obtained from 47°S station at 1 km along 142°E transect (south of Tasmania) in 1997–98 (Antarctic CRC Program; Bray *et al*. 2000) because the AESOPS SAZ I km mooring data was compromised by a mooring accident. SF at SAZ zone from 142°E transect was minimum amount since it was model calculated without observing the winter data.

Remineralization of POC in the mesopelagic water column

The difference in organic carbon flux between the two trap depths indicates the rate of mineralization taking place in that portion of the water column. The CO_2 from remineralized POC in the euphotic water column is essentially recycled into the atmosphere in a short time. However, the CO_2 that is injected to the interior oceanic layers are stored for a longer period and serves a significant role as the atmospheric CO_2 sink. POC is particularly remineralized at a high rate in the mesopelagic layers and resulting CO_2 can be retained for decades to centuries before being recycled back into the atmosphere. The mineralization rate of POC in the bathypelagic layers are one order of magnitude smaller (Martin *et al*. 1987). However, the volume of bathypelagic water is far larger and the injected CO_2 by remineralization of POC is retained for a far longer period up to a millennium. Comparable examination of the mass of POC that sinks across the boundary between the euphotic and the mesopelagic layers (export production EP) and the export fluxes of settling

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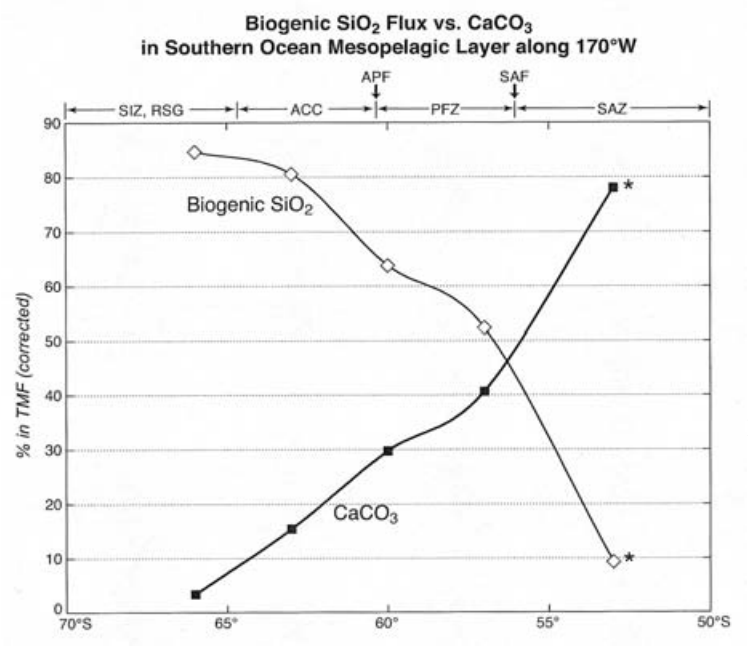

Fig. 6. Latitudinal variability of the percentage of biogenic SiO_2 and $CaCO_3$ in total mass fluxes in the mesopelagic layer along the pelagic 170°W transect (residual water contents were not counted). Year-round (1997–98) export fluxes of opal SiO_2 and $CaCO_3$ was obtained from AESOPS time-series sediment traps deployed at 1 km except the data from SAZ*. The SAZ data was obtained from the AESOPS 2 km trap (Honjo *et al*. 2000).

POC at interior depths, including the deep sea floor underneath, (settling flux SF) is critical in order to understand the workings of the biological pump. However, an *in situ* water column remineralization rate obtained by subtracting the fC_{org} measured by a deep trap from a flux obtained from the shallower trap or EP indicates the minimum remineralization rate since the *in situ* remineralization rate of DOC is not known. We only assume that the latter might be relatively small based upon a report that bacterioplankton biomass is practically limited to the upper 200 m in the Ross Sea (Ducklow *et al*. 2001).

As shown in Table I, the rate of remineralization in 1 m^2 of the euphotic water column obtained by subtracting the EP from the primary production (PP) (both data from Buesseler *et al*. 2003) was as high as 36 mmolC m^{-2} dy^{-1} in the SAZ. In the zones between PFZ and ACC this rate was comparable at 22–25 mmolC m^{-2} dy^{-1} respectively. The rate of remineralization in 1 m^2 ranging from the top of the mesopelagic layer to 1 km deep was very different; the rate of remineralization tended to be higher in the southern stations. The water column remineralization rate from 100 m to 1 km (mesopelagic water column) at the RSG station was 12 mmolC m^{-2} dy^{-1} and was comparable to the ACC station at *c.* 13 mmolC m^{-2} yr^{-1}. The rate of water column remineralizaton in the bathypelagic layer was far lower than the rate in the mesopelagic layer. The remineralization increased at the bottom water-sediment interface (Sayles *et al*. 2001).

Total CO_2 (T-CO_2) can be injected in a 1000 m long ACC mesopelagic water column at the rate of 13 mmolC m^{-2} dy^{-1} by the remineralization of settling POC. T-CO_2 that is produced as a result of the water column remineralization, must be removed by advecting northward with the Antarctic Intermediate Waters (AAIS) forming a T-CO_2 rich extension such as the Upper and Lower Intermediate water in the southern Atlantic (Schmitz 1996). The rate and mass of regenerated CO_2 to be supplied to this sink from the APF, ACC and RSG (SIZ) with the total area of approximately 30 to 34 Mkm^2 (Tréguer & Jacques 1992, Moore *et al*. 2000) (8.3 to 9.4% of the world's pelagic ocean area) is very substantial with respect to the global carbon balance.

The temporal variability of PP over a year-long continuous observation (Dicky *et al*. 1998, Marra *et al*. 1998) and SF by a high resolution time-series sediment trap was studied in the Arabian Sea stations finding that a PP signal reaches the mesopelagic layers within several days (Honjo & Weller 1998). There are no continuous primary productivity measurements throughout a year in the Southern Ocean that can be compared with the 170°W time series sediment trap data thus far. Variability of primary production through a productive season indicates that during the early spring (October–November 1997) the mean primary productivity was 33 mmolC m^{-2} dy^{-1}. In the late spring (December 1997) during bloom conditions, primary productivity along the Southern Ocean zones of the 170°W averaged 67 mmolC and absolute values ranged from 33 to 93 mmolC m^{-2} dy^{-1} depending on the location. In the late summer (February–March 1998) post bloom conditions, the mean productivity was 19 mmolC m^{-2} dy^{-1} along the 170°W (Hiscock *et al*. 2003). The general geographical pattern of productivity during the bloom matches with that of C_{org} in general. However, the detailed comparison of PP and EP must wait until both measurements are synchronized and conducted in close geographic proximity.

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Comparison of export fluxes of particles with the underlying sediment

Carbonate preservation is likely to be better on the sea floor of the AZ at 170°W due to the relatively shallow depth (< 3000 m). Despite this bias, the particles collected by the sediment trap array document the dramatic transition from the carbonate ocean to the silica ocean at the APF that is the crossover latitude of normalized $\%CaCO_3$ and %opal (Fig. 6). Southern Ocean surface sediments north of the SAF typically have high carbonate content (> 80%) above the lysocline, and opal content close to the detection limit. Carbonate content consistently decreases, while opal content increases towards the APF where opal becomes the dominant phase. South of the APF, opal is the principal sedimentary constituent. ^{230}Th-normalized opal fluxes at the seabed reach a maximum just south of the APF in the Atlantic and the central Indian sector of the Southern Ocean which is typically 0.15–0.30 molSi m^{-2} yr^{-1} (Kumar *et al*. 1995, Francois *et al*. 1997). Preliminary ^{230}Th measurements in the sediments of the NZT Sector at 170°W indicate a similar, although somewhat lower, maximum in normalized opal fluxes (Chase *et al*. 2003).

Farther south, opal concentrations decrease again, this time due to dilution by lithogenic materials (e.g. Burckle *et al*. 1982, Yu 1994). The mean annual composition of the settling material intercepted at 1 km (Fig. 2) (expressed in % of the five major constituents) is generally consistent with these trends. In the SAZ along the 170°W, carbonate was 64% to 57%, and opal was 18% of the total mass flux at the 1981 m trap whereas near the SAF, carbonate content decreased to 41% and opal content increased to 52%. Near the APF opal content further increased to 64%, but the carbonate content was still significant at 30%. This trend continued in the AZ where opal content rose to 81%, while carbonate content dropped to 15%. South of the SACCF opal content was similarly high (85%), while carbonate dropped to a very low concentration (3%) (Fig. 6).

Although there was general consistency between settling particle and sediment composition, several differences were observed. First, the percentage of opal in the material collected in the SAZ appears significantly higher than the percentage of opal typically measured in sub-Antarctic sediments (e.g. Charles *et al*. 1991, Yu 1994). This suggests that a significant flux of biogenic silica may occur in the SAZ, but the particles are poorly preserved in the sediments. Likewise, the carbonate content of settling particles remained surprisingly high well south of the APF and into the AZ. This differs from the sediments, as they generally contain very little carbonate south of the APF. If the carbonate fluxes measured here are typical, they suggest a significant export of alkalinity from the upper water column and carbonate dissolution on the sea floor. On the other hand Sayles *et al*. (2001), found that, despite extremely high (> 25) C_{org}/C_{inorg} in the exported particles at the RSG station, (Honjo *et al*. 2000), carbonate still remained in the surface sediment. Their explanation was that most CO_2 was neutralized by CO_3^{2-} from the overlying water rather than by the dissolution of sedimentary CO_2 (Sayles *et al*. 2001).

The lithology of the Southern Ocean sediments typically shifts near the Antarctic continent from siliceous ooze to siliceous silty clay or fine silts, with lower opal concentrations due to dilution by lithogenic material (Cooke & Hays 1982). This transition has been taken as an indication of sea ice presence, based on the assumption that sea ice inhibits diatom production and collects dust particles that are released upon melting (Burckle *et al*. 1982). However, the extremely low lithogenic flux measured at the RSG station in the SIZ (Honjo *et al*. 2000) does not corroborate the purported increase in terrigenous flux associated with a receding ice edge. This observation brings into question whether this lithological boundary established on the sea floor sediment distribution is directly linked to receding sea ice and whether it can be used to reconstruct past changes in sea ice distribution. Rather, the difference of lithology between the export and upper sediment sequence is more likely to be due to the redistribution of sediment by topography and deep current (Sayles *et al*. 2001).

Insights into the Last Glacial Maximum in the Southern Ocean from the present SIZ

Many researchers strongly argue that the SIZ expanded most vigorously during the last glacial maximum period (LGM) among the pelagic environments in the Southern Ocean. For example, Moore *et al*. (2000) estimated that SIZ expanded to 30 Mkm^2 compared to 19 Mkm^2 today (Tréguer & Jacques 1992). The expansion of the SIZ during the LGM would have greatly influenced the total operating mode of the biological pump in the Southern Ocean and thus would have contributed to the formation of the global climatic conditions during that period.

During the LGM while SIZ is expanded, the area underlain by robust sub-zero dichothermal layers (Fig. 5) with a stable mixed zone on top will also increase. If the present condition of RSG is considered to be applicable to the LGM Southern Ocean, this mixed layer fosters an inefficient grazing community so that the phytoplankton bloom is exported to the upper mesopelagic layer with less remineralization, resulting in a high annual export production despite a short open ocean period. The large EP provides relatively large fC_{org} at the oceanic interior and efficiently removes POC from upper layers to the sink layers. The absence of coccolithophorids and near absence of pteropods provides the SIZ an extremely high Si_{bio}/C_{inorg} ratio. Thus the removal of alkalinity from the upper ocean would be minimal and remedies the absorption of the atmospheric CO_2 at the ocean surface. In addition, the extended sea ice cap restrains the ventilation of CO_2 by such

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routes as upwelling from deep water (Francois *et al*. 1997) into the atmosphere. These scenarios hypothesize that the cool temperature during the LGM did not curtail the biological pump in the Southern Ocean but it could absorb even more atmospheric CO_2 unless the primary production was drastically reduced in the SIZ by increased density of sea ice coverage.

Summary

The Southern Ocean, from these studies mainly in the New Zealand–Tasmania (NZT) Sector, consists of two zones each with a specific biological pump. The Antarctic Polar Front (APF) is not only a physical boundary of water characteristics but also serves as a critical biogeochemical border. A highly specialized biological pump is at work in the Southern Ocean south of the APF. In this area the C_{org}/C_{inorg} is > 1, the Si_{bio}/C_{inorg} is >> 1 and diatom frustules play the major role in exporting organic carbon to the interior sink (silica ocean). In the sub-Antarctic Zone (SAZ) that develops in the north of the PFZ, both Si_{bio}/C_{inorg} and C_{org}/C_{inorg} are < 1 and the biological pump is driven by coccoliths and planktonic foraminifera tests (carbonate ocean) continued from the lower latitude oceans.

The organic carbon particle export to the interior layer (1 km deep) in the Southern Ocean zones along 170° at *c*. 170 mmolC m^{-2} yr^{-1} was more consistent from the SAZ to the RSG stations (including 142°E SAZ station). Although no coccoliths or significant exports of foraminifera tests were apparent in the zones south of the APF, pteropod shells were exported to the interior in the ACC. Therefore surface alkalinity could be exported both to lower depths and to the seabed surface in this zone. Inorganic carbon (in $CaCO_3$) export in the interior of the SAZ to the ACC was *c*. 110 mmolC m^{-2} yr^{-1} and was comparable to the North Atlantic. Carbonate export flux abruptly dropped to 6 mmolC m^{-2} yr^{-1} in the RSG because of the near absence of pteropod shell export to the interior. The opal flux (in SiO_2) was highly variable in each zone compared to organic carbon and $CaCO_3$. It increased southward from 17 mmolSi m^{-2} yr^{-1} at the SAZ 142°E station to 926 mmolSi m^{-2} yr^{-1} at the ACC while it was 267 mmolSi m^{-2} yr^{-1} in the RSG. The aerosol lithogenic particle fluxes were very small in all the pelagic stations and apparently were not participating in the present day Southern Ocean biological pump as ballasts nor sources of critical micro-nutrients, such as dissolved Fe.

The euphotic/mixed layer of the Seasonal Ice Zone (SIZ) is underlain by a sub-zero dichothermal layer during the summer seasons and this might be a reason why the RSG was poorly inhabited by zooplankton including pteropods. Limited replenishment of micronutrients through the dichothermal layer during the summer exhausted dissolved Fe in the thin mixed layer (50 m) long before the end of the growing season yet major nutrients still remained. This explains why the annual opal-Si export at the RSG was smaller (267 mmolC m^{-2} yr^{-1}) than that at the ACC. The meagre development of a grazer community passed organic carbon more directly to the layers below the dichothermal layer providing a large Export Production at 100 m (12 mmolC m^{-2} d^{-1}) with an unusually high *f*-ratio (64% during productive season) compared to the northern zones (16% to 38%) (Buesseler *et al*. 2003).

The huge export flux and the primary production of opal at the ACC might also be related to the sub-zero dichothermal layer under the SIZ. More Fe in the upwelling water is passed to the mixed layer of the ACC while the dichothermal layer blocks the bottom of the SIZ during the growing season. This interplay between the dichothermal layer and the biogeochemical staging in the Southern Ocean to the south of the APF possibly enhanced the absorption of atmospheric CO_2 during the LGM when the SIZ double its area.

The regeneration rate of CO_2 in the water column between 100 m to 1 km was about 13 mmolC m^{-2} dy^{-1} in the zones south of the AFZ with the estimated area of about 30 M km^2. This substantial amount of the regenerated CO_2 must be removed by northward advection off the Antarctic Continent.

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