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Characteristics of suspended particulate organic matter in the southwestern Atlantic: Influence of temperature, nutrient and phytoplankton features on the stable isotope signature

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ABSTRACT

Surface particulate organic matter (POM) along a transect from Subantarctic coastal waters on the Argentine shelf to the Bellingshausen Sea was characterized by its organic carbon (POC) and nitrogen (PON) content and δ^{13}C and δ^{15}N signatures in relation to sea surface water temperature (SST), nutrients and plankton. The correlation of δ^{13}C with SST was highly significant for the entire transect but less obvious within Subantarctic shelf ecosystems. Stable isotopes of POM varied from δ^{13}C ~ −12‰ and δ^{15}N ~ 8‰ in Subantarctic shallow waters to δ^{13}C ~ −32‰ and δ^{15}N ~ −2‰ in the sector including the oceanic Subantarctic waters and the Antarctic region. In Argentine shelf waters δ^{13}C was > −24‰ (on average −20.9‰) and more variable than in oceanic Subantarctic and Antarctic waters (average of −27.6‰). High isotopic variability of POM in northern Argentine shelf waters is probably due to a pronounced nutrient gradient. There, a sharp δ^{13}C decrease of ca. 12‰ was associated to an increase of the silicate to nitrate (Si:N) ratio to values > 0.25, and an increase of siliceous phytoplankton. Further south, Si:N ratios > 1 did not significantly affect δ^{13}C, and the influence of the sea surface temperature (SST) was more evident. δ^{15}N in POM of Argentine shelf waters averaged 6.3 ± 2.4‰, and the lowest δ^{15}N values (−1.7‰) occurred in the northern Drake Passage, where they build, together with δ^{13}C around −27‰, a clearly distinct pattern in the western South Atlantic. For the whole transect, SST alone accounted for 74% of the δ^{13}C variability. A multiple regression including SST, ammonium and POC explained 83% of δ^{13}C variance. The fit improvement by ammonium involved the nutrient-poor, regenerative system in the northernmost shallow sector and the Subantarctic shelf. δ^{15}N showed a strong inverse relationship with the fraction of unutilized nitrate, probably due to isotopic enrichment in the nitrate pool by phytoplankton uptake.

1. Introduction

The western South Atlantic Ocean embraces a high diversity of hydrological and ecological systems, e.g. the Brazil and Malvinas (Falkland) currents, the neritic tidal and thermohaline fronts along Argentine shelf waters (Guerrero and Piola, 1997), the Polar Front in the Drake Passage and the Antarctic Circumpolar Current with the Antarctic water masses.

According to its hydrographic and nutrient regimes and dependent plankton assemblages and dynamics this region can be divided into two sectors: north of the Polar Front are the Subantarctic, “low-silicate, high-nitrate, low-chlorophyll”, waters (LSiHNLC, Dugdale and Minas, 1995) with considerable spatial and temporal variance related to the position of major fronts and regional circulations (Acha et al., 2004). South of the Polar Front are the Antarctic water masses, high in nutrients and called the true “high-nutrient, low-chlorophyll” region (HNLC). A steep silicate gradient is found between both sectors (Brzezinski et al., 2005), with strongly decreasing silicate:nitrate ratios from the North across the Antarctic Circumpolar Current (Sarmiento et al., 2004). This, together with iron availability, influences growth conditions and distribution of phytoplankton in the Southern Ocean (Franck et al., 2000 and references therein). Both regions exhibit remarkable internal heterogeneities in terms of abundances and species assemblages (Olguín and Alder, 2004). In general, diatom abundance increases from North to South with increasing nutrient concentration, whereas dinoflagellates and picoplankton follow an inverse pattern (Alder and Franzosi, 2005; Olguín et al., 2005).

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North of the Polar Front, in Argentine shelf water, more than six ecosystems have been described (Carreto, 2001), whose location depends on bathymetry, the interactions of the Brazil and Malvinas currents, and the displacement of nutrient-poor or -rich water bodies related to fronts and upwellings (Acha et al., 2004). Based on temperature, salinity and nutrients, the region north of the Polar Front is also divided into neritic waters of the Argentine shelf and oceanic ones between the Subantarctic and the Polar fronts (Alder and Boltovskoy, 1991). South of the Polar Front, based on planktonic microbial communities and abiotic factors, Alder and Franzosi (2004) identified two sectors, one from the Polar Front to the Antarctic Divergence and the other from the tip of the Antarctic Peninsula to the Bellingshausen Sea. In general, 12 specific diatom assemblages were found in Antarctic waters (Olguín and Alder, 2004).

The southern end of the Argentine shelf is part of the Patagonian Cold Estuarine System. This Pacific–Atlantic system is interconnected by the Cape Horn current, which transports low-salinity water from the Southeast Pacific (Acha et al., 2004), and continues as the Malvinas Current (Longhurst, 1998), which transports oceanic nutrient-rich Subantarctic waters to the Argentine shelf (Silva and Neshiba, 1979). Some variability of the Malvinas current is related to the Antarctic Circumpolar Wave and the ENSO (White and Peterson, 1996; Peterson and White, 1998). Little is known about ENSO effects on fluctuations of the Brazil-Malvinas Confluence, which influence microplankton distribution patterns in oceanic southwestern Atlantic waters (Thompson and Alder, 2005). Thus, if these highly diverse systems suffer significant spatial shifts, changes in suspended particulate organic matter (POM) composition may be preserved in the sediments, helping to reconstruct the occurrence of such events in the past. However, to date there are no available data on tracers of suspended POM such as stable carbon and nitrogen isotopes in Argentine shelf and adjacent oceanic waters.

In this context, a main goal of the present work was to characterize the isotopic composition (δ^{13}C and δ^{15}N) of suspended POM of surface waters along a transect in the western South Atlantic Ocean from Subantarctic coastal, middle and outer Argentine shelf waters to the Bellingshausen Sea in Antarctica. A particular target was to study the relationships of the isotope signature with the silicate:nitrate ratio in the characteristic low-nitrate/low-silicate waters of the north Argentine shelf, and further south under the LSiHNLC and HNLC regimes. The data were discussed also considering their dependence on plankton biomass indicators, taking into account influences of temperature (e.g. Rau et al., 1982) and nitrate availability (Altabet and Francois, 1994) as main driving forces of variations of δ^{13}C and δ^{15}N in marine phytoplankton.

2. Methods

2.1. Study area

During the Austral autumn, in March and April 2005, subsurface water samples (9 m depth) were taken at 38 stations during two transects on the Argentine shelf, the Drake Passage and north and west of the Antarctic Peninsula to the Bellingshausen Sea. The first transect (March 12 to 18) embraced 14 stations with a spatial resolution of about one degree of latitude from the Drake Passage to the Antarctic Peninsula (56–68°S, Sta. 1–14, Fig. 1). The second transect (April 9 to 12) consisted of 24 stations (Sta. 15–38, Fig. 1). Samples were taken every 45′ of latitude on the Argentine Shelf from the Le Maire Strait (~55°S, Sta. 15) to coastal waters off the southern half of the Buenos Aires State (~38°S, Sta. 38).

2.2. Field and analytical methods

At each station, ~60 L of water were collected from the ship's research pumping system. Aliquots were taken for various determinations of chemical and biological parameters. Mostly 2 L aliquots were filtered on board through GF/F filters (Whatman, precombusted at 450 °C, 3 h). Filtrates were poisoned with $HgCl_2$ and stored at 4 °C in 50 mL PE bottles for later nutrient analyses (Kattner, 1999). Nitrate, nitrite, ammonium (all in µM N), silicate (µM Si) and phosphate (µM P) were determined according to seawater standard methods (Kattner and Becker, 1991). Filters were stored frozen at −20 °C.

Filters for the determination of isotopes, carbon (C) and nitrogen (N) content were dried at 50 °C for 4 h and kept at room temperature in a desiccator until analysis. C and N were quantified with an elemental analyser (Fisons, NA 2100). Standard Reference Material 1515 was used for calibration and as a quality standard. Organic C was determined by removing inorganic C by acidification with 1 N HCl. Particulate organic carbon (POC) and nitrogen (PON) are expressed in µM C and µM N, respectively.

Analysis of stable C and N isotopes was carried out with a Thermo Finnigan Delta Plus mass spectrometer coupled to a Flash EA 1112 elemental analyser. GF/F filters containing POM were put in silver vials, acidified with 0.1 N HCl to remove inorganic carbon, dried 12 h at 50 °C and completely oxidised in the elemental analyser by flash combustion at temperatures above 1000 °C under pure O_2. The isotope composition of N_2 and CO_2 was analysed by mass spectrometry. Samples were analysed in duplicate including an internal standard and a blank every four samples. The amount of isotope for each sample was within the analytical linearity range. The relative standard deviation (as coefficient of variation) between the duplicates never exceeded 3%. Results were normalised to the Pee Dee Belemnite (PDB) (Fry and Sherr, 1984) and atmospheric N_2 standards calculating isotope ratios (R), given as ‰ deviation from the standard value (δ^{13}C and $\delta 1^{5}$N) where:

$$R = {}^{13}\mathrm{C}/{}^{12}\mathrm{C} \text{ or } {}^{15}\mathrm{N}/{}^{14}\mathrm{N}, \text{ and}$$

$$\delta(‰) = ((R_{\mathrm{sample}}/R_{\mathrm{standard}}) - 1) \times 1000$$

The isotope ratios were determined with the international standards from the International Atomic Energy Agency (Vienna): IAEA-N1 and IAEA-N2 were used for ^{15}N, NBS 22 and USGS-24 for ^{13}C, and peptone as internal standard.

For the quantification of pigments, filters were frozen and stored in the dark until analysis. Pigment extraction was performed in 90% acetone during 24 h at 4 °C. Chlorophyll *a*, *b* and *c* and phaeopigments were quantified spectrophotometrically, and concentrations were estimated according to Jeffrey and Humphrey's (1975) equations. Unless otherwise specified, chlorophyll is used throughout the text as the sum of *a*, *b* and *c*.

Surface seawater temperature (°C) and salinity data were made available by cruise participants from the Servicio de Hidrografía Naval (Argentina).

3. Results and discussion

The detailed biogeochemical data along the transect from the Argentine shelf to the Antarctic Peninsula embrace very different hydrographical regions and ecosystems. Data on particulate organic matter (POM) and nutrients were in the wide range found in shelf-influenced regions of Argentine and the Antarctic Peninsula, in oligotrophic oceans as well as in the typical Antarctic waters with high nutrients but low-chlorophyll concentrations. Main features of overall trends and particular regions are discussed with special regard on isotopic variability.

3.1. General synoptic trends

The transect covered a range of water depths from 36 to 4950 m. The surface waters had temperatures between 18.8 °C and −0.7 °C

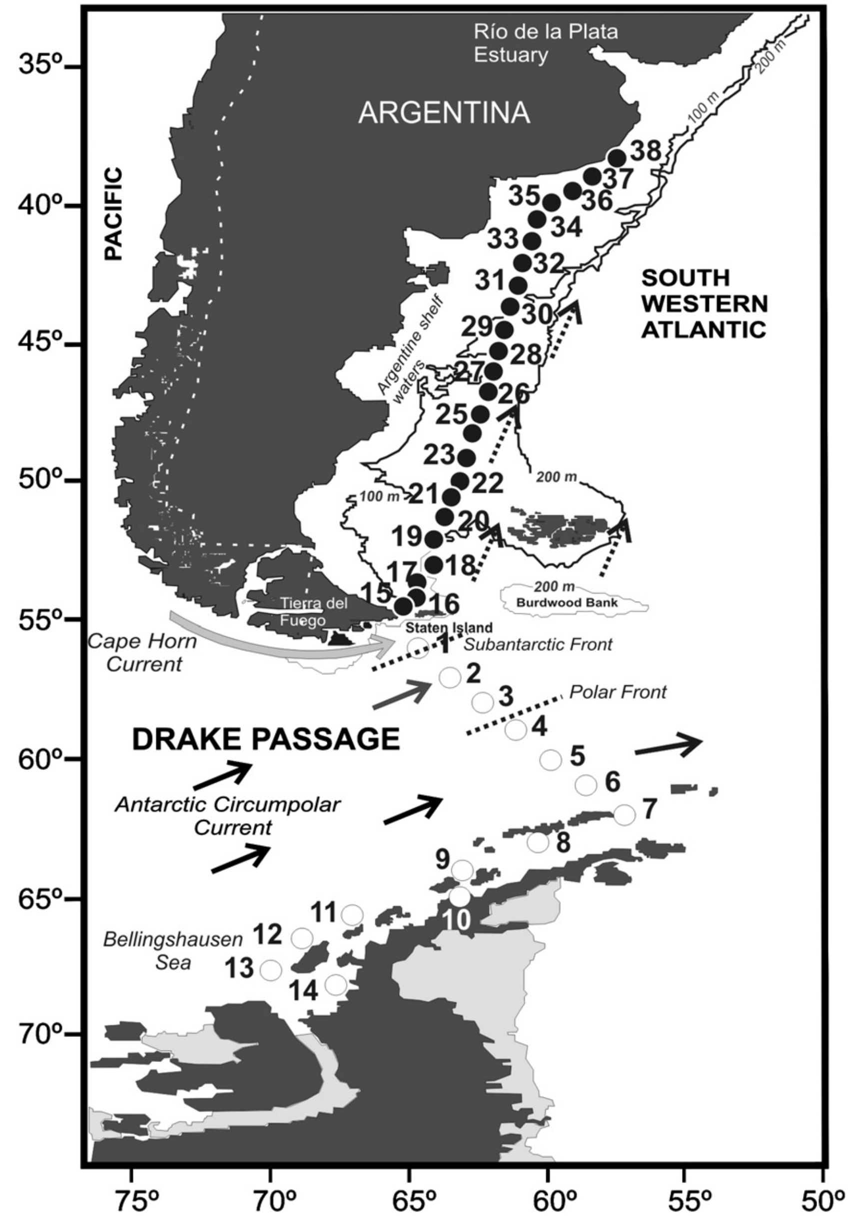

Fig. 1. Location of sampling stations along a transect in the western South Atlantic in the austral autumn 2005.

and salinities ranging 33.90–32.04. Nutrients generally increased with latitude, mostly reaching maximum concentrations south of the Polar Front. An exception was ammonium, which exhibited several peaks of around 1.5 µM N within local trends along the transect.

Chlorophyll values were relatively low and similar to those reported for middle and outer shelf waters during early autumn on the Argentine Shelf (Bianchi et al., 2005; Rivas, 2006) and waters north and west of the Antarctic Peninsula (Meguro et al., 2004).

POC and PON correlated significantly ($r = 0.91$, $n = 38$, $p < 0.001$) (Fig. 2a), and C:N ratios ranged 4.5–8.8. The slope of the regression line was 5.8 and C:N averaged 6.5 ± 1.1. Both values are close to the Redfield value of 6.6 and to that of cells growing at a high rate (Laws et al., 2001), suggesting a generally still active autumn phytoplankton population along most of the transect, excepting probably the northern shallow waters of the Argentine shelf sector (see Southern Buenos Aires and North Patagonian Shelf (BNPA) data subgroup in Fig. 2a and below).

In general there was a predominance of isotopically lighter POM with decreasing surface seawater temperature (SST) along with increasing latitude and increasing nutrient concentrations, however, with highly variable plankton biomass (Fig. 3) down the Argentine shelf to the Drake Passage and Antarctic Peninsula.

Along the transect POM tended to be isotopically heavier with increasing phytoplankton biomass proxies such as POC, PON or chlorophyll (Fig. 2c–f). The isotopically heaviest POM was found in the northern sector together with the highest C:N values (range ~8–9, Fig. 2b, BNPA data subset). In general, the correlation between δ^{13}C and C:N ratio was low, however, statistically highly significant ($r = 0.52$, $p < 0.001$, Fig. 2b). δ^{15}N did not significantly correlate with C:N ratios, but the stations with the highest C:N values corresponded to the uppermost δ^{15}N range, which is consistent with the regenerative character of this region, as discussed below in Section 3.2.1. At the stations on the west side of the Antarctic Peninsula (APE, encircled points in Fig. 2c–f) data were different to the general enrichment in the heavier carbon isotope with increasing biomass. These stations had chlorophyll, POC and PON values in the mid to upper range of the other group, but were isotopically much lighter.

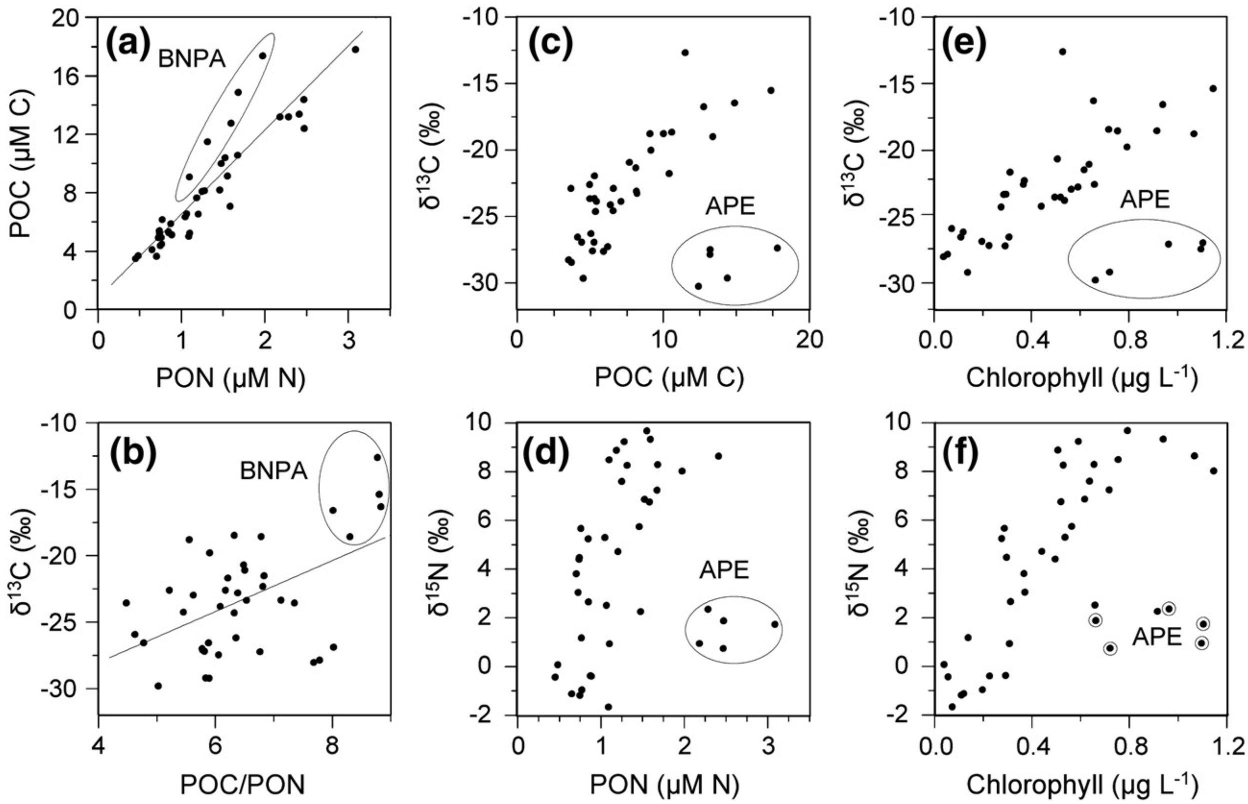

Fig. 2. (a) Regression of all POC data against PON, and (b) between δ^{13}C and the C:N ratio of particulate matter (POC/PON quotient in atoms). Encircled points in (a) and (b) correspond to stations of the Southern Buenos Aires and North Patagonian Shelf (BNPA) sector. Relationship between stable isotopes in suspended particulate organic matter and: (c) particulate organic carbon (POC), (d) particulate organic nitrogen (PON), (e) and (f) chlorophyll. Encircled (APE) points: data from the SW side of the Antarctic Peninsula.

3.2. Individual sectors

3.2.1. Southern Buenos Aires and North Patagonian Shelf (BNPA)

This region extends along the transect from 38° to 43°S (Sta. 38 to 31) with a depth range of 36–75 m and covers mainly waters of the middle shelf (Figs. 1 and 3). The surface waters were characterized by temperatures ranging 18.8 °C–14.5 °C and salinities from 33.70 to 33.30, on average 16.5 °C and 33.45, respectively. Nutrient concentrations were low (silicate <0.25 µM, nitrate mostly <1 µM), with a high contribution of ammonium to dissolved inorganic nitrogen (DIN), ranging from 14 to 70%, on average 47 ± 20%. In this temperate region, nitrogen is the limiting factor for primary production (Carreto et al., 1981; Carreto, 2001), which is mainly based on nutrient regeneration (Carreto et al., 1995). The phytoplankton community is dominated by neritic/cosmopolitan species with preference for warm waters, and the diatom density is low (Olguín and Alder, 2004).

POC and chlorophyll were relatively high (Fig. 3c) compared to the other regions along the transect, but nevertheless correspond to the lowest concentrations reported for this area in summer (February and March; Romero et al., 2006).

In accordance with the regenerative characteristic of this sector, high C:N ratios (mean of 8.5, Fig. 2a and b) suggest a considerable fraction of detritus or recycled components in the POM, which may be in part responsible for the isotopically heavy POM.

δ^{13}C and POC matched well in this sector (Fig. 3a and c), where δ^{13}C strongly varied from −12.5 to −22‰, on average −17.56 ± 2.77‰. This large range of δ^{13}C may be related to phytoplankton metabolism and changes in species composition as adaptation to the low nutrient concentrations as well as variable amounts of detrital material.

δ^{15}N averaged 8.54 ± 0.68‰ and reached the maximum value of 9.68‰ at Sta. 34, in a sector characterized by the highest values of the entire transect, extending into South Patagonian waters (Fig. 3a). The N isotopic signature is probably the result of a combination of different sources of N supporting primary production: on the one hand the low-nitrate concentration would result in a pool of nitrate enriched in the heavier isotope and on the other hand ammonium excreted by consumers would be isotopically lighter (Altabet, 1996).

3.2.2. South Patagonian Shelf (SPA)

This sector extends from 44° to 54°S (Sta. 30 to 15) with depths between 100 and 200 m, temperatures ranging 13.9 °C–7.8 °C and salinities from 33.53 to 32.04, on average 10.5 °C and 33.25, respectively. Salinity at Sta. 15 reached its lowest value in Subantarctic waters and along the transect, reflecting the effect of the Cold Estuarine System.

Nitrate and silicate concentrations increased from North to South (Fig. 3d). This increase represents a transition related to the splitting of the 100 and 200 m isobaths and is most likely associated with the influence of the nutrient-richer, productive waters of the Malvinas Current (Guerrero and Piola, 1997). Accordingly, diatoms are dominated by species typical for cold waters in this sector extending to 57ºS near the Polar Front (Olguín and Alder, 2004).

POC shows an overall decline along this sector while chlorophyll oscillates between roughly 0.5 and 1.5 µg L^{-1} in a jigsaw pattern likely related to front-related patchiness typical for this sector (Acha et al., 2004). The constant and smooth decrease of δ^{13}C between Sta. 30 and 25 approximately followed POC. The chlorophyll maximum at Sta. 25 was not reflected in abrupt variations of δ^{13}C, δ^{15}N or POC, while the increase in chlorophyll from Sta. 23 to 20 was accompanied by a continuous decrease in δ^{15}N from 5.67 to 2.51‰ at constantly low POC values and almost invariant δ^{13}C. Thus, although a phytoplankton composition shift may be partly responsible for the local δ^{15}N decrease, the changes above mentioned occurred at increasing nitrate values, which can be accompanied by variations in the isotopic signature of inorganic nitrogen. Hence, these changes in δ^{15}N of POM

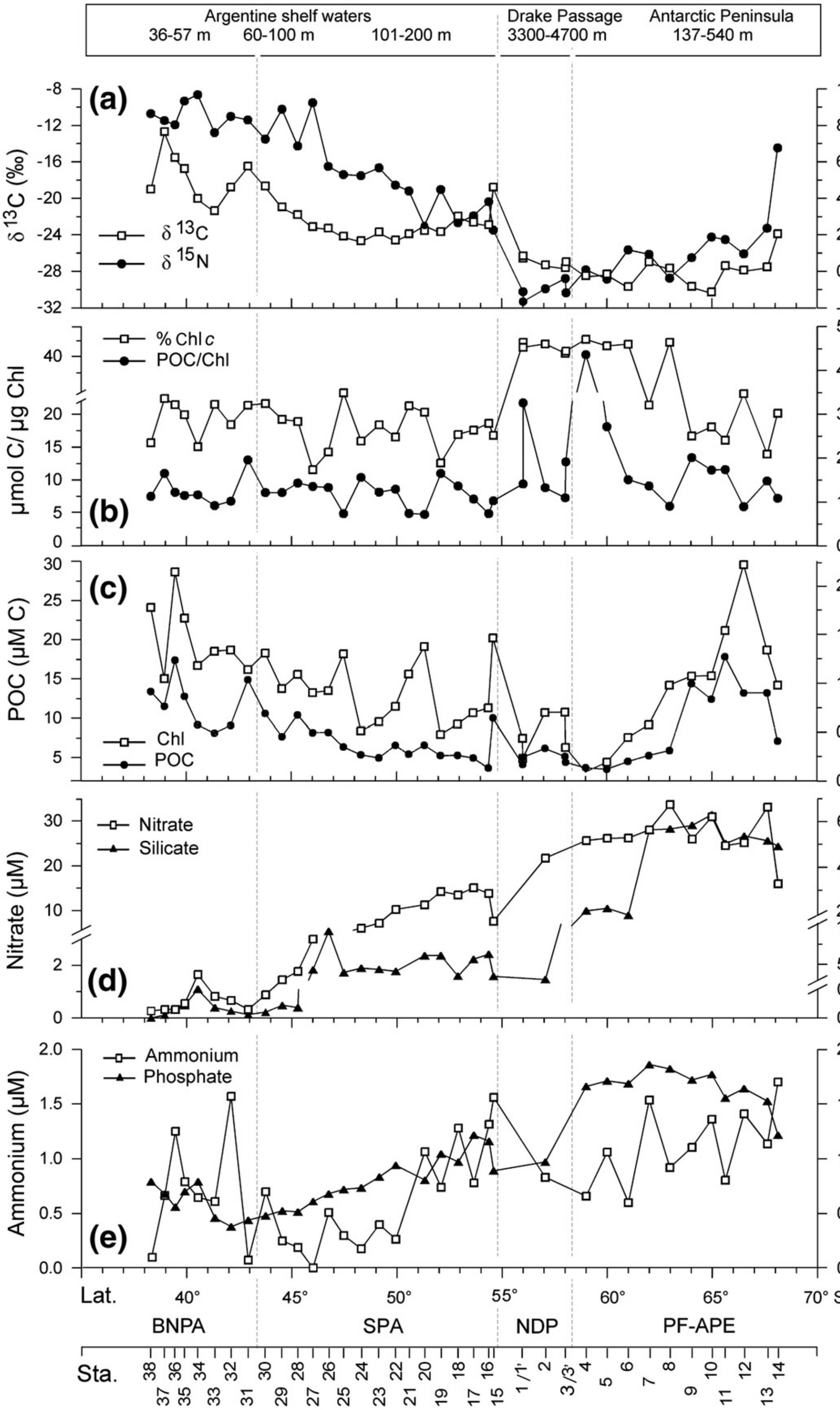

Fig. 3. Latitudinal parameters along a transect covering the sectors: Southern Buenos Aires and North Patagonian Shelf (BNPA), South Patagonian Shelf (SPA), Northern Drake Passage (NDP), Polar Front to Antarctic Peninsula (PF-APE); including range of water depths. Abbreviations: Chl: sum of chlorophyll *a*, *b* and *c*. %Chl *c*: percentage contribution of chlorophyll *c* to total Chl. POC: particulate organic carbon.

could reflect biological fractionation and/or isotopic differences in DIN supply (Sigman et al. 2000). From Sta. 20 to 19 the increase in δ^{15}N from 2.4 to 4.4‰ occurred together with a sharp decrease in chlorophyll, likely due to increased grazing at a frontal zone. From Sta. 19 to 16, chlorophyll gradually increased while POC decreased with an increase of %Chl *c* and a decrease of the POC/Chl ratio. This suggests an increased proportion of autotrophic biomass relative to the heterotrophic plankton species (Hoffmann et al., 2006), however, there was not any major isotopic signal at these stations.

Despite the heterogeneity associated to front situations (Acha et al., 2004) in this region, δ^{13}C generally varied very smoothly and, in contrast to δ^{15}N, did not seem to be significantly affected by front-dependent oscillations of phytoplankton biomass. In the Patagonian shelf waters the highest surface chlorophyll values are associated with a strong depletion of pCO_2 (Bianchi et al., 2005). This should be reflected in isotopically heavier organic matter, but is not obvious in our data set. Concerning the general decreasing trend of δ^{15}N in this sector, it is worth mentioning that besides increasing nitrate also a general increase of ammonium took place from Sta. 24 to 15. Regarding the origin and effect of the ammonium peak at Sta. 16/15, it may be possible that the apparently more steeply declining δ^{15}N values in the southern part of this transect are partly related to an input of isotopically light ammonium by rainfall (Paerl and Fogel, 1994) in the SE Pacific (Acha et al., 2004); thus, this ammonium may be taken up by phytoplankton. Thus, both an increasing Raleigh substrate fractionation with increasing nitrate (Mariotti et al., 1981), together with isotopically light ammonium may have contributed to the enhanced δ^{15}N decrease in POM in this region.

Sta. 15, the last one of this sector, is close to the Le Maire Strait and is partly influenced by the relatively nutrient-poor Cold Estuarine System through the Cape Horn Current (Fig. 1). Here we found an increase of δ^{13}C (−18.76‰ at nitrate 7.6 μM N) and the beginning of a steep decrease in δ^{15}N, together with a simultaneous decrease of all nutrient concentrations except ammonium, accompanied by a chlorophyll peak and the lowest salinity of the transect.

3.2.3. Northern Drake Passage (NDP)

This part of the transect is basically delimited by the Subantarctic Front and the Polar Front and extends from 54.4 to 58°S (Sta. 1, 1′, 2, 3, 3′) with depths between 3000 and 5000 m, temperatures ranging 5.6 °C–4.3 °C and salinities from 33.87 to 33.63, on average 5.1 °C and 33.77, respectively.

Nutrients showed transition values intermediate between the lower Atlantic and high Antarctic concentrations, which was accompanied by decreased POC and total chlorophyll as well as by an abrupt increase in the contribution of chlorophyll *c* to total chlorophyll (% Chl *c*, Fig. 3b).

Both isotopes decreased sharply. δ^{15}N varied between 0.08 and −1.66‰, the latter being the minimum value of the entire transect (Fig. 3a), and δ^{13}C diminished from −18.76 to −26.29‰ (mean of -26.93 ± 0.61‰). The extremely low δ^{15}N values may result from phytoplankton uptake of isotopically light ammonium. Checkley and Miller (1989) found that the decrease of ^{15}N in suspended POM can be due to the excretion of isotopically light N by zooplankton and other pelagic heterotrophs, which is in turn assimilated by phytoplankton. Oceanic zooplankton excretes ammonium that is isotopically light not only relative to their bodies' nitrogen but also to subeutrophic nitrate. Although the contribution of ammonium to DIN and to its average δ^{15}N might be low, Rönner et al. (1983) found in the Scotia Sea that even at high-nitrate concentrations, primary production in the austral summer subsisted predominantly on ammonium. They further indicated that there is a rapid and intensive mineralization of organic matter in surface waters resulting in high recycling of N (8 times) before it is lost from the euphotic zone. Thus, phytoplankton could be enriched in isotopically light nitrogen despite relatively low concentrations of its inorganic source, in this case ammonium. Lourey et al. (2004) reported δ^{15}N values from ~0 to ~−4‰ near the Polar Front in summer, in relation to the production of low ^{15}N-POM by summertime ammonium uptake. In principle, the low δ^{15}N values might be also associated to biological fixation of atmospheric N_2. However, this is unlikely since the density of cyanobacteria was constantly low (Franzosi, unpublished data from this expedition), as it generally is in the whole Drake Passage and in the Southern Ocean (Alder and Franzosi, 2004, 2005).

3.2.4. Polar Front to Antarctic Peninsula (PF-APE)

This part of the transect includes the southern Drake Passage with depths of ~3500 m (Sta. 4–6) and the track along the Antarctic Peninsula with depths of 150–750 m (Sta. 7–14). Temperatures ranged from 2.9 °C to −0.7 °C and salinities from 33.90 to 32.34 (Sta. 14), on average 0.7 °C and 33.45, respectively.

Silicate and nitrate greatly increased, as typical for Antarctic waters. Near the Polar Front (~59°S), chlorophyll reached the lowest values of the whole transect (Sta. 4) with a large increase in the contribution of chlorophyll *c* to total chlorophyll (%Chl *c*, Fig. 3b) extending to about 63°S (Sta. 7–8). Southwards chlorophyll increased again together with higher ammonium values. Around 66°S (Sta. 11 and 12) maximum chlorophyll values with a decrease in %Chl *c* were found.

The outstanding feature of this sector was an inflexion in the δ^{15}N trend. δ^{15}N tended to increase with nitrate concentration (Fig. 3a and d), what is in contrast to the Subantarctic waters off Patagonia and the northern part of the Drake Passage. The change in the δ^{15}N response to nitrate could partly depend on a higher proportion of highly silicified phytoplankton in the frontal zone (Quéguiner and Brzezinski, 2002), since silicate increased steeply, whereas nitrate continued its smooth increase.

The δ^{15}N values ranged from −1.12 to 6.76‰ and δ^{13}C from −30.62 to −23.87‰ (mean of -27.81 ± 1.62‰). At the end of the transect (Sta. 14) δ^{15}N strongly increased, accompanied by a low C:N value of 4.5. This is in agreement with the high microplankton density found in Margarite Bay, one of the most productive areas of the Southern Ocean (Alder, 1995). δ^{13}C showed a sharp increase from −27.5 to −23.4‰, the isotopically heaviest POM of the Antarctic stations. This may be related to the presence of high amounts and dominance of nanoflagellates typical for the Bellingshausen Sea (Mura et al., 1995). Except for this station, δ^{13}C values were much lower than in the Buenos Aires-North Patagonia and South Patagonia sectors.

3.3. Main driving forces of δ^{13}C variability

A highly significant positive correlation was found between SST and δ^{13}C in POM along the entire transect ($r = 0.86$, $n = 38$, $p < 0.001$, Fig. 4a, regression equation in Table 1). Temperature has a significant effect on isotopic fractionation by marine phytoplankton due to its influence on pCO_2 in water (e.g. Lourey et al., 2004 and references therein). Within this context, the data from our transect show a trend in accordance with results of Fontugne and Duplessy (1981). The δ^{13}C data were grouped in clusters corresponding to well-defined water masses or ecosystems (see also Carreto et al., 1981). Although all data show a significant correlation with SST, they were not necessarily correlated within individual systems that can extend over about ten degrees of latitude. Within the BNPA and SPA clusters, no obvious relationship between δ^{13}C and SST was observed (Fig. 4a). However, further South the data from the Drake Passage and Antarctic waters showed a clearer trend towards more negative δ^{13}C values with decreasing SST and most likely increasing $CO_{2(aq)}$.

Similar correlations between δ^{13}C in POM, latitude (Rau et al., 1982) and SST have been reported by several authors, notably by Fontugne and Duplessy (1981), Rau et al. (1991) and Dehairs et al. (1997) (Table 1). The regressions lines of δ^{13}C vs SST from the last two publications are quite similar to ours (Table 1, Fig. 4a), although our

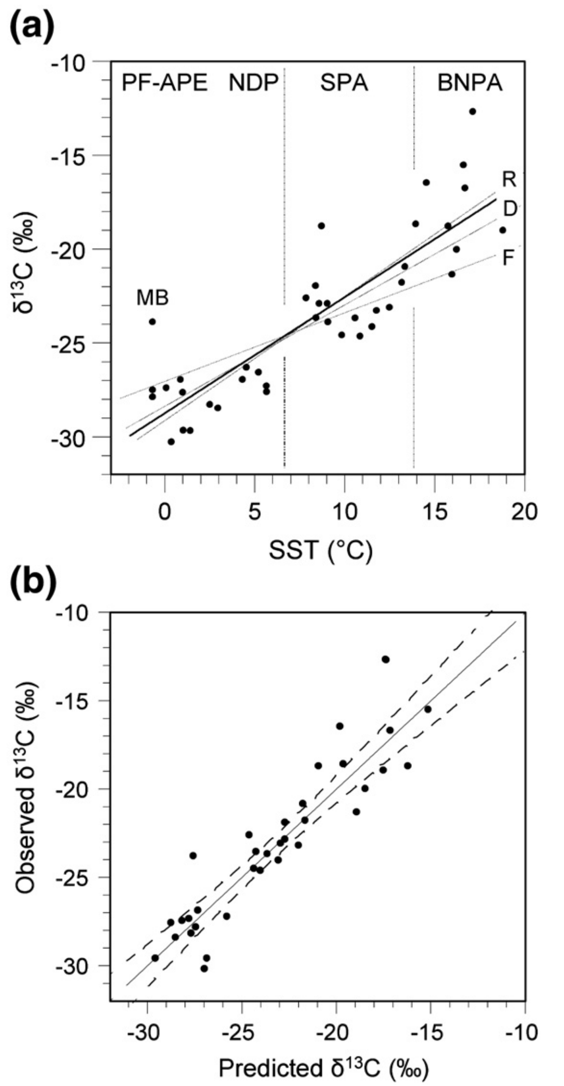

Fig. 4. Relationship of measured $\delta^{13}C$ in suspended particulate organic matter vs. (a) sea surface temperature (SST) in a simple regression and, (b) vs. predicted $\delta^{13}C$ values from a multiple with SST, particulate organic carbon and ammonium as independent variables in. The regression lines in (a) correspond to data from F: Fontugne and Duplessy (1981), R: Rau et al. (1991), D: Dehairs et al. (1997) and full line: this work.

data cover several different ecosystems over 30° of latitude. Despite differences in the four equations, all predict a $\delta^{13}C$ around -24.8 ± 0.11 at a temperature of 6.5 °C, corresponding to a latitude of ~55°S in the Subantarctic frontal zone. This value is in the region of the sharp $\delta^{13}C$ decrease in the northern Drake Passage (this work), as also reported by Rau et al. (1991), who found a 7‰ gradient south of 53.3°S.

Compared to the overall relationship with SST, some $\delta^{13}C$ values in the BNPA were substantially higher, which may be due to several

Table 1
Relationship between $\delta^{13}C$ of surface particulate organic matter and sea surface temperature (SST) from various authors compared with this work.

Regression equations	Region	Reference
$\delta^{13}C=0.35$ SST -27.00	North Atlantic and Indian Ocean	Fontugne and Duplessy (1981)
$\delta^{13}C=0.62$ SST -29.13	Drake Passage	Rau et al. (1991)
$\delta^{13}C=0.52$ SST -28.32	Tasmania to Prydz Bay, Antarctica	Dehairs et al. (1997)
$\delta^{13}C=0.62$ SST -28.73	SW Atlantic and Southern Ocean	This work

reasons. POM at these stations had the highest phaeopigment (not shown) and highest C:N values of the whole transect. This suggests a decaying phytoplankton population and a relative high abundance of detritus in POM, from which N-components are preferentially released and/or mineralized (Lee, 1988). In accordance with this pattern, the contribution of ammonium to DIN was high. When N limitation is relieved by the addition of ammonium, the activity of the enzymes important for the intermittent assimilation of ammonium (phosphoenolpyruvate carboxylase (PEPC) and carboxykinase, PEPCK) is stimulated, what results in less isotopic discrimination and more positive $\delta^{13}C$ values (McCarthy and Goldman, 1979; Guy et al., 1989). Descolas-Gros and Fortugne (1985) measured Rubisco, PEPCK and PEPC activity together with $\delta^{13}C$ values in several diatom and one dinoflagellate species. They found that low $\delta^{13}C$ values were related to high Rubisco activity and high $\delta^{13}C$ values in the algae that were related to high PEPCK and PEPC activities. Further, Descolas-Gros and Oriol (1992) found that diatoms contain only PEPCK, while dinoflagellates contain both PEPC and PEPCK. Therefore, since the silicate-poor northern region of the transect is dominated by dinoflagellates, $\delta^{13}C$ values could be higher than expected by an isotopic fractionation exclusively related to SST and/or $[CO_{2(aq)}]$. Thus, a temperate environmental setting based on regeneration, with relatively high ammonium and abundant dinoflagellates, would favour the production of isotopically heavier POM.

Besides the dependence of $\delta^{13}C$ on temperature and $[CO_{2(aq)}]$, an influence of nutrients on isotopic fractionation is also likely, as discussed above for ammonium. Nevertheless, the general co-variation between $\delta^{13}C$ and nutrients observed along the entire transect (Fig. 3a, d and e) could also be the result of the overall increase in nutrient concentration with decreasing temperatures towards the Antarctic waters. This is reflected by the highly significant correlations ($r>0.90$, $n=35$, $p<0.001$) between temperature and nitrate or phosphate (Figs. 5a and b).

Aside of the cross-correlation between nutrients and temperature, effects of nutrients on the isotopic signatures may be more related to substrate utilization. The tightest correlation between $\delta^{13}C$ and nutrients was observed for nitrate ($r=-0.85$, $n=35$, $p<0.001$ for a linear regression (not shown) and $r=0.89$, $n=35$, $p<0.001$ with ln [nitrate], Fig. 5c). Besides the moderately improved fit, the non-linear approach describes more realistically the relationship between both variables than a linear regression, particularly at low to very low-nitrate concentrations. This reflects a stronger decrease in $\delta^{13}C$ with increasing nitrate at low concentrations, which is less pronounced at higher nitrate values. In the range of nitrate concentrations from 0.3 to 6 µM, $\delta^{13}C$ decreased sharply and consistently from -12.67 to -24.6‰. This decrease took place in the SST range from 18.8–10.8 °C and at silicate concentrations <5 µM (Figs. 4a and 6a, respectively). It is described more sensitively by nitrate than by silicate or SST at such low nutrient concentrations and relatively high water temperatures. At nitrate concentrations between 10 and 15 µM, $\delta^{13}C$ varied around 23.5‰, and at nitrate >20 µM $\delta^{13}C$ averaged ~27.5‰. However, the correlation with nitrate is most likely a sign of the effect of ammonium on $\delta^{13}C$ in a low-nitrate, regenerative setting as mentioned above (see also the best-fit multiple regression including ammonium discussed below).

$\delta^{13}C$ correlated also highly significantly with phosphate ($r=-0.81$, $n=35$, $p<0.001$, Fig. 5d). Bidigare et al. (1997) reported that the correlation between algal carbon isotope fractionation and phosphorus may indirectly reflect primary production limitation by co-depletion of iron and other trace metals. While this cannot be excluded, the correlation between $\delta^{13}C$ and phosphate in our data set might only reflect the co-variation of phosphate and nitrate ($r=0.95$, $n=35$, $p<0.001$, not shown) and of nitrate and $\delta^{13}C$.

The correlation between $\delta^{13}C$ and silicate was also highly significantly ($r=-0.70$, $n=35$, $p<0.001$, Fig. 6a). Even though this correlation is lower as with nitrate and phosphate, it points to a

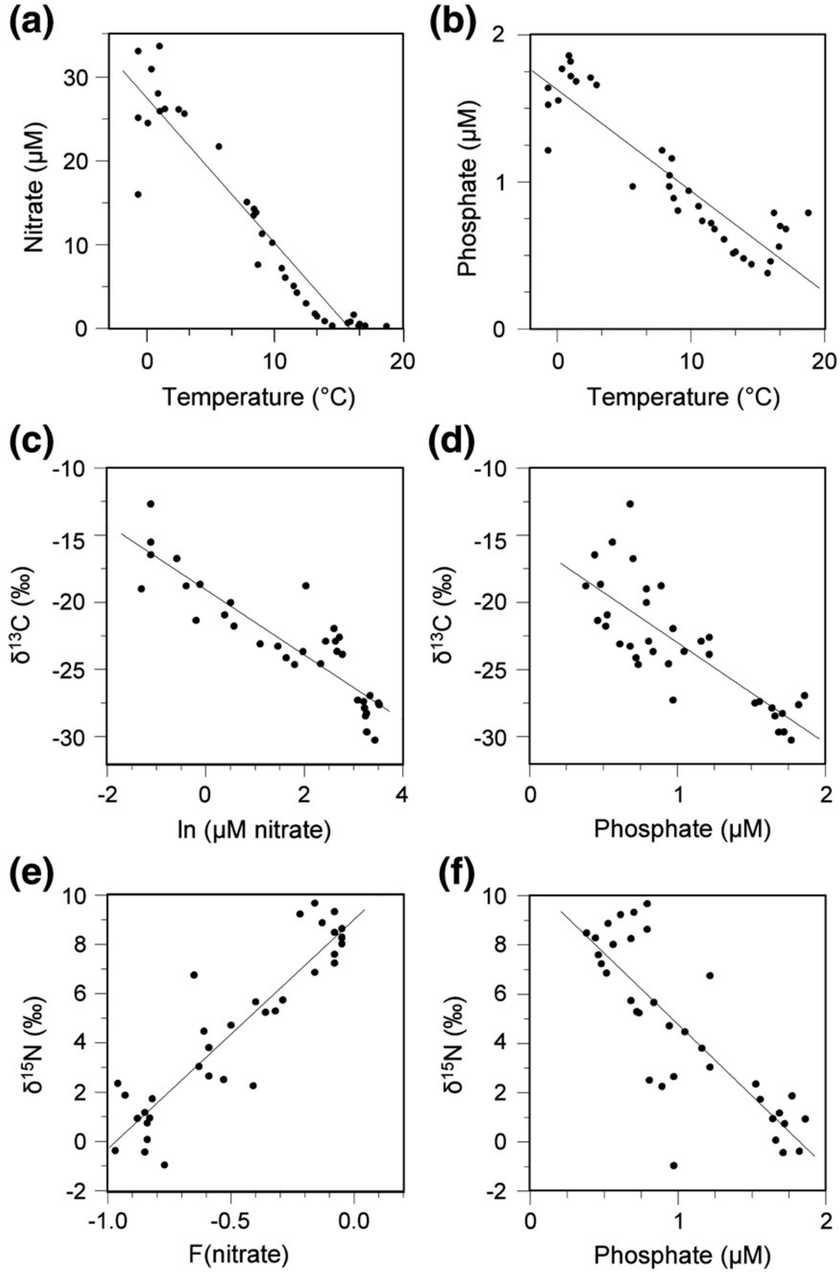

Fig. 5. Linear regression of (a) nitrate and (b) phosphate concentrations in surface seawater vs. water temperature, (c) δ^{13}C vs. the natural logarithm of the nitrate concentration, (d) δ^{13}C vs phosphate concentration, (e) δ^{15}N vs $F = f \ln f/(1-f)$, where $f = [NO_3^-]_{observed}/[NO_3^-]_{initial}$ and $[NO_3^-]_{initial} = 36$ μM N, as originated from the Upper Circumpolar Deep Water, and (f) δ^{15}N vs phosphate concentration.

further link between patterns of phytoplankton distribution and δ^{13}C in POM. In the northern sector, until ~46°S, silicate values of <0.25 μM (mean of 0.08 μM) were accompanied by average δ^{13}C of -18.35 ± 2.8‰. Off South Patagonia up to the southern shelf limit at 54°S, silicate ranged from 3 to 10 μM (mean 5.2 μM), and δ^{13}C averaged -23.07 ± 1.6‰. Further south and in Antarctic waters, silicate increased to 20–60 μM (mean 45.6 μM), and average δ^{13}C further decreased to -27.70 ± 1.7 ‰. Thus, the largest isotopic fractionation gradient was associated with the change in silicate from about 0.1 to 5 μM, probably related to an increase in siliceous phytoplankton. Nelson and Tréguer (1992) reported that silicate concentrations <2.5 μM can limit growth of most diatoms, indicating that silicate availability likely limits diatom productivity in the vicinity of the Polar Front. The low-silicate:nitrate (Si:N) ratio of <0.25 at all stations north of ~46°S further indicates silicate limitation for diatom growth (Gilpin et al., 2004). Therefore, the strong changes in δ^{13}C in the northern sector of the Argentine shelf can be also partly related to the Si:N ratio influencing phytoplankton assemblage composition. An exponential decay relationship between δ^{13}C and Si:N ($r = 0.75$; Fig. 6b) suggests that Si:N ratios >1 do not produce further major decreases in δ^{13}C and that the influence of temperature becomes more obvious, as discussed before. Hutchins and Bruland (1998) examined field data and found that in all three Fe-limited oceanic HNLC regimes, the Si:N ratio of freshly upwelled water is close to or >1, but this ratio drops as water advects away from the upwelling centre. Although most of our Subantarctic stations were situated on shelf and not in oceanic regions, this observation seems to hold also for our data (Fig. 6c), where the main nutrient source is located at higher latitudes and likely influences the isotopic composition of POM northwards.

The main trends of our δ^{13}C data were summarized in regression models following Dehairs et al. (1997). We applied multiple regressions

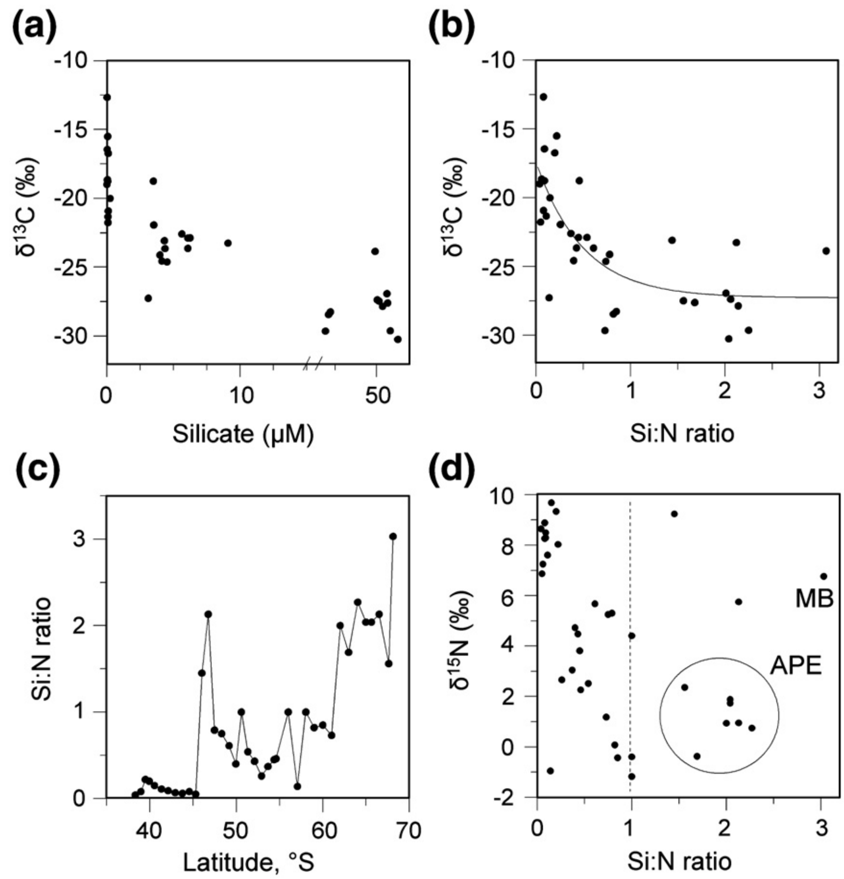

Fig. 6. Relationships between $\delta^{13}C$ and (a) silicate concentration and, (b) the silicate to nitrate ratio (Si:N). (c) Latitudinal variation of the Si:N ratio. (d) Relationship between $\delta^{15}N$ and Si:N ratio. Antarctic Peninsula (APE), Margarite Bay (MB).

of $\delta^{13}C$ relative to temperature, nutrients and biomass indicators. The most relevant examples are summarized in Table 2, including the minimum amount of parameters that had proofed influence on POM-$\delta^{13}C$; did not cross-correlate, and explained the highest amount of $\delta^{13}C$ variance. As expected, temperature alone explained most of the variance in the multiple regressions due to its influence on $[CO_{2(aq)}]$ (Dehairs et al., 1997). The combination with the best-fit and more realistic distribution of predicted values (Fig. 4b) was obtained with temperature, POC and ammonium as independent variables, as discussed in detail below.

For the observed direct proportionality between $\delta^{13}C$ with POM, POC produced a slightly better fit than chlorophyll or any combination of the different pigments, including phaeopigments. Ammonium contributed to a better explanation of the high $\delta^{13}C$ data at nitrate-poor higher latitudes; the values $>-18‰$ are more symmetrically distributed around the regression curve than with SST alone. Interestingly, an improved fit was not only obtained in the low-nitrate, regenerative BNPA region but also in SPA, where 77% of the nitrate values were >2 μM. In SPA, where $\delta^{13}C$ had a wide range of variation from $-18‰$ to $-25‰$, the percentage of $\delta^{13}C$ data points within the 0.95 confidence interval increased from 25% vs SST alone to 30% vs SST and POC, to a maximum of 55% after including ammonium as third independent variable. Although not entirely understood, there is evidence that natural phytoplankton can react to ammonium spiking with reduced discrimination against ^{13}C during the carboxylation process. This is even possible in nitrate-rich Antarctic waters dominated by diatoms (Dehairs et al., 1997). It is not clear to what extent such a process can apply to our data set, but calls attention on the potential relevance of ammonium fluctuations for explaining $\delta^{13}C$ variability in general and not only in nutrient-poor, regenerative systems.

Since in the relationship of $\delta^{13}C$ vs biomass indicators the data from SW Antarctic Peninsula build a separate group, the regressions were run with and without this data subset. Although the best correlation was obtained without SW Antarctic Peninsula data ($r=0.93$ for $n=30$), there were basically no substantial differences between the fit for both data sets ($r=0.92$ for all data, $n=35$, Fig. 4b), which supports the quality of the selected parameters as predictors of $\delta^{13}C$.

Table 2
Correlation coefficients from simple and multiple regressions of $\delta^{13}C$ vs sea surface temperature (SST), particulate organic carbon (POC) and ammonium (NH_4^+).

Independent variables	r ($n=35$) all data	r ($n=30$) without Sta. 9–13 from SW Antarctica
SST	0.86	0.84
SST, POC	0.88	0.90
SST, NH_4^+	0.90	0.89
SST, POC, NH_4^+	0.92	0.93

3.4. Main driving forces of $\delta^{15}N$ variability

A highly significant positive correlation was found between $\delta^{15}N$ and SST ($r=0.81$, $n=38$, $p<0.001$) along the entire transect. $\delta^{15}N$ correlated inversely with phosphate ($r=-0.82$, Fig. 5f), showing higher dispersion than $\delta^{13}C$ (Fig. 5d) and with nitrate ($r=-0.88$, $p<0.001$ for a linear regression, not shown). These relationships are probably mostly the result of the general increase in nutrient concentrations with decreasing temperatures (Fig. 5a and b) and of the highly significant correlation between nitrate and phosphate.

The correlation between δ^{15}N and nitrate has probably the only major functional reason. This is also reported by Altabet and Francois (1994) for large horizontal gradients in surface nutrient concentrations, as across the Polar Front of the Southern Ocean. These authors note that this relation is not a function of nitrate concentration but of the fraction of unutilized substrate ($f = [NO_3^-]_{observed}/[NO_3^-]_{initial}$). The δ^{15}N of produced PON has been assumed to be proportional to $F = f \ln f/(1-f)$ (Needoba et al., 2003), which is based on the Raleigh fractionation equation for the substrate pool (Mariotti et al., 1981). Therefore we reprocessed our δ^{15}N and nitrate data using an estimate of f for the study region. Following Sigman et al. (2000), we adopted a $[NO_3^-]_{initial}$ value of 36 µM, considering the Upper Circumpolar Deep Water as the ultimate nitrate source for much of the Southern Ocean surface. The regression obtained between δ^{15}N and F was highly significant (δ^{15}N-PON = 9.02 + 9.32 F, $r = -0.91$, $p < 0.001$, Fig. 5e). Although being only moderately better, this regression fits probably more meaningfully to our data on a regional basis than if directly based on nitrate concentration. Despite the high correlation between both parameters we did not attempt to derive the overall fractionation factor (ε) from the equation regression, due to the diversity of our sampled regions. This diversity is probably responsible for the "clustered" patterns of data spreading around the regression line (Fig. 5e; see also discussion below on δ^{15}N and Si:N ratios below).

The relationship between δ^{15}N and Si:N follows a partly different trend than for δ^{13}C. For Si:N < 1, the overall trend is also towards isotopically heavier POM with decreasing Si:N ratios (Fig. 6d). However, instead of an asymptotic trend for Si:N > 1 as for δ^{13}C, there is clear separation of δ^{15}N data for most samples from SW of the Antarctic Peninsula (encircled APE data points), and Sta. 14 from Margarite Bay is even more separated. This seems to be related to a different response of both isotopes to increasing nitrate concentrations south of the Subantarctic Front. While δ^{13}C varies only moderately, δ^{15}N inverts its decreasing trend towards higher values, probably due to the changes in phytoplankton composition as discussed before.

4. Summary and conclusions

Most parameters denote clear differences between Subantarctic and Antarctic waters, as well as between the oceanic and shelf environments within the Subantarctic waters. The correlation between δ^{13}C of POM and SST was highly significant along the transect but less obvious within the individual Subantarctic shelf ecosystems, where variations were frequently related to changes in plankton and nutrients. The strong δ^{13}C gradient of about 12‰ between POM from the northern and southern Patagonia shelf regions was associated to the change from low to moderate silicate concentrations, an increase of Si:N ratios to > 0.25, and an increase of siliceous phytoplankton species. Further south, Si:N ratios > 1 did not seem to affect significantly δ^{13}C, and the influence of temperature became more evident. Regarding the overall trend, the strong correlation between δ^{13}C and nutrients is possibly due to their tight inverse co-variation with SST, except of ammonium. The multiple regression model including SST, ammonium and POC explained 83% of δ^{13}C variance. The improvement of the fit by ammonium was not restricted to the nutrient-poor, regenerative system in the northernmost shallow sector but comprised most of the Subantarctic shelf and may be also relevant for Antarctic waters.

δ^{15}N showed an strong inverse relationship with a non-linear transformation of the estimated fraction of unutilized nitrate, most likely due to isotopic enrichment in the nitrate pool by autotrophic uptake. Especially the very low δ^{15}N values of POM in the transition between shelf and oceanic Subantarctic waters, together with δ^{13}C around −27‰, build a clearly distinct pattern in the western South Atlantic. Thus, composition changes in sedimentary POM of the northern Drake Passage can be potentially useful indicators of past shifts of the Brazil and Cape Horn currents and of oscillations in the Antarctic Circumpolar Wave. An open question remains the origin of that signature. In this regard, the determination of δ^{15}N in dissolved inorganic nitrogen could help ascertain and track ammonium input from rainfall and runoff from Chilean waters through the Cape Horn current into the Southwest Atlantic. Thus, signals from ENSO-derived climatic oscillations in the Southeast Pacific and teleconnection lags could be monitored by biogeochemical indicators in surface Subantarctic Atlantic waters shortly after their occurrence.

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