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# Changes in the source of nutrients associated with oceanographic dynamics offshore southern Chile (41°S) over the last 25,000 years



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#### ABSTRACT

In order to obtain a better knowledge of past oceanographic variability offshore southern Chile, this study reappraises the changes in the sources of nutrients over the last 25 ka based on a detailed comparison of previously published nitrogen isotope and microfossil records (dinoflagellate cysts, coccoliths and diatoms) from ODP Site 1233 (41°S). Our findings support the main conclusions of Martinez et al. (2006) in the sense that both the Subantarctic Surface Water and the Gunther Undercurrent are potential sources for the recorded late Quaternary sedimentary  $\delta^{15}$ N signatures at Site 1233, with variable contributions of both sources during different time periods. This study indicates that Subantarctic Surface Water forms the main source for nutrients during the last glacial maximum (25–18.6 cal ka BP), the first part of the deglaciation (18.6–15.7 cal ka BP) and the Holocene (9.8 cal ka BP until present). An increased contribution of Equatorial Subsurface Water as a source of nutrients to the photic zone offshore southern Chile is observed between 14.4 and 9.8 cal ka BP, which is indicative for upwelling conditions at least after 13.2 cal ka BP as indicated by the microfossil data.

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#### Introduction

Nitrogen (N), and mainly nitrate, is one of the main elements regulating marine biological productivity variations in nutrient limited environments such as the low- and mid-latitude oceans (e.g., Hebbeln et al., 2000, 2002; Mohtadi and Hebbeln, 2004; Sarmiento et al., 2004; Pisias et al., 2006: Romero et al., 2006: Mohtadi et al., 2008: Verleve and Louwye, 2010a: Saavedra-Pellitero et al., 2011). At present, nitrate is not completely consumed in the Southern Ocean where the uptake is limited by other factors such as light and the absence of micronutrients (mainly iron) (e.g., Mitchell et al., 1991). This results in a CO<sub>2</sub> efflux from the ocean to the atmosphere. Recent studies indicate that the nutrient load of the Antarctic Circumpolar Current (ACC) during the last glacial maximum was lower than today as a result of a 30% increase in nutrient consumption by phytoplankton in the Southern Ocean (Robinson et al., 2005), which should have limited the release of CO<sub>2</sub> (e.g., Sigman and Boyle, 2000). Nitrate is ultimately removed from the marine ecosystem by microbial denitrification which occurs in oxygen-poor sediments and in suboxic (<5 µM O<sub>2</sub>) water columns of the open-ocean oxygen minimum zones, housed in the eastern (sub)tropical North and South Pacific and the Arabian Sea. Besides the

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regulation of biological production, nitrate removal in oxygen minimum zones also directly impacts global climate by the reduction of nitrate into the greenhouse gas nitrous oxide ( $N_2O$ ), which has a tremendous global warming potential.

During the phytoplankton assimilation and the microbial denitrification, the lighter (<sup>14</sup>N) isotope preferentially undergoes reaction. As the initial nitrate supply is progressively consumed, the <sup>15</sup>N/<sup>14</sup>N of the remaining nitrate increases which leads to a related increase in the N isotopic ratio of the organic matter itself. In the Subantarctic Zone, for instance, the nutrients are supplied through northward lateral advection from the Antarctic Zone and are progressively consumed (Altabet and François, 1994; Sigman et al., 1999) causing a steep north-south nitrate gradient from ~20 µM at the Subantarctic Front to ~4 µM at the Subtropical Front (Garcia et al., 2010a). This equatorward decrease in nitrate availability is accompanied by an increase in the N isotope ratio  $\delta^{15}$ N  $(\delta^{15}$ N =  $[(^{15}N/^{14}N_{\text{sample}})/(^{15}N/^{14}N_{\text{reference}}) - 1] \times 1000$ , with the atmospheric N<sub>2</sub> as the universal reference) of the nitrate pool and of the organic matter produced by phytoplankton. When the surface nutrients are completely consumed, sedimentary  $\delta^{15}N$  is a reflection of the isotopic composition of the nitrate delivered to the surface waters.

In this study, we first compare the sedimentary nitrogen isotope record (25–0 cal ka BP) (Martinez et al., 2006) from ODP Site 1233 (41°S; offshore southern Chile) with high-resolution dinoflagellate cyst assemblage data from Verleye and Louwye (2010a), with additional microfossil records from Mix et al. (2003) and Saavedra-Pellitero et al. (2011) in

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order to give a better constrained interpretation of the nutrient source changes off southern Chile since the last glaciation. A comparison with sedimentary nitrogen isotope records from cores located north and south of our study area (GeoB7139-2 (30°S), De Pol-Holz et al., 2006; E11-2 (54°S), Robinson et al., 2005) gives additional insights into the two main water mass end-members feeding the Southern Chile margin.

ODP Site 1233 is located at the southern margin of the South Pacific eastern boundary current, which is one of the world's most productive marine environments (Berger et al., 1987) (Fig. 1a), and is strongly influenced by both high- and low-latitude biogeochemical processes. The eastern tropical South Pacific houses a large region of water-column denitrification that accounts for approximately 15% of the total N removal from the ocean and distributes <sup>15</sup>N-enriched water toward the south and west in the Pacific (Martinez et al., 2006; Robinson et al., 2007; Kienast et al., 2008; Robinson et al., 2009; Martinez and Robinson, 2010) while less <sup>15</sup>N-enriched surface waters are advected from the Southern Ocean (Fig. 1c). Martinez et al. (2006) suggested that the sedimentary  $\delta^{15}N$  at ODP Site 1233 reflects the isotopic composition of the nitrate delivered to the region. Therefore, the recorded  $\delta^{15}N$  values and nitrate concentrations at Site 1233 depend on the oceanographic dynamics in the source areas and the regional/local oceanographic changes such as upwelling, stratification and the position of the Subtropical Front, This dynamical process regulates the contribution of both the Subantarctic Surface Water (SASW) and the Gunther Undercurrent (GUC) in influencing at once the  $\delta^{15}$ N signature and nitrate availability at Site 1233.

The microfossil data makes a valuable contribution in validating that an increasing influence of SASW lowers nitrate concentrations and might also lower the  $\delta^{15}N$  signature, while a greater GUC contribution likely has the opposite effect. A comparison with late Quaternary

nitrogen isotope records derived from cores north and south of the study area is therefore crucial. In this respect, the record of core E11-2 (54°S) can be interpreted as a Subantarctic end-member and can be indicative for the influence of SASW at Site 1233.

Martinez et al. (2006) suggested that high  $\delta^{15}N$  values between 19 and 10 cal ka BP reflected a stronger lateral advection of heavy nitrates from the more northerly denitrification zones offshore of Peru and northern Chile, while lower isotopic compositions during the Holocene and the last glacial maximum were assumed to be largely controlled by Southern Ocean dynamics. A better understanding of past local oceanographic variability, as obtained by microfossil analyses, can provide more detailed information about the source area of the recorded sedimentary organic matter  $\delta^{15}N$  at Site 1233.

### **Regional setting**

Surface circulation in the SE Pacific offshore Chile is dominated by the equatorward flowing Peru–Chile Current, originating between 40°S and 45°S as a northern branch of the ACC (Boltovskoy, 1976; Strub et al., 1998) (Fig. 1a). North of 35°S, the Peru–Chile Counter Current divides the northward-flowing Peru–Chile Current into a coastal and oceanic branch, which turns off to the west close to the equator to form the South Equatorial Current (Fig. 1a). The ACC, in turn, is a high-nutrient low-chlorophyll area, in which biological productivity is limited by the absence of micronutrients, such as iron (De Baar et al., 1995; Boyd et al., 2000, 2001; Hutchins et al., 2001). The high river discharges associated with hyper-humid conditions of onshore southern Chile result in an increase of iron availability in the coastal surface waters, which in turn increases primary productivity (e.g., Iriarte et al., 2007).

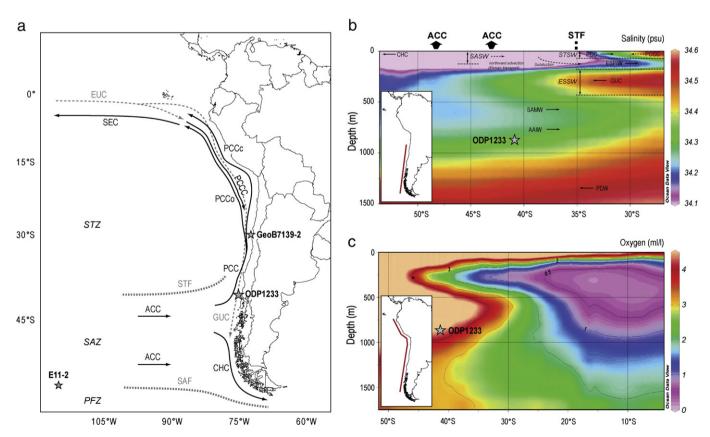


Figure 1. Oceanography of the SE Pacific. (a) Surface currents in the SE Pacific and the location of ODP Site 1233 and other cores (GeoB7139-2, E11-2); (b) vertical profile of the main currents in the upper 1500 m of the SE Pacific between 32°S and 53°S and their salinity characteristics; (c) oxygen concentrations in the upper 1500 m in a vertical profile along a transect in the SE Pacific between 14°S and 51°S. Abbreviations: AAIW, Antarctic Intermediate Water; ACC, Antarctic Circumpolar Current; CHC, Cape Horn Current; ESSW, Equatorial Subsurface Water; EUC, Equatorial Undercurrent; GUC, Gunther Undercurrent; PCC, Peru–Chile Current; PCC, coastal branch of Peru–Chile Current; PCCO, oceanic branch of the Peru–Chile Current; PDW, Pacific Deep Water; PFZ, Polar Frontal Zone; SAF, Subantarctic Front; SAMW, Subantarctic Mode Water; SASW, Subantarctic Surface Water; SAS, Subantarctic Zone; SEC, South Equatorial Current; STF, Subtropical Surface Water; STZ, Subtropical Zone.

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