

Abstract

This paper presents whole water column data for nitrate N, O isotopic composition for the Kerguelen Plateau area and the basin extending east of the Island, aiming at understanding the N-cycling in this naturally iron fertilized area that is characterized by large re-current phytoplankton blooms. The KEOPS 2 expedition (Oct.-Nov. 2011) took place in spring season and complements knowledge gathered during an earlier summer expedition to the same area (KEOPS 1, Feb.-Mar. 2005). As noted by others a remarkable condition of the system is the moderate consumption of nitrate over the season (nitrate remains > 20 µM) while silicic acid becomes depleted, suggesting significant recycling of nitrogen. Nitrate isotopic signatures in the upper water column do mimic this condition, with surprising overlap of spring and summer regressions of $\delta^{18}O_{NQ3}$ vs. $\delta^{15}N_{NQ3}$ isotopic compositions. These regressions obey rather closely the 18 ε /¹⁵ ε discrimination expected for nitrate uptake (18 ε / 15 ε = 1), but regression slopes as large as 1.6 were observed for the mixed layer above the Kerguelen Plateau. A preliminarily mass balance calculation for the early bloom period points toward significant nitrification occurring in the mixed layer and which may be equivalent to up to 47% of nitrate uptake above the Kerguelen Plateau. A further finding concerns deep 44 ocean low $\delta^{18}O_{N03}$ values (<2‰) underlying high chlorophyll waters at the Polar Front Zone and which cannot be explained by remineralisation and nitrification of the local particulate nitrogen flux, which is too small in magnitude. However, the studied area is characterised by a complex recirculation pattern that would keep deep waters in the area and could impose a seasonally integrated signature of surface water processes on the deep waters.

1. Introduction

The Kerguelen Plateau and lee-ward off-shelf areas are characterized by intense seasonal phytoplankton blooms, which are sustained by enhanced iron supply from deep water (Blain et al., 2007; 2008). While these intense blooms result in strong silicic acid depletion, their impact on depletion of the nitrate stocks is much smaller, with end-of-bloom surface water nitrate concentrations still very high, as observed during the KEOPS 1 expedition in late summer 2005 (Blain et al. 2007; Mosseri et al., 2008). Relative to the magnitude of primary production the bloom areas are characterized by enhanced shallow remineralisation and reduced deep sea export, as compared to off-shelf areas located outside the bloom patch (Jacquet et al., 2008). Mosseri et al. (2008) report that despite similar silicic acid and nitrate uptake ratios being close to 1, the apparent nitrate consumption over the season was much lower than the silicic acid consumption, implying significant shallow remineralisation of N, as evidenced by substantial sub-surface ammonium concentrations, reaching up to 2 µM (Mosseri et al., 2008). It is likely that such conditions would also favor a surface ocean development of nitrifying Bacteria and Archaea, with some members of the latter group known to have affinities for ammonium equaling and even exceeding those of diatoms (Martens-Habbena et al., 2009; Stahl and de la Torre, 2012).

Several authors have highlighted that knowledge about nitrate stable isotope composition is an essential asset to resolve the complex suite of processes that control the oceanic N cycle (see e.g., Sigman et al., 1999; DiFiore et al., 2006; 2009; Rafter et al., 2013). During the early season KEOPS 2 expedition (Oct.-Nov.) to the Kerguelen area, we analysed the N and O stable isotope composition of nitrate over the whole water column to investigate possible imprints of the above described shallow remineralisation + nitrification process, as well as imprints of enhanced primary production on deep ocean nitrate isotopic composition. Furthermore, this early season expedition offered the opportunity to investigate the seasonal variability of the nitrate isotopic composition, by comparing results with those obtained earlier by others during the late summer KEOPS 1 expedition to the same area (Trull et al., 2008). This work on nitrate isotopic composition takes advantage of the study of primary production, nitrate and ammonium uptake, carbon export production and remineralization that was conducted by others during the KEOPS 2 expedition (Cavagna et al., 2014; Planchon et al., 2014 and Jacquet et al., 2014).

Confirming previous studies, combined measurement of nitrate dual isotope composition and N-nutrient uptake rate measurements, as performed during KEOPS 2, appears to be particularly useful for investigating surface ocean N-processes. In that aspect this study differs from previous studies on nitrogen cycling using the natural nitrate dual isotopic composition, but lacking information on N-process rates. The present study also adds significantly to the existing data base on nitrate isotopic composition in the Southern Ocean, with new data for the Polar Front region in a naturally iron fertilized area.

2. Methods

2.1 Site description

The studied area covers the broad plateau region stretching between Kerguelen and Heard Island to the SE, and the deep basin to the east of the island (Figure 1). This 98 basin is bound to the south by the Kerguelen Plateau and to the north by a sill (Gallieni Spur) extending from the plateau in north-easterly direction (Figure 1).

Briefly, the studied area to the east of Kerguelen is crossed by the meandering Polar Front, which circumvents the island from the south-west, crosses the shallow (~500m) Kerguelen Plateau (which extends in south easterly direction from the island) and forms a loop extending northward till the sill that borders the basin to the north (Gallieni Spur), thereby enclosing a stable mesoscale meander structure (Figure 1). Surface and subsurface waters closely follow, and actually define the position of the PF. Deep water flow in the area is fed by Circumpolar Deep water flow channeled through the Fawn Tough (Park et al., 2008) and also by the northward directed deep western boundary current in the Australian Antarctic basin east of the Kerguelen Plateau (McCartney and Donohue, 2007; Fukamachi et al., 2010).

For further details about the topography and the large scale circulation in the Kerguelen Island and Plateau areas we refer to Park et al. (2008).

The T-S diagram (Figure 1) highlights the hydrodynamic environment of the Kerguelen area, with profiles characteristic of the Open Ocean Zone. Most salient features are: highest temperatures in surface waters; presence of subsurface temperature minimum Winter Water; increased temperatures in Upper Circumpolar Deep Water; increased 116 salinities in Lower Circumpolar Deep Water; a broad salinity maximum reflecting the remnant North Atlantic Deep Water; slightly less saline and cold Bottom Waters.

2.2 Sampling and Analysis

The KEOPS 2 expedition took place from Oct. till early Nov. 2011 on board R/V Marion Dufresne. The sampling strategy aimed at documenting both the short term temporal evolution of the system during pre- and bloom conditions of selected sites and the broader spatial variability between Plateau and more off-shelf sites (Figure 1b shows the map with the MODIS Chlorophyll pattern superimposed). Short term temporal evolution was followed in a stationary meander of the Polar Front and by revisiting 125 sites above the Plateau, while spatial variability was studied along a W - E section and a N – S section covering the Plateau and the basin east of Kerguelen Island.

The water column was sampled per CTD rosette equipped with 12L Niskin bottles. N-nutrients (nitrate, nitrite, ammonium) were measured onboard using classical spectrophotometric methods (Blain et al. 2015). The samples for nitrate isotopic composition consisted of a sub-fraction (10 ml) of the filtered seawater (Acrodisc; 0.2 131 µm porosity) intended for on-board nitrate + nitrite analysis. These subsamples were kept frozen (-20°C) till analysis in the home-based laboratory. The nitrogen and oxygen isotopic composition of nitrate was determined via the bacterial denitrifier method, using *Pseudomonas aureofaciens* bacteria which reduce nitrate to N2O (Sigman et al., 2001; Casciotti et al., 2002). We aimed at a final homogenous nitrate content of 20 136 nmoles for samples and reference standards alike (see below). The analytical 137 equipment consisted of a custom-build gas bench connected on-line to a set-up for gas 138 conditioning, which involved elimination of volatile organic carbon compounds, $CO₂$ 139 and cryogenic focusing of N₂O, GC separation of CO₂ traces from N₂O, a Con-Flo unit 140 and IRMS (Thermo Delta V). For final calculations we used the USGS 32, 34, 35 and 141 IAEA N3 international reference standards (Sigman et al., 2001; Böhlke et al., 2003) 142 and the two-point normalization procedure as discussed in Casciotti et al. (2002) and 143 Paul et al. (2007). $\delta^{15}N$ values are reported as $[(15N/14N_{sample})/(14N/15N)_{ref}-1]$ *1000, 144 referenced to Air N₂ and $\delta^{18}O$ as $[(^{18}O/^{16}O)_{\text{sample}}/(^{18}O/^{16}O)_{\text{ref}} - 1]^*$ 1000, referenced to 145 VSMOW. Multiple analyses of USGS and IAEA reference solutions indicate average 146 measurement errors for $\delta^{15}N_{NQ3}$ and $\delta^{18}O_{NQ3}$ analyses were 0.17‰ and 0.38‰, 147 respectively. We also analysed 35 duplicate samples from successive CTD casts at same 148 depths yielding median values of the standard deviations being 0.05‰ and 0.28‰ for 149 δ^{15} N and δ^{18} O, respectively.

150 Note that the method measures the isotopic composition of NO_3 plus NO_2 . The 151 presence even of small nitrite amounts would lower the $\delta^{15}N$ and $\delta^{18}O$ values of 152 nitrate + nitrite relative to nitrate only (Casciotti et al., 2007). In the present study the 153 effect of $NO₂$ was neglected since overall nitrite concentrations were small, 154 representing on average <0.5% of the nitrate + nitrite pool (see also DiFiore et al., 155 2009). However, it has been reported that slightly higher nitrite levels reaching 0.8 % 156 of the nitrite + nitrate pool such as observed here for the surface waters can result in a 157 lowering of the $\delta^{15}N$ and $\delta^{18}O$ values by 0.4‰ and 0.2‰ on average (Rafter et al., 158 2013; their supplementary material). We have not corrected our surface water nitrate 159 isotopic values for a possible nitrite effect, as is the case also in work presented by 160 others (see e.g., DiFiore et al. 2009; Rafter et al., 2013), but have considered the 161 impact of this when calculating nitrification (see section 4.5). Information on nitrate, 162 ammonium uptake experiments and C, N Export flux via the 234 Th method is given in 163 the contributions by Cavagna et al. (2014) and Planchon et al. (2014). As part of the 164 analysis protocol for assessing carbon export via the 234 Th method, we also analysed

165 δ^{15} N of suspended particulate nitrogen in the size fractions 1 to 53 µm and > 53 µm, as 166 sampled with large volume in-situ pumps (Planchon et al., 2014).

3. Results

169 The full data set $(\delta^{15}N_{NO3}, \delta^{18}O_{NO3},$ concentrations of NO₃, NO₂, NH₄⁺, Salinity, Tpot) is available in Appendix Table 1.

3.1 Water column profiles

A total of 20 sites were sampled for analysis of nitrate isotopic composition. One site located south-west of Kerguelen, in HNLC waters well outside the Kerguelen bloom was taken as reference site (R-2; Table 1). We differentiate 3 regions (Table 1): (i) Plateau stations located south of the PF, above the shallow Plateau and the margin 177 and underlying the bloom plume (stations A3-1, TNS-8, TEW-4, E-4W, A3-2, E-4W-2); (ii) Polar Front Meander stations in the central part of the basin east of Kerguelen where the bloom had not fully developed yet (stations TNS-6, E-1, TEW-5, TEW-6, E-3, E-4E, E-5, IODA-REC); (iii) Polar Front and north of Polar Front sites (stations TEW-7, TEW-8, F-L). Average upper 100m Chl-a concentrations are highest for the Polar Front stations (2.03 \pm 0.43 µg l⁻¹), followed by the Plateau stations (1.27 \pm 0.54 µg l⁻¹), while 183 the Meander sites had lower Chl-a concentrations (0.85 \pm 0.32 µg l⁻¹), though clearly in 184 excess of values recorded for the HNLC reference station (0.3 μ g l⁻¹) (Table 1). We note 185 that Plateau sites on average have the coldest (2.27 \pm 0.34 °C) and most saline (33.89 \pm 0.02) surface waters (upper 100m), while PF sites have the warmest (3.49 \pm 0.24 °C) 187 and freshest (33.79 \pm 0.02) surface waters (Table 1). Average nitrate values in the upper 100m of water column remain high throughout the study period with average 189 values of 26.6 ± 1.9 ; 26.2 ± 0.9 and 23.1 ± 1.3 µM for Plateau, Meander and PF areas, respectively (Table 1). With increasing depth, nitrate concentrations in general increase to reach maximal values around 37 µM at 500m in Upper Circumpolar Deep

waters (UCDW) (Figure 2a). Concentrations decrease slightly in Lower Circumpolar 193 Deep Waters (around 30 µM) and increase again slightly in bottom waters (around 32 μ M). Profiles of $\delta^{15}N_{NO3}$ mirror the ones of nitrate (Figure 2b): High values in surface 195 waters (reaching up to 7.5 ‰) which decrease to 4.6‰ in the NO_3 maximum and 196 increase slightly to 5‰ till about 2500 m. A slight decrease of $\delta^{15}N_{NO3}$ is noticed in Polar Front bottom waters which also show a slight increase in nitrate concentration (Figure 2a,b). Such values are similar to those observed widely for the deep ocean (see 199 Di-Fiore et al., 2009; Sigman et al., 2000; 2009b; Rafter et al., 2013). Although δ^{18} O_{NO3} values are more scattered, it can be clearly seen that they follow a pattern similar to $\delta^{15}N_{NO3}$, with values up to 6‰ in surface waters, which decrease to <2‰ in the 500 to 1000m depth interval but tend to increase again in deep and bottom waters and stay close to 2‰ (Figure 2c).

204 Differences of the $\delta^{15}N$ and $\delta^{18}O$ gradients between deep ocean and surface are 205 generally visualized by plotting the $\Delta(15-18)$ values, which have been defined (Sigman 206 et al., 2005) as: the difference between δ^{15} N and δ^{18} O (Rafter et al., 2013), keeping in 207 mind that for deep waters the $\delta^{15}N_{NO3} - \delta^{18}O_{NO3}$ difference is close to 3‰.. From 208 Figure 2d it appears that surface waters have $\Delta(15-18)$ values generally <3‰ (range 0.9 209 - 3‰; average = 2.30 ± 0.5 ‰), with lowest values observed for Plateau, PF areas, and 210 Meander stations This indicates that surface water δ^{18} O values have increased more 211 $\,$ than δ^{15} N values. In contrast, the sub-surface waters between 250 m and 1250 m show 212 a majority of data points with $\Delta(15-18)$ values> 3‰, though values are scattered rather 213 widely. Since uptake of nitrate fractionates $15N/14N$ and $18O/16O$ equally (Granger et al., 214 2004; Sigman et al., 2005), another process needs to be invoked to explain the low $215 \quad \Delta(15-18)$ values for surface waters. In the discussion further below we show that these 216 low surface waters $\Delta(15-18)$ values (<3‰) can be attributed largely to a partial 217 utilization of the surface water nitrate pool combined with nitrification in the surface 218 and subsurface waters.

219 For the 250 m to 1500 m depth interval at stations on the PFZ side of the PF (east of 220 74°E) and to a lesser stations close to the plateau margin between 71° and 72°E (Figure

221 3a) we observe low $\delta^{18}O_{NQ3}$ values (<2‰) and high $\Delta(15-18)$ values(> 3‰; Figure 2d). This feature is probably associated with advection of UCDW as discussed later. The occurrence of these signals at the western and eastern borders of the meander possibly reflects the presence of a cyclonic circulation in the basin which confines the meander, as reported by Park et al. (2014). Note that the S to N section between 226 approximately 71° and 72°E also intersects the low $\delta^{18}O_{NO3}$ waters (see Figure 3b).

227 Below 1500m $\Delta(15-18)$ values are close to 3‰, reflecting similar vertical gradients for 228 δ^{15} N and δ^{18} O.

3.2 W-E and S-N Sections

231 Figure 3a,b shows the spatial distribution of the $\delta^{15}N_{\rm NO3}$ and $\delta^{18}O_{\rm NO3}$ signals and nitrate concentration along the W to E and S to N transects. Deep waters (>500m) in the 233 central part of the W to E section, between 72°E and 74°E have $\delta^{15}N_{NO3}$ values close to 5‰, while westward and eastward of this central area, deep waters have slightly lower $\delta^{15}N$ values (Figure 3, top). Lowest $\delta^{15}N_{NO3}$ values are observed in bottom waters (>2000 m) east of 73°E and appear associated with very low temperatures (<1°C). These waters are probably of southerly origin, associated with the Fawn Trough Current, transporting cold Antarctic waters of eastern Enderby origin (Park et al., 2008) and possibly also partly with the Deep Western Boundary Current which is part of the deep cyclonic gyre in the Australian – Antarctic Basin (McCartney and Donohue, 2007; Fukamachi et al., 2010).

4. Discussion

4.1 Nitrate concentration and isotopic composition

245 The clear ${}^{15}N$, ${}^{18}O$ enrichments of nitrate in the upper ocean (Figure 2) suggest a strong effect of isotopic discrimination during nitrate uptake by the phytoplankton (Sigman et

247 al., 1999; DiFiore et al., 2010). The isotope fractionation effect is visualized by plotting 248 $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values vs. the natural logarithm of nitrate concentration (Figure 249 4). The degree of linearity of these relationships is indicative of the degree by which 250 isotopic discrimination approaches closed system Rayleigh fractionation. The slope 251 values of these regressions are equivalent to apparent discrimination factors 252 (ε). Whole water column values are -4.08 \pm 0.17 (\pm se), -4.18 \pm 0.20 and -4.54 \pm 0.21, for 253 Meander, Polar Front and Plateau areas, respectively (Figure 4). When focusing on the 254 upper 250m (this layer partly includes UCDW), slopes are slightly steeper, reaching - 255 -4.62 ± 0.21 , -4.44 \pm 0.23 and -4.76 \pm 0.36, respectively (Figure 4). Slopes for $\delta^{18}O_{NO3}$ are 256 steeper than for $\delta^{15}N$, reaching -6.15±0.37, -6.20 ± 0.39 and -6.75 ± 0.56 for the whole 257 water column and -6.15 ± 0.87 , -5.18 ± 0.52 and -6.13 ± 1.03 , for the upper 250m, for 258 Meander, Polar Front and Plateau, respectively (Figure 4). We thus observe a tendency 259 if or slopes of $\delta^{15}N_{NO3}$ vs LN[NO₃] to increase in shallow waters, while on the contrary 260 slopes for $\delta^{18}O_{NOS}$ vs LN[NO₃] decrease. Largest $\delta^{15}N$, $\delta^{18}O$ slope values are observed 261 for the Plateau sites. Overall such values fit within the range of ε values reported for 262 nitrate uptake by phytoplankton (4 - 10‰ for¹⁵ ε and ¹⁸ ε ; DiFiore et al., 2010; Sigman et 263 al., 2009a,b; Granger et al., 2004, 2010). The high whole water column slope values for 264 δ^{18} O are in part due to the low δ^{18} O values (<2‰) of deep waters (LCDW and bottom 265 vaters) underlying UCDW (Figure 2c). Although δ^{18} O slope values for the upper 250m 266 (Figure 4) tend to be smaller than whole water column slopes, they still clearly exceed 267 those for $\delta^{15}N_{NO3}$.

268 The larger slope values of δ^{18} O vs. LN[NO₃] regressions compared to those for δ^{15} N, at 269 first sight might reflect the fact that the apparent discrimination factors for $^{18}O/^{16}O$ 270 and $^{15}N/^{14}N$ ($^{15} \varepsilon$; $^{18} \varepsilon$) are not similar, as is expected (ε^{15} / ε^{18} = 1) in case nitrate uptake 271 (and also denitrification, but this is irrelevant for the oxygen-rich environment studied 272 here) is the sole process inducing isotopic fractionation (Granger et al., 2004, 2008; 273 Sigman et al., 2009b). The likeliness that nitrification in subsurface waters as well as in 274 the upper mixed layer is responsible for these observations is developed further 275 below. A further process that could divert the ε^{15} / ε^{18} ratio from unity is diazotrophy,

276 evidence of which is discussed by Gonzalez et al. (2014). Dinitrogen fixation would 277 Iower nitrate δ^{15} N without affecting δ^{18} O. N₂ fixation rates for the upper 50 m for the 278 Plateau and R-2 sites do reach at most 0.2 mmol $m⁻² d⁻¹$ (Gonzalez et al., 2014). For the 279 Plateau site this represents only about 1% of the calculated best fit nitrification rate 280 (see later below) of 18 mmol m⁻² d⁻¹. No N₂ fixation rates are available for the Meander 281 sites, but assuming that the rate observed at Plateau and R-2 also applies for the 282 Meander site, N_2 fixation rate for the Meander would represent some 20% of the 283 calculated best-fit nitrification rate (1 mmol $m² d⁻¹$; see further below), which is a 284 significant fraction. For the Meander site, however, the nitrification rate itself is poorly 285 constrained (see below), making it difficult to definitively conclude here on the relative 286 significance of N_2 fixation and nitrification for that site.

287

288 \qquad 4.2 Differential behavior of $\delta^{^{15}}N_{\rm NO3}$ and $\delta^{^{18}}O_{\rm NO3}$ evidenced from $\Delta(15\text{-}18)$

289 Differences between the $\delta^{15}N_{NOS}$ and $\delta^{18}O_{NOS}$ profiles are highlighted even more when 290 plotting the difference between these isotopic compositions (i.e., $\delta^{15}N_{NO3}$ - $\delta^{18}O_{NO3}$ = $291 \Delta(15-18)$; see Figure 2d;). A striking feature that appears from the present data set are 292 the consistently low $\Delta(15-18)$ values (<3‰; range 0.8 - 3) in the upper 250 m for all 3 293 areas, reflecting the proportionally stronger enrichment of nitrate in 18 O than 15 N.

294 Note that the sole effect of nitrate uptake with similar $^{15}N/^{14}N$, $^{18}O/^{16}O$ discrimination 295 would have left $\Delta(15-18)$ unchanged (Sigman et al., 2005), which is not the case here. 296 Such a feature of low $\Delta(15-18)$ values (<3‰) throughout the surface layer where 297 intrate concentrations are mostly \geq 20 µM, appears characteristic not only for the 298 present spring data set, but also for the summer data obtained during KEOPS 1 (Trull et 299 al., 2008) and has not been reported for other Southern Ocean studies. Rafter et al. 300 (2013) report low values (2.5 - 3‰) in subsurface waters (~100 – 400 m; <25µM NO₃) 301 at latitudes around 50°S but these are overlaid with surface waters (<15 μ M NO₃) that 302 have high $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values and $\Delta(15-18)$ values of about 3‰ (see their Fig. 303 4). The latter authors describe the low subsurface $\Delta(15-18)$ values (2.5 -3‰), as being

the result of partial consumption of available nitrate in surface waters, export of low δ^{15} N-PN, and remineralisation - nitrification there. Since nitrate N, O cycles are 306 uncoupled and ambient seawater with a δ^{18} O close to zero (Archambeau et al., 1998) is the main source of oxygen for this 'recycled' nitrate (Sigman et al., 2009b), the latter is 308 relatively more depleted in heavy $15N$ isotope than in heavy $18O$ isotope, and this 309 results in $\Delta(15-18)$ values < 3‰, as discussed by Rafter et al. (2013). However, as stated above, in contrast to the results reported by the latter authors for Open Antarctic Zone and Polar Front Zone surface waters (Pacific sector) we observe that 312 the subsurface trend of lowered $\Delta(15-18)$ continues in the upper mixed layer, reaching 313 values as low as 1‰. We note that the lower $\Delta(15-18)$ values in the upper 200m coincide with higher ammonium and nitrite contents (Figure 5), possibly reflecting effects of nitrification, which could be either a local or imported condition (see section 4.5 below).

317 For the waters between 250 and 1250m (upper mesopelagic), which include the 318 UCDW, a number of $\Delta(15-18)$ data points are slightly in excess of 3‰ (Figure 2d) due 319 to low $\delta^{18}O_{NQ3}$ values (Figures 2d and 3). From Figure 3 it appears that this feature 320 concerns mainly stations at the Polar Front east of 74°E (stations TEW-7; TEW-8, F-L) 321 underlying high chlorophyll surface waters (Figure 1), as well as some sites closer to 322 the Kerguelen margin in the West, around 72°E (stations E-4W; E-5) (Figure 3). The 323 vertical $\delta^{18}O_{NO3}$ profiles for these stations show deep $\delta^{18}O_{NO3}$ values close to 1.65 ‰ 324 (i.e., some 0.35‰ lower than the average deep ocean value of 2‰) (Figure 5). On the 325 other hand stations in the low chlorophyll central part of the PF meander (TEW-5; 326 TEW-6; E-4E; TNS-6; E-1), and also north of the PF (TNS-1) and away from the 327 Kerguelen bloom (R-2), show mesopelagic $\delta^{18}O_{NO3}$ values close to the deep ocean 328 reference value of 2‰. So the question arises what particular process or condition can 329 account for these variations in mesopelagic $\delta^{18}O_{N03}$ values.

330 A simple calculation shows that the lowered $\delta^{18}O_{NQ3}$ values cannot be explained by 331 mesopelagic remineralisation and nitrification of organic N exported over the course of 332 a single production season. For the latter process to increase deep ocean nitrate

333 concentrations (taken as 31 µM) to the mesopelagic average value of 34.5 µM and to 334 decrease $\delta^{18}O_{NQ3}$ from the deep ocean value of 2‰ to 1.65‰ taking a $\delta^{18}O_{\text{water}}$ of -335 0.4‰ (Archambeau et al., 1998) and $\delta^{18}O_{NO3}$ of nitrification = 1.1‰ (Sigman et al., 336 2009b), would require an export and complete remineralisation and nitrification of 337 organic nitrogen in the 250 to 1250m water column layer of some 20 to 100 mmol $m²$ 338 d⁻¹ to fit the observed [NO₃] and $\delta^{18}O_{NOS}$, respectively. This is about 10 to 50 times 339 Iarger than the export flux from the 150 m depth horizon estimated via the 234 Th-340 deficit approach (average PN flux = 1.9 mmol $m⁻² d⁻¹$; Planchon et al., 2014). We 341 speculate that the complex recirculation pattern generated by the basin topography 342 and the presence of the PF induces a multiple season integrative effect on the nitrate 343 isotopic signature of the deep water in the gyre structure. The presence of low δ^{18} O_{NO3} 344 values also at some stations located more to the West (72°E; Figure 3) is in agreement 345 vith a scenario whereby the low mesopelagic $\delta^{18}O_{NQ3}$ signature at the Polar Front is 346 entrained with the cyclonic circulation of the PF meander. This signal transfer could be 347 quite fast considering that shipboard measurements by Lowered Acoustic Doppler 348 Current Profiler revealed a strong eastward current along the northern edge of the 349 basin as associated with a cyclonic circulation. This current stretches over the whole 350 water column and reaches a velocity of 25 cm s^{-1} (Y.H. Park; pers. communic., 2011). 351 Alternatively we could argue that the low $\delta^{18}O_{NO3}$ feature is imported from elsewhere. 352 The mesopelagic waters in the 250 to 1250 m range do comprise UCDW waters (i.e., 353 temperature maximum waters above the salinity maximum waters). As discussed by 354 Rafter et al., (2013) these waters carry heavy $\delta^{15}N_{NO3}$ and decreased $\delta^{18}O_{NO3}$ isotopic 355 signatures acquired at lower latitudes and resulting from a combination of processes 356 including: (i) partial nitrate assimilation in the surface waters feeding northward 357 flowing Antarctic Mode and Intermediate Waters, (Sigman et al., 2009b); (2) flux of 358 partially denitrified waters into surface waters (mainly in the Pacific and Indian oceans) 359 combined with nearly complete consumption of nitrate in the low latitude ocean, 360 yielding high δ^{15} N values for sinking PN (see Sigman et al., 2009a; Rafter et al., 2013). 361 This yields subtropical subsurface waters with high $\delta^{15}N_{NO3}$ and low $\delta^{18}O_{NO3}$, and thus 362 high $\Delta(15-18)$ values. These isotopic signatures are again advected southward with

deep water and become subsequently incorporated in CDW to join the circumpolar 364 circulation (Rafter et al., 2013) explaining the presence of $\Delta(15-18)$ values exceeding 3‰. In the Open Antarctic Zone, CDW upwells and its UCDW branch flows northward to subduct at the Polar Front as SAMW and AAIW (Rafter et al., 2013).

4.3 Low $\delta^{15}N_{NO3}$ values in bottom waters

369 The low $\delta^{15}N_{NO3}$ values in the cold (~ 0.5 °C) bottom waters in vicinity of the Polar Front (Figure 3) may possibly be brought about in case partial nitrification takes place in the sediments and feeds isotopically light nitrate to the bottom waters, as has been described for the Bering Sea Shelf by Granger et al. (2011). However, if such a process is also operating here in the Kerguelen area, we would expect to see the effects more marked in waters hugging the slopes surrounding the basin. Indeed, there is some 375 evidence for isotopically light NO_3^- in the western part of the W-E section (Figure 3), but clearly, the strongest depletions do occur in waters close to, and underlying, the Polar Front in the eastern part of the W-E section and which are quite remote from the slope regions of the basin. These cold bottom waters are likely of southerly origin, associated with the Fawn Trough Current which transports cold Antarctic waters of eastern Enderby origin (Park et al., 2008) and possibly also partly with Deep Western Boundary Current which is part of the deep cyclonic gyre in the Australian – Antarctic Basin (McCartney and Donohue, 2007; Fukamachi et al., 2010). However, values reported for the Polar Antarctic Zone in the Indian and Australian sectors do not show 384 evidence of deep ocean $\delta^{15}N_{NO3}$ values lower than 5‰ (DiFiore et al., 2009). So it 385 Femains uncertain where these low δ^{15} N_{NO3} signatures in bottom waters underlying the Polar Front area at 74-75°E originate from.

In the next sections we focus on the conditions in the upper 250m of water column where our observations provide evidence of significant nitrification.

4.4 Co-variation of $\delta^{15}N_{NO3}$ *-* $\delta^{18}O_{NO3}$

392 Figure 8 shows the regressions of $\delta^{18}O_{NO3}$ vs. $\delta^{15}N_{NO3}$ for the Plateau, Meander and PF areas. As expected from the discussions above, the regression slopes for whole water column are larger than 1 (they vary between 1.4 and 1.5, for PF and Plateau areas, respectively). The black line in Figure 8 reflects the expected regression in case 396 discrimination during nitrate uptake is similar for ${}^{18}O/{}^{16}O$ and ${}^{15}N/{}^{14}N$ and acts upon a 397 initrate source reservoir that has a deep water isotopic signature (i.e., $\delta^{15}N_{NO3}$ = 5‰ 398 and $\delta^{18}O_{N03}$ = 2‰). When focusing on the upper 250m we note that slope values decrease and come close to 1 for the PF area (slope = 1.14), while they are close to 1.3 for Plateau and Meander sites (Figure 8). For all 3 areas, it is clear, however, that data points mostly fall above the expected regression. This condition is also clearly reflected 402 in the $\Delta(15-18)$ values which on average fall below 2.5‰ for the upper 200m of water column (see Figure 2).

Figure 8 also shows the summer data obtained during KEOPS 1 (Trull et al., 2008) superposed on the present KEOPS 2 spring data. This comparison is limited to the upper 250 m of the water column, i.e. the depth range analysed during KEOPS 1 (Trull et al., 2008). The summer data overlap tightly with the spring data but also sit above the 1:1 line, defined above, but in contrast to spring, summer shows a slope value close to 1 (0.98). However, a closer look reveals that the deep summer samples have 410 Slightly more elevated $\delta^{18}O_{NO3}$ values, tilting the regression and thereby decreasing the 411 slope value. These more elevated subsurface $\delta^{18}O_{NO3}$ values may reflect the effect of subsurface nitrification in an area of partial surface nitrate assimilation (Rafter et al., 2013; Sigman et al., 2009b). When focusing on the mixed layer depth, the slopes of the $\delta^{18}O_{NO3}$ vs. $\delta^{15}N_{NO3}$ regressions become even steeper for the Plateau (up to 1.65) and Meander areas and for the KEOPS 1 data set (Figure 8), but not for the PF area. Thus, within the upper 250m and even more so in the upper mixed layer, the variations of 8^{18} O_{NO3} values clearly exceed those for corresponding 8^{15} N_{NO3} values. Such a condition may result from the remineralisation – nitrification organic nitrogen (Sigman et al., 2009b, DiFiore et al., 2009). Also, the absence of a clear differentiation between

summer (KEOPS 1) and spring (KEOPS 2) conditions (Figure 8; we would expect to see 421 the summer condition further up the line with higher $\delta^{15}N$ and $\delta^{18}O$ values) is quite puzzling, and may reflect the fact that the nitrate consumed is being largely replenished from remineralisation coupled to nitrification, thereby dampening the 424 enrichment of $15N$ due to uptake (but enhancing the $18O$ enrichment). We also note that the average deficit of silicic acid and nitrate in the mixed layer vs. the winter 426 values in underlying T_{min} waters are systematically >> 1 (up to 4) for the whole area, 427 while Si(OH)₄/NO₃ uptake ratios are generally close to 1 (0.74 to 1.51) for the Plateau and Meander areas, consistent with iron replete conditions there (Closset et al., 2014; Cavagna et al., 2014). The larger deficit of silicic acid compared to nitrate could thus partly result from shallow recycling of nitrogen. . In fact nitrate contents stay relatively high throughout the growth season and KEOPS 1 summer nitrate values remain generally in excess of 20 µM (Trull et al., 2008), while summer silicic acid 433 concentrations run low to near depletion, despite the $Si(OH)_{4}/NO_{3}$ uptake ratio being close to 1 (Mosseri et al., 2008). This is further evidence for significant nitrification in the upper mixed layer. The combined effect of nitrate uptake and nitrification in the 436 euphotic zone will result in decoupling the $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ signals, thereby decreasing their average deep ocean difference of 3‰.

438 The question can be raised to what extent this is a local or imported condition from an 439 upstream area. At the HNLC reference station, located upstream of the Kerguelen 440 Plateau and Meander areas the upper mixed layer values of $\delta^{15}N$ and $\delta^{18}O$ are 441 increased by about 1.2‰ and 2‰, respectively, relative to local deep waters (Figure 442 2). This results in decreased $\Delta(15-18)$ values (average value upper 100m = 2.25‰), 443 which are similar to values for the Meander $(\Delta(15-18) = 2.39 \pm 0.44\%)$, PF $(\Delta(15-18) =$ 444 $2.44 \pm 0.28\%$) and also Plateau sites sampled during the earlier part of the study 445 period (A3-1; E-4W; TNS-8; TEW-4; $\Delta(15-18) = 2.51 \pm 0.38\%$). Such values, however, 446 are larger than those for Plateau sites sampled toward the end of the study period (E-447 4W-2 and A3-2; average $\Delta(15-18)$ = 1.79 \pm 0.12‰), adding evidence for ongoing 448 nitrification during this early bloom phase, at least above the Plateau. Meander and 449 Polar Front sites on the contrary do not show such evidence as their upper ocean $\Delta(15-$

18) values do not differentiate from the value at the HNLC reference station.

Nitrification could possibly occur at the shelf sediment water column interface, as 452 reported for the low nitrate Bering Sea shelf, characterized by high NH_4^+ levels (Granger et al., 2011; 2013). For instance, at the shallow (< 100m) TEW-1 shelf station (see Figure 6A) ammonium contents are enhanced (up to 1.1 µM) close to the seafloor. 455 We note, however, that $\Delta(15-18)$ values are relatively large, averaging 2.3‰ (Figure 6A; Table A1), a condition that is not indicative of significant nitrification. Furthermore the shallow TEW-1 station is located north of the Polar Front, and surface waters advected from this shallow shelf area flow north, north-east, staying north of the PF (see surface water flow lines in Figure 1), away from A3. Except for this station TEW-1 we do not see evidence for nitrification at the site sediment water column boundary layer elsewhere above the Kerguelen Plateau, though we have no data for the shallow water column (<100m) close to Heard Island located further south on the Plateau, 463 some 400 Km upstream of site A3 (Figure 1a). During KEOPS 1 (summer 2005) NH₄⁺ and NO₂ concentrations at the C1 site close to Heard Island reached up to 0.7 and 0.4 μ M, 465 respectively and a single nitrate isotopic measurement for the C1 site gave a $\Delta(15-18)$ value of 2.13‰ (Trull et al., 2008) so conditions similar to those observed here for site 467 TEW-1. Especially the large $\Delta(15-18)$ values (>2%o) observed for these two shallow (<100m) plateau sites make it unlikely that sediment boundary layer nitrification is a source of nitrate to the mixed layer above the main Kerguelen Plateau area south of 470 the Polar Front. In the next section we evaluate the strength of a possible nitrification in the surface layers.

4.5 Calculating the temporal evolution of $\delta^{15}N_{NO3}$ *and* $\delta^{18}O_{NO3}$ *in the surface mixed layer*

The similarity of the ranges of upper ocean nitrate isotopic compositions during early (KEOPS 1) and late (KEOPS 2) season (Figure 8) raises the question whether the

Kerguelen system had already reached some steady state condition for nitrogen cycling early in the season, with nitrate consumption being mostly balanced by remineralization combined with nitrification. However, earlier studies, suggest that the evidence for significant euphotic zone nitrification in Southern Ocean surface waters is weak (Olson, 1981; Bianchi et al., 1997; Trull et al., 2008; DiFiore et al., 2009). To resolve this apparent controversy we will estimate the strength of nitrification in the 483 upper mixed layer. We apply a mass balance approach for both, $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ in the mixed layer of Plateau and Meander stations where data on temporal evolution are available. We take advantage of the fact that nitrate and ammonium uptake rates were measured during KEOPS 2 (Cavagna et al., 2014) and also that values of isotopic composition of suspended and sinking material are available (Trull et al., 2014; Dehairs, unpublished results) Note that the model calculations presented here cover a limited length of growth period (about one month). More complex model calculations describing the evolution nitrification over the full growth season are presented elsewhere (Fripiat et al., submitted).

We take the upper 100 m nitrate conditions observed during the earliest visit to the Plateau and Meander as the initial conditions (i.e. conditions for stations A3-1 and TNS-6, respectively). Euphotic zone (0.01% PAR; 57 to 137m deep) integrated nitrate uptake rates reported by Cavagna et al. (2014) do show an increase by some 30% for the Meander region (Stations E-1, E-3, E-4E and E-5; 27 day period). For the Plateau region only two N-uptake profiles (stations E-4W; A3-2) were measured, apart by just 4 498 days. Nitrate uptake for the Meander sites are on average 12.4 \pm 2.2 mmol m⁻² d⁻¹ (n = 499 4) while for the Plateau sites they are 36 ± 4.7 (n=2). Ammonium uptake rates are 6.6 500 ± 1.4 mmol m⁻² d⁻¹ (n=4) and 6.2 \pm 1.9 (n=2) for Meander and Plateau sites, respectively. Using these average nitrate uptake rates we calculate the nitrate concentrations (called residual nitrate) that would be present in the upper 100 m at the end of the observation period in case uptake is the sole process affecting the nitrate concentration. Nitrate concentrations at stations A3-1 (Plateau) and TNS-6 (Meander) were considered to represent the initial conditions, whereas concentrations

506 at stations A3-2 (Plateau) and station E-5 (Meander), visited 27 days after A3-1 and 507 TNS-6, respectively, represent the conditions at the end of the observation period. 508 Residual nitrate values are slightly $(\Delta[NO_3]) = 1.8 \mu M = 6\%$; Meander) to significantly 509 Iower $(\Delta[NO_3] = 4.1 \mu M = 25\%$; Plateau) than measured values (see Table 3). The 510 isotopic composition of the residual nitrate is then calculated from the estimated 511 fraction of nitrate remaining, using a discrimination of 5‰ for both $15N/14N$ and 180^{16} O (Sigman et al.,1999; DiFiore et al., 2010) and considering that the surface 513 mixed layer operates as a closed system (Rayleigh fractionation applies). The 514 calculated isotopic compositions of the residual nitrate are heavier than the measured 515 ones. The differences between calculated and observed isotopic values are: for $\delta^{15}N$ 516 0.22‰ and 1.45‰ and for $\delta^{18}O$, 0.10 and 0.98‰ for Meander and Plateau areas, 517 respectively. For the Meander differences are small (close to the analytical precision) 518 and so the calculated nitrification rate is poorly constrained. For the Plateau area the 519 differences are larger and as a result calculated nitrification combined with nitrate 520 upwelling are better constrained.

521 The isotope effects associated with nitrification are taken as follows, assuming a 522 steady state between the production and consumption of both ammonium and nitrite 523 (e.g., Fripiat et al., 2014):

524 For
$$
\delta^{15}N_{NO3}
$$
: Nitrif. $[\delta^{15}N_{PN} - \varepsilon_R + x(\varepsilon_{NH4u} - \varepsilon_{AMO}) + y(\varepsilon_{NiU} - \varepsilon_{NiO})]$ (1)

525 For
$$
\delta^{18}O_{NO3}
$$
: Nitrif. $(\delta^{18}O_{H2O} + 1.1)$ (Sigma et al., 2009b) (2)

526 with Nitrif = the nitrification rate, $\delta^{15}N_{PN}$ = the N isotopic composition of suspended 527 material (1.74‰); $\delta^{^{18}O_{H2O}}$ = the oxygen isotopic composition of ambient water; $\varepsilon_{\rm R}$ = the 528 discrimination during remineralisation (2‰); ε_{NH4U} = the isotope discrimination during 529 NH₄⁺ uptake(5‰); ε_{AMO} = the discrimination during NH₄⁺ oxidation (15‰; ε_{NiU} = the 530 discrimination during nitrite uptake (1‰); ε_{NiO} = the discrimination during nitrite 531 oxidation (-12.5%) ; x = the fractional yield of ammonium uptake relative to 532 ammonium remineralisation (with NH_4 ⁺ remin. = $AmU + AmO$) and $y =$ the fractional 533 yield of nitrite uptake relative to ammonium oxidation oxidation (with AmO = NiU +

534 NiO). Table 2 gives the selected values for the different discrimination factors as taken 535 from the literature.

536 The theoretical in-situ nitrate isotopic values at the end of the observation period are 537 considered to result from the weighted impact of uptake, nitrification and upwelling 538 and were calculated as follows:

539 $\delta^{15}N_{NO3} =$

540
$$
\frac{Uptake(\delta^{15}N_{NOS} - \varepsilon_{NaU}Lnf) + Nitrif[\delta^{15}N_{PN} - \varepsilon_R + x(\varepsilon_{NH4U} - \varepsilon_{AmO}) + y(\varepsilon_{NiU} - \varepsilon_{NiO})] + Upw(\delta^{15}N_{NOST min})}{Uptake + Nitrif + Upwelling}
$$

541

542 and

543
$$
\delta^{18}O_{NO3} = \frac{Uptake(\delta^{18}O_{NO3} - \varepsilon_{NaU}Lnf) + Nitrif(\delta^{18}O_{H2O}) + Upw(\delta^{18}O_{NO3T\min})}{Uptake + Nitrif + Upwelling}
$$

544

545 With the different ε values = the isotopic discriminations; $\delta^{15}N_{NO3Tmin}$ and $\delta^{18}O_{NO3Tmin}$ = 546 isotopic composition for the subsurface temperature minimum waters (ε and δ values 547 are given in Table 2); *f* = fraction of remaining nitrate; *x* and *y*, as defined above; 548 Uptake = nitrate uptake rate; Nitrif = nitrification rate; Upw = rate of vertical advection 549 of nitrate.

550 The best fit between observed and calculated isotopic compositions is searched using a 551 optimization scheme with nitrification, upwelling from subsurface waters (T_{min} waters 552 at 100 to 150 m depth), NH₄⁺ oxidation and NO₂ uptake as adjustable variables.

The matching of observed and calculated nitrate draw down and the matching of NH₄⁺ 553 554 oxidation with $NO₂$ uptake + nitrification are imposed constraints. The best fit 555 calculations yield nitrification rates of 1.7 \pm 2.3 and 17.4 \pm 4.1 mmol m⁻² d⁻¹ for 556 Meander and Plateau, respectively (Table 3). Best fit values are 0 and 5.5 mmol $m^2 d^{-1}$ 557 for NO₂ uptake and 4.0 and 6.1 mmol m⁻² d⁻¹ for NO₃ upwelling, for Meander and 558 Plateau sites respectively (Table 3). We note that the values for nitrate upwelling are 559 quite similar to the value of 7.4 mmol $m² d⁻¹$ we calculate, as based on an Ekman 560 pumping velocity of 3 x 10⁻⁶ m s⁻¹ for the studied KEOPS 2 area, reported by Gille et al. 561 (2014), and an average subsurface (150m) NO_3 concentration of 28.5 μ M. In case the 562 NO₃ upwelling rate is fixed and set equal to the calculated value of 7.4 mmol m⁻² d⁻¹ based on the Ekman pumping velocity, the best fit nitrification rates are slightly smaller 564 but more constrained with values of 1.3 \pm 1.2 and 16.2 \pm 2.4 mmol m⁻² d⁻¹, for Meander and Plateau, respectively. For the Meander site the evidence for nitrification 566 is poor, in agreement with the fact that surface water $\Delta(15-18)$ values remain small and quite constant over the 1 month period of observation and are similar to those for the HNLC R-2 reference station. We also verified the effect of nitrite presence on these 569 calculations. Indeed, Rafter et al. (2012) report a lowering of the true nitrate δ^{15} N and 570 $\,$ $\,$ 6 18 O compositions by 0.4‰ and 0.2‰, respectively, in case nitrite contents amount to some 0.8% of the nitrate content, what is the case here (see also methods section 2.2). It appears that nitrification rates above the Plateau would be reduced by at most 7% due to unaccounted for nitrite.

We performed a sensitivity test to verify the range (minimum – maximum) of nitrification, nitrite uptake and nitrate upwelling rates, taking into account the measurement errors on isotopic compositions (as given in the Methods section) and the observed variability on nitrate and ammonium uptake rates. It appears for the Meander site that the min. – max. range of possible nitrification rates reaches from 0 to 11 mmol m⁻² d⁻¹, a range which narrows from 0 to 4 mmol m⁻² d⁻¹ in case NO₃ upwelling is kept fixed. The situation is quite different for the Plateau site where the 581 min. – max. range of nitrification reaches from 6 to 27 mmol $m⁻² d⁻¹$ which narrows 582 down from 10 to 22 mmol $m² d⁻¹$ when upwelling is kept fixed. From this we conclude for the Plateau area significant surface layer nitrification needs to be invoked to explain the observed nitrate isotopic compositions and which may represent as much as 48% of the nitrate uptake. For the Meander the evidence for nitrification is poor.

The conditions leading to the high upper ocean nitrification above the Plateau are believed to be related with the depth range of the euphotic layer and the mixed layer.

Above the Plateau the euphotic layer (0.1% PAR level) is consistently shallower than the mixed layer and any nitrate produced from nitrification, a process which is supposedly inhibited by light (Olson, 1981; Guerero and Jones, 1996), at the bottom of the euphotic layer therefore becomes retained in the surface mixed layer. This aspect is discussed in more detail in a paper by Fripiat et al. (submitted). The calculated nitrification rate for the Kerguelen Plateau significantly exceeds some earlier estimates and which led to the conclusion that nitrification is a rather minor process equivalent to <10% of phytoplankton nitrate uptake in Southern Ocean waters (Olson, 1981; Trull et al., 2008; DiFiore et al., 2009). In contrast, high nitrification rates reaching levels similar to the phytoplankton nitrate demand appear to be common for oligotrophic systems (see e.g., Yool et al.., 2007; Wankel et al., 2007; Mulholland and Lomas, 2008 and references therein). Nevertheless, conditions for significant nitrification activity appear to be met in the studied Kerguelen area. For one thing, ammonium concentrations are relatively high, reaching up to 0.5, 0.7 and 0.8 µM within the first 100m for the PF, Meander and Plateau sites, respectively (Figure 3) thus providing the substrate for any bacterial and archaeal ammonium oxidizing activity. Furthermore, nitrite concentrations reach up to 0.33 µM in the upper 100m of water column (Table 1), again indicating nitrification activity is ongoing there. Archaea do abound in the Southern Ocean (Church et al., 2003) and may exhibit a specific affinity for ammonia similar to the one for diatoms, as reported for the cultivated marine ammonia oxidizing archeon (*Nitrosopumilus maritimus)* (Martens-Habbena et al., 2009 and Stahl and de la Torre, 2012).

Conclusions

The present data set adds to the existing data set on dual nitrate isotopic composition for the seasonally ice covered Polar Antarctic Zone (DiFiore et al., 2009) and a meridional section in the Pacific sector (Rafter et al., 2013). It also adds information on the seasonal evolution of nitrate isotopic composition in the iron fertilized Kerguelen area, by complementing an earlier study that was conducted during summer in the

same area (Trull et al., 2008). Published work related to the late summer KEOPS 1 study in the same area as investigated in the present study, highlighted the large difference between the seasonal drawdown of silicic acid and nitrate, with the latter being moderate despite similar Si, N uptake rates (Mosseri et al., 2008). Those results pointed toward the occurrence of significant remineralisation and nitrate production. The present work confirms the significance of nitrification in the area, with nitrification equivalent to up to 47% of the nitrate uptake over the Kerguelen Plateau area. This finding of large nitrification rates in nitrate-replete environments was unexpected a priori, in view of the earlier studies outside the Kerguelen area which concluded to minor nitrification effects in Southern Ocean surface waters (Olson, 1981, DiFiore et al., 2009). A direct result of this condition is that estimates of New or Exportable Production which are based on the assumption that all surface water nitrate results from nitrification in the deep ocean and vertical supply to the surface waters, are too high. Correcting New Production for the effect of nitrification would bring closer the estimates of exportable production and Export production during KEOPS 2, as 632 measured with the 234 Th methodology (see papers by Cavagna et al., 2014 and Planchon et al., 2014, both in this issue).

Acknowledgements

We thank the Captain and the crew of Marion-Dufresne as well as KEOPS 2 Chief scientists B. Quéguiner and S. Blain for their assistance and help during the cruise. We are grateful to the Institut Paul Emile Victor (IPEV) for having granted us access to the Marion Dufresne facilities. This work was supported by the French Research program of INSU-CNRS LEFE-CYBER the French ANR(SIMI-6 program, ANR-10-BLAN-0614), the French CNES (Centre National d'Etudes Spatiales) and the French Polar Institute IPEV (Institut Polaire Paul-Emile Victor). The research was conducted with grants from Belgian Science Policy (BELSPO, grant SD/CA/05A); Flanders Research Foundation (FWO; grant G071512N); Vrije Universiteit Brussel, Strategic Research Plan); the Antarctic Climate and Ecosystem Cooperative Research Center (ACE-CRC, Hobart, Australia). The altimeter and colour/temperature products for the Kerguelen area were produced by Ssalto/Duacs and CLS with support from Cnes. F. Fripiat is Post-Doc at FWO, Flanders Research Foundation; C. Fernandez was partially supported by Fondap 15110027 Incar. We acknowledge the help of Natacha Brion, Leen Rymenans and Michael Korntheuer during nitrate and nitrate isotope analyses and thank the two anonymous reviewers for their constructive comments and criticisms.

-
-
- **References:**
- Archambeau, A.-S., Pierre, C., Poisson, A., and Schauer, B.: Distributions of oxygen and carbon stable isotopes and CFC-12 in the water masses of the Southern Ocean at 30°E from South Africa to Antarctica: results of the CIVA1 cruise, J. Mar. Syst., 17, 25-38, 1998.
- Bianchi, M., Feliatra, F., Tréguer, P., Vincendeau, M.-A., and Morvan, J.: Nitrification rates, ammonium and nitrate distribution in upper layers of the water column and in sediments of the Indian sector of the Southern Ocean, Deep-Sea Res. Pt. II, 44, 1017-1032, 1997.
- Blain, S., Capparos, J., Guéneuguès, A., Obernosterer, I., and Oriol, L.: Distributions and stoichiometry of dissolved nitrogen and phosphorus in the iron fertilized region near Kerguelen (Southern Ocean), Biogeosciences, 12, 623-635. doi:10.5194/bg-12- 623-2015, 2015.

Blain, S., Quéguiner, B., Armand, L., Belviso, S., Bombled, B., Bopp, L., Bowie, A., Brunet, C., Brussaard, C., Carlotti, F., Christaki, U., Corbière, A., Durand, I., Ebersbach, F., Fuda, J.-L., Garcia, N., Gerringa, L., Griffiths, B., Guigue, C., Guillerm, C., Jacquet, S., Jeandel, C., Laan, P., Lefèvre, D. , Lo Monaco, C., Malits, A., Mosseri, J., ObernostererI., ParkY.-H., Picheral, M., Pondaven, P., Remenyi, T., Sandroni, V., Sarthou, G., Savoye, N., Scouarnec, L., Souhaut, M., Thuiller, D., Timmermans, K., Trull, T., Uitz, J., van Beek, P., Veldhuis, M., Vincent, D., Viollier, E., Vong, L., and Wagener, T.: Effect of natural iron fertilization on carbon sequestration in the Southern Ocean, Nature, 446, 1070-1074, 2007.

- Blain, S., Quéguiner, B., and Trull, T.: The natural iron fertilization experiment KEOPS (Kerguelen Ocean and Plateau compared Study): An overview, Deep-Sea Res. Pt. II, 55, 559-565, 2008.
- Böhlke, J., Mroczkowski, S., and Coplen, T.B.: Oxygen isotopes in nitrate: New 683 reference materials for ${}^{18}O:{}^{17}O:{}^{16}O$ measurements and observations on nitrate-water equilibrations, Rapid Comm. Mass Sp., 17, 1835-1846, 2003.
- Buchwald, C., and Casciotti, K.L.: Oxygen isotopic fractionation and exchange during bacterial nitrite oxidation, Limnol. Oceanogr., 55, 1064-1074, 2010.
- Casciotti, K.L.: Inverse kinetic isotope fractionation during bacterial nitrite oxidation, Geochim. Cosmochim. Acta, 73, 2061-2076, 2009.
- Casciotti, K.L., Böhlke, J.K., McIlvin, M.R., Mroczkowski, S.J. and Hannon, J.E.: Oxygen Isotopes in Nitrite: Analysis, Calibration, and Equilibration, Anal. Chem., 79, 2427- 2436, 2007.
- Casciotti, K.L., Sigman, D.M., Hastings, M. G., Böhlke, J.K., and Hilkert, A.: Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method, Anal. Chem., 74, 4905-4912, 2002.
- Casciotti, K.L., Sigman, D.M., and Ward, B.B.: Linking diversity and stable isotope fractionation in ammonia-oxidizing bacteria, Geomicrobiol. J., 20, 335-353, 2003.
- Cavagna, A.J., Lefèvre, D., Dehairs, F., Elskens, M., Fripiat,F., Closset, I., Lasbleiz, M., Flores-Leive L., Cardinal, D., Leblanc, K., Fernandez, C., Oriol, L., Blain, S., and Quéguiner, B.: Biological productivity regime in the surface water around the

Kerguelen Island in the Southern Ocean – from the use of an integrative approach, Biogeosciences Discuss., 11, doi:10.5194/bgd-11-18073-2014, 2014.

Church, M.J., DeLong, E.F., Ducklow, H.W., Karner, M.B., Preston, C.M., and Karl, D.M.:

Abundance and distribution of planktonic Archaea and Bacteria in the waters west of the Antarctic Peninsula, Limnol. Oceanogr., 48, 1893-1902, 2003.

- Closset, I., Lasbleiz, M., Leblanc, K., Quéguiner, B., Cavagna, A.-J., Elskens, M., Navez, J., and Cardinal, D.: Seasonal evolution of net and regenerated silica production around a natural Fe-fertilized area in the Southern Ocean estimated from Si isotopic approaches, Biogeosciences, 11, 5827–5846, doi:10.5194/bg-11-5827- 2014, 2014.
- DiFiore, P.J., Sigman, D.M., and Dunbar, R.B.: Upper ocean nitrogen fluxes in the Polar Antarctic Zone: constraints from the nitrogen and oxygen isotopes of nitrate, Geochem., Geophys. Geosyst., 10, doi:10.1029/2009GC002468, 2009.
- DiFiore, P.J., Sigman, D.M., Karsh, K.L., Trull, T.W., Dunbar, R.B., and Robinson, R.S.: Poleward decrease in the isotope effect of nitrate assimilation across the Southern Ocean, Geophys. Res. Lett., 37, L17601, doi:10.1029/2010GL044090, 2010.
- DiFiore, P.J., Sigman, D.M., Trull, T.W., Lourey, M.J., Karsh, K., Cane, G., and Ho, R.: Nitrogen isotope constraints on subantarctic biogeochemistry, J. Geophys. Res., 111, C08016, doi:10.1029/2005JC003216, 2006.
- Fogel, M.L., and Cifuentes, L.A.: Isotope fractionation during primary production, in: Organic Geochemistry, edited by Engel, M.H., and. Macko, S.A, Plenum Press, N.Y., 73-98, 1993.
- Fripiat, F., Sigman, D. M., Fawcett, S. E., Rafter, P. A., Weigand, M. A. and Tison, J.-L.: New insights into sea ice nitrogen biogeochemical dynamics from the nitrogen isotopes, Global Biogeochem. Cy., 28, DOI: 10.1002/2013GB004729, 2014.
- Fukamachi, Y., Rintoul, S. R., Church, J. A., Aoki, S., Sokolov, S., Rosenberg, M. A., and Wakatsuchi, M.: Strong export of Antarctic bottom water east of the Kerguelen Plateau, Nat. Geosci., 3, 327–331, 2010.
- Gille, S. T., Carranza, M. M., Cambra, R., and Morrow, R.: Wind-induced upwelling in the Kerguelen Plateau Region, Biogeosciences, 11, 6389–6400, 2014doi:10.5194/bg-11-6389-2014, 2014.
- Granger, J., Prokopenko, M.G., Mordy, C.W., and Sigman, D.M., The proportion of remineralized nitrate on the ice-covered eastern Bering Sea shelf evidenced from the oxygen isotope ratio of nitrate, Global Biogeochem. Cy., 27, 962 – 971, doi:10.1002/gbc.20075, 2013.
- Granger, J., Prokopenko, M. G., Sigman, D. M., Mordy, C. W., Morse, Z. M., Morales, L.
- V., Sambrotto, R. N., and Plessen, B.: Coupled nitrification-denitrification in 737 Sediment of the eastern Bering Sea shelf to ^{15}N enrichment of fixed N in shelf waters, *J. Geophys. Res.,* 116, doi:10.1029/2010JC006751, 2011.
- Granger, J., Sigman, D. M., Needoba, J. A., and Harrison, P. J.: Coupled nitrogen and oxygen isotope fractionation of nitrate during assimilation by cultures of marine phytoplankton, Limnol. Oceanogr., 49, 1763–1773, 2004.
- Granger, J., Sigman, D.M., Lehmann, M.F., and Tortell, P.D.: Nitrogen and oxygen isotope fractionation during dissimilatory nitrate reduction by denitrifying bacteria, Limnol. Oceanogr., 53, 2533–2545, 2008.
- Granger, J., Sigman, D. M., Rohde, M. M., Maldonado, M. T., and Tortell, P. D.: N and O 746 isotope effects during nitrate assimilation by unicellular prokaryotic and eukaryotic

plankton cultures, Geochim. Cosmochim. Ac., 74, 1030–1040, 2010.

- Guerrero, M. A., and Jones, R. D.: Photoinhibition of marine nitrifying bacteria 1. Wavelength-dependent response, Mar. Ecol. Prog. Ser. 141, 183–192, 1996.
- Hoch, M. P., Fogel, M. L., and Kirchman, D. L.: Isotope fractionation associated with ammonium uptake by a marine bacterium, Limnol. Oceanogr., 37, 1447–1459, 1992.
- Jacquet, S. H. M., Dehairs, F., Savoye, N., Obernosterer, I., Christaki, U., Monnin, C., and Cardinal, D.: Mesopelagic organic carbon remineralization in the Kerguelen Plateau region tracked by biogenic particulate Ba, Deep-Sea Res. Pt. II, 55, 868– 879, 2008.
- Jacquet, S. H. M., Dehairs, F., Cavagna, A. J., Planchon, F., Monin, L., André, L., Closset, I., and Cardinal, D.: Early season mesopelagic carbon remineralization and transfer 759 efficiency in the naturally iron-fertilized Kerguelen area, Biogeosciences Discuss., 11, 9035–9069, 10doi:10.5194/bgd-11-9035-2014, 2014.
- Kendall, C.: Tracing nitrogen sources and cycling in catchments, in: Isotope Tracers in Catchment Hydrology, edited by: Kendall, C., and McDonnell, J. J., Elsevier, 519– 576, 1998.
- Knapp, A.N., Sigman, D.M., Lipschultz, F., Kustka, A.B., and Capone, D.G.: Interbasin 765 isotopic correspondence between upper - ocean bulk DON and subsurface nitrate and its implications for marine nitrogen cycling, Global Biogeochem. Cy., 25, GB4004, doi:10.1029/2010GB003878, 2011.
- Lasbleiz, M., Leblanc, K., Blain, S., Ras, J., Cornet-Barthaux, V., Hélias Nunige, S., and Quéguiner, B.: Pigments, elemental composition (C, N, P, Si) and stoichiometry of particulate matter, in the naturally iron fertilized region of Kerguelen in the Southern Ocean, Biogeosciences, 11, 5931–5955, doi:10.5194/bg-11-5931-2014, 2014.
- Martens-Habbena, W., Berube, P. M., Urakawa, H., de la Torre, J. R., and Sath, D. A.:
- Ammonia oxidation kinetics determine niche separation of nitrifying Archaea and Bacteria, Nature, 461, 976–979, 2009.
- McCartney, M. S. and Donohue, K. A.: A deep cyclonic gyre in the Australian–Antarctic Basin, Prog. Oceanogr., 75, 675–750, 2007.
- 778 Möbius, J.: Isotope fractionation during nitrogen remineralization (ammonification): Implications for nitrogen isotope biogeochemistry, Geochim. Cosmochim. Ac., 105, 422-432, 2013.
- Mosseri, J., Quéguiner, B., Armand, L., and Cornet-Barthaux, V.: Impact of iron on silicon utilization by diatoms in the Southern Ocean: a case of Si/N cycle decoupling in a naturally iron–enriched area, Deep-Sea Res. Pt. II, 55, 801–819, 2008.
- Mulholland, M. R. and Lomas, M. W.: Nitrogen uptake and assimilation, in: Nitrogen in the Marine Environment, edited by: Mulholland, M. R. and Capone, D. J., Elsevier, 303–384, 2008.
- 787 Olson, R. J.: N tracer studies of the primary nitrite maximum, J. Mar. Res., 39, 203–226, 1981.
- Olson, R. J.: Differential photoinhibition of marine nitrifying bacteria a possible mechanism for the formation of the primary nitrite maximum, J. Mar. Res., 39, 227–238, 1981.
- Park, Y.-H., Durand, I., Kestenare, E., Rougier, G., Zhou, M., d'Ovidio, F., Cottéa, C., and Lee, J.-H.: Polar Front around the Kerguelen Islands: an up-to-date determination and associated circulation of surface/subsurface waters, J. Geophys. Res.–Oceans, 119, DOI: 10.1002/2014JC010061, 2014.
- Park, Y.-H., F. Roquet, I. Durand, and Fuda, J.-L.: Large-scale circulation over and around the Northern Kerguelen Plateau, Deep-Sea Res. Pt. II, 55, 566–581, 2008.
- Paul, D., Skrzypek, G., and Fórizs, I.: Normalization of measured stable isotopic compositions to isotope reference scales – a review, Rapid Commun. Mass Sp., 21, 3006–3014, 2007.
- 801 Pennock, J. R., Velinsky, D. J., Ludlam, J. M., and Sharp, J. H.: Isotopic fractionation of ammonium and nitrate during uptake by Skeletonema costatum: implications for δ^{15} N dynamics under bloom conditions, Limnol. Oceanogr., 41, 451–459, 1996.
- Planchon, F., Ballas, D., Cavagna, A.-J., Van Der Merwe, P., Bowie, A., Trull, T., Laurenceau, E., Davis, D., and Dehairs, F.: Carbon export in the naturally iron-806 **Fertilized Kerguelen area of the Southern Ocean using** 234 Th-based approach, Biogeosciences Discuss., doi:10.5194/bgd-11-15991-2014, 2014.
- Rafter, P. A., DiFiore, P. J., and Sigman, D. M.: Coupled nitrate nitrogen and oxygen 809 isotopes and organic matter remineralization in the Southern and Pacific Oceans, J. Geophys. Res.–Oceans, 118, 4781–4794, doi:10.1002/jgrc.20316, 2013.
- 811 Sigman, D. M., Altabet, M. A., McCorkle, D. C., Francois, R., and Fischer, G.: The δ^{15} N of nitrate in the Southern Ocean: Consumption of nitrate in surface waters, Global Biogeochem. Cy., 13, 1149-1166, 1999.
- 814 Sigman, D. M., Altabet, M. A., McCorkle, D. C., Francois, R., and Fischer, G.: The δ^{15} N of nitrate in the Southern Ocean: Nitrogen cycling and circulation in the ocean interior, J. Geophys. Res.-Oceans, 105, 19,599-19,614, 2000.
- Sigman, D. M., Casciotti, K. L., Andreani, M., Barford, C., Galanter, M., and Böhlke, J. K.: A bacterial method for nitrogen isotopic analysis of nitrate in seawater and freshwater, Anal. Chem., 73, 4145–4153, 2001.
- 820 Sigman, D., Granger, J., DiFiore, P., Lehmann, M. M., Ho, R., Cane, G., and van Geen, A.: Coupled nitrogen and oxygen isotope measurements of nitrate along the eastern 822 Morth Pacific margin, Global Biogeochem. Cy., 19, GB4022, doi:10.1029/2005GB002458, 2005.
- Sigman, D. M., Karsh, K. L., and Casciotti, K. L.: Nitrogen isotopes in the ocean, in: Encyclopedia of Ocean Sciences, edited by: Steele, J. H., Turekian, K. K., and Thorpe, S. A., Elsevier, 25, 40–54, 2009a.
- Sigman, D. M., DiFiore, P. J., Hain, M. P., Deutsch, C., Wang, Y., Karl, D. M., Knapp, A. N., Lehmann, M. F., and Pantoja, S.: The dual isotopes of deep nitrate as a 829 constraint on the cycle and budget of oceanic fixed nitrogen, Deep-Sea Res. Pt. I, 56, 1419–1439, 2009b.
- 831 Stahl, D. A. and de la Torre, J.: Physiology and diversity of ammonia-oxidizing archaea, Annu. Rev. Microbiol., 66, 88–101, 2012.
- 833 Trull, T. W., Davies, D., and Casciotti, K.: Insights into nutrient assimilation and export in naturally iron-fertilized waters of the Southern Ocean from nitrogen, carbon and oxygen isotopes, Deep-Sea Res. Pt. II, 55, 820–84, 2008.
- Trull, T.W., Davies, D., Dehairs, F., Cavagna, A.-J., Lasbleiz, M., Laurenceau, E.C., d'Ovidio, F., Planchon, F., Leblanc, K., Quéguiner, B., and Blain, S.: Chemometric perspectives on plankton community responses to natural iron fertilization over and downstream of the Kerguelen plateau in the Southern Ocean, Biogeosciences Discuss., doi:10.5194/bgd-11-13841-2014, 2014.
- 841 Wankel, S. D., Kendall, C., Pennington, J. T., Chavez, F. P., and Paytan, A.: Nitrification in the euphotic zone as evidence by nitrate dual isotopic composition; 843 Observations from Monterey Bay, California, Global Biogeochem. Cy., 21, GB2009, doi:10.1029/2006GB002723, 2007.
- Waser, N. A. D., Harrison, P. J., Nielsen, B., Calvert, S. E., and Turpin, D. H.: Nitrogen isotope fractionation during the uptake and assimilation of nitrate, nitrite, ammonium and urea by a marine diatom, Limnol. Oceanogr., 43, 215–224, 1998.
- 848 Waser, N. A., Yu, Z., Yin, K., Nielsen, B., Harrison, P. J., Turpin, D. H., and Calvert, S. E.: Nitrogen isotopic fractionation during a simulated diatom spring bloom: 850 importance of N- 15 starvation in controlling fractionation, Mar. Ecol.-Prog. Ser., 179, 291–296, 1999.
- Yool, A., Martin, A.P., Fernández, C., and Clark, D.R.: The significance of nitrification for oceanic new production, Nature, 447, 999-1002, 2007.

Table headings:

858 $\frac{\text{Table 1}}{8}$: Average values for Sal, Tpot, Chl-a, NO₂, NH₄⁺, NO₃, Si(OH)₄, $\delta^{15}N_{NO3}$, 859 $\delta^{18}O_{NO3}$ in the upper 100m, for the Plateau, Polar Front Meander, Polar Front sites and the HNLC Reference station. Nutrient data are from the shipboard nutrient 861 team (Blain et al., 2015); Chl-a data are from Lasbleiz et al. (2014); ML depth values 862 are from Y.-H. Park pers. communic..

Table 2: Considered isotopic discrimination factors for model calculations.

Table 3: Plateau and Meander sites: Observed initial and final conditions of nitrate concentrations isotopic compositions; Observed nitrate and ammonium uptake 868 rates (from Cavagna et al., 2014); Calculated nitrification, nitrite uptake, nitrate upwelling rates required to explain the observed nitrate isotopic compositions and nitrate concentrations at the end of the considered growth period.

872 Appendix Table A1: Complete data set. Salinity; Tpot; density; $\delta^{15}N_{NO3}$; $\delta^{18}O_{NO3}$; 873 concentrations of NO_3 ; NO_2 ; NH_4 ⁺. Nutrient data are from Blain et al. (2015).

Figure legends:

Figure 1: (a) Kerguelen area with KEOPS 2 sampling grid. Blue dots = 'Plateau' stations; Red dots = 'Meander' stations; Green dots = stations at the Polar Front and north of the PF; black dot = 'Reference' station; Orange dots = stations outside the 881 Plateau and Meander areas. The black line marks the position of the Polar Front; (b) MODIS Chlorophyll distribution for second half of November 2011 (colour bar: μ ug $\lceil \cdot^1 \rceil$ arrows represent the current speed, with scale marked by the small black arrow (30cm/sec) below the figure (courtesy F. d'Ovidio & Y.-H. Park); (c) T-S 885 diagram (all stations) with $[NO₃]$ superimposed. (ODV-AWI, R. Schlitzer).

886 Figure 2: Water column profiles of (a) NO₃ (μM); (b) δ¹⁵N_{NO3}; (c) δ¹⁸O_{NO3}, and (d) Δ(15-18); Complete data set. Blue circles = Plateau stations; Red circles = Meander 888 stations; Green circles = Polar Front and north of PF stations; Filled black circle = Reference station (R-2).

890 Figure 3: Whole water column distributions of $\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$, NO $_3$, Tpot and Salinity; (a) West to east section starting on the Kerguelen Plateau and crossing the Polar Front Meander; the Polar Front loop is crossed at about 71.3°E and at 74°E; (b) South to North section along about 72°E. (ODV-AWI, R. Schlitzer)

894 • Figure 4: Regressions of $\delta^{15}N$ (left) and $\delta^{18}O$ (right) vs. LN[NO₃]; Top row: whole water column; bottom row: upper 250m, Blue circles: Plateau stations; Red circles: Meander stations; Green circles: Polar Front and north of Polar Front stations.

897 Figure 5: Profiles of $\delta^{18}O_{NO3}$ and Chl-a (µg l⁻¹) profile for stations underlying the high Chlorophyll plume in the vicinity of the Polar Front (green circles; stations TEW-7, TEW-8, F-L) and in the central part of the Polar Front Meander (red circles; stations TNS-6, TNS-1, TEW-6) and the Reference station (black circles; station R-2).

901 • Figure 6: Sections of NH₄⁺, NO₂, $\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$ and $\Delta(15-18)$ in the upper 600m of water column; (a) West to East section; (b) South to north section. $NH_4{}^+$ and $NO_2{}^-$ data are from Blain et al. (2015). (ODV-AWI, R. Schlitzer).

904 Figure 7: Profiles of NH₄⁺ (μ M) and NO₂ (μ M) in the upper 500m for Plateau (blue circles); Meander (red circles); Polar Front (green circles). Superimposed are the

906 late season data for the Plateau region as recorded during KEOPS 1 (open circles; 907 Trull et al., 2008).

908 Figure 8: $\delta^{18}O_{NQ3}$ vs. $\delta^{15}N_{NQ3}$; Blue = Plateau; Red = Meander; Green = Polar Front and 909 north of PF; (a) whole water column; (b) Upper 250 m; (c) Mixed Layer; Grey circles 910 in (B) and (C) represent the late season Plateau values recorded during KEOPS 1

911 (Trull et al., 2008); the black line with slope = 1 represents the evolution of

912 Teference deep water nitrate with $\delta^{15}N_{NO3}$ = 5‰ and $\delta^{18}O_{NO3}$ = 2‰ in case the

913 $15N/14N$ and $18O/16O$ fractionation factors are similar.

915 Table 1: Average values for Sal, Tpot, Chl-a, NO₃, NO₂, NH₄⁺, Si(OH)₄, $\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$ in the upper 100m, for the Plateau, Polar Front Meander, Polar Front sites and the 916 HNLC Reference station. Nutrient data are from the shipboard nutrient team (Blain et al., 2015); Chl-a data are from Lasbleiz et al. (2014); ML depth values are from Y.-H. 917 Park, pers. communic...

918

922 Table 1: Continued

923

924

925

928

930

 $*$ for low ammonium concentrations (<10 μ M)

931

933 Table 3: Plateau and Meander sites: Observed initial and final conditions of nitrate concentration and isotopic composition; Observed nitrate and ammonium uptake rates (from Cavagna et
934 al., 2014); Calculated nitrif

934 al., 2014); Calculated nitrification, nitrite uptake, nitrate upwelling rates required to explain the observed nitrate isotopic composition and nitrate concentration at the end of the
935 considered growth period. considered growth period.

^a average rates from Cavagna et al. (2014)

 $^{\rm b}$ matching with observed value at T $_{\rm end}$ is imposed

 $\mathrm{c}\,$ Nitrate upwelling fixed at 7.4 mmol m $\mathrm{c}\,$ d $\mathrm{d}\,$, based on the Ekman pumping velocity in Gille et al. (2014)

Station Name	Lon °E	Lat °S	Seafloor, m	$\mathsf{CTD}\ \mathsf{N}^\circ$	Depth, m	Salinity	Tpot °C	Density, σ_{θ}	$\delta^{15}N_{NO3}$, ‰	$\delta^{18}\!O_{N03}$, $\%$	$[NO3], \mu M$	$[NO2]l \mu M$	$[NH_4^+]$, μ M
$A3-1$	72.08	-50.63	530	$\overline{4}$	469	34.359	2.184	27.443	5.28	3.08	35.4	0.05	0.05
					352	34.254	2.106	27.366	5.37	2.99	34.9	0.04	0.01
					278	34.137	1.821	27.294	5.61	3.71	33.7	0.03	0.03
					252	34.099	1.744	27.270	5.45	2.92	33.4	0.04	0.01
					227	34.062	1.769	27.238	5.65	3.37	32.9	0.04	\sim
					202	34.011	1.693	27.203	5.63	3.20	32.1	0.05	0.04
					173	33.934	1.670	27.142	5.79	\sim	30.7	0.2	0.06
					151	33.915	1.740	27.122	5.74	3.31	29.9	0.26	0.16
					101	33.904	1.727	27.114	5.85	3.55	29.7	0.26	0.12
					41	33.897	1.698	27.111	5.89	3.43	29.2	0.27	0.08
					12	33.896	1.695	27.110	5.80	3.22	28.8	0.27	0.11
TNS-8	72.24	-49.46	1030	$\, 8$	992	34.660	2.169	27.686	5.08	3.36	34.7	0.04	\blacksquare
					903	34.642	2.201	27.669	5.00	2.64	34.7	0.03	\blacksquare
					702	34.565	2.257	27.602	4.93	\sim	34.7	0.03	
					601	34.528	2.283	27.571	5.09	2.11	36.2	0.03	
					501	34.466	2.268	27.523	5.17	2.19	36.7	0.03	
					401	34.374	2.182	27.456	5.27	2.41	36.2	0.03	$\pmb{0}$
					303	34.244	1.954	27.369	5.42	2.31	35.7	0.04	$\pmb{0}$
					251	34.113	1.909	27.268	5.40	2.50	34.2	0.04	$\pmb{0}$
					203	33.912	1.796	27.116	5.89	4.15	30.0	0.18	0.17
					149	33.877	1.903	27.079	6.10	3.81	29.5	0.26	0.26
					101	33.870	2.055	27.062	6.15	3.52	28.4	0.27	0.19
					41	33.867	2.126	27.054	6.10	3.74	28.6	0.28	0.19
					12	33.867	2.126	27.054	6.07	3.41	28.1	0.28	0.20

936 Table A1: Complete data set. Salinity; Tpot; density; $\delta^{15}N_{NOS}$; $\delta^{18}O_{NOS}$; concentrations of NO₃; NO₂; NH₄⁺; Nutrient data are from Blain et al. (2015).

944

948

951

952

962

963

979

982

983

992 Figure 2

996 Figure 3a

1003

1004 Figure 4

 $48°S$

 47° S

 $49°S$

 50° S

depth [m]

1013

1014 Figure 6b

1021 Figure 8