

The $\delta^{15}\text{N}$ of chlorophyll to reconstruct the cycle in Adélie Land, East Antarctica, over the last 2000 years

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Authors response to referee #1

Major comments

Reviewer 1 - Comment 1. Sutre et al present a new Southern Ocean $\delta^{15}\text{N}$ record based on chlorophyll, which, to the best of my knowledge, is the first of its kind and the first $\delta^{15}\text{N}$ record in the Southern Ocean to cover the last 2000 kyr. As such, the dataset is sufficiently novel and deserves publication in a journal such as Biogeoscience. However, several clarifications are required before the manuscript can be accepted.

Reviewer 1-Response 1. We thank anonymous referee 1 for the interest given to this dataset and its novelty. We considered all their comments and suggestions and will modify the paper according the responses detailed below.

R1-C2. First, the discussion of the factors controlling chlorophyll $\delta^{15}\text{N}$, in Section 5.1, should be rewritten in light of the existing literature. It is unclear why the authors focus on N_2 fixation and denitrification, given that these processes are not considered to control nitrate $\delta^{15}\text{N}$ (and exported $\delta^{15}\text{N}$) in the Antarctic Zone. Several studies, including (Altabet and Francois, 1994; DiFiore et al., 2009; Fripiat et al., 2019; Sigman et al., 1999), have shown that nitrate $\delta^{15}\text{N}$, and exported organic $\delta^{15}\text{N}$, are controlled to first order by the degree of nitrate consumption and the associated isotopic discrimination.

R1-R2. We thank the reviewer for this comment and agree that the discussion of the factors controlling chlorophyll $\delta^{15}\text{N}$ should be better aligned with the existing literature. The revised section will now first focus on nitrate utilisation and isotopic discrimination (Altabet and François, 1994; Sigman et al., 1999; DiFiore et al., 2009; Fripiat et al., 2019), before discussing processes occurring within the phytoplankton cells that may further modify the relationship between nitrate $\delta^{15}\text{N}$ and chlorophyll $\delta^{15}\text{N}$ (Needoba and Harrison, 2004; Needoba et al., 2004; DiFiore et al., 2006; DiFiore et al., 2010; Fripiat et al., 2019; Ohkouchi et al., 2024). This revised structure will place the dominant controls on the proxy first while retaining the additional processes necessary to discuss the specific

characteristics of the chlorophyll $\delta^{15}\text{N}$ signal. This will provide a more direct framework for interpreting our chlorophyll $\delta^{15}\text{N}$ downcore record.

In our initial discussion, we briefly introduced the different sources and sinks involved in the marine nitrogen cycle before focusing on the chlorophyll $\delta^{15}\text{N}$ proxy. We agree that it overemphasised processes such as N_2 fixation and nitrification, which are not expected to be primary controls on nitrate $\delta^{15}\text{N}$ in the Antarctic Zone. We will substantially reduce the discussion of these secondary processes and move it later in the discussion. However, we chose not to remove it entirely, as both N_2 fixation and denitrification have been reported in certain sectors of the Antarctic Zone and may locally - to a still unknown extent - influence the nitrogen cycle.

R1-C3. I would also recommend a more detailed discussion of the offset between chlorophyll $\delta^{15}\text{N}$ and exported organic $\delta^{15}\text{N}$. First, the observed offset appears broadly consistent with literature estimates, for example $5.3 \pm 1.6\text{‰}$ in Sachs et al. (1999), and this should be clearly discussed. Second, Sachs et al. (1999) report variability in this offset, with a standard deviation of 1.6‰ . The authors should rule out that this variability can explain the variability reported in their records, and add some discussion on the factors that can control such an offset (growth rates, shifts in species composition, etc).

R1-R3. We agree that the original discussion placed too much emphasis on external factors such as the different nitrate sources, instead of the internal processes and offsets that control variations in $\delta^{15}\text{N}_{\text{chl}}$. In the revised manuscript, we will therefore better detail the isotopic relationships between chlorophyll, exported organic matter, and the primary source of nitrogen (i.e. nitrates supplied by the LCDW) (Needoba and Harrison, 2004; Needoba et al., 2004; DiFiore et al., 2006; DiFiore et al., 2010; Fripiat et al., 2019; Ohkouchi et al., 2024). Establishing these relationships provides a more robust framework for interpreting both the absolute values and the temporal variations in the $\delta^{15}\text{N}_{\text{chl}}$. It also demonstrates that $\delta^{15}\text{N}_{\text{chl}}$ can be used to estimate $\delta^{15}\text{N}_{\text{phyto}}$, as a diagenetic-free signal, and reconstruct surface ocean conditions at the time of nitrate assimilation.

To better constrain the isotopic composition of exported biomass, we will add a new figure showing estimates of $\delta^{15}\text{N}_{\text{phyto}}$ derived from $\delta^{15}\text{N}_{\text{chl}}$ after correcting for the fractionation associated with chlorophyll synthesis (Figure R1):

$$\delta^{15}\text{N}_{\text{phyto}} = \delta^{15}\text{N}_{\text{chl}} - \gamma_{\text{chl}},$$

where $\gamma_{\text{chl}} = -4.7 \pm 1.7\text{‰}$, the fractionation associated with chlorophyll *a* synthesis relative to biomass as measured by Ohkouchi et al. (2024). These estimates are compared with $\delta^{15}\text{N}_{\text{bulk}}$ measurements obtained from the same sediment samples. Although $\delta^{15}\text{N}_{\text{bulk}}$ integrates nitrogen from multiple sources and is likely to be substantially affected by diagenetic alteration, the estimated $\delta^{15}\text{N}_{\text{phyto}}$ exhibits a more limited downcore variability, consistent with the preservation of a more stable chlorophyll-derived signal. Considering both the uncertainty associated with γ_{chl} and the analytical uncertainty ($\sim 0.6\text{‰}$), some $\delta^{15}\text{N}_{\text{phyto}}$ values overlap with the $\delta^{15}\text{N}_{\text{bulk}}$ range in the upper part of the core. This suggests that both proxies preserve a common primary nitrogen signal near the sediment surface, whereas the progressive enrichment of $\delta^{15}\text{N}_{\text{bulk}}$ downcore further highlights the increasing influence of diagenetic alteration.

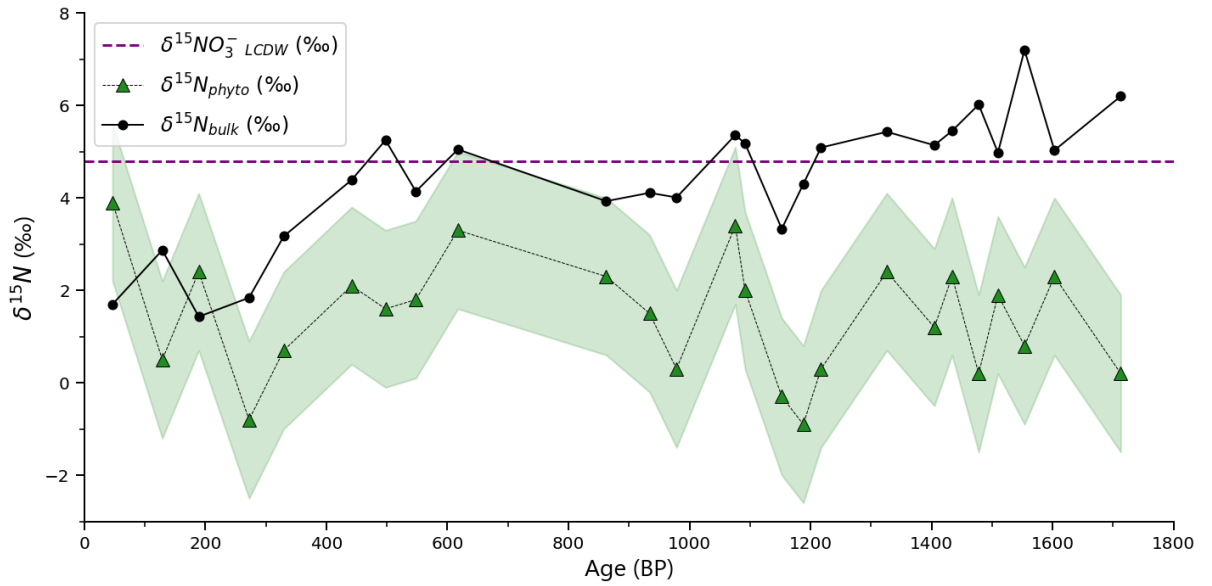


Figure R1. Comparison of $\delta^{15}\text{N}$ records of bulk nitrogen and phytoplankton (calculated) relative to the modern $\delta^{15}\text{N}$ of nitrates from the LCDW (Lower Circumpolar Deep Water). The green envelope represents the uncertainty of the γ_{chl} fractionation factor. Both records share the same analytical precision ($\sigma = \pm 0.6\text{‰}$).

For this comparison, we will only use $\delta^{15}\text{N}_{\text{bulk}}$ measurements obtained from the same depths as the chlorophyll measurements, thus allowing both records to represent the same temporal interval over the last ~2000 years. Although this comparison indicates that $\delta^{15}\text{N}_{\text{bulk}}$ may preserve more of its primary isotopic signal than previously assumed, $\delta^{15}\text{N}_{\text{chl}}$ remains the more informative proxy. Indeed, the reconstructed $\delta^{15}\text{N}_{\text{phyto}}$ values remain below the $\delta^{15}\text{N}$ signature of nitrate supplied by mCDW (derived from LCDW), as expected from isotopic fractionation during nitrate assimilation, whereby phytoplankton biomass is depleted in ^{15}N relative to its nitrate source. This relationship provides the mechanistic basis for reconstructing nitrate utilisation from the chlorophyll $\delta^{15}\text{N}$ record. Conversely, $\delta^{15}\text{N}_{\text{bulk}}$ values are above the source value below 500 years BP, indicating a diagenetic impact.

We will further discuss isotopic fractionation during nitrate assimilation to relate the $\delta^{15}\text{N}_{\text{phyto}}$ to past nutrient conditions, based on the following offset: $\delta^{15}\text{N}_{\text{NO}_3^-} = \delta^{15}\text{N}_{\text{phyto}} + \epsilon$, with ϵ the fractionation factor associated with nitrate assimilation. We will give insights into ϵ 's potential dependence on interspecific differences, phytoplankton physiology, and environmental conditions. Changes in species composition are difficult to quantify, as species-specific fractionation factors are not well constrained for all taxa. In the Adélie Land region, diatoms dominate the phytoplankton productivity (Wright and van den Enden, 2000; Beans et al., 2009). In diatoms, we note that *Chaetoceros* resting spores (CRS) have a particularly high fractionation factor and result in low $\delta^{15}\text{N}$ diatom-bound values (Dove et al., 2025). However, the increase in CRS at 1450-1150 and 450-150 yrs BP, from ~20% to ~40%, is not large enough to explain the low $\delta^{15}\text{N}_{\text{chl}}$ values at ~1200 and 300 yrs BP. Overall, current evidence suggests that interspecific differences in isotopic fractionation have relatively small influence on $\delta^{15}\text{N}$ signals of mixed communities (Jones et al., 2022; Robinson et al., 2025). The isotope effect associated with nitrate assimilation is also sensitive to phytoplankton physiological state. In particular, light limitation can reduce growth (Vives et al., 2022) and decouple nitrate uptake from intracellular nitrate reduction, increasing nitrate efflux and thereby enhancing the expression of nitrate isotope discrimination (Needoba and Harrison, 2004). Reduced growth rate alone does not

necessarily imply a larger isotope effect, as demonstrated by experiments under nutrient limitation (Needoba et al., 2004). We will revise part 5.1 of the discussion (i.e. rationales) to relate the different offsets to environmental conditions such as light availability, stratification, and mixing (DiFiore et al., 2010). Having identified these factors contributing to the variability of the $\delta^{15}\text{N}_{\text{chl}}$ record, we will move on to section 5.2 of the discussion, where we will reconstruct the paleoenvironmental conditions that may exacerbate these factors and explain the high variability.

R1-C4. Second, I would be caution regarding some of the interpretations of the records. The authors infer an influence of sea ice and modes of atmospheric variability, but overall, I am not convinced that the records fully support these statements. For example, in Fig. 3a, do the different periods highlighted by the grey shaded areas really exhibit statistically distinct chlorophyll d15N values? This is unclear to me and would require a more thorough assessment of variability and trends.

R1-R4. We thank the reviewer for pointing out this ambiguity. We agree that the grey-shaded areas in Fig. 3, which were intended to represent periods of atmospheric and sea-ice variability following Crosta et al. (2021), may have given the misleading impression that these intervals bear statistically distinct $\delta^{15}\text{N}_{\text{chl}}$ ranges. This is particularly problematic for the 1100–1500 yr BP interval, during which both high and low $\delta^{15}\text{N}_{\text{chl}}$ values occur despite the diatom proxies indicating generally low sea-ice cover. To address this issue, we will remove the grey-shaded areas from the revised figure and no longer use these predefined intervals as the basis for our interpretation. This will avoid implying distinct phases that are not supported by the new data.

We will nevertheless consider the influence of atmospheric variability on sea-ice conditions and, consequently, on nutrient supply, as an important aspect of the interpretation. Accordingly, we will retain the discussion of the influence of the westerlies but will moderate our interpretation of the respective roles of El Niño and the Southern Annular Mode (SAM).

As the discussion will no longer be structured around predefined intervals, we will revise Figure 3 (Figure R2) to better emphasise the similarities and differences between $\delta^{15}\text{N}_{\text{chl}}$ and the other proxy records. The red and blue areas depict positive and negative departure from the mean value of each proxy rather than representing predefined periods. In addition, we will remove the CRS dataset as it conveys a similar information as the abundance of *F. curta* + *F. cylindrus*. Overall, the revised multi-proxy approach will focus on the relationship between $\delta^{15}\text{N}_{\text{chl}}$, export productivity, and sea-ice variability rather than on discrete time intervals. This will provide a stronger and more objective framework for evaluating the influence of sea ice and atmospheric variability, and ocean circulation while avoiding overinterpretation of individual intervals.

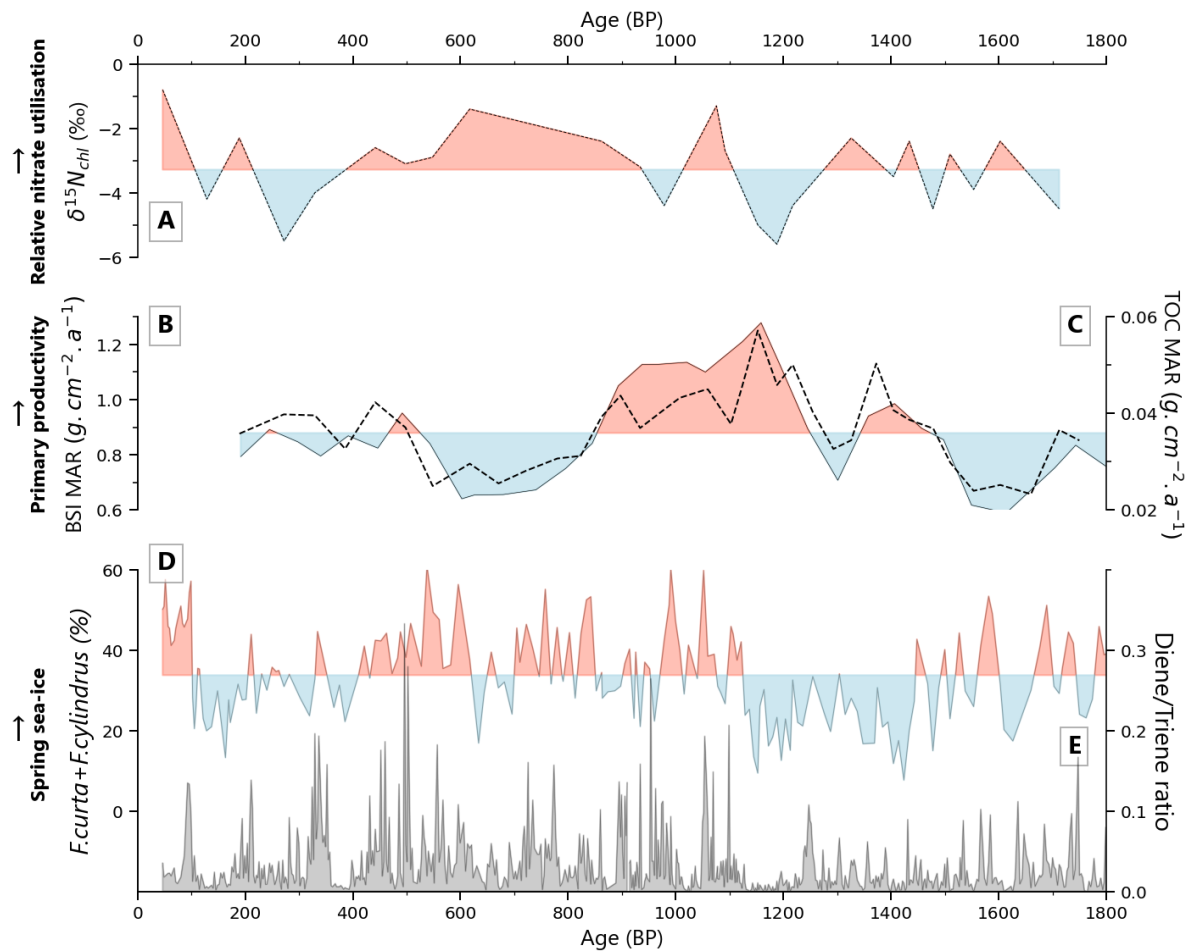


Figure R2. Intercomparison of relative nitrate utilisation, export productivity, and sea-ice records from Site IODP U1357B. A) $\delta^{15}\text{N}_{\text{chl}}$ (this study). B) Mass Accumulation Rates of total organic carbon (TOC, in black) (this study). C) Mass Accumulation Rates of biogenic silica material (BSi, in green) (Johnson et al., 2021). D) Relative abundance of the combined *Fragilariopsis curta* and *Fragilariopsis cylindrus* group (Crosta et al., 2021) E) Di-unsaturated HBI (C25:2; Diene)/tri-unsaturated HBI isomer (C25:3; Triene) ratio (Ashley et al., 2021).

Minor comments:

R1-C5. Introduction: I am not an expert in pigment $\delta^{15}\text{N}$, but I would have appreciated a more thorough description of how chlorophyll $\delta^{15}\text{N}$ differs from others, such as chlorin $\delta^{15}\text{N}$ (e.g., Higgins et al., 2011, 2010).

R1-R5. We agree that the specific characteristics of chlorophyll *a* and its distinction from other pigment-based $\delta^{15}\text{N}$ proxies should be better introduced. We will therefore add a brief description to the introduction, while keeping the more detailed discussion of the proxy and its isotopic offsets in the rationale section. For instance, Chlorophyll *a* and its degradation products, often referred altogether as chlorins (e.g., pheophytin *a* and pyropheophytin *a*), have been used to reconstruct past changes in nutrient utilisation, as they are relatively well preserved in sediments (Higgins et al., 2010; Higgins et al., 2011). However, these chlorin compounds may also be transported and remobilised from other areas of the continental shelf. This process may be particularly important

in the Antarctic coastal environment, where lateral transport by the Antarctic Coastal Current (ACC; see modification below in Figure R3) can transport chlorins from algal blooms further to the east, as well as remobilise marine sediment. As a result, we may observe an additional spatial and temporal offset between the isotopic composition of the source nitrate and that recorded by the different chlorins extracted from the sediment (Ohkouchi et al., 2002). In contrast, chlorophyll *a* is particularly labile and requires relatively rapid export and burial to be preserved in sediments. Its preservation therefore provides a direct link to the local surface-water conditions at the time of production. This characteristic is particularly relevant to our study site collected in a sediment drift.

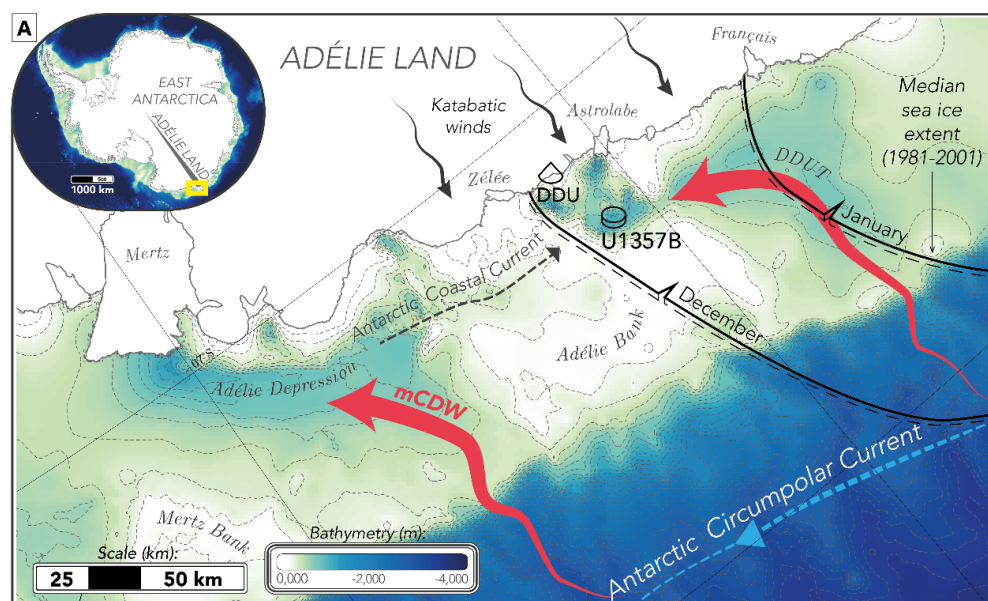


Figure R3. A) Regional map of Adélie Land, East Antarctica. Red arrows: modified Circumpolar Deep Water (mCDW) trajectory through the depressions. Cylinder: IODP U1357 coring site. Cone: Dumont d'Urville (DDU) scientific station. Elevation from Matsuoka et al. (2021), bathymetry modified from Beaman et al. (2011), sea Ice extent from Fetterer et al. (2017).

R1-C6. Lines 19-20: The authors suggest that elevated d15N values could be explained by increased sea ice and delayed sea-ice melt. However, such conditions are typically associated with stronger light limitation, which would be expected to reduce the degree of nutrient consumption rather than enhance it (i.e., to explain high d15N).

R1-R6. We agree that the wording in lines 19–20 was too conclusive and could imply a direct relationship between increased sea-ice cover and enhanced nitrate consumption. We will revise this statement in the manuscript following the arguments presented below. Sea-ice cover can increase light limitation by reducing light penetration, particularly during early spring blooms. However, previous studies have shown that blooms and export generally occur in late spring and summer in the Adélie Land region (Massé et al., 2011), when sea ice has retreated and light availability is stronger. Here, strong wind stress and sea-ice meltwater strongly influence the stratification and mixed-layer depth in which the phytoplankton is exposed to sunlight. Increased sea-ice persistence and later melt extends the period of stable, stratified surface waters, resulting in a shallower mixed layer during a shorter growing season (Venables and Meredith, 2014; Droste

et al., 2025). Under these conditions, prolonged stratification may favour phytoplankton growth and nitrate consumption during the summer. Conversely, when the ice-free season is longer, the period during which stratification can be disrupted by wind-driven mixing is extended and the mixed layer deepens. Such mixing events can resupply nitrate to the surface waters and favour late-season blooms. We will therefore consider that the relationship between sea-ice persistence, light availability, stratification, and nitrate consumption is not unidirectional. The revised text will present this mechanism more cautiously and avoid directly attributing high $\delta^{15}\text{N}_{\text{chl}}$ values to increased sea-ice cover alone.

R1-C7. Line 73: I would recommend replacing “phytoplankton pump” with “biological pump,” as export is an ecosystem-level process.

R1-R7. The revised introduction will be modified accordingly.

R1-C8. Line 97: Here and throughout the manuscript, greater care should be taken with the use of references. For example, DiFiore et al. (2009) did not investigate wintertime convection, but rather the controls on nitrate $\delta^{15}\text{N}$ in the polar Antarctic Zone. Similarly, on line 106, Sigman et al. (1999) is cited in relation to the typical range of summer MLD in the Antarctic Zone, which is not the focus of this study.

R1-R8. We will carefully revise the references throughout the manuscript to ensure that each citation directly supports the corresponding statement. In particular, DiFiore et al. (2009) has been removed from the discussion of wintertime convection and replaced with references specifically addressing wintertime convection in the Southern Ocean (Toole, 1981). Similarly, references concerning circulation associated with polynyas (Snow et al., 2016) and modern summer mixed-layer depths in Antarctic coastal waters (Williams et al., 2011) have been added where appropriate. More generally, we will review the references throughout the manuscript and replace or supplement citations where necessary, with particular attention to their geographical and seasonal relevance to our study.

R1-C9. Figure 2: It would be helpful to connect the symbols with lines to make the trends easier to discern.

R1-R9. Figure 2 will be modified accordingly, with the addition of analytical uncertainties for $\delta^{15}\text{N}$ records (cf. Figure R4).

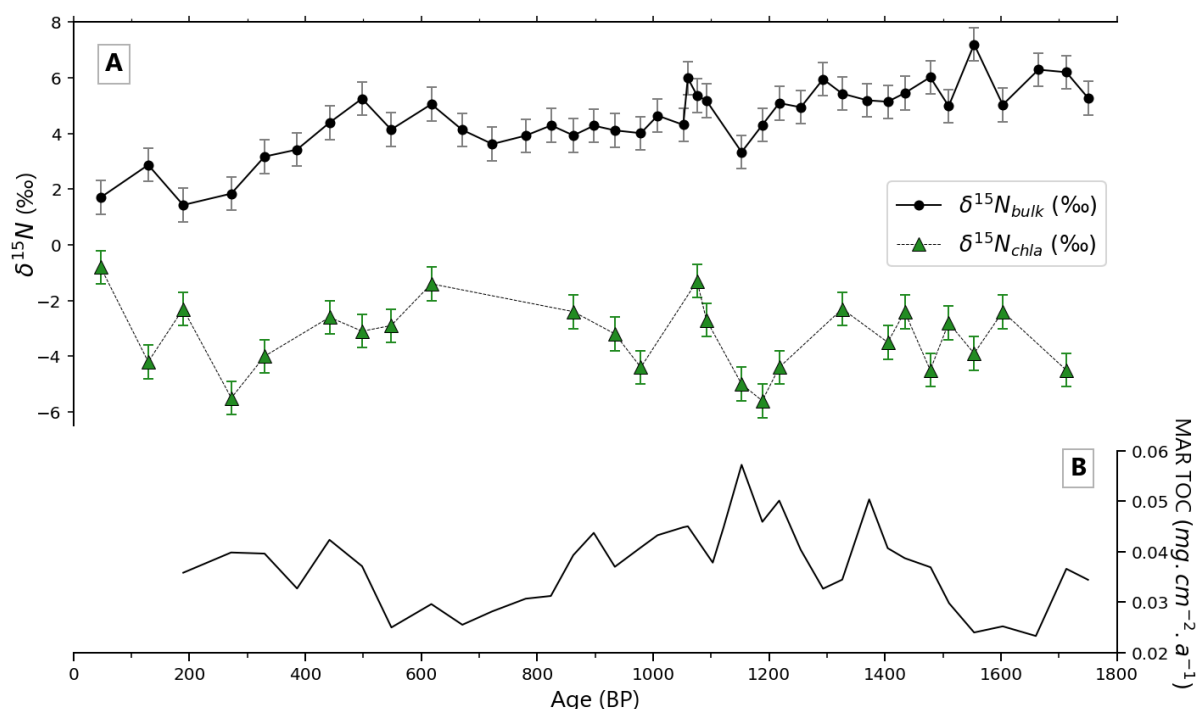


Figure R4. A) $\delta^{15}N$ records of bulk nitrogen and chlorophyll *a*. B) mass accumulation rates of total organic carbon measured from IODP core site U1357B over the last 2,000 years. This figure represents the new Figure 2.

R1-C10. Lines 204-217: I am not convinced that this discussion of N₂ fixation and denitrification is necessary. It is well established that nitrate and organic N d₁₅N in the Southern Ocean are primarily controlled by nitrate assimilation and export (Altabet and Francois, 1994; DiFiore et al., 2009; Fripiat et al., 2019; Sigman et al., 1999). In addition, whether denitrification occurs in the water column or in the sediments has a strong influence on nitrate d₁₅N (Lehmann et al., 2007), and this is not discussed. Finally, the presence of functional genes does not imply that they are expressed or that the associated processes are quantitatively significant.

R1-R10. Please refer to our answer in **R1-R2**.

R1-C11. Lines 223: It is unlikely that penguins exert a significant control on nitrate $\delta^{15}N$ (or fixed N) at such remote sites. To the best of my knowledge, their impact has only been demonstrated in the immediate vicinity of penguin colonies. Given the large reservoir of nitrate (and fixed N) in the Antarctic Zone, such localized inputs are likely to be rapidly diluted offshore. At a minimum, the authors should provide references demonstrating a measurable impact at remote locations. In addition, sea ice represents only a minor reservoir of fixed N within the mixed layer. It is therefore unlikely to exert a strong influence on sedimentary d₁₅N. If the authors wish to argue otherwise, this interpretation should be supported with additional references and, ideally, quantitative estimates (i.e., mass and isotopic balance calculation).

R1-R11. We agree that penguin colonies and sea ice are minor sources of N and are unlikely to exert a significant control on the nitrate $\delta^{15}N$ signal at our study site, given the large nitrate

reservoir in the Antarctic Zone and the distance of the core site from penguin colonies (~30 km from rookeries around the DDU station). Our intention was not to propose these sources as major controls on the sedimentary $\delta^{15}\text{N}_{\text{chl}}$ record, but rather to mention them as potential minor sources of nitrogen that could theoretically contribute to the surface nutrient pool during periods of intense phytoplankton production. We agree that the original wording did not make this distinction sufficiently clear. We will therefore revise this section to explicitly state that the dominant source of nitrate to the study area is the supply from deeper waters, whereas nitrogen inputs associated with rookeries will be ignored and sea-ice processes will be described as negligible. The revised text will focus on the dominant role of subsurface nitrate supply and avoid attributing extreme $\delta^{15}\text{N}_{\text{chl}}$ values to minor nitrogen sources for which there is insufficient evidence at our site.

R1-C12. Line 239: I think the close agreement between the isotopic offset observed here (between chlorophyll and bulk N d15N) and literature estimates (e.g., Sachs et al., 1999) should be stated more clearly. The similarity appears strong and would help the reader better understand the systematic underlying chlorophyll d15N.

R1-R12. Please refer to our answer in **R1-R3**.

R1-C13. That said, while this correspondence is encouraging, other processes may also influence this offset (e.g., growth rate, shifts in species composition, etc.). I would therefore encourage the authors to discuss these potential effects and assess whether they could account for, or alternatively be ruled out as drivers of, the variability recorded in chlorophyll d15N.

R1-R13. Please refer to our answer in **R1-R3**

R1-C14. Line 250: Please revise terms such as “highly available 14N.” All 14N in nitrate is available, and the concept of availability is not directly related to isotope fractionation.

R1-R14. We agree with the referee’s comment to stop using the concept of availability of one isotope over another. It will also be revised in section 5.2 to prevent any misunderstanding.

R1-C15. On line 274, and throughout this discussion, biogenic silica appears to be treated as a proxy for nitrate uptake, which is not strictly accurate. In contrast, d15N is more directly related to nitrate utilization (e.g., Altabet and Francois, 1994). I would therefore recommend using more cautious and precise wording. This link (biogenic silica and nitrate uptake) should be better described, with a consideration of possible biases (e.g., variable Si:N ratios; Hutchins and Bruland, 1998).

R1-R15. We understand the reviewer’s concern and will revise the wording throughout the manuscript. We reckon that it is not strictly accurate to use BSi as a proxy for nitrate uptake, as other phytoplankton also take up N and there is a loss of material during settling. However, the correspondence between MAR-BSi and MAR-TOC indicates that diatoms are the main phytoplankton off Adélie Land, in agreement with modern studies (Wright and van den Enden,

2000; Beans et al., 2009). Second, the shallow depositional setting of our core (~700 m deep) and the highly seasonal blooms favour efficient export and preservation, as demonstrated by the presence of laminae (Maddison et al., 2012). We will mention these limitations.

Changes in iron supply to the Southern Ocean and associated changes in the Si/N uptake ratio (Brzezinski et al., 2003) are at the origin of the silicic leakage hypothesis (Brzezinski et al., 2002), an open ocean process essentially active at the glacial-interglacial timescale (Matsumoto et al., 2002). The Antarctic shelf environments are much less iron-limited because of several sources including sea-ice and glacier melts, resuspension of sediment, and oceanic supply (Sambrotto et al., 2003). Therefore, there is no support for great changes in the Si/N uptake ratio over the last 2000 years.

We will retain MAR-BSi and MAR-TOC as indicators of paleoproductivity, as done in many publications from the open Southern Ocean (Jaccard et al., 2013; Studer et al., 2015, 2018) where remineralisation is much higher than on the Antarctic shelf (Ragueneau et al., 2000). In these publications, BSi (or any other proxy of productivity) is used as a direct proxy for N uptake, irrespective of any bias, to ultimately reconstruct the oceanic N supply via the SO upwelling (Ai et al., 2020; Fripiat et al., 2026). We will build on these studies to similarly document changes on N supply via the mCDW in a much better controlled oceanic setting.

R1-C16. Line 278: “The discrepancy between the chlorophyll d15N record and both MAR signals (Fig. 3a, 3b & 3c) indicates that the degree of nitrate uptake by the regional productivity is unlikely to be the primary driver of chlorophyll d15N variability off Adélie Land.” This sentence is inconsistent with the established relationship between nitrate d15N (and organic N) and the degree of nitrate consumption (Altabet and Francois, 1994; DiFiore et al., 2009; Fripiat et al., 2019; Sigman et al., 1999). Nitrate remains the ultimate source of N for phytoplankton and must control the mass and isotopic balance of newly produced biomass and their regenerated products. To be a proxy, in my view, chlorophyll d15N should be related to biomass d15N, so the authors should clarify this statement.

R1-R16. The $\delta^{15}\text{N}$ traces the relative utilisation of N as a balance between supply (here, mainly the upwelling of mCDW) and uptake (here, diatoms). If one endmember is characterised, it is possible to infer changes in the other. Although not strictly accurate, MAR-BSi and MAR-TOC records reflect changes in the N uptake over the last 2000 years, which allows apprehending congruent changes in the vertical supply, as done in many publications in the open ocean (Studer et al., 2015, 2018; Ai et al., 2024; Fripiat et al., 2026). However, more careful wording and mention of potential limitations (see **R1-R15**) will be used in the revised manuscript.

We will also better explain how chlorophyll $\delta^{15}\text{N}$ relates to biomass $\delta^{15}\text{N}$. Please refer to our answer in **R1-R2**.

R1-C17. In addition, relatively little variation in nutrient consumption can be expected over such timescales, given that nutrient utilization is, on average, very low in the coastal Antarctic Zone. It would therefore be valuable to estimate the extent to which such variability could influence biomass d15N (i.e., the accumulated product in Rayleigh fractionation kinetics; see figure 1 in Sigman and Fripiat, 2019). This aspect warrants further discussion to better assess the sensitivity of chlorophyll d15N to changes in nutrient utilization under nutrient-replete conditions such as those prevailing in the coastal Antarctic Zone.

R1-R17. We thank the reviewer for highlighting this critical point. To better assess the sensitivity of $\delta^{15}\text{N}_{\text{chl}}$ to changes in nitrate utilisation, we will add new calculations estimating the fraction of nitrate utilised by phytoplankton (u-ratio). As surface-water conditions in the coastal Antarctic Zone can vary from strongly stratified conditions in early spring to episodically strongly mixed conditions in summer, it is difficult to determine whether the exported chlorophyll was produced under closed- or open-system conditions with respect to nitrate supply. We therefore calculated the u-ratio using both Rayleigh fractionation for a closed system and the steady-state model for an open system following Altabet and François (1994). The uncertainty envelopes shown in the new figure (Figure R5) combine the uncertainties associated with the main parameters used in these calculations:

$\delta^{15}\text{NO}_3^-_{\text{LCDW}} = 4.8 \pm 0.2\text{‰}$, representing the mean isotopic composition of nitrate in Lower Circumpolar Deep Water (Sigman *et al.*, 1999; DiFiore *et al.*, 2009);

$\varepsilon = 5.0 \pm 0.7\text{‰}$, representing the fractionation factor associated with nitrate assimilation by phytoplankton in the PAZ mixed layer (Difiore *et al.*, 2009);

$\gamma_{\text{chl}} = 4.7 \pm 1.17\text{‰}$, representing the fractionation associated with chlorophyll *a* synthesis relative to biomass (Ohkouchi *et al.*, 2024).

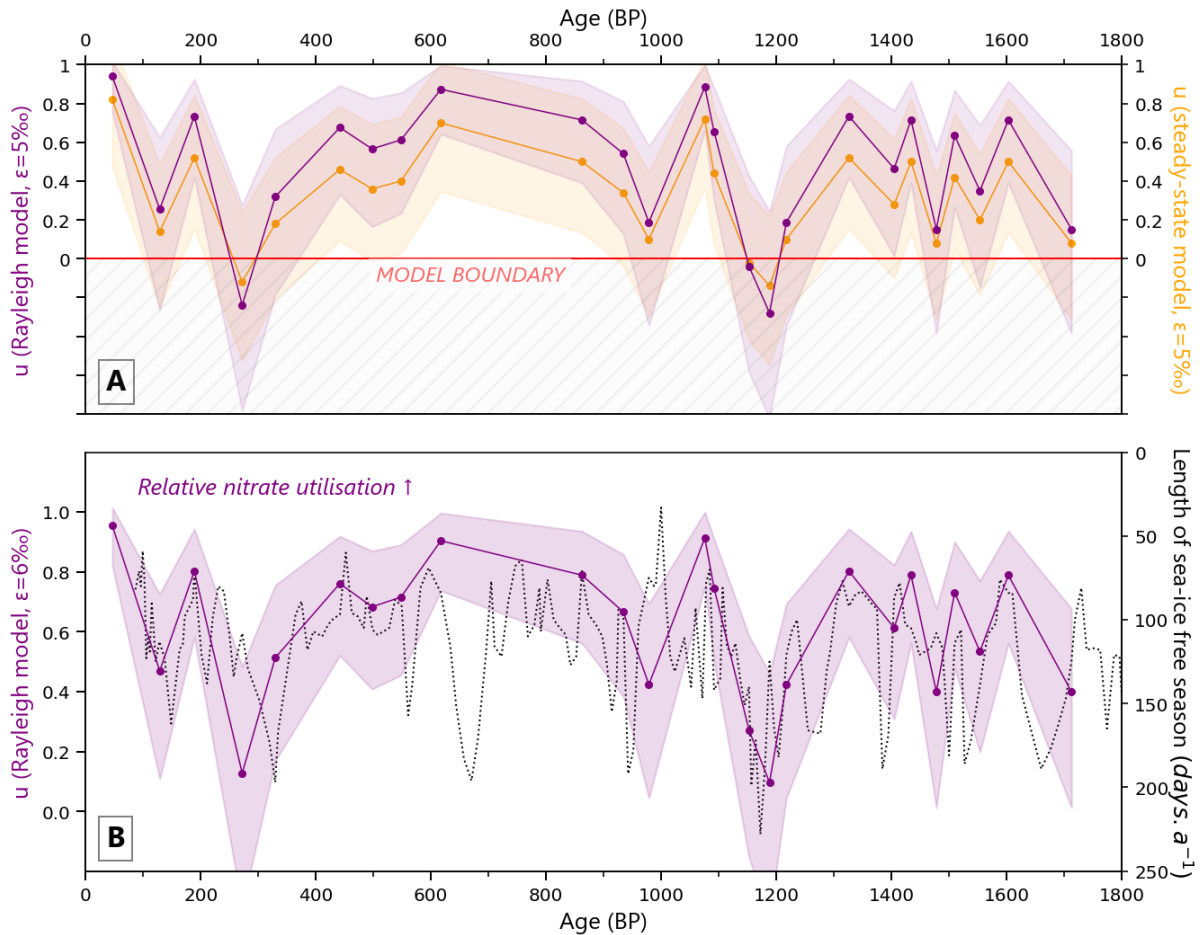


Figure R5. A) Degree of nitrate utilisation (u) calculated from $\delta^{15}\text{N}_{\text{chl}}$ in Site core IODP U1357B in a context of closed (Rayleigh model, purple line) and open (steady-state model, orange line) system. The corresponding envelopes represent the quadratic sum of the uncertainties under consideration. B) Comparison of the degree of nitrate utilisation (u) calculated from $\delta^{15}\text{N}_{\text{chl}}$ in a closed system (Rayleigh model, purple line) and the length of sea-ice free season calculated from

the relative abundance of open-water diatoms in site core IODP U1357B (Crosta et al., 2021). This figure's position in the paper has not yet been decided.

The calculations show that, using such isotopic signatures and fractionation factors representative of modern coastal Antarctic conditions, some of the observed $\delta^{15}\text{N}_{\text{chl}}$ values would correspond to utilisation ratios outside the theoretical range of the models, including negative apparent utilisation. Other values would correspond to utilisation ratios >0.8 , which appear unlikely even under strongly stratified conditions. These results indicate that the observed $\delta^{15}\text{N}_{\text{chl}}$ values cannot be explained solely by changes in nitrate utilisation from productivity alone, within the range expected from the modern Antarctic conditions considered here. Instead, they suggest that variations in the isotopic composition of the nitrate supplied to the surface waters and/or changes in the fractionation associated with nitrate assimilation need to be considered when interpreting the record. For example, as shown in Fig. B above, increasing the mean assimilation fractionation factor (ϵ) from 5‰ to 6‰ is sufficient to bring the reconstructed u-ratios back within the theoretical range of the models. This illustrates the sensitivity of the u-ratio estimates to variations in ϵ . Rather than interpreting these values as direct estimates of nitrate utilisation, or discussing them through offset uncertainties alone, we therefore use the most unrealistic estimates to identify periods during which variations in the parameters controlling the isotopic composition of chlorophyll may have influenced our record.

As part of our multiproxy approach, we will also compare these results with the duration of the ice-free season over the last 1800 years, based on the extended data of Crosta et al. (2021). The duration of the ice-free season is reconstructed from open-ocean diatoms, a proxy totally independent of $\delta^{15}\text{N}_{\text{chl}}$. The resulting record shows a strong correspondence with both the reconstructed u-ratios and $\delta^{15}\text{N}_{\text{chl}}$ variations. We can now unambiguously show that a shorter sea-ice season would favour earlier weakening of stratification and more frequent mixing of the surface layer. Under these conditions, late-summer blooms following nitrate resupply may occur more frequently, as observed in the Adélie region (Sambrotto et al., 2003). Chlorophyll *a* exported during such blooms would integrate a recently replenished nitrate pool with a lower $\delta^{15}\text{N}$ signature. This mechanism could therefore explain the low $\delta^{15}\text{N}_{\text{chl}}$ values observed during periods of reduced sea-ice presence. Overall, these new calculations highlight the importance of considering changes in nutrient supply, mixing, and isotope fractionation associated with phytoplankton growth when interpreting the chlorophyll $\delta^{15}\text{N}$ record.

R1-C18. Discussion in general: While the authors discuss the role of sea ice in driving buoyancy fluxes, they should also consider additional forcings, such as buoyancy input from Antarctic Ice Sheet meltwater (e.g., Bronselaer et al., 2020, 2018). Moreover, factors such as changes in the westerlies and nutrient fertilization are also considered important in explaining variations in sedimentary $\delta^{15}\text{N}$.

R1-R18. Very little is known about the dynamics of the regional ice sheet over the last 2000 years. $\delta^{18}\text{O}$ analysis in diatom frustules preserved in the nearby core MD03-2601 suggests a glacial retreat at ~1700 yrs BP (Crespin et al., 2014) that is not reflected in the new $\delta^{15}\text{N}_{\text{chl}}$ and in the diatom census counts in cores U1357B and MD03-2601. Fatty acid δH_2 values in site U1357 increased over the last 4000 years, suggesting less glacial ice meltwater from the Ross Sea during the Neoglacial (Ashley et al., 2021). This period is generally associated with glacial readvances in East Antarctica (Ingolfsson et al., 1998). Overall, we do not expect important changes in regional ice sheet and associated glacial meltwater and iron load over the last 2000 years.

Final response to anonymous referee #2

R2-C1. This manuscript presents the first Antarctic record of chlorophyll-bound nitrogen isotopes ($\delta^{15}\text{N}_{\text{chl}}$) from IODP Site U1357B off Adélie Land. The study is novel and potentially important because $\delta^{15}\text{N}_{\text{chl}}$ may provide a more direct and less diagenetically altered record of nitrogen cycling than bulk sediment $\delta^{15}\text{N}$. The dataset is valuable, the manuscript is generally well written, and the interpretation is placed within an interesting multi-proxy framework.

However, I have several concerns regarding the interpretation of the $\delta^{15}\text{N}_{\text{chl}}$ signal, and I therefore recommend **major revisions** before publication.

R2-R1. We thank anonymous referee 2 for their positive opinion on the novelty of our study. Many comments raised by the two referees are comparable, and we invite referee 2 to read our response to referee 1 where applicable.

Major comments:

R2-C2. The central conclusion that $\delta^{15}\text{N}_{\text{chl}}$ primarily reflects changes in nitrate supply rather than nitrate utilisation is not yet fully convincing. The lack of correspondence between $\delta^{15}\text{N}_{\text{chl}}$ and MAR-TOC/MAR-BSi does not necessarily exclude utilisation effects, as export production is not a direct measure of nitrate consumption. Alternative explanations should be discussed more thoroughly.

We never meant that nitrate uptake was not important. As mentioned in R1-R16, the $\delta^{15}\text{N}$ traces the relative utilisation of N as a balance between supply (here, mainly the upwelling of mCDW) and uptake (here, diatoms). If one endmember is characterised, it is possible to infer changes in the other. Although not strictly accurate, MAR-BSi and MAR-TOC records reflect changes in the N uptake over the last 2000 years, which allows apprehending congruent changes in the vertical supply, as done in many publications in the open ocean (Studer et al., 2015, 2018; Ai et al., 2024; Fripiat et al., 2026). However, more careful wording and mention of potential limitations (see **R1-R15**) will be used in the revised manuscript.

Additionally, we will revise the discussion to explicitly consider the potential influence of nitrate utilisation and the processes that can modify the relationship between nitrate $\delta^{15}\text{N}$ and $\delta^{15}\text{N}_{\text{chl}}$. In particular, we will include a semi-quantitative assessment of nitrate utilisation and discuss the sensitivity of the reconstructed utilisation ratios to changes in the fractionation factor associated with nitrate assimilation (see **R1-C17**). We will expand the discussion to include changes in phytoplankton growth rates and species composition, which can modify isotopic fractionation under different light and nutrient conditions, as well as changes in the frequency of mixing events and nutrient recycling associated with variations in the duration of the ice-free season. The revised interpretation therefore does not consider $\delta^{15}\text{N}_{\text{chl}}$ to be controlled exclusively by nitrate supply. Rather, we propose that variations in nitrate supply and utilisation, together with changes in phytoplankton physiology and surface-water conditions, can contribute to the observed signal. We believe this more cautious interpretation is appropriate for this first application of $\delta^{15}\text{N}_{\text{chl}}$ to a coastal Antarctic sedimentary record, especially for such a specific study site.

R2-C3. The authors attribute the strongly negative $\delta^{15}\text{N}_{\text{chl}}$ values to incomplete nitrate utilisation and isotopic fractionation during chlorophyll synthesis, but no quantitative framework is provided. A simple isotope mass-balance calculation demonstrating whether the observed values are realistic under modern Antarctic conditions would strengthen the interpretation.

R2-R3. Please refer to our answer in **R1-R17**.

R2-C4. Potential effects of changes in phytoplankton community composition (e.g. diatoms versus *Phaeocystis antarctica*) are largely dismissed. Given known differences in isotopic fractionation among phytoplankton groups, this possibility deserves more discussion.

R2-R4. We understand the reviewer's argument that changes in phytoplankton community composition could potentially influence $\delta^{15}\text{N}_{\text{chl}}$ through differences in isotopic fractionation among phytoplankton groups, and that this possibility was not sufficiently discussed in the original manuscript. Direct information on the species-specific fractionation factors of the dominant phytoplankton groups in the study region is limited, and we do not have records of past quantitative *Phaeocystis antarctica* abundance (Ashley et al., 2021). Diatoms are the dominant species of the modern phytoplankton assemblage in the Adélie Land region, especially at the Dumont d'Urville Trough (Sambrotto et al., 2003; Beans et al., 2008; Riaux-Gobin et al., 2011). The close correlation between MAR-TOC and MAR-BSi does support the assumption that diatoms most likely dominated in the past, as changes in total organic matter export broadly followed changes in diatom-derived export. We therefore consider large changes in the dominant phytoplankton community to be unlikely over our site core. While contribution from *Phaeocystis* export cannot be excluded, as material from the eastern Commonwealth Bay and Mertz Polynya could potentially be transported towards the study site by the ACC, its associated chlorophyll is probably degraded at the time of deposition at our core site, meaning that this species has little influence on our $\delta^{15}\text{N}_{\text{chl}}$. We will therefore revise the discussion to acknowledge these limitations, and to consider shifts in species composition among diatoms (cf. **R1-R13**), together with growth-rate-dependent fractionation, conditions of nutrient supply and recycling, as potential contributors to the observed $\delta^{15}\text{N}_{\text{chl}}$ variability.

R2-C5. The proposed link between sea-ice conditions, stratification, nutrient supply, and $\delta^{15}\text{N}_{\text{chl}}$ is plausible, but the discussion occasionally presents this mechanism too definitively. Alternative pathways and uncertainties should be acknowledged more explicitly.

R2-R5. We agree that the proposed relationship between sea-ice conditions, stratification, nutrient supply, and $\delta^{15}\text{N}_{\text{chl}}$ should be presented more accurately. As clarified above, we will develop the discussion to acknowledge alternative pathways and uncertainties, including changes in nitrate utilisation, resupplies, growth-rate-dependent fractionation, and nutrient recycling. As described in our response to **R1-C17**, the new nitrate-utilisation calculations clearly show that utilisation alone cannot explain the full range of observed $\delta^{15}\text{N}_{\text{chl}}$ values. We therefore now present the sea-ice influence on mixing conditions and diatom growth rate as a possible pathway rather than a unique control.

R2-C6. Clarify the distinction between nitrate supply, nitrate availability, and nitrate utilisation throughout the manuscript.

R2-R6. We will take care to distinguish more clearly between these terms to avoid any confusion. The term ‘availability’ will be specifically avoided, in line with our response in **R1-C14**.

R2-C7. Consider including quantitative correlations between $\delta^{15}\text{N}_{\text{chl}}$ and the environmental proxy records shown in Figure 3.

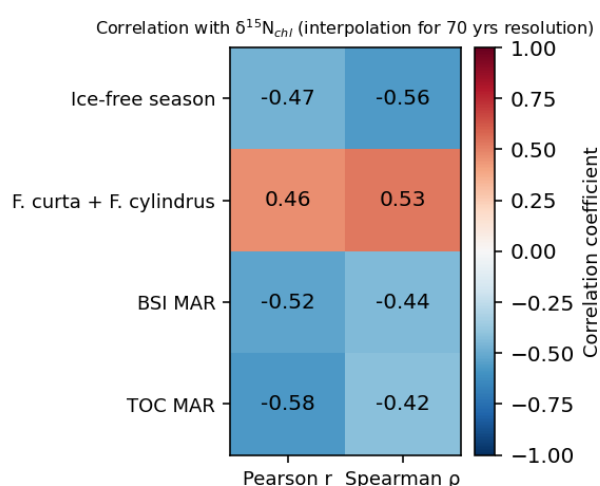


Figure R5. Correlation matrix between $\delta^{15}\text{N}_{\text{chl}}$ and various records and calculations from sediment core U1357B, using $\delta^{15}\text{N}_{\text{chl}}$ as the interpolation reference at 70-year resolution.

R2-R7. We thank the reviewer for this suggestion. We calculated correlations between $\delta^{15}\text{N}_{\text{chl}}$ and the sea-ice and productivity proxies shown in **R1-R4**. However, quantitative correlations are affected by the different temporal resolutions and sampling depths of the records, as interpolation to common depths requires choosing a common resolution. We chose to show the correlation tests based on the $\delta^{15}\text{N}_{\text{chl}}$ record’s average resolution of ~70 years (SD ~45 years). The correlations with the sea-ice diatom abundance, MAR-BSi, and MAR-TOC records are relatively consistent and significant across the tested resolutions, with positive correlations with sea-ice diatoms and negative correlations with MAR-BSi and MAR-TOC (Figure R5). Despite the correlation with the MAR records is partly favoured by their similar sampling resolution to $\delta^{15}\text{N}_{\text{chl}}$, we will be less categorical about the absence of a relationship between these proxies. The diatom-based sea-ice record (and the ice-free season) bears similar correlation values than those of the MAR records. However, these values may be debilitated by the temporal resampling at 70 years. The R5 figure nevertheless places greater emphasis on the indirect role of sea ice on $\delta^{15}\text{N}_{\text{chl}}$ through regulating nutrient inputs and the conditions under which phytoplankton develops. We will include the correlation results as a table in the Supplementary Materials and discuss their limitations in the manuscript.

R2-C8. The discussion of future ecosystem responses to sea-ice decline is somewhat speculative and should be toned down.

R2-R8. We agree with the referee's comment. We will refrain ourselves to the discussion of future ecosystem changes (please see **R2-R4**).

R2-C9. A careful language edit would improve readability in several sections.

R2-R9. We will carefully edit the revised version to improve flow and avoid overly complex phrasing.

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