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Key Points:

- Upwelling along the Chilean Margin brings nutrient rich Southern Ocean water to the surface promoting productivity
- Preformed Southern Ocean nitrate is seemingly transported throughout the South Pacific, promoting productivity
- Results complicate proposed hypotheses about the relationship between Southern Ocean biological pump efficiency and atmospheric CO_2

Supporting Information:

Supporting Information may be found in the online version of this article.

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Southern Ocean Biological Pump Role in Driving Holocene Atmospheric CO_2: Reappraisal

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Abstract Changes in Southern Ocean biological pump efficiency are frequently invoked as a source of glacial/interglacial CO_2 variability. It was recently suggested that Southern Ocean biological pump weakening also contributed to Holocene CO_2 increase. Here we test the causes and downstream effects of biological pump inefficiency during the Holocene. We first provide evidence that a southward shift of the South Westerly Winds, was likely the cause of increasing upwelling in the Southern Ocean leading to local biological pump weakening as reflected in fossil-bound $\delta^{15}N$. We then introduce a series of ultra-high resolution (6 m/ky) productivity records from the Chilean Margin to determine the fate of Southern Ocean nutrients. A compilation of records from Pacific sites supports export and complete consumption of preformed Southern Ocean nutrients, which might have reduced the contributions of Southern Ocean marine source to the Holocene increase in atmospheric CO_2.

Plain Language Summary The extent of Southern Ocean biological productivity's role in determining atmospheric CO_2 concentrations is still debated. Previous work hypothesized that changes to biological nutrient utilization drove large CO_2 variability and recently even the Holocene CO_2 increase. Here, we seek to better understand the role of Southern Ocean productivity in atmospheric CO_2 concentrations. To start, we tie nutrient use inefficiency to wind position and upwelling, identifying a force for change. Then, we create a series of high resolution productivity records to investigate downstream effects of said changes. We find that Southern Ocean nutrients are upwelled to the Chilean Margin surface to promote productivity. We further demonstrate that unused Southern Ocean nutrients continue to fuel increases in productivity and low nitrogen isotopic signatures of organic matter throughout the South Pacific. Our results therefore suggest that while the Southern Ocean was a CO_2 source during the Holocene and likely contributed to the contributed to the Holocene CO_2 increase, other regions mitigated this release via biologic consumption.

1. Introduction

The degree of Southern Ocean biologically available nitrogen utilization, or the biological pump efficiency, has been linked to changes in atmospheric carbon dioxide (CO_2) concentrations (Knox & McElroy, 1984). Upper Circumpolar Deep Water upwelling brings macronutrients like carbon, nitrogen, and phosphorous to the Southern Ocean surface where they can fuel productivity (Sigman, Altabet, McCorkle, et al., 1999). Despite an abundance of macronutrients in Antarctic surface waters, iron availability and light is low and exerts a key control on primary productivity at present and possibly also in the past (Boyer et al., 2018; Martin et al., 1990; Mitchell et al., 1991). The "leaky biological pump" hypothesis posits that when upwelling strength increases, nutrients become abundant in the Southern Ocean surface because primary producers cannot effectively utilize all that is present (Sigman & Boyle, 2000). Nutrients that are not fully consumed by primary producers remain in the surface layer, leaving CO_2 to freely exchange with the atmosphere while the excess nutrients are exported to the lower latitudes (Sarmiento & Toggweiler, 1984).

Biological pump efficiency has been explored as a mechanism for glacial/interglacial CO_2 changes. The position of the Southern Westerly Winds (SWW) plays a key role in global climate variability owing to the link between latitudinal shifts in the SWW and Southern Ocean upwelling, which leads to CO_2 outgassing (Ai et al., 2020; Marshall & Speer, 2012; Sigman & Boyle, 2000). Modeling studies generally support the link between SWW intensity (Tschumi, et al., 2008) and/or position (Huiskamp et al., 2016; Persch et al., 2023), Southern Ocean ventilation, and atmospheric CO_2 concentration albeit with some disagreement about the sign of changes. They do, however, agree on the shared roles of the physical and biological pumps in determining atmospheric CO_2 concentrations. Decreased upwelling and nutrient delivery to the Southern Ocean in glacial periods when the SWW are farther north allow for more complete nitrogen utilization, a more efficient biological pump, and a CO_2 decrease at the proper magnitude for G/IG changes (Studer et al., 2015; Wang et al., 2017). The opposite is true for interglacial periods. A combination of proxy data and modelling mechanistically supports the importance of biological pump efficiency in G/IG climate variability by demonstrating that southward SWW movement since the last deglaciation increased Southern Ocean upwelling, nitrate delivery to the surface ocean, and CO_2 release to the atmosphere (Anderson et al., 2009; Gray et al., 2021).

Nitrogen isotopes ($\delta^{15}N$) trace the degree of nutrient consumption in the surface ocean when nutrients are incompletely consumed. The lighter ^{14}N isotope is preferentially incorporated by organisms leaving the surface pool progressively enriched in ^{15}N with greater nutrient utilization (Sigman & Fripiat, 2019). Thus $\delta^{15}N$ in sediment organic matter (Altabet & Francois, 1994) or fossil-bound (FB-$\delta^{15}N$) (Martínez-García et al., 2014; Sigman, Altabet, Francois, et al., 1999; Wang et al., 2017) reflects the degree of nitrate utilization; higher (lower) ^{15}N values reflect higher (lower) nutrient utilization (Ai et al., 2020; De Pol-Holz et al., 2009; Martínez-García et al., 2014; Robinson & Sigman, 2008; Sigman, Altabet, Francois, et al., 1999; Studer et al., 2015). When available nutrients are completely consumed, there is no fractionation and surface ocean values reflect the source water nitrate composition (Sigman & Fripiat, 2019). Other processes that may influence $\delta^{15}N$ as measured in bulk sediment or fossils are nitrogen fixation which introduces relatively light atmospheric nitrogen into the marine nitrate pool, and water column denitrification which utilizes ^{14}N for respiration, leaving the surrounding water enriched in ^{15}N. Sedimentary denitrification does not affect $\delta^{15}N$ values because this is a complete process.

The notable increase in atmospheric CO_2 toward the late Holocene, which is not observed in previous integlacials, has been attributed to early human activities, primarily the large-scale conversion of natural lands to agriculture in southeast Asia (Ruddiman, 2003). The idea has been challenged mainly because the $\delta^{13}C$ values of air, reconstructed from ice core CO_2, do not decrease as would be expected with an anthropogenic or terrestrial carbon source and instead align with a natural CO_2 release with a neutral isotopic signature (Broecker & Stocker, 2006). Alternatively, Studer et al. (2018), documenting a decrease in FB-$\delta^{15}N$ from the last deglaciation throughout the late Holocene in sites around the Southern Ocean, which consistently reflect a progressive decrease in biological pump efficiency, have proposed that this could be the source for the increase in Holocene CO_2. Given increasing or constant productivity they conclude that higher nitrate concentrations are likely the result of increasing upwelling from southward SWW migrations, but lack of consensus about SWW movements of at that time warranted caution (Lamy et al., 2010; Moreno et al., 2010). Recently, however, Riechelson, Bova, et al. (2023) constructed a high resolution record of SWW position along the Chilean Margin that reconciled conflicting interpretations from regional records and demonstrated southward migration of the SWW across the Holocene, supporting the inferred role of SWW migration on the biological pump efficiency.

A key question surrounding the "leaky biological pump" hypothesis, however, has been whether preformed nutrients exported from the Southern Ocean increased downstream productivity thereby compensating for reduced Southern Ocean nutrient utilization. "Preformed" nutrients are brought to a region by advection as opposed to "regenerated nutrients" which are provided through respiration and therefore act to increase the local CO_2 sink. The Chilean Margin region is immediately downstream of the Southern Ocean, and thus affected by the advected preformed nutrients that can fuel primary productivity and nutrient consumption there. In fact, low nitrate concentrations in the modern suggest that the upwelled nutrients in this region are efficiently utilized (Figure 1). Further, nutrients not utilized on the Chilean Margin may be transported farther downstream to the western Pacific warm pool (WPWP) and to the highly productive Eastern Equatorial Pacific (EEP) upwelling regions via Subantarctic Mode Water and/or Antarctic Intermediate Water (AAIW) to promote productivity in these locations (Talley, 2013). Chilean Margin surface nitrate is supplied by both northern and southern sourced water and a change in one of these end members would influence local nitrate concentrations (De Pol-Holz et al., 2009) (Figure S1 in Supporting Information S1). Various studies have suggested that Chilean Margin chemical signals can be transported to the WPWP and EEP surface by "tunneling" through intermediate waters (Bova et al., 2015; Lambert et al., 2022; Pena et al., 2013). For biological pump efficiency to play a role in global CO_2 concentrations, decreased efficiency in one location must not be compensated elsewhere.

Here, we address two questions: (a) Are the SWW responsible for changes to Southern Ocean nutrient availability within the Holocene? and (b) What is the fate of nutrients that are not utilized in the Southern Ocean? We use XRF

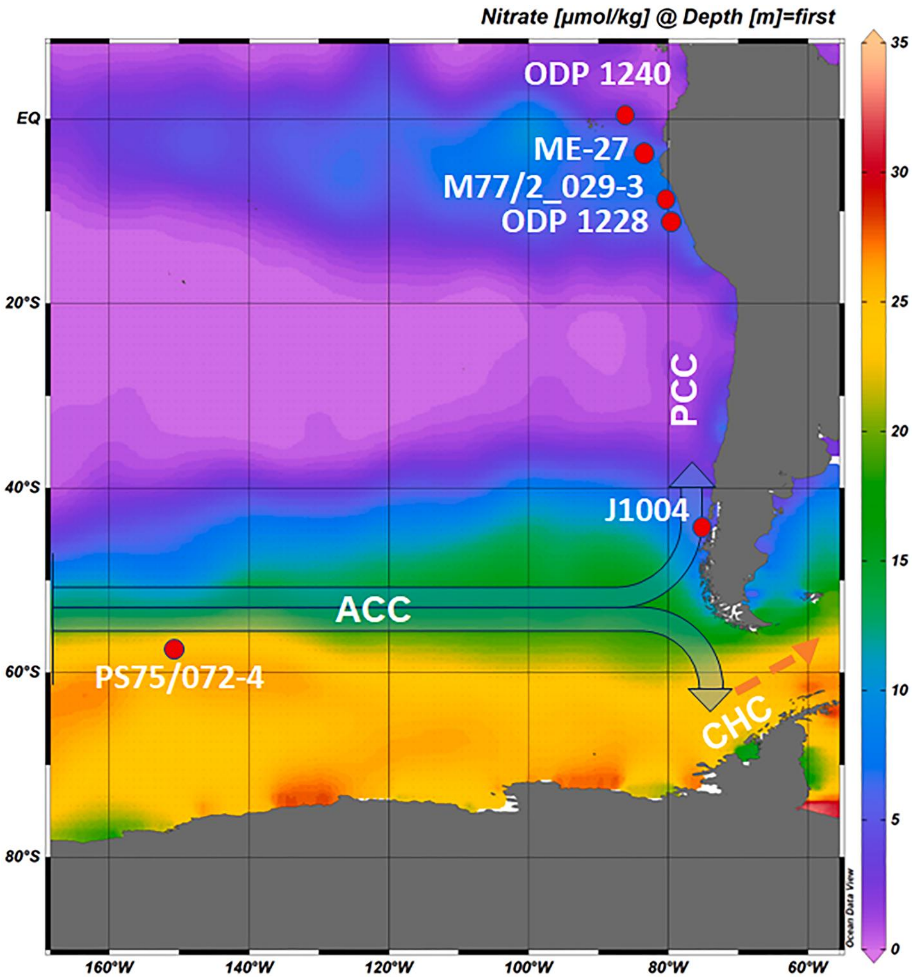

Figure 1. Location of Chilean Margin Site J1004 (this study), Southern Ocean Site PS75/072-4, Eastern Equatorial Pacific Sites ODP 1240 and ME-27, Peru Margin Sites M77/2_029-3 and ODP 1228, and western Pacific warm pool Sites MD01-2392 and MD06-3052 plotted on top of surface nitrate (Agnihotri et al., 2006; Doering et al., 2016; Jia & Li, 2011; Saavedra-Pellitero et al., 2022; Studer et al., 2018; Studer, Mekik, Ren, Hain, Oleynik, Martínez-García, et al., 2021; Xu et al., 2020). Transparent arrows show the modern mean annual position of the Antarctic Circumpolar Current and its bifurcation along the Chilean Margin into the Peru-Chile Current and Cape Horn Current. Figure made using WOA 18 in Ocean Data View (Boyer et al., 2018; Schlitzer, 2018).

data from a core on the southern Chilean margin to assess the co-variation between the SWW, upwelling, and Southern Ocean $\delta^{15}N$, and examine what forces this variability. We provide a new set of productivity and nutrient utilization data from the southern Chilean Margin to assess downstream effects of Southern Ocean biological pump inefficiency. If Southern Ocean surface nitrate is transported and promotes productivity downstream, the additional carbon sink may have partially counteracted the increased Southern Ocean CO_2 source, complicating the scenario proposed in Studer et al. (2018). Finally, we trace the nutrients farther downstream to the WPWP, EEP, and Peru Margin. In doing so, we contribute new insights into the role of biological pump efficiency in atmospheric CO_2 concentrations.

2. Setting and Methods

Site J1004 (44.0005°S, 75.1511°W) is located close to the South American continent at 1,124 m water depth, and thus influenced by Pacific Deep Water (PDW). The Antarctic Circumpolar Current (ACC) is a wind-driven current whose core lies between 50 and 55°S (Toggweiler & Russell, 2008). The ACC is disrupted at its northern boundary by the South American continent and bifurcates into northward and southward moving branches termed the Peru-Chile Current (PCC) and Cape Horn Current respectively. J1004 is north of this bifurcation, so it is influenced by the PCC at the surface (Figure 1). The northward current leads to upwelling along the shore due to Ekman pumping. Changes to the SWW location and intensity shift ACC position, which can alter the proportion and strength of water moving north or south (Lamy et al., 2015). AAIW forms in the Southeast Pacific and flows northward in the subsurface (Figure S1 in Supporting Information S1) (Bostock et al., 2013). Subantarctic Mode Water (SAMW) forms along the subantarctic front and moves north above AAIW.

The SWW can migrate ∼10° in latitude seasonally (Adler et al., 2018). SWW southward (northward) migration forces increased (decreased) Southern Ocean upwelling (Marshall & Speer, 2012). As the SWW migrate southward, they shift the location of the oceanic Subpolar Front, which increases the upwelling of nutrient and CO_2 rich PDW within the ACC and Upper Circumpolar Deepwater around the Antarctic continent (Talley, 2013). At the J1004 location, sea surface temperature satellite data indicate frontal movement and enhanced coastal upwelling in the austral summer and fall when the SWW are located farther south (Saldías et al., 2021). During modern austral winter the SWW conditions, the winds blow directly onshore at 44°S. When the SWW shift southward in austral summer, the onshore movement occurs to the south and some of the air is deflected northward parallel to the coast (Pérez-Santos et al., 2019). The Coriolis Effect deflects the northward flowing PCC westward, which brings subsurface water to the surface via Ekamn pumping.

The sedimentation rate at J1004 is relatively constant, ∼5.9 m/kyr, for the entire record which spans from 85 years BP to∼11,300 years BP (Riechelson, Bova, et al., 2023). The sediment core from Site J1004 was analyzed on the ITRAX XRF core scanner (Cox Analytical Laboratories) at Lamont Doherty Earth Observatory using Cr X-Ray tubing at 1 cm resolution set to 30 kV and 55 mA, at a 15 s count time. Q-spec software was then used to convert the energies to elemental intensities.

The %Al record shown here and its interpretations as a proxy for SWW movements are discussed in detail in Riechelson, Bova, et al. (2023). Here, we add the XRF record of sedimentary bromine (Br), which has been shown to reflect the abundance of marine organic matter in sediments (Ziegler et al., 2008), and thus can be linked to variations in marine productivity (Frugone-Álvarez et al., 2017). Br counts measured via XRF core scanning may be calibrated to the weight percent of total organic carbon (%TOC) in the core to produce a high-resolution record of marine productivity if the organic matter is primarily marine-derived. The origin of the organic matter can be ascertained by analyzing the carbon to nitrogen ratio (C/N) of the organic matter; a value ranging from 4 to 10 is typical of marine sourced organic matter, whereas land plants have much higher C/N values (Meyers, 1994). We analyzed 35 samples scattered throughout J1004 for %TOC. Twenty eight of the samples were freeze dried and dessicated with HCl to remove inorganic carbon. They were then analyzed on a Carlo Erba Elemental Analyzer at the Rutgers Inorganic Analytical Laboratory and calibrated with Acetanilide with 0.72 wt% reproducibility. An additional 7 samples were prepared in the same manner and analyzed shipboard on the JOIDES Resolution for %C, %N, and %inorganic carbon (%IC) with a ThermoElectron Corporation FlashEA 1112 and calibrated with a Buffalo Mountain soil standard with reproducibility of <0.04 wt% for TC, and <0.02 wt% for TN. The %$CaCO_3$ was obtained using shipboard CO_2 coulometer. Reproducibility on the %$CaCO_3$ was better than 0.8 wt%. To calculate %TOC for shipboard data, %IC was subtracted from TC. Error on %TOC was 1%.

Despite a substantial terrestrial input that results in a high sedimentation rate (5.9 m/kyr) at Site J1004, we measure an average C/N ratio of 8.1 (Figure S2 in Supporting Information S1), which indicates the organic carbon is dominantly marine in origin. This is supported by data from other TOC studies from the Chilean Margin that find primarily marine carbon despite high terrestrial input (Hebbeln et al., 2000). %TOC at J1004 is therefore representative of marine productivity, and can be utilized to calibrate the bromine data, which is representative of marine, not terrestrial, productivity (Rothwell & Croudace, 2015). The correlation between %TOC and Br is $R^2 = 0.795$ and the resulting linear equation was used to convert higher resolution Br XRF data into %TOC (Figure S3 in Supporting Information S1). The %TOC was then converted to organic carbon flux by calculating the mass accumulation rate (MAR) with the following equation:

$$\text{TOC Accumulation rate} = \text{LSR} \times \text{DBD} \times \text{TOC (wt\%)}$$

where LSR is the linear sedimentation rate calculated from our age model and DBD is dry bulk density obtained from the shipboard data (Bova et al., 2019). $CaCO_3$ MAR was calculated shipboard using the same formula.

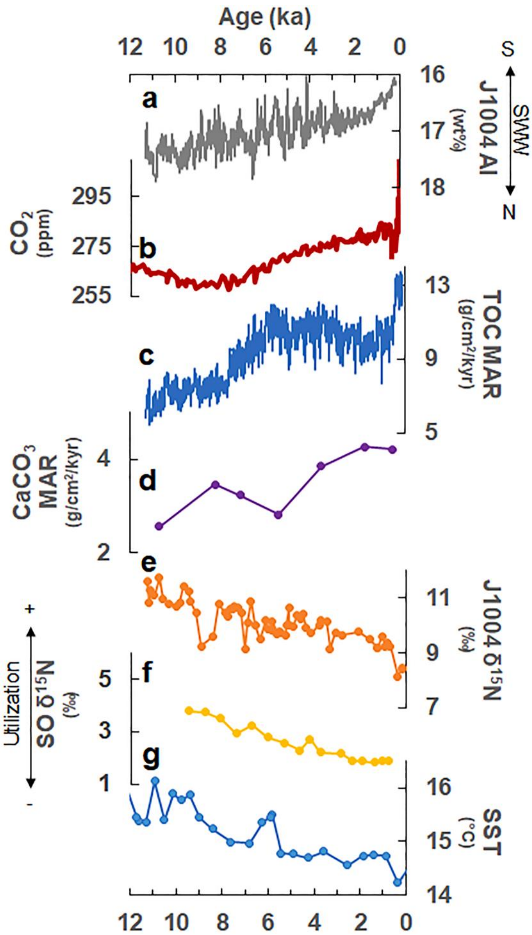

Figure 2. (a) Holocene profile of J1004 Al wt% representing Southern Westerly Winds migrations (Riechelson, Rosenthal, et al., 2023) plotted with (b) Atmospheric CO_2 from EPICA Dome C ice core (Bereiter et al., 2015), (c) J1004 carbon mass accumulation rate (MAR) calculated by calibrating J1004 Br XRF data to TOC data and corrected for the sedimentation rate and dry density (this study), (d) J1004 shipboard $CaCO_3$ MAR (Bova et al., 2019), (e) J1004 $\delta^{15}N$ data (this study), (f) Southern Ocean pennate $\delta^{15}N$ from Core PS75/072-4 (Studer et al., 2015), (g) alkenone SST from Site ODP 1233 (Lamy et al., 2002).

We have measured bulk sediment $\delta^{15}N$ rather than FB-$\delta^{15}N$ because foraminifera from J1004 were utilized for other analyses and the analysis of bulk sediments allows for high resolution records. For bulk sediment nitrogen isotope analysis, we freeze dried and homogenized 25–30 mg from 68 samples evenly distributed throughout the core. Samples were then tightly packed into tin boats and subsequently a second tin boat to ensure full combustion. We then analyzed the samples by continuous flow isotope ratio mass spectrometry using a GVI Isoprime coupled to a Eurovector Elemental Analyzer. Standards are calibrated using multiple analyses of standards IAEA N1, IAEA N3, and USGS certified reference material SGR 1b with an error <0.3‰.

3. Results

At ∼44°S along the Chilean Margin, J1004 bulk sediment $\delta^{15}N$ values reflect end member mixing between the equatorial sourced water (∼12.0‰) and SAMW (∼6.3‰) (Rafter et al., 2012). Surface $\delta^{15}N$ values decrease moving southward with distance from the EEP oxygen minimum zone, demonstrating decreasing denitrification and increasing utilization influence (De Pol-Holz et al., 2009). In the present there is no oxygen deficient zone in this region, and productivity is higher today than at any point over the Holocene. For this reason, any denitrification signal, both today and in the past, is likely transported from the south Pacific oxygen minimum zone located to the north off Peru and northern Chile (Boyer et al., 2018).

In shallow, rapidly-accumulating sediments, where diagenetic effects are minimal, FB-$\delta^{15}N$ and bulk sediment $\delta^{15}N$ values are expected to be comparable though not necessarily equal (De-Pol Holz et al., 2007; Robinson et al., 2012). The sedimentation rate at J1004 is almost 3 times higher than nearby Chilean Margin sites ODP 1233, where the high sedimentation rate was used as evidence that the impact of alteration on bulk sediment $\delta^{15}N$ values was negligible (Martinez et al., 2006). To further examine the effects of alteration within the sediments at J1004, we compare %TN to %TOC (Figure S2 in Supporting Information S1). The resulting line goes through zero within error at even 1 SD, suggesting that the inorganic contributions are minimal. The constant sedimentation rate and long term C/N (Figure S2 in Supporting Information S1) together indicate that terrestrial supply is constant across the Holocene with minimal effect on $\delta^{15}N$.

Concomitant with the $\delta^{15}N$ decrease, J1004 total organic carbon accumulation rate and $CaCO_3$ MAR increase toward the present, both suggesting an increase in primary productivity (Figure 2). The particularly large increase in TOC MAR in the Late Holocene is the result of more extreme SWW migration as demonstrated in the J1004 Al wt% as well as in western Atlantic records (van der Bilt et al., 2022). Most likely, this productivity increase is the result of an influx of nitrate to the surface. Near zero modern surface nitrate concentrations indicate that the decreasing $\delta^{15}N$ values are likely not the result of local changes (i.e., decreasing utilization), but rather an advected preformed signal (Boyer et al., 2018). The magnitude of the $\delta^{15}N$ change at J1004 is comparable to the $\delta^{15}N$ decrease in the Southern Ocean, consistent with complete consumption of upwelled nutrients on the Chilean Margin, with variability inherited from the source region.

4. Discussion

4.1. The SWW and Southern Ocean Nutrient Utilization

A comparison of Southern Ocean $\delta^{15}N$ with J1004 Al wt%, an indicator of SWW position along the Chilean Margin, suggests Southern Ocean upwelling increases across the Holocene as a result of SWW southward movement, confirming an idea proposed by Studer et al. (2018) (Figure 2) (Riechelson, Bova, et al., 2023). The SWW migrate in response to changes in the interhemispheric and equator-to-pole latitudinal temperature gradient

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(Lu et al., 2010). When the SWW move southward, as they did through the Holocene, Southern Ocean upwelling increases (Marshall & Speer, 2012) leading to greater nitrate delivery to the surface ocean and a reduction in the Southern Ocean biological pump efficiency due to iron limitation.

4.2. Testing the Leaky Biological Pump Hypothesis

Nutrients may be supplied from the Southern Ocean to the Chilean Margin via local upwelling. Satellite sea surface temperature data of the Chilean Margin reveal seasonal coastal Ekman upwelling near our core site in austral summer (Saldías et al., 2021). Normal winds between 41 and 45°S are perpendicular to the coast, but during austral summer the winds move northward parallel to the coast, causing enhanced coastal Ekman upwelling (Pérez-Santos et al., 2019). Given the relationship between the SWW and coastal upwelling today, we expect that as the SWW migrated southward across the Holocene, coastal upwelling near J1004 would have increased, bringing nutrient rich southern-sourced waters from the subsurface to the surface. So as the SWW migrate south, both Southern Ocean upwelling and Chilean Margin coastal upwelling increase. Decreasing sea surface temperatures and $\delta^{15}N$ values on the Chilean Margin throughout the Holocene documented in nearby Site ODP 1233 could be caused by upwelling or advection of southern sourced water (Lamy et al., 2002; Martinez et al., 2006). Antarctic surface water advection via the PCC is unlikely because it would require that the ACC be located farther north. This is improbable given southward SWW movement (Lamy et al., 2004). Assuming that there is an increase in local coastal upwelling across the Holocene, not only is the source $\delta^{15}N$ changing as a result of decreasing utilization efficiency in the Southern Ocean, but the amount of Southern Ocean nitrate delivered to the Chilean Margin surface is changing as well.

Studer et al. (2018) suggest enhancing Southern Ocean upwelling and decreasing biological pump efficiency caused the Southern Ocean CO_2 sink to become less and less efficient across the Holocene, leaving more CO_2 in the atmosphere. However, exported Southern Ocean preformed nutrients could have increased productivity and enhanced CO_2 uptake downstream, potentially compensating for reduced efficiency at the Southern Ocean source. At Site J1004 along the Chilean Margin, downstream of the Southern Ocean, we find that productivity increases across the Holocene, as indicated by greater organic and inorganic ($CaCO_3$) carbon fluxes. This is in agreement with consistently increasing biogenic silica wt% over the last 7,000 years at nearby core GeoB3313-1 (Lamy et al., 2002). Given near surface nitrate depletion in the present when nutrient delivery is presumably at its highest given Southern Ocean incomplete utilization and Chilean Margin productivity at maximum, it is likely that nutrient consumption was complete across the Holocene (Boyer et al., 2018).

However, only a portion of the nutrients advected from the Southern Ocean region via intermediate and mode waters are upwelled to the Chilean Margin surface, and the majority likely continue downstream. SAMW and AAIW water masses flow north and westward until they arrive in the western equatorial region, then travel eastward to the EEP subsurface (Bostock et al., 2013; Bova et al., 2015; Rafter et al., 2012). When southern sourced waters enter the EEP, nutrients from SAMW are transported into the thermocline through diapycnal mixing where they are brought to the surface by Ekman upwelling (Rafter & Sigman, 2016; Rafter et al., 2012). In the EEP, like in the Southern Ocean, nitrate utilization is tied to upwelling and productivity is limited by iron deficiency (Martin, 1990). Local upwelling dominates nitrate supply along the equator and with stronger upwelling, nutrients are less completely consumed (Rafter & Sigman, 2016). From the EEP, nutrients may be transported south in subsurface water.

We investigate nutrient transport through the south Pacific by plotting $\delta^{15}N$ and measures of primary productivity following the water flow path (Figure 3). Although only selected records are presented in Figure 3, other records support the observed trends on the Chilean Margin (Martinez et al., 2006), WPWP (Kienast et al., 2008; Lambert et al., 2022), EEP (Pichevin et al., 2009), and Peru Margin (Glock et al., 2018). The Southern Ocean, Chilean Margin, WPWP, and EEP all generally show a similar decrease in $\delta^{15}N$, which may reflect complete nutrient consumption and a changing Southern Ocean end member. On the Chilean Margin and in the WPWP, this is paired with increasing primary productivity, supporting increasing nutrient export from the Southern Ocean. Productivity in the EEP is thought to decrease as a result of weakening wind-driven upwelling, which explains how water carries a seemingly Southern Ocean $\delta^{15}N$ signal, but primary productivity decreases (Saavedra-Pellitero et al., 2022). Though more nutrients are trapped in the subsurface and fewer are upwelled to the surface to promote productivity, the nitrate brought to the surface generally displays the Southern Ocean trend. The Peru Margin seems to share no features with other regional records, which is understandable given the heavy

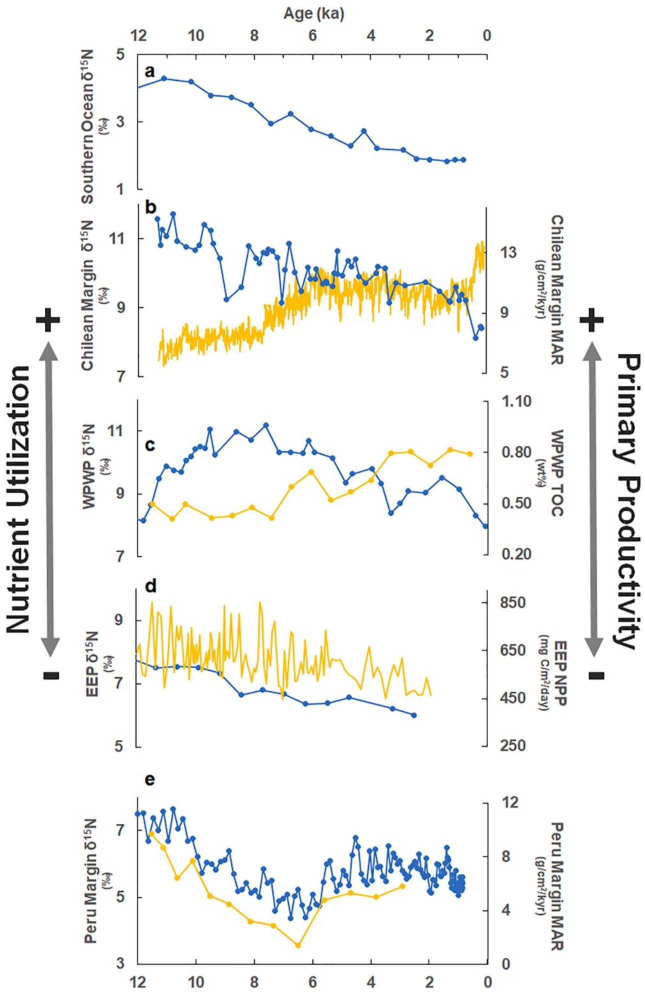

Figure 3. A compilation of $\delta^{15}N$ records and various measures of productivity in the order of flow path from top to bottom. The Southern Ocean (a) is represented by PS75/072-4 (Studer et al., 2018), the Chilean Margin (b) by J1004 (this study), the western Pacific warm pool (c) $\delta^{15}N$ by MD 01–2386 (Jia & Li, 2011) and %TOC by MD 06–3052 (Xu et al., 2020), the Eastern Equatorial Pacific (d) $\delta^{15}N$ by ME-27 (Studer, Mekik, Ren, Hain, Oleynik, Martínez-García, et al., 2021) and NPP by ODP 1240 (Saavedra-Pellitero et al., 2022), and finally the Peru Margin (e) by $\delta^{15}N$ by ODP 1228 (Agnihotri et al., 2006) and TOC flux M77/2_029-3 (Doering et al., 2016).

denitrification influence which would overprint any existing signal. In total, the trends described here support a decrease in nitrate utilization in the Southern Ocean and a subsequent increase in the export of preformed nutrients from the Southern Ocean across the Holocene. We further suggest the decreasing $\delta^{15}N$ trends of similar magnitude to that observed in the Southern Ocean results from complete consumption of Southern Ocean nutrients and thus the $\delta^{15}N$ signature of the Southern Ocean source.

To determine the potential influence of the Southern Ocean on downstream signals, we subtracted the Southern Ocean $\delta^{15}N$ from the J1004, WPWP, EEP, and Peru Margin $\delta^{15}N$ records to remove the end member signal (Figure S4 in Supporting Information S1). We did so by interpolating all records to the same age intervals, then normalizing to the Southern Ocean record. In J1004, the WPWP, and the EEP, correcting to the Southern Ocean removes the long term decreasing trend in the data, indicating that the change in each of these locations is of similar magnitude to the Southern Ocean change and thus likely an advected Southern Ocean signal. With greater distance from the Southern Ocean, there are likely additional effects acting on the $\delta^{15}N$ signal and thus we may have overcorrected the Southern Ocean signal. Nonetheless, the normalized records generally support the proposed advected signal and complete consumpton in these locales. Dissimilar pattern in the Peru Margin indicates that the Southern Ocean signal unsurprisingly does not influence the $\delta^{15}N$ pattern.

If nutrients were incompletely consumed downstream, it might indicate that changes in the Southern Ocean carbon sink was not compensated elsewhere. Conversely, if all of the exported nutrients promoted productivity and utilization downstream, it would imply that the decrease in the Southern Ocean CO_2 sink was compensated elsewhere. More realistically, what we are left with is a scenario more complicated than that proposed in Studer et al. (2018) wherein the Southern Ocean source might have been compensated by increasing productivity downstream although the magnitude of both remain difficult to estimate.

5. Conclusions

In this paper we seek to better understand the impact of the Southern Ocean leaky biological pump on Holocene atmospheric CO_2 concentrations. By comparing Southern Ocean nutrient utilization with SWW migration reconstructed from Al wt%, we confirm that Holocene changes to biological pump efficiency are driven by a southward SWW migration. We then determine that unutilized Southern Ocean nutrients do promote productivity downstream on the Chilean Margin, WPWP, and EEP and are probably completely consumed implying that exported nutrients from the Southern Ocean increased carbon sinks downstream. Therefore, the relationship between Southern Ocean biological pump efficiency and atmospheric CO_2 is likely more complex than proposed by Studer et al. (2018). Nevertheless, given that the Holocene atmospheric $\delta^{13}C$ record is consistent with a marine source of CO_2, it would imply that the Southern Ocean source was possibly not completely compensated likely contributing to the Holocene CO_2 increase.

Data Availability Statement

XRF, organic carbon, and nitrogen isotope data are available in the NOAA World Data Service for Paleoclimatology offered through the National Centers for Environmental Information (Riechelson, Rosenthal, et al., 2023).

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