A rise in surface nutrient concentrations in the Southern Ocean over the Holocene

Anja S. Studer¹-*,†, Daniel M. Sigman², Alfredo Martínez-García¹, Lena M. Thôle³, Elisabeth Michel⁴, Samuel L. Jaccard³, Jörg A. Lippold⁵, Alain Mazaud⁴, Xingchen T. Wang², Laura F. Robinson⁶, Jess F. Adkins⁷, Gerald H. Haug¹,⁸.

¹Max Planck Institute for Chemistry, Climate Geochemistry Department, Mainz, Germany. ²Department of Geosciences, Princeton University, Princeton, NJ, USA. ³Institute of Geological Sciences and Oeschger Center for Climate Change Research, University of Bern, Bern, Switzerland. ⁴Laboratoire des Sciences du Climat et de l’Environnement (LSCE), Gif-sur-Yvette Cedex, France. ⁵Institute of Earth Sciences, University of Heidelberg, Heidelberg, Germany. ⁶Bristol Isotope Group, School of Earth Sciences, University of Bristol, Bristol BS8 1RJ, United Kingdom. ⁷Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125. ⁸Geological Institute, Department of Earth Sciences, ETH Zurich, Zurich, Switzerland.

* Corresponding author: anja.studer@unibas.ch
† now at: Department of Environmental Sciences, University of Basel, Basel, Switzerland.

A ~20 parts per million rise in atmospheric carbon dioxide concentration over the course of the Holocene has long been recognized as exceptional among interglacials and in need of explanation. Previous hypotheses involved natural or anthropogenic changes in terrestrial biomass, carbonate compensation in response to deglacial outgassing of oceanic CO₂, and enhanced shallow water carbonate deposition. Here, we compile new and previously published fossil-
bound nitrogen isotope records from the Southern Ocean that indicate a rise in surface nitrate concentration through the Holocene. When coupled with increasing or constant export production, these data suggest an acceleration of nitrate supply to the Southern Ocean surface from underlying deep water. This change would have weakened the ocean’s “biological pump” that stores CO$_2$ in the ocean interior, possibly explaining the Holocene atmospheric CO$_2$ rise. Over the Holocene, the circum-North Atlantic region cooled and the formation of North Atlantic Deep Water seemingly slowed. Thus, the “seesaw” in deep ocean ventilation between the North Atlantic and the Southern Ocean that has been invoked for millennial scale events, deglaciations, and the last interglacial period may have also operated, albeit in a more gradual form, over the Holocene.

There is growing evidence for ongoing changes in Southern Ocean overturning$^1$, and these changes in turn affect the rates at which anthropogenic CO$_2$ penetrates into the deep ocean and naturally stored deep ocean CO$_2$ is vented to the atmosphere. Unraveling these dynamics is central to predicting the trajectory of ocean CO$_2$ uptake and the atmospheric concentration of CO$_2$ in the coming decades and centuries. Paleoceanographic reconstructions over the relatively climatically stable Holocene period have the potential to provide information on the variability of Southern Ocean circulation and biogeochemistry and their interaction with climate that is easier to interpret than over glacial cycles, when diverse aspects of the Earth system were changing markedly.

Recent work has shown that the Holocene, while stable in comparison to recent glacial cycles and most previous interglacials, did host significant changes in both physical
climate and the global carbon cycle. Compilation of temperature records suggests a cooling of roughly 1°C since 8,000 yrs, focused in the Northern Hemisphere (NH). Ice core reconstructions indicate substantial changes in atmospheric CO$_2$: after an initial deglacial rise from 180 to 270 ppm between ~18,000 and 11,000 yrs, CO$_2$ declined by 10 ppm from 11,000 to 8,000 yrs before increasing from 260 ppm to a pre-industrial concentration of 280 ppm.

The early Holocene atmospheric CO$_2$ decline from 11,000 to 8,000 yrs has been suggested to result from re-growing terrestrial biosphere in the aftermath of glacial retreat, while both terrestrial and oceanic processes have been proposed to explain the subsequent 20 ppm rise since 8,000 yrs. A decline in terrestrial biomass has been proposed and attributed to either natural climate change or deforestation by humans. An alternative proposal is that ocean alkalinity decreased due to a pulse of deep sea calcium carbonate burial, itself a response to an increase in terrestrial biomass earlier in the Holocene. Another ocean alkalinity-based hypothesis is that rising sea level led to enhanced deposition of coral reefs and other shallow water carbonates since 8,000 yrs, lowering ocean alkalinity and thus raising atmospheric CO$_2$ (ref 8).

The modern Southern Ocean is characterized by high surface nutrient (e.g., nitrate) concentrations, which reflects the rapid circulation-driven exchange between surface waters and the nutrient-rich ocean interior. Phytoplankton are unable to consume the wealth of nutrients, as their growth in the region is limited by iron. Thus, the nutrient excess of the Southern Ocean surface provides a potential indicator of overturning changes in the past. Moreover, the incomplete consumption of nutrients combines with the high overturning rate in the Southern Ocean to lower the efficiency of the global
ocean’s “biological pump” of carbon, reducing the quantity of CO₂ that is sequestered in the deep ocean through the production and remineralization of sinking organic matter. As a result, the Southern Ocean, its biogeochemical conditions, and its relative importance in the ventilation of the ocean interior have long been recognized as a potential driver of atmospheric CO₂ change on time scales of hundreds and thousands of years. Given the importance of the Southern Ocean in setting atmospheric CO₂ and the hypothesis that Southern Hemisphere (SH) westerly wind strength is a critical climate-sensitive determinant of Southern Ocean overturning, Moreno et al. used South American pollen assemblage changes to infer that westerly wind strengthening could have increased Southern Ocean CO₂ release over the Holocene, contributing to the Holocene atmospheric CO₂ rise. This hypothesis can be seen as an extension of the proposal that the SH winds played a similar role in the rise of CO₂ during the last deglaciation. However, so far, reconstructions of Holocene changes in westerly wind strength remain controversial.

In high nutrient regions such as the Southern Ocean, the nitrogen (N) isotope composition of exported organic matter reflects the degree to which the gross nitrate supply is assimilated by phytoplankton growth. The consumption of surface nitrate causes its δ¹⁵N to rise as its concentration declines (δ¹⁵N = [(¹⁵N/¹⁴N)_{sample} / (¹⁵N/¹⁴N)_{atm} N₂ - 1] * 1000 ‰). This δ¹⁵N rise is recorded in the biomass of the phytoplankton such as diatoms that consume the nitrate. Thus, the δ¹⁵N of the organic matter bound and preserved within the siliceous frustules of diatoms (δ¹⁵N_{db}) provides a means for reconstructing past changes in the relative degree of nitrate consumption. In regions such as the Antarctic Zone (AZ) where the deep ocean is ventilated, a higher δ¹⁵N_{db}
would imply a rise in nitrate consumption and an increase in the efficiency of the global ocean’s biological pump and thus more deep ocean storage of CO₂.

We report two new $\delta^{15}N_{db}$ records from the Indian sector of the Southern Ocean and compile them with previously published Southern Ocean nitrogen isotope data\textsuperscript{16,17,18}. Sediment core MD11-3353 is from the Indian sector of the AZ, and core MD12-3396CQ is from the Indian sector of the Polar Frontal Zone (PFZ), just to the North of the AZ (Figure 1). The other records in the compilation are (1) a $\delta^{15}N_{db}$ record from core PS75/72-4 in the Pacific sector of the AZ\textsuperscript{17}, (2) a foraminifera-bound $\delta^{15}N$ ($\delta^{15}N_{fb}$) record from ODP Site 1090 in the Atlantic sector of the Subantarctic Zone (SAZ) to the North of the PFZ\textsuperscript{16}, and (3) Pacific sector compilations of deep sea coral-bound $\delta^{15}N$ ($\delta^{15}N_{cb}$) in the AZ (Drake Passage) and SAZ (Drake Passage and south of Tasmania)\textsuperscript{18}.

**Holocene decline in fossil-bound $^{15}N/^{14}N$**

Over the last 10,000 yrs, $\delta^{15}N_{db}$ declined in all AZ records, by $\sim2\%_o$, and AZ $\delta^{15}N_{cb}$ appears consistent with this amplitude of decline (Figure 2). The $\delta^{15}N_{fb}$ record from the Atlantic SAZ and the $\delta^{15}N_{cb}$ data from the Pacific SAZ suggest that the nitrate $\delta^{15}N$ decline extended northward into this region as well, although weakening northward, e.g., to a $\sim1\%_o$ decrease at ODP Site 1090. Whereas the high rate of nitrate supply to the AZ surface is dominated by upwelling of underlying subsurface waters, the SAZ receives nitrate from both the AZ surface and underlying Circumpolar Deep water. Thus, the northward decline in the $\delta^{15}N$ decrease is consistent with the AZ as the origin of the $\delta^{15}N$ decrease.
Our observations derive from $\delta^{15}N$ measurements in three fossil types (i.e., diatoms, foraminifera and corals), with records from each of the basins of the Southern Ocean. Nevertheless, previous work did not clearly show a Holocene $\delta^{15}N$ decline. There is a range of plausible explanations for this disconnect between recent and earlier measurements. First, it is common for Southern Ocean sediment cores to lack a complete Holocene, and radiocarbon dates are often sparse or absent in Antarctic cores due to a lack of foraminiferal carbonate. For example, several of the first bulk sediment $\delta^{15}N$ records extending back to the last ice age$^{19}$ have subsequently been found to lack the latter half of the Holocene$^{20}$. The second category of explanations relates to proxy characteristics and analytical methods. Bulk sedimentary $\delta^{15}N$ measurements can be affected by exogenous N inputs$^{21,22}$ and variable isotope fractionation associated with diagenesis$^{16}$, interfering with their ability to robustly record the Holocene trend$^{16}$. The accuracy of the earliest combustion-based $\delta^{15}N_{db}$ measurements$^{23,24}$ was compromised by gaseous N absorption on the opal$^{25}$, and the precision of current methods has significantly improved over time$^{26}$, which is critical for recording modest changes. In addition, opal from non-diatom material can contaminate the $\delta^{15}N_{db}$ signal in intervals with low diatom flux$^{26}$, and diatom assemblage changes may lead to artifacts$^{27}$. Importantly, diatom assemblage separation has been performed on all $\delta^{15}N_{db}$ records reported here, confirming that the Holocene trend is not an artifact of diatom species abundance changes or of non-diatom opal contamination (Supplementary Figure S1).

It is also possible that the regional extent of the reconstructed Holocene nitrate $\delta^{15}N$ decrease did not apply to all sectors of the Southern Ocean. In particular, the $\delta^{15}N_{db}$ record at core TN057-13 in the Atlantic AZ does not show a Holocene decline$^{27}$ (although $\delta^{15}N_{fb}$ at ODP Site 1090 does (Fig. 2c)).
Finally, all of our AZ records are from near the Polar Front, so it is possible that the Holocene $\delta^{15}\text{N}$ decline did not extend further southward into the more polar AZ, potentially explaining the lack of a clear Holocene decline in some other previous $\delta^{15}\text{N}_{\text{db}}$ records. Due to the convergence of Southern Ocean waters to flow through the Drake Passage, the $\delta^{15}\text{N}_{\text{cb}}$ decline observed in the Drake Passage argues that the more polar AZ also experienced this $\delta^{15}\text{N}$ change. However, the most polar sites in the Drake Passage do not have a high density of corals through the Holocene, so this argument is preliminary.

The Holocene $\delta^{15}\text{N}$ decline in the Southern Ocean might be suspected to derive from a decline in the $\delta^{15}\text{N}$ or a rise in the concentration of the subsurface nitrate that is upwelled to the surface. Upper Circumpolar Deep Water (UCDW) upwells in the AZ near the Polar Front, while Lower Circumpolar Deep Water (LCDW) upwells further poleward in the AZ. The modern range in nitrate $\delta^{15}\text{N}$ among pure North Atlantic Deep Water (NADW), LCDW, and UCDW is less than 0.5 ‰ (ref. 29), with Pacific Deep Water in the low latitude South Pacific expanding the deep nitrate $\delta^{15}\text{N}$ range to 1 ‰ at maximum. The nitrate $\delta^{15}\text{N}$ and concentration differences among these water masses are weakened by circulation and remineralization in the Southern Ocean. With regard to nitrate concentration, even though NADW has a low nitrate concentration of ~17.5 $\mu$mol/kg when measured in the low latitude Atlantic, the nitrate concentration of LCDW that most directly derives from it is only slightly lower than that of UCDW (~32 vs. 34 $\mu$mol/kg in the Indian and Pacific). Changing the nitrate concentration of LCDW or UCDW substantially (e.g., by 10-20 $\mu$mol/kg) would require a comparable change in the global nitrate reservoir, which is unlikely. What remains a greater concern is the
assumption of a constant mean ocean nitrate $\delta^{15}$N across the Holocene. Some non-Southern Ocean records show decreasing trends across the Holocene$^{33}$, and a decline in whole ocean nitrate $\delta^{15}$N cannot be ruled out. However, previous studies do not provide evidence for a mean ocean decrease approaching 2‰ (refs. 22, 33).

**Increase in the supply rate of nitrate**

Thus, the Holocene decline in Southern Ocean fossil-bound $\delta^{15}$N is best interpreted as an increase in the proportion by which the nitrate supply to the surface ocean exceeded its demand by phytoplankton, resulting in a rise in surface nitrate concentration. If this change was driven by changing eolian iron supply, then the iron supply would have needed to decline over the late Holocene, for which there is no evidence$^{34,35}$. Moreover, opal fluxes in the three cores with $\delta^{15}$N$_{db}$ records suggest constant or increasing export production over the Holocene (Figure 2d, although the available Southern Ocean opal flux records appear heterogeneous, Supplementary Figure S2). A decline in the degree of nitrate consumption coupled with stable or weakly rising export production points to a Holocene rise in the rate of gross nitrate supply into the Antarctic surface and thus an increase in water flux from the subsurface into the surface.

As noted above, sediment core TN057-13 from the Atlantic AZ has $\delta^{15}$N$_{db}$ and opal flux records that are inconsistent with those we report from the Indian and Pacific AZ$^{13,27}$. With regard to opal flux, TN057-13 shows a decline since the last deglaciation$^{13}$, in contrast to our observations of stable or rising opal flux (Figure 2d, Supplementary Figure S2). We tentatively propose that the observed differences in opal flux trends and absolute values derive from the between-sector differences in (1) the sources of upwelled water and/or (2) basin-level constraints on the net upwelling rate. With
regard to upwelling sources, the silicate concentration in the water to be upwelled in the Atlantic AZ – and thus the biogenic opal flux – is reduced by the inflow of low-silicate NADW, such that deglacial changes in opal flux may be affected by changes in NADW formation\textsuperscript{36}. With regard to upwelling rates, Atlantic sector AZ upwelling may be limited by eddy compensation, which itself may be sensitive to the rate of NADW formation. In detail, an increase in northward wind-driven transport in the Southern Ocean, absent a parallel increase in NADW formation, would have led to a thickening of the low latitude Atlantic thermocline and an associated steepening of isopycnals at the northern boundary of the Southern Ocean\textsuperscript{37}. This would have increased southward eddy transport and thus prevented a rise in nitrate supply to the Southern Ocean surface due to a decline in the residual circulation\textsuperscript{38}. Because this North Atlantic-driven feedback is more remote in the Indian and Pacific than in the Atlantic basin, upwelling in the Indian and Pacific Southern Ocean may have had more freedom to increase over the Holocene. In any case, the possibility of basin-to-basin variations in the Holocene nitrate evolution of the Southern Ocean should be pursued further.

\textbf{CO$_2$ leakage to the atmosphere}

For almost all changes in circulation that would increase nitrate supply to and nitrate concentrations in the Southern Ocean surface, there would be increased leakage of biologically stored CO$_2$ from the Southern Ocean and a resulting increase in atmospheric CO$_2$ concentration\textsuperscript{39}. The Holocene change might be considered a gradual continuation of the AZ changes that have been proposed to explain the glacial-to-interglacial increases in atmospheric CO$_2$ in general. A comparison with previous box model and ocean general circulation model results suggests that, for a range of scenarios, the reconstructed Holocene change could generate the observed 20 ppm rise in atmospheric
CO₂ (Supplementary Information). A more specific assessment awaits clarity as to whether the reconstructed increase in surface nitrate concentration applied to the more polar AZ.

Other carbon cycle-related data do not as yet compellingly support or disprove our hypothesis. First, a release of biologically light carbon from the ocean adequate to explain the 20 ppm atmospheric CO₂ rise should cause the δ¹³C of atmospheric CO₂ to decline by 0.2 ‰, more than the observed ~0.05 ‰ decline over the last 7,000 yrs⁴⁰ (Supplementary Figure S3). However, there are other potential contributors to the history of atmospheric CO₂ δ¹³C, including changes in the terrestrial biosphere, ocean temperature, and the isotopic characteristics of air/sea CO₂ exchange, each with uncertainties⁴⁰. Second, in terms of radiocarbon constraints, slow air/sea equilibration at the AZ surface probably explains the deep sea coral-based observation of a relatively weak Holocene difference in radiocarbon content between the upwelling UCDW and Antarctic Intermediate Water, the latter forming from AZ surface water near the Antarctic Polar Front⁴². The existing data appear to suggest a weak decline in this difference through the Holocene, consistent with faster Southern Ocean overturning⁴². Third, abyssal Indian Ocean carbonate ion concentration decreased over the Holocene⁴³, whereas a weakening of the biological pump in itself would have transiently raised deep ocean carbonate ion⁴⁴. However, deep ocean carbonate ion also depends on terrestrial biosphere size, shallow carbonate burial, and compensation of these by deep ocean CaCO₃ burial rate⁷. Fourth, a weakening of the ocean’s biological pump over the Holocene should have decreased the surface to deep ocean dissolved inorganic carbon δ¹³C gradient, consistent with observations⁴⁵. Finally, weakening of the ocean’s biological pump should have raised ocean interior oxygen concentrations. However, the
existing redox-sensitive proxies may not record changes at the relatively high absolute oxygen concentrations that have characterized the deep ocean throughout the Holocene.\textsuperscript{19}

A weakening of the biological pump was not the sole change affecting atmospheric $\text{CO}_2$ across the Holocene. However, when superimposed on terrestrial biosphere and ocean alkalinity changes,\textsuperscript{5-8,45} it can generate the net 20 ppm increase. This may explain why Earth system models – which do not hindcast a Holocene trend in Antarctic overturning – fail to produce the different trends in atmospheric $\text{CO}_2$ for the Holocene and previous interglacial MIS 5e (~128,000-115,000 yrs), during which atmospheric $\text{CO}_2$ declined by $\leq$10 ppm:\textsuperscript{46} no decline in AZ $\delta^{15}\text{N}_{\text{db}}$ (i.e. nitrate consumption) is evident over the course of MIS 5e.\textsuperscript{17}

**Possible Northern Hemisphere driver**

Data indicate a NH cooling of 2°C since 7,000 yrs (Figure 2e) that was focused in the circum-North Atlantic\textsuperscript{4} (Supplementary Figure S4). This cooling and North Atlantic grain size and magnetic susceptibility data suggest a decline in NADW formation into the later Holocene\textsuperscript{47-49} (Figure 2f), to which the mid-Holocene increase in Antarctic overturning may have been a response. The same connection has been proposed for the Heinrich events of the last ice age and upon deglaciation\textsuperscript{14,36,50}.

One possible scenario connecting NADW reduction to Antarctic overturning enhancement involves the winds: at the deglaciations and during NH stadials, reduction of NADW formation caused SH warming and southward migration of the SH westerly winds, which in turn drove an increase in Antarctic overturning.\textsuperscript{11,13,14} For the Holocene,
there is not yet clarity as to the sense of SH temperature change (Supplementary Figure S4) or the strength and position of the westerly winds\textsuperscript{12,15}. An alternative mechanism for a North Atlantic/Southern Ocean teleconnection is through the ocean interior. The seeming reduction in NADW formation over the Holocene may have lowered the density of the deep ocean, accelerating Antarctic surface-to-deep overturning through the “density vacuum” mechanism\textsuperscript{36,50}.

The climate of the Holocene appears to be more stable than that of most other late Pleistocene interglacials, with a weaker tendency for the post-deglacial cooling that characterizes interglacials\textsuperscript{52}, a characteristic that may have facilitated the development of complex human civilizations. It has been proposed that the rise in atmospheric CO\textsubscript{2} over the Holocene, which also appears to be a unique feature among interglacials, may help to explain Holocene climate stability\textsuperscript{53}. Thus, the evidence reported here for Southern Ocean change, if it indeed explains the Holocene CO\textsubscript{2} rise, provides an oceanographic mechanism for the remarkable stability of Holocene climate.
Figures and figure legends

Fig. 1: Sediment core and deep sea coral locations relative to austral summer surface nitrate concentrations and oceanic fronts. Core locations of the diatom-bound $\delta^{15}$N and opal flux records are shown in white with a black rim, locations of the ODP Site 1090 foraminifera-bound $\delta^{15}$N record and of the coral-bound $\delta^{15}$N measurements are shown in white, and sediment cores with published opal flux data mentioned in the text are shown in dark grey. APF, Antarctic Polar Front; SAF, Subantarctic Front; STF, Subtropical Front. Fronts are after Orsi et al.\textsuperscript{54}. 
Fig. 2: Holocene records of fossil-bound δ¹⁵N and biogenic opal flux from the Southern Ocean, compared with climate- and circulation-related records from the Northern Hemisphere and with atmospheric CO₂. a, Atmospheric pCO₂ composite⁵⁵. b, δ¹⁵N records from the Antarctic Zone of the Southern Ocean. Diatom-bound δ¹⁵N
records are shown in green, from the Pacific Antarctic\textsuperscript{17} (circles, PS75/72-4), the Indian Antarctic (triangles, MD11-3353) and the Indian Polar Frontal Zone (diamonds, MD12-3396CQ). A compilation of coral-bound $\delta^{15}$N data\textsuperscript{18} (Drake Passage) is shown in blue. \textbf{c,} Published fossil-bound $\delta^{15}$N records from the Subantarctic Zone of the Southern Ocean. Red, foraminifera-bound $\delta^{15}$N record from ODP Site 1090 in the Atlantic\textsuperscript{16}, dark-blue, coral-bound $\delta^{15}$N compilation from the Drake Passage\textsuperscript{18}, light-blue, coral-bound $\delta^{15}$N compilation from Tasmania\textsuperscript{18}. \textbf{d,} Thorium-normalized opal flux records from cores PS75/72-4 (circles, ref. 17), MD12-3396CQ (diamonds) and MD11-3353 (triangles). \textbf{e,} Temperature anomaly from 30-90°N relative to the 1961-1990 common era (CE) instrumental mean\textsuperscript{4}. \textbf{f,} Mean grain size of the sortable silt fraction, a proxy for near-bottom flow speed, from core MD99-2251 from the Gardar Drift at 2620m water depth\textsuperscript{48} (orange) and mean relative grain size from a stacked record from 13 sediment cores located South of Iceland\textsuperscript{47} (grey), indicative of the relative strength of the Iceland-Scotland overflow and thus North Atlantic Deep Water formation. Data in \textbf{a} and \textbf{e} are shown for the period prior to 1900 CE.
Methods

Data availability. The authors declare that data supporting the findings of this study are available within the article and its supplementary information files. Data are also available on Pangaea.

δ¹⁵Ndb analysis. The N isotopic composition of the diatom fraction was measured at Princeton University with the persulfate-denitrifier technique. The diatom separation and cleaning protocol is given in detail in the Supplementary Information.

Biogenic opal concentration and opal fluxes. Opal concentrations were measured using the wet digestion technique, and opal fluxes were evaluated by correcting for sediment focusing with Th-normalization.

Age models and radiocarbon dating. Sediment core PS75/72-4 was recovered in the Antarctic Zone of the Pacific sector of the Southern Ocean (57°33.51′ S, 151°13.17′ W, 3099m water depth). The Holocene portion of the age model is constrained by four accelerator mass spectrometry (AMS) radiocarbon ages on Neogloboquadrina pachyderma (sin.) for the past 11,000 years. Sediment core MD12-3396CQ is located in the Polar Frontal Zone of the Indian sector of the Southern Ocean (47°43.88′ S, 87°41.71′ E, 3615m water depth). The stratigraphy of the sediment core is based on 16 AMS radiocarbon dates on monospecific planktonic samples chosen within the abundance peak of the species, with four replicates on different species (Supplementary Table S1). The calendar age model is obtained using a deposition model with OxCal, using calibration curve SH2013 and a marine reservoir age for the core location during the Holocene of 900±100 years following GLODAP. Sediment core MD11-3353 was retrieved in the Antarctic Zone of the Indian sector of the Southern Ocean (50.57°S,
68.39°E, 1568m), south of Kerguelen Island. The age model was constructed by correlating distinctive features in the potassium (K) X-ray Fluorescence scanning record of MD11-3353 to those observed in core MD12-3396CQ (Supplementary Figure S5).
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**Correspondence and requests for materials** should be addressed to A.S.S.  
[anja.studer@unibas.ch].

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**Author contributions**

A.S.S., D.M.S., A.M.G. and G.H.H. designed the study. A.S.S. performed the $\delta^{15}$N db analyses and wrote the first draft of the manuscript with D.M.S., A.M.G and G.H.H. L.M.T, S.L.J and J.L. contributed the $^{230}$Th-normalized opal flux data. E.M. and A.M. provided access to the sediment cores and measured the radiocarbon ages for the construction of the age model. X.T.W. provided coral-bound $\delta^{15}$N data that aided interpretation of our data. All authors contributed to the interpretation of the data and provided input to the final manuscript.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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