A well oxygenated eastern tropical Pacific during the warm Miocene

Authors: Anya V. Hess[1]*, Alexandra Auderset[2,5], Yair Rosenthal[1,3], Kenneth G. Miller[1], Xiaoli Zhou[4], Daniel M. Sigman[5], Alfredo Martínez-García[2]

Affiliations:
[1]Department of Earth and Planetary Sciences, Rutgers the State University of New Jersey; New Brunswick, NJ, USA.
[2]Climate Geochemistry Department, Max Planck Institute for Chemistry; Mainz, Germany.
[3]Department of Marine and Coastal Sciences, Rutgers the State University of New Jersey; New Brunswick, NJ, USA.
[4]State Key Laboratory of Marine Geology, Tongji University; Shanghai, China.
[5]Department of Geosciences, Princeton University; Princeton, NJ, USA.
* Email: anya.hess@rutgers.edu

Summary

The oxygen content of the oceans is susceptible to climate change, and has declined in recent decades [1], with the largest effect in oxygen deficient zones (ODZs) [2], mid-depth ocean regions with oxygen concentrations <5 µmol/kg (ref. 3). Earth system model simulations of climate warming predict that ODZs will expand until at least 2100. The response on timescales of 100s–1000s of years, however, remains uncertain [3–5]. Here, we investigate changes in the response of ocean oxygenation during the warmer-than-present Miocene Climatic Optimum (17.0–14.8 Ma). Our planktic foraminifera I/Ca and $\delta^{15}N$ data, paleoceanographic proxies sensitive to ODZ extent and intensity, indicate that dissolved oxygen concentrations in the eastern tropical Pacific exceeded 100 µmol/kg during the Miocene Climatic Optimum. Paired Mg/Ca-derived temperature data suggest that an oxygen deficient zone developed in response to an increased west-to-east temperature gradient and shoaling of the eastern tropical Pacific thermocline. Our records align with model simulations of data from recent decades to centuries [6,7] that suggest weaker equatorial Pacific trade winds during warm periods may lead to decreased equatorial upwelling, causing equatorial productivity to be less concentrated in the east. These findings shed light on how warm climate states like during the Miocene Climatic Optimum may affect ocean oxygenation. If the MCO is considered as a possible analogue to future warming, our findings seem to support models suggesting that the recent deoxygenation trend and expansion of the eastern tropical Pacific oxygen deficient zone may eventually reverse [3,4].

Introduction

Loss of ocean oxygen over the past 50 years, attributed to warming, has adversely affected coastal environments and intensified oxygen deficient zones (ODZs), especially in the eastern tropical Pacific (ETP) [2,8]. ODZs are water masses characterized by low dissolved oxygen concentrations (generally <5 µmol/kg) at ~200–700 meters water depth. They form in regions where upwelling high-nutrient waters fuel high biological productivity [9]. The remineralization of sinking organic matter further drives down oxygen concentration in poorly ventilated intermediate waters, forming the ODZ [9]. Earth system model simulations of atmospheric CO_2-

induced warming consistently predict that ODZs will expand until at least 2100 in response to warming-induced decreased solubility. The response on timescales of 100s–1000s of years is uncertain [3–5]. Some models simulate that enhanced ventilation from the Southern Ocean and/or a concomitant decrease in biological export production in the tropical ocean will reverse the recent deoxygenation trend [3,4], whereas others predict persistent ODZ expansion [5]. Here we investigate the response of the ETP ODZ (Fig. 1) to the Miocene Climatic Optimum (MCO; 17.0–14.8 Ma), a potential analog for future warming when temperatures were warmer than today (e.g., bottom water temperatures up to 9°C warmer than present) [10], and compare it with the response during subsequent cooling in the Mid-Miocene Climatic Transition (MMCT; 14.8–12.6 Ma).

In planktic foraminifera shells, we measured iodine-to-calcium ratios (I/Ca) and the isotopes of shell-bound organic nitrogen (FB-$\delta^{15}N$ for "foraminifera-bound $\delta^{15}N$"), paleoceanographic proxies sensitive to ODZ extent [11,12], and magnesium-to-calcium ratios (Mg/Ca) as a proxy for temperature in Ocean Drilling Program Site 845 (9°34.950'N, 94°35.448'W), which underlies the core of the northern lobe of the ETP ODZ (Fig. 1). I/Ca is sensitive to changes in ODZ intensity [13]. It relies on the fact that in suboxic conditions, (generally ~2–10 μmol/kg but perhaps up to 100 μmol/kg; refs. [13,14]), such as occur in ODZs, iodate (IO_3^-) is reduced to iodide (I^-) [15]. Because iodine oxidation is relatively slow (months to years), waters mixing upwards from the ODZ retain relatively low iodate concentrations despite the high oxygen concentrations above the ODZ [16]. This is recorded by foraminifera living above the ODZ as low I/Ca because their calcitic shells incorporate iodate but not iodide [11]. FB-$\delta^{15}N$ has been used to detect past changes in denitrification [17,18], in which bacteria use nitrate (NO_3^-) instead of oxygen (O_2) as the electron acceptor for the oxidation of organic matter; its occurrence in the water column is largely restricted to the ODZs. Denitrification discriminates against ^{15}N, so its occurrence in the ODZs leaves the remaining nitrate pool with a high $^{15}N/^{14}N$ ratio (or $\delta^{15}N$, where $(\delta^{15}N = ((^{15}N/^{14}N)_{sample}/(^{15}N/^{14}N)_{atm\ N2} - 1)) \times 1{,}000‰$). When this high-$\delta^{15}N$ nitrate is upwelled or mixed into surface waters, it is recorded in surface ocean plankton, including the tissue and shell-bound organic matter of foraminifera [12,19], and the shell-bound $\delta^{15}N$ is preserved over millions of years [17,18].

Miocene Oxygenation History

We analyzed surface- and subsurface-dwelling foraminifera *Dentoglobigerina altispira* and *Dentoglobigerina venezuelana*, respectively, from Site 845. Both species record relatively high I/Ca values during the MCO (4.9±1.0 and 4.9±0.7 μmol/mol, respectively, during 15.1–16.0 Ma) followed by significantly lower values during MMCT cooling (1.8±0.4 and 1.4±0.4 μmol/mol, respectively, during 14.8–11.7 Ma) (Fig. 2a). Core top calibrations suggest that I/Ca >~4 μmol/mol characterizes areas where the minimum oxygen concentration in the water column ($[O_2]_{min}$) exceeds 100 μmol/kg [13,20]. In contrast, in the ETP, $I/Ca_{subsurface}$ <1.5 μmol/mol indicates local oxygen concentrations of <7 μmol/kg [14]. Based on the current I/Ca-$[O_2]_{min}$ calibration [13,20], our records suggest that the ETP ODZ was well oxygenated during the warm MCO, with apparently >100 μmol/kg oxygen, similar to the modern South Pacific subtropical gyre where there is no ODZ, and subsequently decreased to <7 μmol/kg during MMCT cooling (Extended Data Fig. 3). The sharp transition from well oxygenated to poorly oxygenated conditions spans ~250 ky recorded in 7.2 m of sediment core and is therefore not artificially prolonged by sediment mixing.

In the modern ocean, in areas without a strong ODZ, iodate concentration is relatively constant through the water column (~100 nM range) except for moderate depletions in the mixed layer due to consumption by biological productivity [21]. In the ETP, iodate concentration is relatively constant in the upper thermocline and mixed layer (<20 nM range), with a strong iodate chemocline in the lower thermocline (~200 nM shift over ~50 water depth) [22]. The similarity in I/Ca of the two species is consistent with the findings of Boscolo-Galazzo et al. (ref. [23]) suggesting that *D. altispira* and *D. venezuelana* occupied a depth habitat within the upper 200 m of the water column in the ETP during the MCO and MMCT.

The FB-δ^{15}N records confirm the Middle Miocene deoxygenation trend and further constrain its timing and magnitude. FB-$\delta^{15}N_{venezuelana}$ values at Site 845 are relatively low during the MCO and rise by 3.1‰ from 14.7 to 12.6 Ma (Fig. 2b), suggesting little to no ETP water column denitrification during the MCO and increasing denitrification beginning at 14.7 Ma. The lag in FB-δ^{15}N rise after the I/Ca shift is consistent with the higher reduction potential of iodate than nitrate [11] (i.e., reduction of iodate at less than ~70 µmol/kg O_2 and nitrate at less than ~5 µmol/kg) [13] and progressive deoxygenation of the ODZ. At Site 872, at the western edge of the northern lobe of the ETP ODZ (Fig. 1), FB-$\delta^{15}N_{altispira}$ begins to rise at 13.6 Ma (Fig. 2) [18], suggesting gradual expansion of ^{15}N-enriched waters westward from the ODZ. The difference in FB-δ^{15}N values between sites may involve the cores' locations relative to the ODZ (Fig. 1). In any case, the values measured at both sites during the MCO are lower than expected in close proximity to a denitrifying environment [12,24]. While the FB-δ^{15}N record from Site 872 shows decreased dentrification during the MCO, suggesting more restricted geographical extent of the Pacific ODZ [18], the new I/Ca and FB-δ^{15}N records suggest that the ETP ODZ was fully oxygenated during the MCO. A full-scale ODZ with significant denitrification developed only after the transition to a cooler climate.

Taken together, these data show that during the warm part of the Miocene (16.0–15.1 Ma) the ETP was well oxygenated. By 15.1 Ma, oxygen concentration had begun to fall and by 14.7 Ma reached levels conducive to denitrification. By 13.6 Ma, the signal of denitrification in the ODZ increased to the point of strongly impacting nitrate δ^{15}N in the western tropical Pacific, indicating a spatial extent more comparable to today.

Proposed Mechanism

The rapidity of changes recorded in the foraminifera I/Ca and δ^{15}N proxies suggest that climate, rather than tectonics, was the primary driver of Miocene ODZ changes. The Central American Seaway, connecting the ETP with the Caribbean, remained open to even deep-water throughflow until the Late Miocene, with no MCO-MMCT-related changes [25]. The direct effect of warmer MCO temperatures would have been to augment deoxygenation due to reduced oxygen solubility [26], which in itself would have tended to expand, not contract, the MCO ODZ. Thus, we must turn to changes in ocean circulation and biological productivity to propose explanations for ODZ contraction during the MCO. Models suggest two mechanisms that could enhance ocean oxygenation in warmer climates: (i) increased deep-ocean ventilation from the high-latitude oceans and/or (ii) decreased biological export production in the tropical Pacific [3–5], which has been attributed to weaker tropical Pacific trade winds (i.e., Walker Circulation) under warmer climates in the past [27] and under anthropogenic global warming [28]. Although the two mechanisms are not mutually exclusive, our Mg/Ca temperature reconstructions, measured alongside I/Ca, provide evidence that the latter played a role during the MCO.

Planktic foraminifera Mg/Ca-derived sea-surface temperatures (SSTs) show weak gradients during the MCO zonally along the equatorial Pacific and meridionally from the equatorial Pacific to the Southern Ocean, with these gradients strengthening during the MMCT

(Fig. 3a). West tropical Pacific SST was relatively stable over the study period, with ~2°C cooling at 13.8–13.3 Ma. In contrast, the Southern Ocean cooled by ≥6°C from ~14.2–11.7 Ma, and the ETP cooled by ~4°C throughout the 16.5–11.5 Ma study interval. The equatorial Pacific SST gradient increased between ~15.5 and 12 Ma, in step with global cooling (Fig. 3a). Subsurface temperatures in the ETP cooled more than the surface and became more variable starting at ~14.6 Ma (Fig. 3b), reflecting that in addition to global cooling there was concomitant shoaling of the thermocline and increased upwelling during the MMCT, as suggested previously on the basis of foraminiferal oxygen and carbon isotopes [29,30]. More variability in $\delta^{18}O_{venezuelana}$ during the MMCT at nearby Site U1337 has been attributed to increased upwelling [30], consistent with this interpretation. While we cannot rule out that *D. venezuelana* migrated to a deeper depth habitat, the similar I/Ca values for both species throughout our record suggest it did not migrate out of the depths with stable iodate concentrations (i.e., to below the upper thermocline [22]).

In the modern ETP, fewer nutrients are introduced into the photic zone when the upwelling is reduced (e.g., during El Niño events) due to a reduction in the upward water transport. In addition, there is an accompanying deepening of the thermocline and therefore a decrease in the capacity of the upward water transport to entrain nutrients from below the thermocline water into the subsurface. These coupled changes reduce ETP biological productivity and the flux of sinking organic matter, which in turn allows the ODZ to contract [6]. A reduction in trade winds-driven upwelling, caused by the warmer climate, may explain the contraction of the ETP ODZ during the MCO. An increase in ventilation of the high-latitude sourced equatorial intermediate-depth water might have further contributed to the oxygenation of the ODZ at that time.

The reduction in tropical temperature gradients and increased thermocline depth may have been partly due to weakening of the trade winds and thus a deeper thermocline in the ETP during the MCO, resulting in reduced nutrient supply to the surface. As a result, export production was likely less focused in the ETP, leading to lower oxygen consumption in the poorly ventilated thermocline waters of this region and thus contraction and possibly collapse of the ODZ as suggested by our proxy records. During the MMCT, stronger equatorial trade winds raised the ETP thermocline, allowing for greater upwelling and nutrient supply, which focused remineralization and associated oxygen consumption in the ETP, leading to the formation of a strong ODZ (Fig. 4).

The rise in FB-$\delta^{15}N$ during the MMCT was weaker at Site 845 than at Site 872, despite the proximity of Site 845 to the ETP ODZ. Given the paleolocation of Site 845 (Fig. 1), an enhancement of ETP upwelling after the MCO may have allowed for incomplete nutrient consumption at the surface. Partial nutrient consumption, with its associated preference for ^{14}N [31], may have lowered the $\delta^{15}N$ of plankton and foraminifera relative to the subsurface nitrate pool, thus counteracting a portion of the $\delta^{15}N$ rise arising from the expansion of the ODZ and thus explaining the smaller FB-$\delta^{15}N$ rise at Site 845 than at Site 872. This interpretation of the FB-$\delta^{15}N$ records offers further preliminary support for ETP upwelling changes as the cause of ODZ expansion after the MCO.

While investigations of Miocene ETP productivity have not identified a consistent change in productivity from the MCO to the MMCT [32,33], the preservation of such a signal is never assured. For example, barite particles used for reconstructing productivity can be reduced to a soluble form and remobilized under suboxic conditions. Also, because remineralization of sinking organic particles happens more quickly in warmer temperatures, relatively warm temperatures during the Miocene may have caused less organic matter to reach the sediment [23]. We note that a high-resolution record from site U1338 shows prolonged (~150 ky) periods of enhanced opal accumulation centered at ~14 and 13.8 Ma, coincident with the major cooling of the MMCT. Increased benthic foraminifera accumulation rates after ~13.83 Ma also coincide with the increased opal accumulation rates, offering further support to the hypothesized increased export production during the global cooling step [34].

Implications

To the extent that we can use the MCO as an analog for a future warm world, the oxygenation of the ETP at that time supports models arguing that recent deoxygenation trends may reverse in the future, leading to weaker ODZs under global warming. A caveat in this interpretation is that processes with long time scales that were involved in the MCO changes might not be relevant to the coming century. Both upper ocean and deep ocean mechanisms have been proposed for weakening the ETP ODZ under warmer climates [18]. Our data provide preliminary evidence for one of the upper ocean mechanisms, specifically, a weakening of the tropical Pacific trade winds during warming [27,28]. This mechanism operates on interannual and decadal time scales [6,7], suggesting that our findings of ODZ oxygenation during the MCO are relevant for the coming decades and centuries of anthropogenic global warming. If so, then the recent (1979–2014) strengthening of the ETP ODZ will give way to ODZ contraction as anthropogenic global warming continues [7,35].

Data Availability Statement: All data generated during this study are available as source data files for figures in which they appear and in the NOAA database (data doi link).

Competing Interest Statement: The authors declare no competing interests.

Figure. 1. Map showing areal distribution and intensity of the ETP ODZ. Oxygen concentrations are reported from the depth of maximum depletion. Shown are the locations of Site 845 at the heart of the northern lobe of the ETP ODZ and Site 872 at its westward extension. Made in Ocean Data View[36] using GLODAP 2019[37,38] data by DIVA gridding data points shown as gray dots using 3:2 x:y grid cell size and excluding outliers.

Brief title: Map showing areal distribution and intensity of the ETP ODZ

Figure 2. Geochemical proxies relevant to Middle Miocene ETP oxygenation from sites 845 (eastern tropical Pacific; all solid lines, with or without filled circles) and 872 (western tropical Pacific; dashed line and diamonds). Darkness indicate species. Data includes replicates. (**a**) I/Ca, with average and ±1 standard deviation for the 16.0–15.1 and 14.8–11.7 Ma intervals. (**b**) FB-δ^{15}N. Oxygen (**c**) and carbon (**d**) isotopes are included for reference, labeled with carbon maxima (CM) events [39] and Miocene maxima (Mi) [40].

Brief title: Geochemical proxies relevant to Middle Miocene ETP oxygenation from sites 845 and 872

Figure 3. Middle Miocene temperature. (**a**) Average sea-surface temperature (SST) anomalies by region. Zonal and meridional SST gradients are the differences between curves. Smoothed using 100 ky bins to match resolution at Site 845, presented relative to their 15–16 Ma averages. See Extended Data Figure 6 for records at individual sites. (**b**) Surface and subsurface temperatures in the ETP. Vertical temperature gradient between surface and subsurface species, a measure of the thermocline depth, highlighted with gray shading. Data include replicates.

Brief title: Middle Miocene temperature

Figure 4. Conceptual model for (**a**) a strong ETP ODZ during MMCT cooling and (**b**) ETP oxygenation during the warm MCO.

Brief title: Conceptual model

[Additional references from main figures: [41–44]]

References

1. Eyring, V. *et al.* Human influence on the climate system. In Climate change 2021: The physical science basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change. in *IPCC Sixth Assessment Report* (eds. Masson-Delmotte, V. et al.) (Cambridge University Press, 2021).
2. Schmidtko, S., Stramma, L. & Visbeck, M. Decline in global oceanic oxygen content during the past five decades. *Nature* **542**, 335–339 (2017).
3. Yamamoto, A. *et al.* Global deep ocean oxygenation by enhanced ventilation in the Southern Ocean under long-term global warming. *Global Biogeochem. Cycles* **29**, 1801–1815 (2015).
4. Fu, W., Primeau, F., Keith Moore, J., Lindsay, K. & Randerson, J. T. Reversal of increasing tropical ocean hypoxia trends with sustained climate warming. *Global Biogeochem. Cycles* **32**, 551–564 (2018).
5. Frölicher, T. L. *et al.* Contrasting upper and deep ocean oxygen response to protracted global warming. *Global Biogeochem. Cycles* **34**, (2020).
6. Deutsch, C., Brix, H., Ito, T., Frenzel, H. & Thompson, L. Climate-forced variability of ocean hypoxia. *Science* **333**, 336–339 (2011).
7. Deutsch, C. *et al.* Centennial changes in North Pacific anoxia linked to tropical trade winds. *Science* **345**, 665–668 (2014).
8. Stramma, L. & Schmidtko, S. Tropical deoxygenation sites revisited to investigate oxygen and nutrient trends. *Ocean Sci.* **17**, 833–847 (2021).

9. Karstensen, J., Stramma, L. & Visbeck, M. Oxygen minimum zones in the eastern tropical Atlantic and Pacific oceans. *Progress in Oceanography* **77**, 331–350 (2008).

10. Steinthorsdottir, M., Jardine, P. E. & Rember, W. C. Near-future pCO_2 during the hot Miocene Climatic Optimum. *Paleoceanogr Paleoclimatol* **36**, (2021).

11. Lu, Z., Jenkyns, H. C. & Rickaby, R. E. M. Iodine to calcium ratios in marine carbonate as a paleo-redox proxy during oceanic anoxic events. *Geology* **38**, 1107–1110 (2010).

12. Ren, H., Sigman, D. M., Thunell, R. C. & Prokopenko, M. G. Nitrogen isotopic composition of planktonic foraminifera from the modern ocean and recent sediments. *Limnol. Oceanogr.* **57**, 1011–1024 (2012).

13. Lu, W. *et al.* Refining the planktic foraminiferal I/Ca proxy: Results from the Southeast Atlantic Ocean. *Geochimica et Cosmochimica Acta* **287**, 318–327 (2020).

14. Hardisty, D. S. *et al.* Limited iodate reduction in shipboard seawater incubations from the Eastern Tropical North Pacific oxygen deficient zone. *Earth and Planetary Science Letters* **554**, 116676 (2021).

15. Rue, E. L., Smith, G. J., Cutter, G. A. & Bruland, K. W. The response of trace element redox couples to suboxic conditions in the water column. *Deep Sea Research Part I: Oceanographic Research Papers* **44**, 113–134 (1997).

16. Chance, R., Baker, A. R., Carpenter, L. & Jickells, T. D. The distribution of iodide at the sea surface. *Environ. Sci.: Processes Impacts* **16**, 1841–1859 (2014).

17. Kast, E. R. *et al.* Nitrogen isotope evidence for expanded ocean suboxia in the early Cenozoic. *Science* **364**, 386–389 (2019).

18. Auderset, A. *et al.* Enhanced ocean oxygenation during Cenozoic warm periods. *Nature* **609**, 77–82 (2022).

19. Smart, S. M. *et al.* Ground-truthing the planktic foraminifer-bound nitrogen isotope paleo-proxy in the Sargasso Sea. *Geochimica et Cosmochimica Acta* **235**, 463–482 (2018).
20. Zhou, X., Hess, A. V., Bu, K., Sagawa, T. & Rosenthal, Y. Simultaneous determination of I/Ca and other elemental ratios in foraminifera using sector field ICP-MS. *Geochemistry, Geophysics, Geosystems* **23**, e2022GC010660 (2022).
21. Jickells, T. D., Boyd, S. S. & Knap, A. H. Iodine cycling in the Sargasso Sea and the Bermuda inshore waters. *Marine Chemistry* **24**, 61–82 (1988).
22. Moriyasu, R., Evans, N., Bolster, K. M., Hardisty, D. S. & Moffett, J. W. The distribution and redox speciation of iodine in the eastern tropical North Pacific Ocean. *Global Biogeochemical Cycles* **34**, e2019GB006302 (2020).
23. Boscolo-Galazzo, F. *et al.* Temperature controls carbon cycling and biological evolution in the ocean twilight zone. *Science* **371**, 1148–1152 (2021).
24. Sigman, D. M. *et al.* Coupled nitrogen and oxygen isotope measurements of nitrate along the eastern North Pacific margin. *Global Biogeochemical Cycles* **19**, (2005).
25. O’Dea, A. *et al.* Formation of the Isthmus of Panama. *Sci. Adv.* **2**, 11 (2016).
26. Garcia, H. E. & Gordon, L. I. Oxygen solubility in seawater: Better fitting equations. *Limnol. Oceanogr.* **37**, 1307–1312 (1992).
27. Yan, Q. *et al.* Large shift of the Pacific Walker Circulation across the Cenozoic. *National Science Review* **8**, nwaa101 (2021).
28. Vecchi, G. A. *et al.* Weakening of tropical Pacific atmospheric circulation due to anthropogenic forcing. *Nature* **441**, 73–76 (2006).
29. Nathan, S. A. & Leckie, R. M. Early history of the Western Pacific Warm Pool during the middle to late Miocene (~13.2–5.8 Ma): Role of sea-level change and implications for

equatorial circulation. *Palaeogeography, Palaeoclimatology, Palaeoecology* **274**, 140–159 (2009).

30. Tian, J., Ma, W., Lyle, M. W. & Shackford, J. K. Synchronous mid-Miocene upper and deep oceanic δ13C changes in the east equatorial Pacific linked to ocean cooling and ice sheet expansion. *Earth and Planetary Science Letters* **406**, 72–80 (2014).
31. Altabet, M. A. & Francois, R. Sedimentary nitrogen isotopic ratio as a recorder for surface ocean nitrate utilization. *Global Biogeochemical Cycles* **8**, 103–116 (1994).
32. Cortese, G., Gersonde, R., Hillenbrand, C.-D. & Kuhn, G. Opal sedimentation shifts in the World Ocean over the last 15 Myr. *Earth and Planetary Science Letters* **224**, 509–527 (2004).
33. Lyle, M. & Baldauf, J. Biogenic sediment regimes in the Neogene equatorial Pacific, IODP Site U1338: Burial, production, and diatom community. *Palaeogeography, Palaeoclimatology, Palaeoecology* **433**, 106–128 (2015).
34. Kochhann, K. G. D., Holbourn, A., Kuhnt, W. & Xu, J. Eastern equatorial Pacific benthic foraminiferal distribution and deep water temperature changes during the early to middle Miocene. *Marine Micropaleontology* **133**, 28–39 (2017).
35. Wu, M. *et al.* A very likely weakening of Pacific Walker Circulation in constrained near-future projections. *Nat Commun* **12**, 6502 (2021).
36. Schlitzer & Reiner. Ocean Data View. (2021).
37. Olsen, A. *et al.* The Global Ocean Data Analysis Project version 2 (GLODAPv2) – an internally consistent data product for the world ocean. *Earth System Science Data* **8**, 297–323 (2016).
38. Olsen, A. *et al.* GLODAPv2.2019 – an update of GLODAPv2. *Earth System Science Data* **11**, 1437–1461 (2019).

39. Holbourn, A., Kuhnt, W., Schulz, M., Flores, J.-A. & Andersen, N. Orbitally-paced climate evolution during the middle Miocene "Monterey" carbon-isotope excursion. *Earth and Planetary Science Letters* 17 (2007).

40. Miller, K. G., Feigenson, M. D., Wright, J. D. & Clement, B. M. Miocene isotope reference section, Deep Sea Drilling Project Site 608: An evaluation of isotope and biostratigraphic resolution. *Paleoceanography* **6**, 33–52 (1991).

41. Sosdian, S. M. & Lear, C. H. Initiation of the Western Pacific Warm Pool at the Middle Miocene Climate Transition? *Paleoceanography and Paleoclimatology* **35**, (2020).

42. Holbourn, A. *et al.* Does Antarctic glaciation force migration of the tropical rain belt? *Geology* **38**, 783–786 (2010).

43. Sosdian, S. M., Babila, T. L., Greenop, R., Foster, G. L. & Lear, C. H. Ocean carbon storage across the middle Miocene: a new interpretation for the Monterey Event. *Nat Commun* **11**, 134 (2020).

44. Leutert, T. J., Auderset, A., Martínez-García, A., Modestou, S. & Meckler, A. N. Coupled Southern Ocean cooling and Antarctic ice sheet expansion during the middle Miocene. *Nat. Geosci.* **13**, 634–639 (2020).

Methods

Carbon and Oxygen Isotope Stratigraphy

Carbon and oxygen isotopes ($\delta^{13}C$ and $\delta^{18}O$, respectively) were measured in benthic foraminifera *Cibicidoides mundulus sp.* (4–6 foraminifera per sample from the 212–300 µm size fraction) to better constrain the age-core depth relationship for Site 845 (Extended Data Figs. 1–2). Foraminifera were sonicated in deionized water to remove fine particles (e.g., coccolithophores) then analyzed using the dual-inlet Optima IR-MS at Rutgers University. Long-term 1-sigma precision for carbon and oxygen isotopes is 0.05‰ and 0.08‰, respectively.

I/Ca and Mg/Ca

I/Ca and Mg/Ca analyses were done on 11–20 monospecific specimens per sample from the 300–355 µm size fraction. I/Ca was measured in surface- and subsurface-dwelling foraminifera *Dentoglobigerina altispira* and *Dentoglobigerina venezuelana*, respectively, at Site 845. Foraminifera were gently crushed between glass plates to open the chambers. Chemical cleaning and analysis procedures follow those outlined by Zhou, Hess et al. [20]. The new method allows for the simultaneous measurements of I/Ca and other paleoceanographic proxies, including Mg/Ca. Zhou, Hess et al. [20] show that core-top I/Ca data generated with the new method not only successfully differentiate oxygen-depleted from oxygen-enriched waters but also produce comparable I/Ca data to those used in existing calibrations [13] (Extended Data Fig. 3). Chemical cleaning procedures are those typical for trace element analysis [45,46]. This involves rinses with ultrapure water to remove fine particulates, rinses with methanol to remove clays, reductive cleaning with ammonium hydroxide, citric acid/ammonia, and hydrazine to remove metal oxides, oxidative cleaning with ammonium hydroxide and hydrogen peroxide to remove organic matter, and a weak acid leach to remove authigenic carbonate. Values were corrected for the effect of reductive cleaning using the equation $I/Ca_{corrected}=I/Ca_{reductive} * 1.3$ of Zhou, Hess et al. [20].

Immediately before each run, the foraminifera were gradually dissolved in trace metal clean 0.065N HNO_3 (OPTIMA®) and 100 µl of this solution was diluted with 300 µl trace metal clean 0.5N HNO_3 to obtain a Ca concentration of 4±2 mmol/L. Samples were analyzed by Finnigan MAT ElementXR Sector Field Inductively Coupled Plasma Mass Spectrometer (ICP-MS) operated in low resolution ($m/\Delta m=300$) following the method outlined by Rosenthal et al. [47]. Al/Ca, Ti/Ca, Mn/Ca and Fe/Ca were measured to monitor for sedimentary contamination. Direct determination of elemental ratios from intensity ratios requires control of the sample Ca concentration; in each run six standard solutions with identical elemental ratios but variable Ca concentrations, which covered the range of Ca concentrations of the samples, were included. These solutions allowed us to quantify and correct for the effects of variable Ca concentrations in a sample solution on the accuracy of El/Ca measurement (so-called matrix effects) based on the sample's Ca concentration. Matrix corrections were typically <5% for Mg/Ca and I/Ca. Instrument precision was determined by repeated analysis of three consistency standards over the course of this study. To reduce the iodine memory effect and improve washout efficiency, anhydrous ammonia gas was injected into a high purity quartz cyclonic spray chamber (Elemental Scientific, ESI), raising the pH of the injected sample (>9.14). The ammonia gas also likely stabilized the iodate in the solution [20,48]. The long-term precision of the consistency standard is 0.36 µmol/mol for I/Ca and 0.13 mmol/mol for Mg/Ca. Black bar in Figure 2a is the average standard deviation of replicate sets from all runs. Replicates are sets of foraminifera from the same sediment sample. Student's t-tests for the populations of data from 15.1–16.0 Ma compared to those from 14.8–11.7 Ma show that the populations are statistically different, with p-values of 4.7×10^{-8} (n=12 variance=1.0 for MCO and n=16 variance=0.16 for MMCT) and

2.2×10^{-6} (n=7 variance=0.52 for MCO and n=24 variance=0.078 for MMCT) for *D. altispira* and *D. venezuelana*, respectively (one-sided two-sample t-tests assuming unequal variances).

Mg/Ca-derived temperatures were calculated using the equation

$$Mg/Ca_{foraminifera} = ((3.43/5.2) * 0.41) * 0.38\ e^{0.09 * T},$$

where T is calcification temperature. This methodology is consistent with recent Mg/Ca studies for the Miocene [41,43,49]. This equation is based on the multi-species equation of Anand et al. [50]:

$$Mg/Ca_{foraminifera}{}^{50} = 0.38\ e^{0.09\ T}.$$

Although no correction is applied for salinity and pH, it has been shown that temperature estimates derived from the multi-species equation of Anand et al. [50] are consistent with estimates using those corrections [51]. To adjust for different Mg/Ca in seawater (Mg/Ca_{sw}) during the Miocene, we included a species-specific power term (H) from Evans and Müller [52]:

$$(Mg/Ca_{sw\ Miocene} / Mg/Ca_{sw\ modern})^{H}$$

For consistency with recent studies using Mg/Ca during the Miocene [43,49], we used Miocene Mg/Ca_{sw} of 3.43 from fluid inclusions and the species-specific constant H for *Globigerinoides sacculifer* of 0.41. To generate the curves presented in figures, temperature data were smoothed using a Savitzky–Golay filter with a third order polynomial and 100 ky time steps.

Nitrogen Isotopes

For each sample, 100–400 individual foraminifera from the species *D. venezuelana* were picked from the 250–400 µm size fraction. 2.5–8.5 mg of foraminifer tests were gently crushed and prepared for analysis, following the adjusted persulfate oxidation denitrifier method for FB-$\delta^{15}N$ first described for planktic foraminifers by Ren et al. [53] and recently updated and described in more detail in Auderset et al. [18]. The protocol involves treatment with Na-polyphosphate solution (*p*H 8) to remove clays, reductive cleaning with dithionite-citric acid solution to remove metal oxides, and oxidative cleaning with potassium persulfate/sodium hydroxide solution to remove organic matter.

Next, 2–5 mg of cleaned shell fragments were weighed and dissolved in hydrochloric acid to release organic matter for analysis. Subsequently, nitrogen was oxidized to nitrate by adding basic potassium persulfate solution. Finally, 5 nmol nitrogen of nitrate in the sample solution was converted to nitrous oxide using the denitrifier method, and its $\delta^{15}N$ was measured by gas chromatography-isotope ratio mass spectrometry [54–57].

To quantify the precision and accuracy of the corrected isotope values, for the series of 26 samples, 3 different in-house (MPIC) foraminifer and coral laboratory standards were analyzed: the coral standard from the taxon *Porites* (PO-1) with $\delta^{15}N$ of 6.2 ± 0.3 ‰, a coral standard from the taxon *Lophelia* with $\delta^{15}N$ of 10.01 ± 0.4 ‰ [58], and a mixed foraminifer standard (63–315 µm size fraction) from the North Atlantic (MSM58-17-1) with $\delta^{15}N$ of 5.84 ‰ (uncertainty not yet assessed). After calibration with international nitrate isotopic references IAEA-NO3 and USGS-34 and correction for the oxidation blank, the analytical precision for PO-1 was ± 0.16 ‰, for *Lophelia* ± 0.14 ‰ and for the foraminifer standard ± 0.4 ‰ (for each standard 1SD, n=6). The oxidation blank per oxidized sample was typically between 0.2–0.5 nmol nitrogen. Because of the limited number of foraminifera, it was not possible to measure replicate samples. The black bar in Figure 2b is the standard deviation of the mixed foraminifer standard for each run, averaged across runs.

ODP Site 845

Ocean Drilling Program Site 845 is closest to the center of the EEP ODZ and the only site in the northern lobe of the ODZ, with sediments from the Middle Miocene. The age-depth model for Site 845 is based on paleomagnetic reversals, biostratigraphy (nannofossils, diatoms, foraminifera), and carbon isotopes (Extended Data Fig. 1). Carbon isotope stratigraphy is correlated to the Holbourn et al. [59] record from nearby Site U1338 (Extended Data Fig. 2). Mapped paleo-locations of Site 845 are from Shipboard Scientific Party [60]; paleo-locations for other sites are from ODSN Plate Tectonic Reconstruction Service (https://www.odsn.de/odsn/services/paleomap/paleomap.html) (Fig. 1 and Extended Data Fig. 5). Mi and CM events labeled in figures are from Miller et al. [61] and Holbourn et al. [39], respectively.

Preservation of foraminifera is generally moderate to poor throughout the study interval [62]. Qualitative microscope analysis shows fluctuations in planktic/benthic ratio likely resulting from dissolution of planktic foraminifera at intervals throughout the section. However, there is no overall change in preservation coincident with the geochemical changes noted at 15.1–14.7 Ma and no systematic change in preservation throughout the study interval (Extended Data Fig. 4). In this section, we compare data from two species with different preservation potential at Site 845 and we compare our data from Site 845 with data from nearby Sites U1337/U1338, where foraminifera are well preserved.

I/Ca of foraminifera is robust to diagenetic alteration [63]. It has been suggested that, if anything, I/Ca ratios might be lowered if significant secondary calcite is precipitated in oxygen-depleted pore waters [63,64]. *D. altispira* have a higher surface-area/shell-volume ratio (lower weight for tests from the same size fraction) than do *D. venezuelana*. Their values are therefore more susceptible to diagenetic alteration due to encrustation [65,66]. That $I/Ca_{altispira}$ and $I/Ca_{venezuelana}$ show the same pattern and that *D. altispira*, which lived in more oxygenated waters further above the ODZ, has consistently higher I/Ca values than *D. venezuelana* for samples with data from both species further supports our interpretation of I/Ca values as primary.

The intracrystalline organic matter of foraminifera is well preserved. It has been shown that the nitrogen content and nitrogen isotopic composition are not affected by oxidative degradation, fossil dissolution, or thermal alteration, making FB-$\delta^{15}N$ a proxy insensitive to diagenesis [67]. The relatively small variation in nitrogen content over millions of years observed in previous studies [17,18] and the lack of correlation between nitrogen content and FB-$\delta^{15}N$ in Site 845 samples further strengthens the assumption that selective degradation of ^{14}N can be excluded as a potential secondary influence on the nitrogen isotopic composition.

Extended Data Figure 1. Age-depth correlation for Site 845 Hole A. Size and shape of red boxes for carbon isotope correlation points indicate uncertainty. Oxygen and carbon isotopes are from *Cibicidoides mundulus* sp. measured at this site.

Brief Title: Age-depth correlation for Site 845.

Extended Data Figure 2. Correlation of carbon isotope curves between (**a**) Site U1338 and (**b**) Site 845. Site U1338 data from Holbourn et al. [59]. Correlation points labeled 1–4; horizontal bars indicate uncertainty, which is also shown as box sizes in Extended Data Figure 1.

Brief Title: Correlation of carbon isotope curves between Site U1338 and Site 845.

Extended Data Figure 3. Calibration of I/Ca and minimum water column oxygen concentration, i.e. oxygen concentration at depth of maximum depletion ($[O_2]_{min}$). Boxes indicate the ±1SD range of I/Ca values for the Miocene Climatic Optimum (MCO) and Mid-Miocene Climatic Transition (MMCT) at Site 845 (Fig. 2a) and their interpreted $[O_2]_{min}$ from this plot, in the case of the MCO, and from deductions in Hardisty et al. [14] and nitrogen isotopes, in the case of the MMCT. Shading for $[O_2]_{min}$ matches that in Figure 1. Modified from Zhou, Hess et al. [20].

Brief Title: Calibration of I/Ca and minimum water column oxygen concentration.

Extended Data Figure 4. Scanning electron microscope images of planktic foraminifera from Site 845 showing outside, inside, and cross-sectional views. Note similar quality of preservation (moderate to poor) throughout the study interval. Scale bars are 50 µm.

Brief Title: Scanning electron microscope images of planktic foraminifera from Site 845.

Extended Data Figure 5. Map showing location of sites used in regional sea-surface temperature compilation. Basemap is modern sea surface temperature from NOAA[68]. Site 845 paleo-locations from Pisias et al. [69], other paleo-locations from ODSN Plate Tectonic Reconstruction Service.

Brief Title: Map showing location of sites used in regional sea-surface temperature compilation.

Extended Data Figure 6. Data used to construct Figure 3a. Sea-surface temperature by region relative to their averages from 16–15 Ma, smoothed using 100 ky bins. Inverted triangles indicate age control points, colored by site. To compare Mg/Ca data from different foraminifer species, some without modern equivalents and therefore lacking species-specific temperature calibrations, we calculate temperatures using the same multi-species equation at all sites (see Methodology). Temperatures derived from TEX_{86} data are only available for one site and so are presented using the original authors' calibrations [44]. In constructing Figure 3A, for site with TEX_{86} data, those temperatures are used rather than Mg/Ca-derived temperatures and in this figure Mg/Ca-derived temperatures are dashed. (**a**) West Pacific warm pool. (**b**) Eastern tropical Pacific. (**c**) Southern Ocean.

Brief Title: Sea-surface temperature by region.

Source Data attached as separate Excel files

[Additional references from Extended Data Figures and their associated Source Data: [42,69–74]]

Methods References

45. Boyle, E. A. & Keigwin, L. D. Comparison of Atlantic and Pacific paleochemical records for the last 215,000 years: changes in deep ocean circulation and chemical inventories. *Earth and Planetary Science Letters* **76**, 135–150 (1985).

46. Rosenthal, Y., Boyle, E. A. & Labeyrie, L. Last Glacial Maximum paleochemistry and deepwater circulation in the Southern Ocean: Evidence from foraminiferal cadmium. *Paleoceanography* **12**, 787–796 (1997).

47. Rosenthal, Y., Field, M. P. & Sherrell, R. M. Precise determination of element/calcium ratios in calcareous samples using sector field inductively coupled plasma mass spectrometry. *Analytical chemistry* **71**, 3248–3253 (1999).

48. Winkelbauer, H. *et al.* Foraminifera iodine to calcium ratios: Approach and cleaning. *Geochem Geophys Geosyst* **22**, (2021).

49. Fox, L. R., Wade, B. S., Holbourn, A., Leng, M. J. & Bhatia, R. Temperature gradients across the Pacific Ocean during the Middle Miocene. *Paleoceanogr Paleoclimatol* **36**, (2021).

50. Anand, P., Elderfield, H. & Conte, M. H. Calibration of Mg/Ca thermometry in planktonic foraminifera from a sediment trap time series: Calibration of Mg/Ca thermometry in planktonic foraminifera. *Paleoceanography* **18**, 28-1 28-15 (2003).

51. Rosenthal, Y., Bova, S. & Zhou, X. A user guide for choosing planktic foraminiferal Mg/Ca-temperature calibrations. *Paleoceanography and Paleoclimatology* **37**, 17 (2022).

52. Evans, D. & Müller, W. Deep time foraminifera Mg/Ca paleothermometry: Nonlinear correction for secular change in seawater Mg/Ca: Deep-time Mg/Ca thermometry. *Paleoceanography* **27**, (2012).

53. Ren, H. *et al.* Foraminiferal isotope evidence of reduced nitrogen fixation in the ice age Atlantic Ocean. *Science* **323**, 244–248 (2009).

54. Sigman, D. M. *et al.* A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater. *Anal. Chem.* **73**, 4145–4153 (2001).

55. Casciotti, K. L., Sigman, D. M., Hastings, M. G. & Bo, J. K. Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method. **74**, 4905–4912 (2002).

56. McIlvin, M. R. & Casciotti, K. L. Technical updates to the bacterial method for nitrate isotopic analyses. *Anal. Chem.* **83**, 1850–1856 (2011).

57. Weigand, M. A., Foriel, J., Barnett, B., Oleynik, S. & Sigman, D. M. Updates to instrumentation and protocols for isotopic analysis of nitrate by the denitrifier method. *Rapid Communications in Mass Spectrometry* **30**, 1365–1383 (2016).

58. Leichliter, J. N. *et al.* Nitrogen isotopes in tooth enamel record diet and trophic level enrichment: Results from a controlled feeding experiment. *Chemical Geology* **563**, 120047 (2021).

59. Holbourn, A. *et al.* Middle Miocene climate cooling linked to intensification of eastern equatorial Pacific upwelling. *Geology* **42**, 19–22 (2014).

60. Shipboard Scientific Party. Site 845. in *Proceedings of the Ocean Drilling Program, Initial Reports* vol. 138 189–263 (1992).

61. Miller, K. G., Wright, J. D. & Fairbanks, R. G. Unlocking the ice house: Oligocene-Miocene oxygen isotopes, eustasy, and margin erosion. *J. Geophys. Res.* **96**, 6829–6848 (1991).

62. Vincent, E. & Toumarkine, M. Data report: Miocene planktonic foraminifers from the eastern equatorial Pacific. in *Proceedings of the Ocean Drilling Program, 138 Scientific Results* (eds. Pisias, N. G., Mayer, L. A., Janecek, T. R., Palmer-Julson, A. & van Andel, T. H.) vol. 138 895–907 (Ocean Drilling Program, 1995).

63. Zhou, X., Thomas, E., Rickaby, R. E. M., Winguth, A. M. E. & Lu, Z. I/Ca evidence for upper ocean deoxygenation during the PETM. *Paleoceanography* **29**, 964–975 (2014).

64. Hardisty, D. S. *et al.* Perspectives on Proterozoic surface ocean redox from iodine contents in ancient and recent carbonate. *Earth and Planetary Science Letters* **463**, 159–170 (2017).

65. van Raden, U. J., Groeneveld, J., Raitzsch, M. & Kucera, M. Mg/Ca in the planktonic foraminifera Globorotalia inflata and Globigerinoides bulloides from Western Mediterranean plankton tow and core top samples. *Marine Micropaleontology* **78**, 101–112 (2011).

66. Stainbank, S. *et al.* Assessing the impact of diagenesis on foraminiferal geochemistry from a low latitude, shallow-water drift deposit. *Earth and Planetary Science Letters* **545**, 116390 (2020).

67. Martinez-Garcia, A. *et al.* Laboratory assessment of the impact of chemical oxidation, mineral dissolution, and heating on the nitrogen isotopic composition of fossil-bound organic matter. *Geochemistry, Geophysics, Geosystems* (2022) doi:10.1002/essoar.10510728.1.

68. National Oceanic and Atmospheric Administration (NOAA), National Environmental Satellite Data and Information Service. Geo-polar blended 5 km SST analysis for the full globe. (2021).
69. Pisias, N. G., Mayer, L. A. & Mix, A. C. Paleoceanography of the eastern equatorial Pacific during the Neogene: Synthesis of Leg 138 drilling results. in *Proceedings of the Ocean Drilling Program, 138 Scientific Results* (eds. Pisias, N. G., Mayer, L. A., Janecek, T. R., Palmer-Julson, A. & van Andel, T. H.) vol. 138 5–21 (Ocean Drilling Program, 1995).
70. Shevenell, A. E., Kennett, J. P. & Lea, D. W. Middle Miocene Southern Ocean cooling and Antarctic cryosphere expansion. *Science* **305**, 1766–1770 (2004).
71. *Geologic Time Scale 2020*. vol. 2 (Elsevier BV, 2020).
72. Barron, J. A. Planktonic marine diatom record of the past 18 My: Appearances and extinctions in the Pacific and Southern Oceans. *Diatom Research* **18**, 203–224 (2003).
73. Shevenell, A. E. & Kennett, J. P. Paleoceanographic change during the Middle Miocene climate revolution: An Antarctic stable isotope perspective. in *Geophysical Monograph Series* (eds. Exon, N. F., Kennett, J. P. & Malone, M. J.) vol. 151 235–251 (American Geophysical Union, 2004).
74. Shipboard Scientific Party. Site 1171. in *Proceedings of the Ocean Drilling Program, Initial Reports* (ed. Scroggs, J. M.) vol. 189 176 (2001).

End Notes

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Correspondence and requests for materials should be addressed to AVH or YR.

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