Oxygen minimum zone expansion in the eastern tropical North Pacific during deglaciation

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[1] During deglaciation at ∼17 ka the intensity and footprint of the oxygen minimum zone (OMZ) increased in the Eastern Tropical North Pacific (ETNP) before a subsequent expansion on the California Margin. Evidence for the earlier increase is found in trace metal concentrations, lamination preservation and $\delta^{15}N$ values from cores located between 540–750 m water depth in the Gulf of Tehuantepec, Southern Mexico. These results differ from similar proxies found even 5°N of the site, where there is evidence for OMZ changes related to rapid climate change in the Northern Hemisphere. Instead, OMZ expansion in the Gulf was contemporaneous with changes in sea ice extent and zonal wind shifts around Antarctica, pointing to Subantarctic Mode Water and Antarctic Intermediate Water as likely sources of oxygen-depleted water. These observations reinforce the importance of the Southern Ocean as a primary modulator of northern hemisphere ocean climate, as far as 15°N in the ETNP.
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1. Introduction

[2] The close relationship between climate change and the North Pacific Oxygen Minimum Zone (OMZ) has been related to both intermediate water ventilation and productivity [*Behl and Kennett*, 1996; *Ortiz et al.*, 2004]. Intermediate water formation in the Western North Pacific (i.e. Sea of Okhotsk) increased during cool intervals of the Last Glacial [*Keigwin*, 1998], ventilating intermediate water depths in the North Pacific. At the same time, it has been hypothesized that the California Undercurrent diminished, reducing the flow of low O_2 water northwards along the margin from the Eastern Tropical North Pacific (ETNP [*Hendy and Kennett*, 2003; *Kienast et al.*, 2002].

[3] Productivity shifts add a further layer of complexity to oxygenation history, given the relationship between nutrient delivery to the euphotic zone, the settling flux of carbon and O_2 consumption in the underlying waters. Export production was reduced during cool intervals on the western margin of North America, and enhanced during periods of warmth [*Hendy et al.*, 2004; *Ortiz et al.*, 2004]. The role of the ETNP in modulating related variations in ventilation and nutrient fluxes can be resolved by comparing the histories of intermediate water O_2 concentrations in the ETNP (south of 20°N) with that on the California Margin. Because O_2 cannot be restored to intermediate water without exchange with the atmosphere, the coeval existence of low O_2 levels in the ETNP with high O_2 concentrations on the California Margin would demonstrate that the two regions were not bathed by the same intermediate water mass.

[4] The Gulf of Tehuantepec is marked by a well-defined OMZ between ∼300 and ∼800 m water depth that is generated by oxidative respiration of organic matter and poor ventilation of subsurface waters. O_2 concentrations lie between 0.4 and 0.1 ml/l in these waters. $\delta^{15}NO_3$ increases from ∼8 to >16‰ in the OMZ, as NO_3 concentrations decrease through the process of denitrification [*Thunell and Kepple*, 2004]. Intermediate waters in the ETNP do not have a simple northern source, as North Pacific Intermediate Water (NPIW) that circulates clockwise in the North Pacific gyre is deflected westward at 20°N in the Eastern Pacific. South of ∼20°N in the ETNP, shallow continental slope sediments are overlain by an intermediate-water mass that is transported west to east across the Pacific via the Equatorial Undercurrent [*Reid*, 1997; *Reid and Mantyla*, 1978; *Tsuchiya and Talley*, 1996; *Wijffels et al.*, 1998]. Consequently the Gulf of Tehuantepec, located between 14 and 16°N off the coast of Southern Mexico, is bathed today by intermediate waters that are different to those on the California, Baja California and Mazatlan margins.

[5] Was this situation different in the past? Here we present the first record of ETNP OMZ strength through the last deglaciation south of the modern influence of NPIW. Trace metal concentration profiles and $\delta^{15}N$ measurements from cores collected on the continental slope of the Gulf of Tehuantepec demonstrate significant differences between the ETNP and more northern sites. These contrasts in turn shed new light on ocean climate in the Pacific during the deglacial transition.

2. A Deglacial Low Oxygen Event in the Gulf of Tehuantepec

[6] Sediment redox chemistry is a common method of reconstructing past bottom water O_2 conditions. Here we present an OMZ reconstruction based on two redox sensitive trace metals, Re, and Mo, and a third, Cd, that is reactive in the presence of dissolved sulfide. Rhenium enrichments in sediments occur when $Re(VII)O_4^-$, a conservative anion in the ocean, is chemically reduced under suboxic conditions (i.e. prior to sulfate reduction), and precipitated, perhaps as $Re(IV)O_2$ [*Crusius et al.*, 1996]. The flux into the sediments is supported by downward

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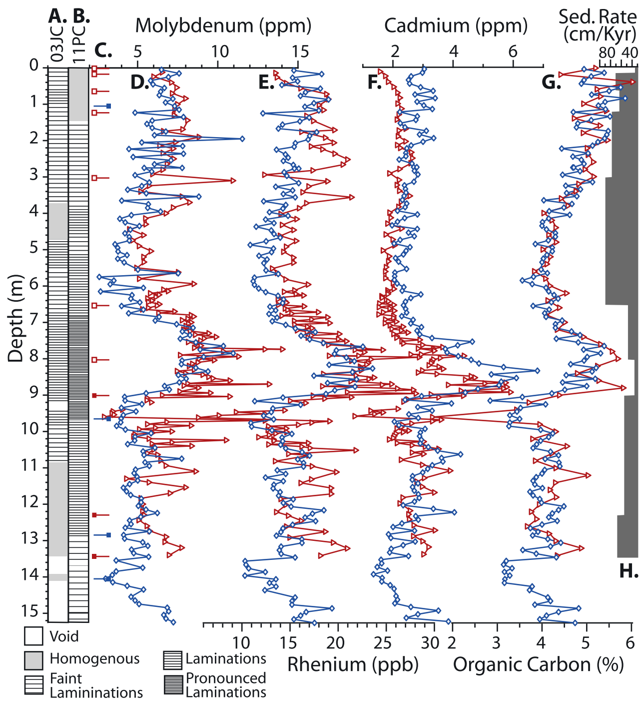

Figure 1. Core stratigraphy and bulk sediment geochemistry by depth from the Gulf of Tehuantepec. (a) Lamination stratigraphy from ME0005A 3JC (740 m water depth). (b) lamination stratigraphy from ME0005A 11PC (540m water depth). (c) ^{14}C dates from 3 JC (red) and 11PC (blue) where filled boxes are planktonic and open boxes are benthic. Redox chemistry in the Gulf is demonstrated by (d) Mo concentrations (11PC; blue diamonds and 3JC red triangles), (e) Re concentrations (11PC; blue diamonds and 3JC red triangles), (f) Cd concentrations (11PC; blue diamonds and 3JC red triangles), (g) % Corg (11PC; blue diamonds and 3JC red triangles [*Thunell and Kepple*, 2004]), and (h) sedimentation rate for 3 JC.

diffusion from the overlying bottom waters [*Calvert and Pedersen*, 1993]. Porewater sulfide concentrations regulate Mo precipitation in anoxic marine sediments [*Zheng et al.*, 2000], with enrichment (>10 mg/g) being associated with Fe-sulfides where a threshold H_2S concentration of ~11 μM [*Erickson and Helz*, 2000] is exceeded. The oceanic distribution of cadmium is similar to phosphate, implying an association with the soft parts of marine flora [*Boyle et al.*, 1976]. Sedimentary Cd enrichments result from the release of Cd during degradation of biogenic material, diffusion into sediments where sulfate reduction occurs at relatively shallow sub-surface depths and precipitation as a sulfide [*Rosenthal et al.*, 1995; *van Geen et al.*, 1995]. Thus, sedimentary Cd enrichments can be attributed to both shallow H_2S presence and export productivity.

[7] Cores ME0005A 11PC (95.29°W,15.71°N, 574 m water depth) and 3JC (95.28°W,15.65°N, 740 m water depth) show surprisingly similar sedimentation rates, δ^{15}N values, trace metal (Mo, Re, and Cd), and Corg (Figure 1) concentrations over the last 20 kyr suggesting relatively homogeneous water column chemistry and sedimentation during that time. Sedimentation rates in the Gulf of Tehuantepec cores are high (see supplemental material[1] for ^{14}C based age model description). At 3JC, the Holocene sedimentation rate was ~60 cm kyr^{-1}, and ~55 cm kyr^{-1} in the last glacial, while the average sedimentation rate at 11PC was ~55 cm kyr^{-1}. Due to the associated high resolution, geochemical responses of the OMZ to rapid deglacial climate events are readily recorded in the sedimentary record.

[8] Last Glacial Maximum trace metal values are similar to Holocene levels. As trace metal concentrations are controlled by Corg flux, bottom water O_2 concentrations and rates of diffusion through sediment pore waters (influenced by sedimentation rate and porosity), the metals data imply is that these processes did not change significantly during the last glacial. Indeed Corg concentrations and sedimentation rate profiles at both sites support this argument and therefore it is reasonably assumed that there was little enhancement of ventilation in the Gulf during the last glacial. However, a significant increase in trace metal concentration above the lattice-bound background occurs during the deglacial interval (7.5 to 9 m sub-bottom depth) starting at ~16.5 ka. Cd, Re and Mo behave similarly at the initiation and across this event (Figure 1). Moreover, the trace metal enrichments occur coincidently with distinct sediment laminations, a strong indicator of very low O_2 in bottom waters (Figure 1). Lamination strength was based on visual observations during sampling as well as shipboard core descriptions. The laminations are most commonly produced by regular shifts in sediment composition, associated with annual changes in productivity or regional precipitation, but are only preserved in the absence of benthic macrofauna due to low bottom water O_2 concentrations.

[9] δ^{15}N values rise in both cores at ~17.5 ka, a thousand years prior to the trace metal increases (Figure 2e [*Thunell and Kepple*, 2004]). Heaviest δ^{15}N values occur in Core 11PC prior to the Bølling, along with high concentrations of trace metals and pronounced laminations. The high δ^{15}N values reflect enhanced denitrification in waters at 200 to 400 m water depth, subsequent uptake by phytoplankton of isotopically heavy residual nitrate that wells up to the mixed layer, and the transfer of this denitrification signal to the underlying sediments [*Altabet et al.*, 1999]. Thus, the coincidence of the δ^{15}N maximum with the laminations and high trace metal contents collectively provides very strong evidence of O_2 depletion in subsurface waters that had a profound effect on the sediments as well as the biogeochemistry of the water column.

[10] It may be argued that strengthening of the OMZ in the Gulf of Tehuantepec prior to the Bølling is an artifact of the age model used. ^{14}C measurements at both sites—a mixed planktonic date at 17.3 ka (11PC) and two *N. dutertrei* derived dates (15.7 and 21.6 ka; 3JC; supplementary material) yield the same age for the shift in OMZ intensity. To resolve this issue, further ^{14}C dating is required. Corg concentrations increase modestly at 16.5 ka in both Tehuantepec cores alongside low-O_2 concentration indicators implying that increased productivity may have played a role in the drawdown of sedimentary O_2 (Figure 1). However, the sedimentation rate

[1]Auxiliary material datasets are available at ftp://ftp.agu.org/apend/gl/2006gl025975. Other auxiliary material files are in the HTML.

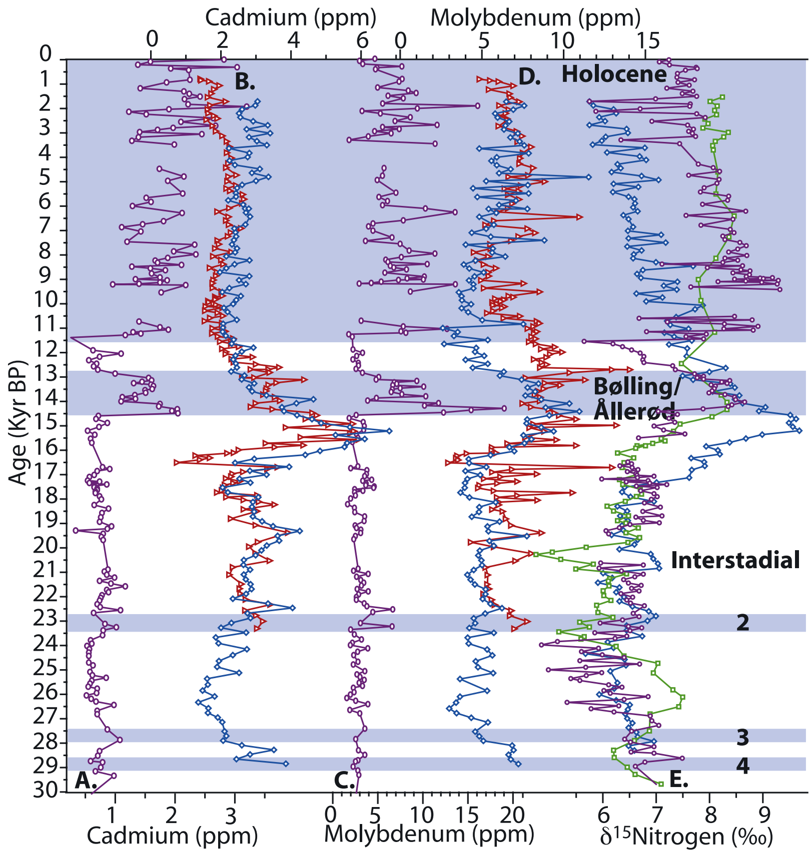

Figure 2. Comparison of the OMZ history along the North American Margin. (a) Cd concentrations from Santa Barbara Basin (ODP Hole 893A; purple circles [*Ivanochko and Pedersen*, 2004]) and (b) the Gulf of Tehuantepec (ME0005A 11PC; blue diamonds and 3JC red triangles). (c) Mo concentrations from ODP Hole 893A (purple circles[*Ivanochko and Pedersen*, 2004]) and (d) 11PC (blue diamonds) and 3JC (red triangles). (e) $\delta^{15}N$ records from 11PC (blue diamonds), Mazatlan Margin (green squares [*Ganeshram and Pedersen*, 1998]), and Santa Barbara Basin (purple circles [*Emmer and Thunell*, 2000]). Climatic events are identified, while blue shading represents warm climatic intervals. At 10 to 13 Ka trace metal differences between the cores most likely result from the paucity of dates in core 11PC at that time.

is significantly lower in this interval and the opal concentration remains <10 wt. % and varies independently of the metal contents (data not shown). These observations imply a net reduction in Corg accumulation on the sea floor at the time, and in turn suggest that local or regional export productivity played a minor role in promoting the trace-metal enrichments.

3. Oxygen Minimum Zones of the North Pacific

[11] The Tehuantepec records suggest that unlike more northerly OMZ records from the North American Margin, the ETNP was not well ventilated during the last glacial. Based on the age model presented here, the data imply the ETNP OMZ became more intense at 17 ka while at the same time, a high O_2 intermediate water mass was present in Santa Barbara Basin (sill depth 540 m; Figure 2 [*Ivanochko and Pedersen*, 2004]) and Baja California [*van Geen et al.*, 2003]. Thus it would appear that the ETNP was bathed by an intermediate water masses with what is inferred to be a significantly different dissolved O_2 concentration during the Last Glacial Maximum. At ~15 ka (the Bølling) O_2 concentrations abruptly decreased and the OMZ expanded in intermediate waters off the California Margin [*Ivanochko and Pedersen*, 2004; *Hendy and Pedersen*, 2005]. At sites on the central California and Oregon Coast, the expansion is indicated by the only preservation of laminations within the latest Quaternary [*van Geen et al.*, 2003]. However, the expansion of the OMZ did not affect the Baja California Margin, where the O_2 concentration of intermediate waters remained relatively high, according to downcore Cd and Mo distributions [*Dean et al.*, 2006].

[12] Similarly distinct differences occur between $\delta^{15}N$ records north of 20°N and the Gulf of Tehuantepec. The northern sites do not show an increase in $\delta^{15}N$ that signals the onset of denitrification until ~16.5 ka, and maximum values are not reached until after the decline in the Gulf of Tehuantepec $\delta^{15}N$ profile at the glacial termination, or ~14.5 Ka (Figure 2e [*Emmer and Thunell*, 2000; *Ganeshram and Pedersen*, 1998; *Hendy et al.*, 2004; *Thunell and Kepple*, 2004]). These data reinforce the inference that the ETNP OMZ has a distinctly different history to the more northerly OMZ. Furthermore, there cannot have been any significant exchange of intermediate water between the ETNP and the California Margin prior to

the Holocene. Although redox chemistry alone cannot exclude local influences, intermediate water history has long been conjectured as the origin of O_2 concentration changes. Therefore, to explore the origin of these differences we must examine the source of intermediate waters that bathe the ETNP.

4. North Pacific Intermediate Water Sources

[13] Intermediate water O_2 concentration is influenced by a number of variables including; temperature/productivity shifts at upstream sources [*Meissner et al.*, 2005], the duration of isolation from the atmosphere, the pattern of subsurface circulation, and the intensity of the organic matter rain during water mass transit. Geochemical expressions of O_2 variability in the Pacific have supported previous discussions of source characteristics, circulation and productivity history, for example, waters emanating from the Sea of Okhotsk [*Crusius et al.*, 2004]. High $\delta^{15}N$ values at 17.5 ka in the Gulf of Tehuantepec are similar to $\delta^{15}N$ records between 11 and 14°S for the same interval on the Peru Margin [*Higginson and Altabet*, 2004] that have been interpreted to represent a substantial reduction in remotely forced Subantarctic Mode Water (SAMW) ventilation (thus, O_2 flux) during the deglaciation.

[14] In contrast to California Margin intermediate waters transported south under the North Pacific gyre, the Gulf of Tehuantepec bottom waters are transported east across the Pacific via the Equatorial Undercurrent. This subsurface water mass includes contributions from SAMW and Antarctic Intermediate Water (AAIW), ~15 Sverdrups of which leak through the equatorial zone via western boundary undercurrents near Papua New Guinea, before spreading back eastward in the Northern Hemisphere tropics [*Reid*, 1997; *Reid and Mantyla*, 1978; *Tsuchiya and Talley*, 1996; *Wijffels et al.*, 1998].

[15] What impact would changes in gas exchange or productivity in the source regions of SAMW and AAIW have on the Gulf of Tehuantepec? We hypothesize that the Tehuantepec records reflect a reorganization of intermediate and mode water circulation during deglaciation that directly links the ETNP to Antarctic climatic change. The cool, low salinity AAIW forms through mixing with Antarctic Surface Water [*Santoso and England*, 2004] and subduction at the Antarctic Polar Frontal Zone [*Sverdrup et al.*, 1942]. As Antarctica began to warm at 19 ka, surface water temperatures increased and westerly winds weakened, and sea-ice production retreated poleward reaching a minimum extent at 17 ka [*Shemesh et al.*, 2002]. Thus we speculate that in the region of AAIW formation, key factors that affect O_2 transfer to surface waters and the rate of intermediate water production [*Meissner et al.*, 2005] sea ice and wind strength [*Santoso and England*, 2004] changed, possibly reducing the O_2 flux at intermediate water depths in the general south to north direction.

[16] While this can explain the $\delta^{15}N$ and trace metal distributions in Gulf of Tehuantepec sediments during the deglaciation, it does not explain the distributions of such proxies off California and Baja. It follows that those more northerly regions must have fallen more directly under the influence of northern-source intermediate waters at that time. Thus, a physical boundary must have existed in the ETNP at ~20°N during the deglaciation that kept northern and southern-source water masses separate.

5. Conclusions

[17] Strengthening of the OMZ in the ETNP at ~17 ka occurred prior to California Margin OMZ expansion as demonstrated by trace metal concentrations, lamination preservation and $\delta^{15}N$ values from cores located between 540 and 750 meters water depth in the Gulf of Tehuantepec, Southern Mexico. No evidence for OMZ waxing and waning in concert with Northern Hemisphere rapid climate change is found in these high resolution cores, a significantly different result from northerly sites. Instead OMZ expansion in the Gulf was temporally similar to sites on the Peru Margin that have been linked to changes in sea ice extent and zonal wind shifts around Antarctica. This suggests SAMW and AAIW may have been sources of poorly ventilated water during deglaciation as far north as 15°N.

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