



Centennial to millennial-scale changes in oxygenation and productivity in the Eastern Tropical South Pacific during the last 25,000 years



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ABSTRACT

Oxygen minimum zones (OMZ) have expanded in all tropical oceans during the last 50 years resulting in habitat contraction and considerable changes in marine biogeochemistry. However, for a better understanding of the OMZ dynamics under the current climate change, two questions are relevant: 1) how do the magnitude and temporal changes in oceanic dissolved oxygen of the last few decades compare to the natural variability on longer timescales, and 2) what were the local and remote factors driving OMZ changes in the past. In the present study we use a stacked record covering the last 25 kyr from the Eastern Tropical South Pacific (ETSP) OMZ to reconstruct changes in oxygenation and productivity. We use a suite of proxies including the presence of laminations, redox sensitive metals (U, Mo, Re, Ni and Cu), total organic carbon and $\delta^{15}\text{N}$ measurements. Water column denitrification and sediment redox conditions show pronounced centennial to millennial-scale variability during the last 25 kyr, with oxygenation levels as low as at present. Global cold periods at different timescales such as the Last Glacial Maximum (23–19 kyr BP) and the Little Ice Age (1500–1850 AD) were associated with a weak OMZ and low export production, while warm intervals such as the deglaciation, part of the Medieval Climate Anomaly and the last 100 years are associated with a stronger OMZ and high export production. Water column denitrification and sediment redox conditions were strongly coupled during the last 25 kyr BP apart from one remarkable exception: during the Antarctic Cold Reversal, sediments were less reducing but the water column denitrification was high resulting in a strong but shallow OMZ. This may have been produced by an enhanced Antarctic Intermediate Water flow. Contrary to our expectations and modeling predictions for the next few decades, we observe a weak ETSP-OMZ during the warm mid-Holocene, which may have been the result of a stronger Walker Circulation that brought oxygen-rich waters to intermediate depths off Peru via Equatorial undercurrents. In combination with other paleoceanographic reconstructions, our results show that oxygenation variability in the ETSP-OMZ was influenced by ocean circulation changes in the Tropical Pacific, high latitude oceanographic and climatic changes, and local productivity.

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1. Introduction

Oxygen concentration in the ocean affects marine biogeochemical processes and the behavior and distribution of marine biota (Stramma et al., 2008, 2010b; Gilly et al., 2013). In the Eastern

Tropical Pacific, a strong and shallow oxygen minimum zone (OMZ) is maintained at intermediate depths as a result of weak ocean ventilation and the decay of organic matter as a result of intense biological production (Pennington et al., 2006; Karstensen et al., 2008). The low oxygen concentration modifies microbial processes and the cycles of the macronutrients nitrogen and phosphorus. Although OMZ waters constitute only ~0.1% of the ocean volume, up to 40% of the total loss of the ocean's bioavailable nitrogen, a macronutrient limiting primary productivity, occurs in these zones (Kuypers et al., 2005; Lam et al., 2009). During the last 50 years, OMZs have expanded both horizontally and vertically in all tropical oceans, likely due to anthropogenic impacts (Stramma et al., 2008, 2010). Global warming is expected to further reduce the oxygen supply to the oceans, producing a continuous expansion of the OMZs and resulting in habitat contraction and considerable changes in marine biogeochemistry (Gilly et al., 2013). However, it is still an open question as to how the magnitude and temporal changes in oceanic dissolved oxygen of the last few decades compare to the natural variability on longer timescales. Moreover, it is not clear how the OMZ in the Eastern Tropical South Pacific (ETSP) responded to prior episodes of climate changes, and the local and remote driving factors remain unknown. In the present work, we reconstruct changes in oceanic oxygenation and export production for the last 25,000 years before present (kyr BP), using sediment cores retrieved from the ETSP-OMZ. We then compare our records with other paleoceanographic reconstructions to identify local and remote driving factors for changes in OMZ intensity.

Reconstructions of past oxygenation in the sediments are based on the use of proxies that record the redox state at the sediment–water interface, such as laminations, redox-sensitive trace metals, and foraminiferal species assemblages (Jaccard et al., 2014). These proxies are likely to detect either changes in the magnitude and distribution of biological export production and/or modifications in ventilation through bottom currents. The presence of laminae provides strong evidence for low oxygen concentrations ($<7 \mu\text{mol kg}^{-1}$, Schönfeld et al., 2015), as low oxygen contents and high sedimentation rates impede sediment reworking by benthic organisms. By contrast, the absence of laminae is not necessarily a proof of oxygenation, but is more likely related to a complex interplay of factors including turbidite flows, slumps, winnowing by strong currents, bioturbation, and a lack of regular variation in terrigenous and biological material (Salvatelli et al., 2014a). Benthic redox conditions are generally recognized to have a dominant influence on the accumulation of authigenic trace metals (e.g., molybdenum, rhenium, and uranium) in marine sediments (Algeo and Tribouillard, 2009). The solubility of redox-sensitive metals decreases under reducing conditions. Reducing conditions commonly occur within the upper centimeters of the sediments, thus the presence or absence of these elements in sedimentary deposits is used to infer past reducing conditions (McManus et al., 2006). Benthic foraminifer assemblages are indicative of past changes in oxygen under certain conditions, but sediments from the Peruvian margin show extensive periods of benthic and planktonic foraminifera dissolution, limiting the use of this proxy to reconstruct high resolution changes in past oxygen concentration (Rein et al., 2005). Consequently, the most reliable approach to infer past oxygenation changes is the combined use of several proxies (Hendy and Pedersen, 2006; Nameroff et al., 2004; Algeo and Tribouillard, 2009; Helz and Adelson, 2013; Jaccard et al., 2014; Scholz et al., 2014; Little et al., 2015).

Water column denitrification has also been indirectly inferred through the use of $\delta^{15}\text{N}$ in sedimentary organic matter (Higginson and Altabet, 2004; Chazen et al., 2009; Scholz et al., 2014). In oxygen-deficient waters ($<2\text{--}10 \mu\text{mol O}_2 \text{ L}^{-1}$), N-loss processes,

such as denitrification ($\text{NO}_3^- \rightarrow \text{N}_2$ via NO_2^-) and anammox (anaerobic ammonia oxidation; $\text{NO}_2^- \rightarrow \text{NH}_4^+ \rightarrow \text{N}_2$; Lam et al., 2009) take place. Under these conditions, NO_3^- is used as an oxidant during organic matter degradation resulting in isotopically light N_2 and N_2O and isotopically heavier residual NO_3^- . This heavy NO_3^- is upwelled to the surface, used by phytoplankton, and eventually deposited into the sediments. Thus, in sites where high sedimentation rates and low oxygen concentrations prevail, a bulk sediment $\delta^{15}\text{N}$ analysis can be used to reconstruct past changes in N-loss (Higginson and Altabet, 2004; Mollier-Vogel et al., 2012). Although the relative importance of denitrification and anammox is strongly debated for the Peruvian OMZ, both of them are denitrification reactions driven by an intense OMZ (Lam et al., 2009; Zehr, 2009). However, other processes that are not influenced by oxygen concentrations contribute to the $\delta^{15}\text{N}$ signal, most importantly the partial NO_3^- utilization by phytoplankton (Mollier-Vogel et al., 2012; Ehlert et al., 2015). During photosynthesis, phytoplankton preferentially take up NO_3^- containing the lighter isotope; therefore, the produced organic matter is depleted in ^{15}N relative to the upwelled NO_3^- . A low relative NO_3^- utilization results in lower particulate organic matter $\delta^{15}\text{N}$ values compared to upwelled NO_3^- $\delta^{15}\text{N}$ values, independent from oxygen conditions in the water column (Waser et al., 1998). Currently, off central and northern Peru, water column measurements show that NO_3^- and PO_4^{3-} concentrations do not limit phytoplankton growth, thus partial NO_3^- utilization occurs (Moore et al., 2013). It is therefore likely that $\delta^{15}\text{N}$ in bulk sediments in this region reflects both water-column N-loss increasing the $\delta^{15}\text{N}$ of upwelled NO_3^- (indicating low-oxygen conditions), and, subsequent partial utilization causing $\delta^{15}\text{N}$ in the organic matter to be lower than upwelled NO_3^- $\delta^{15}\text{N}$ (Mollier-Vogel et al., 2012; Ehlert et al., 2015). Although we are aware of the different processes controlling $\delta^{15}\text{N}$ values in sediments, we will, for simplicity, use the term “denitrification” as a proxy for water column oxygenation.

Paleoceanographic reconstructions indicate that the ETSP-OMZ water column denitrification and sediment redox conditions vary strongly at multi-decadal and centennial (Gutierrez et al., 2009; Salvatelli et al., 2014b), millennial (Higginson and Altabet, 2004; Chazen et al., 2009), and glacial-interglacial timescales (Scholz et al., 2014), in response to climate fluctuations however, the underlying mechanisms are still unclear. Global cold periods such as the Last Glacial Maximum (LGM; 23–19 kyr BP) and the Little Ice Age (LIA; 1500–1850 AD) were generally associated with an OMZ contraction, while warm intervals such as the deglaciation (~17–13 kyr BP), part of the Medieval Climate Anomaly (MCA; 900–1350 AD) and the last 100 years were associated with an OMZ expansion (Higginson and Altabet, 2004; Gutierrez et al., 2009; Salvatelli et al., 2014b). Oxygen reconstructions for the last 2 millennia, both in the water column and the sediments, have been done at multidecadal sampling (Gutierrez et al., 2009; Salvatelli et al., 2014b). This approach can be used to reconstruct changes in ventilation below the OMZ by assessing the coupling/decoupling of oxygenation in the water column and sediments. Several mechanisms have been proposed to explain the observed oxygenation variability. The reduced denitrification (i.e. OMZ weakening) during glacial stages, for example, is attributed to decreased export production and lower oxygen demand, in addition to increased oxygen solubility due to lower surface temperature (Galbraith et al., 2004). Nevertheless, reconstructing changes in oxygen remains complicated due to the above-mentioned restrictions of the different proxies. Moreover, the multiple discontinuities and limitations in the accuracy of ^{14}C measurements in the sediments from the Peruvian margin, prevent the establishment of robust age models. Thus, this prevents comparison with other well-dated records. For these reasons, the understanding of the main processes

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