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

3

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18

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20 upwelling ecosystem, paleoceanography.

21

22 **ABSTRACT**

23

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

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55

56 1. INTRODUCTION

57

58 Oxygen concentration in the ocean affects marine biogeochemical processes and the
59 behavior and distribution of marine biota (Stramma et al., 2008; 2010b; Gilly et al., 2013). In
60 the Eastern Tropical Pacific, a strong and shallow oxygen minimum zone (OMZ) is
61 maintained at intermediate depths as a result of weak ocean ventilation and the decay of
62 organic matter as a result of intense biological production (Pennington et al., 2006;
63 Karstensen et al., 2008). The low oxygen concentration modifies microbial processes and the
64 cycles of the macronutrients nitrogen and phosphorus. Although OMZ waters constitute only
65 ~0.1% of the ocean volume, up to 40% of the total loss of the ocean's bioavailable nitrogen, a
66 macronutrient limiting primary productivity, occurs in these zones (Kuypers et al., 2005; Lam
67 et al., 2009). During the last 50 years, OMZs have expanded both horizontally and vertically
68 in all tropical oceans, likely due to anthropogenic impacts (Stramma et al., 2008; 2010).
69 Global warming is expected to further reduce the oxygen supply to the oceans, producing a
70 continuous expansion of the OMZs and resulting in habitat contraction and considerable
71 changes in marine biogeochemistry (Gilly et al., 2013). However, it is still an open question
72 as to how the magnitude and temporal changes in oceanic dissolved oxygen of the last few
73 decades compare to the natural variability on longer timescales. Moreover, it is not clear how
74 the OMZ in the Eastern Tropical South Pacific (ETSP) responded to prior episodes of climate
75 changes, and the local and remote driving factors remain unknown. In the present work, we
76 reconstruct changes in oceanic oxygenation and export production for the last 25 000 years
77 before present (kyr BP), using sediment cores retrieved from the ETSP-OMZ. We then
78 compare our records with other paleoceanographic reconstructions to identify local and
79 remote driving factors for changes in OMZ intensity.

80

81 Reconstructions of past oxygenation in the sediments are based on the use of proxies
82 that record the redox state at the sediment-water interface, such as laminations, redox-
83 sensitive trace metals, and foraminiferal species assemblages (Jaccard et al., 2014). These
84 proxies are likely to detect either changes in the magnitude and distribution of biological
85 export production and/or modifications in ventilation through bottom currents. The presence
86 of laminae provides strong evidence for low oxygen concentrations ($<7 \mu\text{mol kg}^{-1}$, Schönfeld
87 et al., 2015), as low oxygen contents and high sedimentation rates impede sediment
88 reworking by benthic organisms. By contrast, the absence of laminae is not necessarily a
89 proof of oxygenation, but is more likely related to a complex interplay of factors including

90 turbidite flows, slumps, winnowing by strong currents, bioturbation, and a lack of regular
91 variation in terrigenous and biological material (Salvatteci et al., 2014a). Benthic redox
92 conditions are generally recognized to have a dominant influence on the accumulation of
93 authigenic trace metals (e.g., molybdenum, rhenium, and uranium) in marine sediments
94 (Algeo and Tribovillard, 2009). The solubility of redox-sensitive metals decreases under
95 reducing conditions. Reducing conditions commonly occur within the upper centimeters of
96 the sediments, thus the presence or absence of these elements in sedimentary deposits is used
97 to infer past reducing conditions (McManus et al., 2006). Benthic foraminifer assemblages
98 are indicative of past changes in oxygen under certain conditions, but sediments from the
99 Peruvian margin show extensive periods of benthic and planktonic foraminifera dissolution,
100 limiting the use of this proxy to reconstruct high resolution changes in past oxygen
101 concentration (Rein et al., 2005). Consequently, the most reliable approach to infer past
102 oxygenation changes is the combined use of several proxies (Hendy and Pedersen, 2006;
103 Nameroff et al., 2004; Algeo and Tribovillard, 2009; Helz and Adelson, 2013; Jaccard et al.,
104 2014; Scholz et al., 2014; Little et al., 2015).

105

106 Water column denitrification has also been indirectly inferred through the use of $\delta^{15}\text{N}$
107 in sedimentary organic matter (Higginson and Altabet, 2004; Chazen et al., 2009; Scholz et
108 al., 2014). In oxygen-deficient waters ($<2\text{--}10 \mu\text{mol O}_2 \text{ L}^{-1}$), N-loss processes, such as
109 denitrification ($\text{NO}_3^- \rightarrow \text{N}_2$ via NO_2^-) and anammox (anaerobic ammonia oxidation; $\text{NO}_2^- \rightarrow$
110 $\text{NH}_4^+ \rightarrow \text{N}_2$; Lam et al., 2009) take place. Under these conditions, NO_3^- is used as an oxidant
111 during organic matter degradation resulting in isotopically light N_2 and N_2O and isotopically
112 heavier residual NO_3^- . This heavy NO_3^- is upwelled to the surface, used by phytoplankton, and
113 eventually deposited into the sediments. Thus, in sites where high sedimentation rates and
114 low oxygen concentrations prevail, a bulk sediment $\delta^{15}\text{N}$ analysis can be used to reconstruct
115 past changes in N-loss (Higginson and Altabet, 2004; Mollier-Vogel et al., 2012). Although
116 the relative importance of denitrification and anammox is strongly debated for the Peruvian
117 OMZ, both of them are denitrification reactions driven by an intense OMZ (Lam et al., 2009;
118 Zehr, 2009). However, other processes that are not influenced by oxygen concentrations
119 contribute to the $\delta^{15}\text{N}$ signal, most importantly the partial NO_3^- utilization by phytoplankton
120 (Mollier-Vogel et al., 2012; Ehlert et al., 2015). During photosynthesis, phytoplankton
121 preferentially take up NO_3^- containing the lighter isotope; therefore, the produced organic
122 matter is depleted in ^{15}N relative to the upwelled NO_3^- . A low relative NO_3^- utilization results

123 in lower particulate organic matter $\delta^{15}\text{N}$ values compared to upwelled NO_3 $\delta^{15}\text{N}$ values,
124 independent from oxygen conditions in the water column (Waser et al., 1998). Currently, off
125 central and northern Peru, water column measurements show that NO_3 and PO_4
126 concentrations do not limit phytoplankton growth, thus partial NO_3 utilization occurs (Moore
127 et al., 2013). It is therefore likely that $\delta^{15}\text{N}$ in bulk sediments in this region reflects both
128 water-column N-loss increasing the $\delta^{15}\text{N}$ of upwelled NO_3 (indicating low-oxygen
129 conditions), and, subsequent partial utilization causing $\delta^{15}\text{N}$ in the organic matter to be lower
130 than upwelled NO_3 $\delta^{15}\text{N}$ (Mollier-Vogel et al., 2012; Ehlert et al., 2015). Although we are
131 aware of the different processes controlling $\delta^{15}\text{N}$ values in sediments, we will, for simplicity,
132 use the term "denitrification" as a proxy for water column oxygenation.

133

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

156 records. For these reasons, the understanding of the main processes controlling oxygenation
157 changes remains unresolved.

158

159 The present study is based on a stacked record covering the last 25 kyr to reconstruct
160 changes in oxygenation and productivity using a suite of proxies including the presence of
161 laminations, redox sensitive metals and $\delta^{15}\text{N}$. Moreover, we carefully examined the sediment
162 records with X-ray images, to identify laminated, banded, slumped, and mixed sediment
163 sequences to develop a strong and reliable age model constructed with 60 ^{14}C calibrated ages
164 taken only from laminated sequences to avoid age inversions. The past 25 kyr comprise
165 periods of global ocean circulation and climate changes. The comparison of contrasting
166 climate and ocean circulation conditions provides insight into the underlying mechanisms
167 producing changes in productivity and OMZ intensity. The objectives of the present study
168 are: 1) to reconstruct centennial to millennial scale changes in oxygenation and productivity,
169 2) to assess the coupling-decoupling between water column and sediment redox conditions,
170 and 3) to unravel the main processes controlling oxygenation changes in the ETSP by
171 comparing our record with other relevant records from the literature. A sound understanding
172 of these processes is fundamental for projecting potential future scenarios of the ETSP-OMZ.

173

174 **2. OCEANOGRAPHIC CONTEXT OF STUDY SITE**

175

176 The Peruvian upwelling ecosystem (PUE) is an eastern boundary system characterized by
177 a shallow surface mixed layer and high productivity driven by the upwelling of cold, nutrient-
178 rich and oxygen-poor waters from intermediate depths (Fig. 1A and B; Pennington et al.,
179 2006). The intense upwelling of waters rich in nitrate, phosphate, silicic acid and iron to
180 surface waters induces massive phytoplankton blooms, which at times extend over the shelf
181 offshore (Bruland et al., 2005). The main source of the upwelled water is the nutrient-rich
182 poleward undercurrent (PUC) located between 50 and 400 meters depth, which is in contact
183 with shelf sediments (Bruland et al., 2005; Karstensen and Ulloa, 2009). Approximately 30%
184 of the PUC originates from the primary and secondary Southern Subsurface Countercurrents
185 (SSCCs) and to a considerably lesser degree, from the Equatorial Undercurrent (EUC). The
186 remaining 70% of the PUC is composed of alongshore recirculation associated with flows
187 below it and of weak diffuse currents south of $\sim 9^\circ\text{S}$ (Montes et al., 2010). Changes in the
188 intensity, ventilation, and nutrient concentrations of water in these countercurrents affect the

189 oxygen content and nutrient availability in the subsurface waters off Peru, which eventually
190 fuel the euphotic layers.

191

192 The ETSP-OMZ is defined by an oxygen saturation level of $<\sim 10\%$ of that at the sea
193 surface (Gilly et al., 2013), which corresponds to an oxygen concentration of $<20 \mu\text{mol kg}^{-1}$
194 (0.5 ml L^{-1} ; Helly and Levi, 2004; Fuenzalida et al., 2009). On average, the ETSP-OMZ
195 ranges from ~ 50 to 500 meters depth, and is thickest off Peru between 5° and 13°S (Fig. 1B;
196 Fuenzalida et al., 2009). The upper boundary is shallowest off Peru, shoaling towards the
197 coast and in some cases overlapping the euphotic zone (Fuenzalida et al., 2009). However it
198 varies on seasonal and interannual timescales, allowing for the intrusion of benthic fauna
199 from the upper slope that recurrently causes sediment mixing (Gutierrez et al., 2008). During
200 the strong El Niño event of 1997–98, the upper OMZ boundary deepened to 190 m causing a
201 mild oxygenation of an otherwise anoxic upper slope (200–300m) allowing the presence of
202 benthic fauna (Sanchez et al., 2000; Levin et al., 2002). The ETSP-OMZ is supplied with
203 oxygen-rich water from zonal tropical currents: near the equator, EUC, the SSCCs and the
204 Southern Intermediate Countercurrents (SICC; Furue et al., 2007). These currents provide a
205 net oxygen supply to the ETSP-OMZ (Stramma et al., 2010a).

206

207 **3. MARINE GEOCHEMICAL BEHAVIOR OF TRACE METALS**

208

209 Reconstructions of paleo-redox conditions are usually based on several redox-
210 sensitive metals. However, one of the difficulties in using these elements as proxies for past
211 geochemical conditions is that sedimentary reducing conditions may be controlled by two
212 complementary processes: low dissolved oxygen availability above the sediments and the
213 delivery of reactive organic carbon to the seafloor (McManus et al., 2006). The
214 concentrations of redox-sensitive metals in sediment records have been used to discern
215 paleoredox conditions, with higher trace metal enrichments suggesting more reducing
216 conditions (Tribovillard et al., 2006; Morford et al., 2012). Redox classification of the
217 depositional environments can be subdivided into oxic ($>2.0 \text{ m O}_2 \text{ L}^{-1}$), dysoxic or suboxic
218 ($\sim 0.2\text{--}2 \text{ ml O}_2 \text{ L}^{-1}$), anoxic non-sulfidic ($<0.2 \text{ ml O}_2 \text{ L}^{-1}$, $0 \text{ ml H}_2\text{S L}^{-1}$), and anoxic-sulfidic or
219 euxinic ($0 \text{ ml O}_2 \text{ L}^{-1}$, $>0 \text{ ml H}_2\text{S L}^{-1}$) conditions (Savrda and Bottjer, 1991; Tribovillard et al.,
220 2006; Algeo and Tribovillard, 2009). The sum of the measured metal concentrations contains
221 a detrital background and an authigenic fraction (i.e. the part in excess of the detrital
222 background; Tribovillard et al., 2006). The authigenic (or non-lithogenic) fraction is mainly

223 enriched by syn- or post-depositional redox reactions, and each element exhibits different
224 sensitivities to the redox conditions along the oxic to sulfidic gradient. As in some cases,
225 trace elements present a strong detrital fraction, thus we focus on the authigenic trace element
226 content.

227

228 3.1 Molybdenum

229 In modern seawater, molybdenum (Mo) is present as the stable and largely unreactive
230 molybdate oxyanion (MoO_4^{2-} /Mo(VI)), with a seawater concentration of ~ 104 nmol kg⁻¹, a
231 residence time of 8.7×10^5 yr, and a conservative behavior (Colodner et al., 1993; Algeo and
232 Tribovillard, 2009; Miller et al., 2011). The uptake mechanisms of authigenic Mo (Mo_{auth})
233 by sediments are well understood (Morford et al., 2005; Algeo and Tribovillard, 2009).
234 Mo_{auth} enrichment is limited in oxic environments, whereas under anoxic-sulfidic conditions
235 (i.e. above a hydrogen sulfide concentration of ~ 50 – 250 $\mu\text{M HS}^-$), Mo becomes activated
236 facilitating the conversion of molybdate to thiomolybdates ($\text{MoO}_x\text{S}_{4-x}^{2-}$, $x=0$ to 3) (Helz et al.,
237 1996; Zheng et al., 2000; Algeo and Tribovillard, 2009). During shallow diagenesis,
238 considerable amounts of Mo sorb onto and become incorporated into pyrite, an authigenic
239 mineral that can endure oxidation during sediment burial (Sundby et al., 2004; Helz and
240 Adelson, 2013). There are three main factors influencing the Mo_{auth} uptake by sediments: 1)
241 benthic redox conditions including the mean redox state and the degree of redox variability,
242 2) the operation of a particulate shuttle linked to Mn-Fe redox cycling, scavenging Mo from
243 the water column, thereby raising its concentration near the sediment surface and speeding its
244 diffusion into sediments, and 3) changes in the chemistry of the overlying water column
245 (Algeo and Tribovillard, 2009; Scholz et al., 2013; Helz and Adelson, 2013). The behavior
246 of Mo in sediments strongly suggests that Mo is a reliable proxy for benthic redox conditions
247 at localities with, at minimum, sporadically sulfidic conditions (Scholz et al., 2011; Helz and
248 Adelson, 2013).

249

250 3.2 Uranium

251 In modern seawater, uranium (U) is present as the chemically unreactive uranyl
252 carbonate ($\text{UO}_2(\text{CO}_3)_3^{4-}$, U (VI)), with a seawater concentration of ~ 13 nmol kg⁻¹, a
253 residence time of 4.5×10^5 yr, and conservative behavior (McManus et al., 2006; Algeo and
254 Tribovillard, 2009; Miller et al., 2011). In oxic environments, U enrichment is limited,
255 whereas under anoxic conditions U (VI) is reduced to U (IV) forming either the highly

256 soluble uranyl ion UO_2^+ or the less soluble uranous fluoride complexes (Algeo and
257 Tribovillard, 2009). This reduction occurs in the sediments suggesting that the reduction
258 process may take place on particle surfaces, possibly catalyzed by enzymes produced by iron
259 and sulfate-reducing bacteria (Algeo and Tribovillard, 2009; Morford et al., 2009; Scholz et
260 al., 2011). The uptake of U_{auth} by sediments may occur through the formation of organic-
261 metal ligands in humic acids or by precipitation of crystalline uraninite (UO_2) or its
262 precursor (Zheng et al., 2002; Algeo and Tribovillard 2009). The reduction of U starts at the
263 Fe(II)-Fe (III) redox boundary and is likely controlled by microbially –mediated Fe reduction
264 rather than by the presence of HS^- (Zheng et al., 2002; Algeo and Tribovillard, 2009). This
265 indicates that the onset of U_{auth} enrichment occurs under less reducing conditions compared to
266 Mo and at shallower depths (Morford et al., 2009; Algeo and Tribovillard, 2009). In the
267 water column, U is not influenced by the Mn-Fe redox cycling, therefore, most of the U_{auth} in
268 anoxic sediments is delivered by diffusion across the sediment–bottom water interface
269 (McManus et al., 2006; Algeo and Tribovillard, 2009; Scholz et al., 2011).

270

271 3.3 Rhenium

272 In modern seawater, rhenium (Re) is present as the oxyanion perrhenate (ReO_4^-) (VII),
273 with a seawater concentration of ~ 40 pmol kg^{-1} , a residence time of 7.2×10^5 yr, and
274 conservative behavior (Colodner et al., 1993; Algeo and Tribovillard, 2009; Miller et al.,
275 2011; Helz and Adelson, 2013). Whereas Re does not accumulate in oxic sediments, it can
276 be highly enriched in anoxic and suboxic sediments, with concentrations exceeding the
277 crustal average by 100 to 1000 times (i.e. 0.2 to 2 $ng.g^{-1}$; Colodner et al., 1993; Böning et al.,
278 2004; Helz and Dolor, 2012; Helz and Adelson, 2013). This characteristic renders Re a
279 promising proxy to record redox conditions in the sediments, although it has hitherto received
280 little attention in this context (Crusius et al., 1996; Nameroff et al., 2004; Böning et al., 2004;
281 Helz and Adelson, 2013). The enrichment process involves the reduction of ReO_4^- to an
282 insoluble Re(IV) oxide or sulfide in suboxic and anoxic environments (Helz and Dolor,
283 2012). In contrast to Mo, Re is not adsorbed by Mn oxides and Fe oxyhydroxides surfaces in
284 the water column (Morford et al., 2005; Helz and Adelson, 2013). During shallow diagenesis,
285 Re tends to associate with organic matter, and during organic matter decomposition Re can
286 be remobilized (Colodner et al., 1992; Helz et al., 2012; Helz and Adelson, 2013).

287

288 3.4 Nickel

289 In oxic marine environments, nickel (Ni) behaves as a micronutrient with a nutrient-
290 like oceanic distribution. It is mostly present as a soluble Ni carbonate (NiCO₃) (II) or
291 adsorbed to humic and fulvic acids, and is present in high amounts in plankton and sinking
292 particles (Böning et al., 2004; Tribovillard et al., 2006). The main removal mechanism of Ni
293 to reducing sediments seems to be settling with organic matter; Ni is brought to sediments
294 from the ETSP-OMZ pre-concentrated on biodebris settling through the water column
295 (Tribovillard et al., 2006; Böning et al., 2004; 2015). During organic matter diagenesis Ni is
296 released from organometallic complexes to pore waters. In moderately reducing sediments,
297 Ni is released from the sediments to the overlying waters, whereas under (sulfate-) reducing
298 conditions, Ni is likely to be incorporated as the insoluble NiS into pyrite (Böning et al.,
299 2004; Dean et al., 2006; Tribovillard et al., 2006; Little et al., 2015).

300

301 3.5 Copper

302 In oxic seawater, copper (Cu) is present as an organometallic ligand, and its
303 concentration increases approximately linearly with depth, with a profile that is intermediate
304 between scavenged and nutrient-like (Tribovillard et al., 2006; Little et al., 2015). Copper
305 exhibits a complex geochemical behavior (Little et al., 2015), where it is both bioessential,
306 and toxic to all photosynthesizing microorganisms at Cu²⁺ ion concentrations > 10⁻¹³ M
307 (Little et al., 2015). Cu is also present in high amounts in plankton and sinking particles
308 (Böning et al., 2004). The main removal mechanism of Cu to reducing sediments is settling
309 with organic matter, this metal is brought to sediments from the ETSP-OMZ pre-concentrated
310 on biodebris settling through the water column (Tribovillard et al., 2006; Böning et al.,
311 2004; 2015). Copper complexation with organic matter as well as adsorption to particulate
312 Fe-Mn oxyhydroxides, accelerates scavenging and thus sediment enrichment (Tribovillard et
313 al., 2006; Böning et al., 2015; Little et al., 2015). During organic matter diagenesis or
314 reductive dissolution of Fe-Mn-oxyhydroxides, Cu is released to pore waters. Under reducing
315 conditions, Cu is likely to be incorporated into pyrite or may form its own sulfide phase (CuS
316 and CuS₂; Tribovillard et al., 2006). Nickel and Cu have high concentrations in the lithogenic
317 fraction of sediments in contrast to Mo, U and Re, resulting in relatively low EF values
318 (Böning et al., 2004; 2015). Thus, time periods associated with low Ni and Cu EFs could also
319 be the result of processes not related to biogenic flux, such as fluctuations in the lithogenic
320 sediment source and fluctuations in mineralogy.

321

322 4. MATERIAL AND METHODS

323

324 **4.1 Stacked record, age model and subsampling**

325 We reconstructed changes in productivity, sediment oxygenation, and water column
326 denitrification over the last 25 kyr at unprecedented resolution levels using a stacked record
327 from three sediment cores retrieved at 14°S (Fig. 1). The stacked record is composed of cores
328 G14 (390 m depth; 14.38°S, 76.42°W), G10 (312 m depth; 14.23°S, 76.4°W) and B14 (301
329 m depth; 14.27°S, 76.43°W). Cores G10 and G14 were retrieved during the Galathea-3
330 expedition in 2007 and core B14 was taken during the Paleo-3 cruise in 2005 (Salvatteci et
331 al., 2012; 2014a).

332

333 The complicated stratigraphy of sediment cores from the Peruvian margin strongly
334 suggests the need for a detailed identification of the sediment structures using X-ray images
335 prior to sub-sampling (Salvatteci et al., 2014a). This approach guarantees that the analyzed
336 sediments are a result of deposition from the water column and not from reworking of
337 upslope deposits. The identification of laminated, slumped, and homogeneous sequences
338 must be done with X-ray images because these structures cannot be correctly identified with
339 conventional photographic images or a visual description of the cores (see supp. mat.).
340 Moreover, the dating of the sediment samples in laminated/banded sequences is essential to
341 avoid age inversions.

342

343 The age models for cores G10 and G14 were done using 31 and 29 ¹⁴C analyses,
344 respectively, and are based on cumulative mass-depth due to large downcore changes in
345 sediment density. Given the complicated sedimentological patterns of cores retrieved from
346 the Peruvian shelf (Salvatteci et al., 2014a), we first carried out a detailed stratigraphic
347 analysis based on careful examinations of X-ray images to identify laminated, banded,
348 slumped, bioturbated, and winnowed sections (see supp. mat.). The ¹⁴C analyses and all
349 proxies were only developed on the laminated and banded sections of the core, because
350 slumped sections cannot be accurately dated and their mixed sediments may result in
351 erroneous paleoceanographic interpretations (Salvatteci et al., 2014a). Core G10 covers the
352 Holocene from 10.3 to 0.4 kyr BP, and G14 covers the glacial-interglacial transition from
353 25.2 to 13.4 kyr BP. Sediment corresponding to the last 13.4 kyr were not present in core
354 G14, likely as a consequence of sub-marine landslides, which are common in this area.
355 Sedimentation rates ranged from 0.3 mm.y⁻¹ to 0.7 mm.y⁻¹ for sediment samples
356 corresponding to the LGM and to the Late Holocene respectively. The high sedimentation

357 rates in the stacked record allows for high-resolution reconstructions. A detailed description
358 of the age model is shown in the supplementary material. The age model for the last 2
359 millennia, showing the overlap between cores B14 and G10, is shown in Salvattecì et al.
360 (2014b). Data for core B14 used in the stacked record was taken from Salvattecì et al.
361 (2014b). The strong age model developed in the stacked record allows for the comparison
362 with other high-resolution records.

363

364 Sub-sampling for trace elements and $\delta^{15}\text{N}$ was done following the stratigraphy of the
365 stacked record avoiding the slumped sections. Laminated, banded and some homogeneous
366 sequences were subsampled every 1 cm for trace elements and every 2 cm for $\delta^{15}\text{N}$ analyses.
367 This sub-sampling strategy resulted in 363 trace element analyses and 268 $\delta^{15}\text{N}$
368 measurements. Uranium was not measured in core B14. A detailed description of the
369 subsampling of cores G10 and G14 is provided in the supplementary material. The
370 subsampling criteria for B14 are described in Salvattecì et al. (2012; 2014b).

371

372 **4.2 Sediment structures as a record of benthic oxygenation**

373 Sediment cores retrieved from the core of the ETSP-OMZ often show homogeneous
374 sequences between laminae packages. They have been suggested to be the result of
375 bioturbation, (Brodie and Kemp, 1994), but a careful examination of multiple cores revealed
376 that most of these sequences resulted from instantaneous downslope depositions (Salvattecì et
377 al., 2014a). Therefore, in the present work we rely only on the laminated and banded
378 sequences as a proxy for low oxygen concentration. In order to identify the mechanisms
379 producing sediment homogenization, a detailed comparison with nearby cores would be
380 required, however this would go beyond the scope of the present study.

381

382 In order to examine the sediment structures, digital X-ray images (i.e. SCOPIX) were
383 obtained (Migeon et al., 1990) at the EPOC (Environnements et Paléoenvironnements
384 Océaniques et Continentaux) Laboratory, University of Bordeaux 1, France. Sediment
385 structures in cores G10 and G14 were described following the nomenclature by Brodie and
386 Kemp (1994). The lithology of the cores was classified into three categories: "isolated
387 laminae", "irregularly spaced laminae" and "slumped sequences". The "isolated laminae"
388 consisted of solitary diatom ooze (a few mm thick), enclosed in homogeneous mud. The
389 "irregularly spaced laminae" were packs of laminae (several cm to a few decimeters thick)
390 separated by intervals of homogeneous sediments (several cm to a few decimeters thick).

391 These laminae packs comprised alternations between diatom oozes and diatomaceous mud
392 (with higher contents of clay minerals). Finally, sediment sequences showing internal
393 deformation of the laminae (i.e. unconformable layers and angular discontinuities) were
394 classified as "slumped sequences". While the different types of structures are found
395 throughout the cores, their relative abundances were used to characterize each of the time
396 intervals of interest.

397

398 **4.3 Trace element measurements**

399 Trace elements (U, Mo, Re, Cu and Ni) concentrations were analyzed by ICP-MS
400 (Ultramass Varian) after hot-plate acid digestion in Polytetrafluoroethylene (PTFE) vessels.
401 Organic matter was eliminated and silicates were removed using acid treatments (HF, HNO₃
402 and HClO₄; Jarvis et al., 1992). A detailed description of the methodology employed is
403 described in Salvattecchi et al. (2014b). The accuracy of the trace element concentration
404 measurements was determined by comparison with MESS-3 (Marine sediment reference
405 material for trace elements, National Research Council of Canada). The measurement
406 precision was determined by performing duplicate analyses. The average values of replicate
407 digestions were well within the recommended ranges with relative standard deviations (RSD)
408 being <1% for Mo, U, Ni, and Cu, and <2.5% for Re.

409

410 The chemical composition of andesite is an appropriate representation of the detrital
411 background of the sediments along the Peruvian margin (Böning et al., 2004; Scholz et al.,
412 2011). We therefore used the element contents of andesite to obtain the authigenic
413 concentration of each trace element taken from the GEOROC database (Sarbas and Nohl,
414 2009), taking into account the element concentrations in andesite from whole rocks from the
415 central Andean volcanic zone in Peru. Rhenium concentration in andesite displays the lowest
416 values of all metals studied in the present work (100-176 ppt; Alves et al. 2002). The trace
417 elements to aluminum mass ratios in andesite are as follows: Ni/Al x10⁻⁴ = 2.55, Cu/Al x 10⁻⁴
418 = 4.39, U/Al x 10⁻⁴ = 0.34, Re/Al x 10⁻⁹ = 1.93, and Mo/Al x10⁻⁴ =0.25. Then, the detrital
419 metal fraction was calculated as: $X_{\text{detrital}} = (X/Al)_{\text{andesite}} * Al_{\text{sample}}$. Finally, the authigenic
420 fraction of element X in a sample was calculated as $X_{\text{total}} - X_{\text{detrital}}$. We calculated the
421 enrichment factor (EF) of the elements to determine if they are depleted or enriched relative
422 to andesite. The EFs were calculated using the formula: $EF_{\text{element } x} = (X/Al)_{\text{sample}} /$
423 $(X/Al)_{\text{andesite}}$ (Tribovillard et al., 2006). If EF_x is > (<) 1, then the element X is enriched
424 (depleted) relative to andesite.

425

426 **4.4 $\delta^{15}\text{N}$ measurements**

427 Water column denitrification was inferred through $\delta^{15}\text{N}$ measurements of sedimentary
428 organic matter. The analyses for cores G10 and G14 were performed in the Department of
429 Geosciences at the University of Arizona, USA. $\delta^{15}\text{N}$ values were measured in untreated
430 sediment samples (i.e. no acidification methods were used) on a continuous-flow gas-ratio
431 mass spectrometer (Finnigan Delta PlusXL) coupled to an elemental analyzer (Costech).
432 Standardization was based on laboratory standard acetanilide and the precision was better
433 than ± 0.2 (1s). $\delta^{15}\text{N}$ data from core B14 were published previously by Salvatelli et al.
434 (2014b).

435

436 **4.5 Organic matter quantification and characterization**

437 Total organic carbon (TOC) reflects the amount of organic carbon present in the sediment
438 and can be used to infer past export production. The quantification and characterization of
439 organic matter were done using Rock-Eval 6 (Lafargue et al., 1998). During a programmed
440 pyrolysis, three fractions (S1, S2 and S3) are identified. S1 represents the thermo-vaporized
441 free hydrocarbons contained in the sample released during the isothermal temperature step at
442 300 °C; S2 represents the hydrocarbons resulting from the cracking of sedimentary organic
443 matter, released between 300 and 650 °C; and S3 represents CO_2 generated at temperatures
444 up to 390 °C (Lafargue et al., 1998; Behar et al., 2001; Peters, 2005). TOC is determined by
445 summing the pyrolysable organic carbon (i.e. S1+S2+S3) and the residual organic carbon
446 (Behar et al.; 2001). Normalization of TOC to the concentration of a refractory element (e.g.
447 Al) may correct for variable dilution effects and has the potential to give estimates of organic
448 material input (Martinez and Robinson, 2010). The hydrogen index (HI, mg HC/g TOC) is an
449 indicator of organic matter preservation. It reflects the amount of hydrocarbons released
450 during pyrolysis and is calculated as $(\text{S2} \times \text{TOC}^{-1}) \times 100$. The H-rich organic matter is the most
451 labile and thus will be the first to be consumed by aerobic and anaerobic decomposition
452 (Dean et al., 1994). High values of HI (>400 mg HC.g⁻¹ TOC) are interpreted as an indicator
453 of enhanced preservation of lipid-rich organic matter (Arthur et al., 1998).

454

455 **5. RESULTS**

456 **5.1 $\delta^{15}\text{N}$ record**

457 There were large changes in $\delta^{15}\text{N}$ values during the last ~25 kyr with higher (lower)
458 values during globally warm (cold) periods at different timescales, except during the globally

459 warm mid-Holocene, where low $\delta^{15}\text{N}$ values were recorded (Fig. 2A). Both the Early Glacial
460 (23-26 kyr BP) and the LGM (19-23 kyr BP) were characterized by low $\delta^{15}\text{N}$ values (Table
461 1). From 18.4 to 16.6 kyr BP, there was an increase from 6.2 to 11.4‰ in $\delta^{15}\text{N}$. During this
462 period, the high $\delta^{15}\text{N}$ values exhibited strong multi-centennial-scale variability, followed by a
463 gradual decrease. The Early Holocene was characterized by relatively high $\delta^{15}\text{N}$ values,
464 followed by a tendency towards lower $\delta^{15}\text{N}$ values, reaching a mid-Holocene (~6.5 kyr BP)
465 minimum of 4.8 ‰. The rest of the mid-Holocene was characterized by very low $\delta^{15}\text{N}$ values.
466 During the Late Holocene, $\delta^{15}\text{N}$ values exhibited temporal variability from ~3 kyr BP
467 onwards: low $\delta^{15}\text{N}$ values (5.2‰) were achieved during the LIA, as low as during the Mid-
468 Holocene, and the highest values (10‰), as high as during the Termination 1 period, during
469 the LIA – Current Warm Period (CWP) transition. Although $\delta^{15}\text{N}$ values increased again
470 during the last 150 years, the average for the last 100 years remained relatively low
471 ($6.7 \pm 0.3\%$) compared to the entire record.

472

473 **5.2 Lithology of the composite record**

474 Sediments from H1S, the Early and the Late Holocene showed more laminations
475 compared to sediments from the Early Glacial, the LGM and the mid-Holocene (Fig. 2B).
476 The most common sediment structures observed in the cores were the "irregularly spaced
477 laminae", "isolated laminae" and "slumped sequences" (see supplementary material for
478 details). The "irregularly spaced laminae" that contained finely laminated sequences were
479 present throughout the record, but were better preserved during the H1S, and the Early and
480 Late Holocene. By contrast, during the Early Glacial and the LGM the "isolated laminations"
481 (which include banded sequences) were more frequent, even though laminated sequences
482 were also sporadically observed (e.g., at ~25 kyr BP). Finally, the mid-Holocene was
483 characterized by the absence of finely laminated sequences, the presence of isolated
484 laminations, and sequences that contained reworked material.

485

486 **5.3 Trace element record**

487 5.3.1 Data presentation

488 In the present study, we show trace element values as EFs (Enrichment Factors).
489 Normalization of trace element concentrations as a ratio with Al, or the calculation of EFs
490 may increase, decrease or even change the sign of the correlations between unmodified
491 variables (Van der Weijden, 2002). Subtle changes in some correlations between
492 concentrations and normalized variables were observed (Table 2 and 3). In some cases, the

493 correlation variables were slightly higher in the normalized data set (e.g. correlation between
494 trace elements and TOC), most likely as a result of having the same common denominator
495 (Al). By contrast, weak correlations between unmodified variables were weaker in the
496 normalized dataset (e.g., correlation between $\delta^{15}\text{N}$ and trace elements). Thus, in order to
497 minimize the normalization biases we focus on stratigraphic variation in EFs rather than on
498 absolute values as suggested by Tribovillard et al. (2006). Nonetheless we calculated the
499 average EF of each element in the whole record to identify the elements with highest
500 enrichment relative to andesite (Table SM2). Re and Mo showed high EFs (373 ± 167 and
501 34.7 ± 30.6 respectively), U and Ni showed moderate enrichment (5.9 ± 3.4 and 4.3 ± 2.5
502 respectively) and finally Cu showed low enrichment (1.1 ± 0.7).

503

504 5.3.2 Temporal variability of the trace elements

505 The EFs of the trace elements U, Re, Mo, Ni, and Cu showed pronounced variability
506 during the last 25 kyr BP (Fig. 2C to G; authigenic concentrations of each element: Figure
507 SM7, complete data set Table SM2). Uranium and Re showed similar enrichment patterns,
508 with their concentrations being higher than andesite throughout the core. Mo was enriched
509 throughout the core and exhibited low EFs during the glacial-deglacial period and during the
510 mid-Holocene. Nickel and Cu displayed similar enrichment patterns, with high values during
511 the Holocene and low values (and even depletions) during the glacial-deglacial period.
512 Overall, U, Re, Mo, Ni, Cu showed higher enrichment during the Holocene compared to the
513 glacial-deglaciation period (Fig. 2C to G). There was a striking difference between U, Re, Ni
514 and Cu on the one hand, and Mo on the other: during the recorded part of the mid-Holocene
515 U, Re, Ni and Cu showed relatively higher values compared to the glacial-deglacial period
516 and the Early Holocene, whereas Mo showed lower enrichments, which was consistent with
517 the low $\delta^{15}\text{N}$ values in this part of the record. Moreover, Mo showed the highest correlation
518 with $\delta^{15}\text{N}$ during the Holocene ($r=0.75$, $n=153$), compared to that of U ($r=0.4$, $n=133$), Re
519 ($r=0.30$, $n=153$), Ni ($r=0.53$, $n=153$), and Cu ($r=0.55$, $n=153$) with $\delta^{15}\text{N}$. Additionally, during
520 the Late Holocene, all trace elements (as well as $\delta^{15}\text{N}$) exhibited higher temporal variability
521 compared to the preceding periods. The centennial-scale minimum trace metal EFs during the
522 Late Holocene were as low as during the glacial-deglaciation period.

523

524 **5.4 Organic matter quantification and preservation**

525 The TOC/Al values as well as the HI showed large changes throughout the record,
526 with higher values during the Holocene compared to the glacial-deglaciation period (Fig. 2H

527 and I). Low TOC values characterized the Early Glacial (0.3 ± 0.1) and the LGM (0.4 ± 0.1)
528 and were associated with low HI values (300 ± 28 , 305 ± 21 mg.HC.g⁻¹ TOC, respectively). A
529 small increase in TOC was observed during the H1S (0.6 ± 0.2) and the Antarctic Cold
530 Reversal (0.6 ± 0.1) which was associated with relatively high HI values (400 ± 38 and 400 ± 31
531 mg.HC.g⁻¹ TOC respectively). During the Holocene, there was an increasing trend in average
532 TOC/Al from the Early Holocene to the Late Holocene (0.9 ± 0.2 , 1.2 ± 0.4 and 1.4 ± 0.5),
533 strong centennial-scale variability in TOC/Al values is observed during the Late Holocene.
534 The HI values were similar during the Early Holocene, mid-Holocene and Late Holocene
535 (427 ± 25 ; 428 ± 26 and 427 ± 34 31 mg.HC.g⁻¹ TOC respectively), however strong centennial-
536 scale variability in the HI was observed during the Late Holocene. Finally, the CWP
537 exhibited the highest TOC/Al (3.1 ± 0.3) and HI values (472 ± 17 mg.HC.g⁻¹ TOC). In general,
538 TOC/Al showed high correlations with the trace elements EFs (Table 2 and 3); however, the
539 correlations of TOC (percentages or TOC/Al) with Ni and Cu were slightly higher than with
540 Mo, U, and Re.

541

542 **6. DISCUSSION**

543

544 We used a stacked record covering the last 25 kyr BP, retrieved from the core of the
545 current ETSP-OMZ, to reconstruct changes in water column denitrification, sediment redox
546 conditions, and export production as inferred from a suite of proxies including $\delta^{15}\text{N}$, presence
547 of laminations, TOC, and redox sensitive metals (Fig. 3). In the following sections, we
548 discuss 1) the use of the sediment record stratigraphy as a proxy for benthic oxygenation, 2)
549 changes in benthic redox conditions and productivity during the last 25 kyr, 3) a potential
550 mechanism producing oxygenation changes during the glacial times and the deglaciation, 4)
551 potential mechanisms controlling oxygenation and productivity changes in the ETSP-OMZ
552 during the Holocene, and 5) the implications of the present study in the context of current
553 global warming.

554

555 **6.1 Assessing the sediment core stratigraphy as a proxy for benthic oxygenation**

556

557 The presence of laminations in the stacked record suggests reducing conditions during
558 parts of Termination 1, and the Early and Late Holocene (Fig. 3B). The presence of laminae
559 has been used as strong evidence of low oxygen concentrations off Peru, off California, in the
560 Gulf of California, and elsewhere, but it must be stressed that the absence of laminae, at least

561 off Peru, cannot be used as an evidence of high oxygen concentration as suggested in several
562 studies (Brodie and Kemp, 1994; Van Geen et al., 1996; Schönfeld et al., 2015). For example,
563 as illustrated in core B14 (Fig. SM2), the last 100 years of the record show very few distinct
564 laminations but the proxies for water column and sediment oxygenation indicate strong
565 reducing conditions (Salvatteci et al., 2014b). Moreover, finely laminated sequences are
566 sometimes associated with less reducing conditions in the sediments and reduced water
567 column denitrification, as for example during the LIA (Fig. SM2; Gutierrez et al., 2009;
568 Salvatteci et al., 2014b). The absence of laminae is not simply related to increased bottom-
569 water oxygenation, but more likely to a complex interplay of factors including turbidite
570 flows, slumps, winnowing by strong currents, bioturbation, and a lack of regular variation in
571 terrigenous and biological material (Salvatteci et al., 2014a). Thus, whereas the presence of
572 laminae is a reliable indicator of reducing conditions, the absence of laminae as a proxy of
573 enhanced oxygenation needs to be validated with other proxies such as redox-sensitive
574 metals.

575

576 **6.2 Oxygenation and export production changes during the last 25 kyr**

577

578 **6.2.1 Molybdenum EF, and Mo and U EFs ratios**

579

580 The use of Mo_{auth} concentrations or EFs in the core of the ETSP-OMZ is a useful tool
581 to draw inferences concerning paleoredox conditions since the uptake of Mo by the sediments
582 is mainly driven by benthic redox conditions (Algeo and Tribovillard, 2009; Scholz et al.,
583 2011, Scholz et al., 2014). The operation of the particulate Mn-Fe-oxyhydroxide shuttle is an
584 important mechanisms in sediments from the Peruvian shelf, scavenging Mo from the water
585 column, and raising its concentration near the sediment surface, promoting its diffusion to the
586 sediments (Scholz et al., 2011; Helz and Adelson, 2013). In the core of the OMZ (~300 m
587 depth), sediments receive little Mn-bound particulate Mo, since Mn reduction is largely
588 completed in the water column and Mo pore-water profiles at this depth indicate a downward
589 flux to the sediments (Scholz et al., 2011). Although the evolution of aqueous trace-metal
590 chemistry is an important mechanism in, e.g., the Black Sea, it is not significant in open
591 marine systems like the ETSP (Algeo and Tribovillard, 2009).

592

593 The Mo EFs plot indicated less reducing conditions during the Early Glacial, LGM
594 and the deglaciation periods, whereas strong reducing conditions prevailed during parts of the

595 Early, mid- and Late Holocene (Fig. 3C). In our stacked record, high Mo EFs (Fig. 2C)
596 coincide with good organic matter preservation (Fig. 2I), suggesting that an increase in Mo
597 EF (and other trace elements) is mainly driven by changes in redox conditions and not by an
598 increase in organic matter decomposition. During the Early Glacial, LGM, H1S, and ACR,
599 the Mo EFs were relatively low but enriched relative to andesite, suggesting less reducing
600 conditions compared to the Early and Late Holocene (Table SM2). However, there were two
601 multidecadal-scale maxima during the H1S (at 17.03 and 15.39 kyr BP) with EFs similar to
602 those observed during the Holocene (Table SM2). On average, the Early and Late Holocene
603 showed more reducing conditions compared to the recorded part of the Mid-Holocene (Fig.
604 3C). Finally, the Late Holocene exhibited strong centennial-scale variability in Mo EFs, with
605 shifts from sub-oxic to anoxic benthic redox conditions.

606

607 Concordant with the Mo EF record, the cross-plot of Mo versus U EFs shows that
608 sediments from the Early Glacial, LGM and ACR were sub-oxic whereas sediments from the
609 H1S, Early Holocene, mid-Holocene and Late Holocene were anoxic and in some cases
610 sulfidic (Fig. 4). Cross-plots give additional insights of past redox oscillations, as in
611 sediments of the OMZ core the relationship of redox conditions to authigenic Mo-U
612 enrichment is straight forward: 1) suboxic conditions result in sediments with modest Mo and
613 U enrichments, and with $(\text{Mo}/\text{U})_{\text{auth}}$ ratios lower than the seawater ratio, and 2) anoxic
614 conditions result in sediments with strong Mo and U enrichments accompanied by
615 progressively higher $(\text{Mo}/\text{U})_{\text{auth}}$ ratios as total authigenic concentrations increase (McManus
616 et al., 2006; Algeo and Tribovillard, 2009; Scholz et al., 2011). During the Early Glacial,
617 LGM, and ACR, $(\text{Mo}/\text{U})_{\text{auth}}$ ratios below the concentration of seawater were recorded, as a
618 consequence of modest U EFs, but relatively lower Mo EFs (Fig. 2C and E). By contrast,
619 during (at least parts of) the H1S, Early, Mid- and Late Holocene, $(\text{Mo}/\text{U})_{\text{auth}}$ ratios were
620 sometimes 3 times above the ratio of these elements in seawater. The pattern of redox
621 variations from the sediments of the present study (Fig. 4) is very similar to multiple
622 continental margin sites in the Eastern Tropical Pacific (Algeo and Tribovillard, 2009),
623 further indicating that the $(\text{Mo}/\text{U})_{\text{auth}}$ ratio is a valid proxy for reconstructing changes in
624 benthic redox conditions. Moreover, no evidence for an enhanced Mo supply with metal
625 (oxyhydr)oxides (i.e. particule shuttle) has been found (Algeo and Tribovillard, 2009; Scholz
626 et al., 2011).

627

628 Multidecadal to centennial-scale periods characterized by sulfidic conditions in the
629 sediments where reached several times during the last 25 kyr, as indicated by the $(\text{Mo}/\text{U})_{\text{auth}}$
630 and Mo EFs (Figs. 3C, D and 4). A shift from suboxic to sulfidic benthic redox conditions
631 enhances uptake of both Mo and U, but a stronger accumulation of Mo results in a
632 disproportional increase in the $(\text{Mo}/\text{U})_{\text{auth}}$ ratio. A preferential uptake of U over Mo takes
633 place when redox conditions at the sediment/water interface are suboxic, and of Mo over U
634 when benthic redox conditions are strongly and/or frequently sulfidic (Algeo and
635 Tribovillard, 2009). The $(\text{Mo}/\text{U})_{\text{auth}}$ record shows values below the seawater ratio during the
636 Early Glacial, LGM, and during ACR indicating suboxic conditions, whereas the higher
637 values during parts of the H1S, Early mid-and Late Holocene indicate sulfidic conditions
638 (Fig. 3D). The mid-Holocene shows $(\text{Mo}/\text{U})_{\text{auth}}$ ratios slightly above the seawater ratio
639 suggesting more reducing conditions compared to the Early Glacial and LGM, but less
640 reducing conditions compared to the H1S, and parts of the Early and Late Holocene. The
641 high Mo EFs (up to 230), during periods of poor oxygenation in the Early and Late Holocene
642 were the result of strong sulfidic conditions in the near-surface sediment (Scholz et al., 2014).
643 Finally, the last 100 years show strong sulfidic conditions (inferred by the high Mo EFs, Fig.,
644 3C), and indicate that these conditions were not unprecedented.

645

646 **6.2.2 Rhenium-molybdenum ratios**

647

648 The Re/Mo ratio can potentially be used to distinguish between suboxic and sulfidic
649 conditions in the sediments given the different behavior of Re and Mo under reducing
650 conditions (Crusius et al., 1996). Sediments that are enriched in Re and/or Mo with a Re/Mo
651 ratio higher than the seawater ratio ($0.4 \text{ ng.}\mu\text{g}^{-1}$) were deposited under suboxic conditions,
652 while Re/Mo ratios equal to or less than the seawater value were deposited under sulfidic
653 conditions (Crusius et al., 1996). However, interpretations derived from Re/Mo ratios should
654 be taken with caution, for example Re and Mo accumulations from a core retrieved from the
655 OMZ in the Eastern Tropical North Pacific suggested anoxic conditions, but Re/Mo ratios
656 suggested intermediate reducing conditions (Nameroff et al., 2002). Thus, Re/Mo ratios
657 should be used in combination with other redox sensitive proxies to infer past reducing
658 conditions (Nameroff et al., 2002; Morford et al., 2005).

659

660 The interpretations from the Re/Mo record are strikingly concordant with those
661 derived from the Mo EF and the Mo/U ratio (Fig. 3E). High Re/Mo ratios (and relatively low

662 Mo and Re EFs), indicative of suboxic conditions, characterize the Early Glacial and LGM,
663 which is also in agreement with the poor laminae preservation and low Mo/U ratios (Fig. 3B
664 and D). The start of the H1S showed a Re/Mo decline to ratios below the seawater ratio and
665 then a trend towards increased values until the end of the ACR, interrupted by low values
666 around ~15.4 kyr BP (Table SM2). The relatively high Re/Mo ratios from ~16.5 to 13.5 kyr
667 BP, indicative of suboxic conditions, is consistent with relatively low Mo EFs and Mo/U
668 ratios. On average, the Early (0.9 ± 0.3) and Late Holocene (0.3 ± 0.1) showed lower Re/Mo
669 ratios compared to the recorded part of the mid-Holocene (1.2 ± 0.3). The high Re/Mo ratios
670 during the mid-Holocene suggests more reducing conditions compared to the Early Glacial
671 and LGM, but less reducing conditions compared to the H1S, and parts of the Early and Late
672 Holocene, as also suggested by the $(\text{Mo}/\text{U})_{\text{auth}}$ ratios (Fig. 3D).

673

674 The combined evidence from the lithology of the record, Mo EFs and Mo/U records
675 (Fig. 3) support the use of Re/Mo to distinguish between suboxic and sulfidic conditions in
676 sediments from the ETSP. While the Mo/U systematics has been commonly used to
677 distinguish between suboxic and sulfidic conditions (e.g., Algeo and Tribovillard, 2009;
678 Scholz et al., 2014), only a few studies have used the Re/Mo systematics for this purpose
679 (e.g., Salvatucci et al., 2014b). The use of Re/Mo systematics is promising because Re and
680 Mo show the highest degree of enrichment in reducing sediments relative to crustal values in
681 the ETSP, as well as and in other reducing settings (Crusius et al., 1996; Nameroff et al.,
682 2002; Böning et al., 2004). The signal is best-preserved when buried rapidly (Crusius et al.,
683 1996), and it appears that Re accumulation in sediments is solely due to the extent of
684 reducing conditions (Morford et al., 2005).

685

686

687 **6.2.3 Coupling-decoupling between water column denitrification and sediment redox** 688 **conditions**

689

690 The large changes in the intensity of water column and benthic redox conditions
691 showed a similar pattern during most of the record except from the ACR, indicating a strong
692 coupling between water column denitrification and sediment redox conditions (Fig. 3). The
693 weak water column denitrification (Fig. 3A) during the Early Glacial and the LGM is
694 consistent with the suboxic conditions inferred from the Mo EF, the Mo/U and the Re/Mo
695 ratio, and the banded nature of the sediments (Fig. 3B to E). During the Holocene, the $\delta^{15}\text{N}$
696 (Fig. 3A) and the Re/Mo ratios (Fig. 3D) are strongly correlated ($r=-0.74$, $n=153$, $p<0.005$),

697 implying a strong coupling between water column denitrification and sediment redox
698 conditions. The more laminated nature of the sediments during the Early and Late Holocene
699 and the presence of bands and more homogeneous sediments during the mid-Holocene (Fig.
700 3B) are also consistent with the $\delta^{15}\text{N}$ values, and the Mo/U and Re/Mo ratios. In general, this
701 implies a strong coupling between water column denitrification and benthic redox conditions
702 during the Early Glacial, LGM, and the Holocene. By contrast, the strong water column
703 denitrification during the ACR (Fig. 3A) is clearly opposed to the less reducing conditions in
704 the sediments (Fig. 3B to E) inferred from the lithology and the redox sensitive metals,
705 indicating a decoupling between water column denitrification and benthic sediment redox
706 conditions. Taken together, the proxies indicate a stronger OMZ during the H1S, Early and
707 Late Holocene, and a weaker OMZ during the glacial periods and during the mid-Holocene
708 (Fig. 3). During the ACR, the decoupling between water column denitrification and sediment
709 redox conditions suggests a strong but shallow OMZ.

710

711 **6.2.4 Export production changes and coupling-decoupling between productivity and** 712 **oxygenation**

713

714 Nickel has recently been recognized as an indicator of the organic sinking flux in
715 sediments from upwelling regions (Böning et al., 2015). It has been shown that Ni 1) is
716 associated with enzymes involved in photoautotrophic production, and 2) is a proxy for the
717 original chlorophyll flux to the sediments (Böning et al., 2015). The strong correlation ($r^2 >$
718 0.80) between Ni with TOC in organic-rich sediments from upwelling systems of Peru,
719 Namibia, Chile and from the Gulf of California suggests that Ni is a clear indicator of the
720 organic sinking flux (Böning et al., 2004; 2015). The preferential preservation of Ni over
721 TOC in Peru sediments strongly supports paleo-productivity estimates based on Ni EFs
722 (Tribovillard et al., 2006; Böning et al., 2015). In this sense, Ni is a better indicator of export
723 production than Cu because Ni is less affected by secondary overprints related to sulfur
724 cycling (Böning et al., 2015). Nickel EFs are likely to represent the original presence of
725 organic matter even if it is partially lost after deposition (Tribovillard et al., 2006), as likely
726 occurred in several samples of our composite record associated with poor organic matter
727 preservation (Fig. 2I).

728

729 The export production, represented by the Ni EF, showed a similar pattern to other
730 redox sensitive proxies throughout the record: lower values during the last glacial-interglacial

731 transition and high values (with high temporal variability) during the Holocene (Fig. 3F).
732 Very low export production characterized the Early Glacial and the LGM. The start of the
733 H1S (17–18 kyr BP) showed a small increase in productivity compared to the earlier periods,
734 but from 17–14.5 kyr BP export production was low and comparable to the Early Glacial and
735 the LGM. In some samples of the Early Glacial and LGM, Ni and especially Cu were
736 depleted relative to andesite (Fig. 2F and G), but this is likely to be a result from the masking
737 of the non-lithogenic metal component by rather high lithogenic metal concentrations (Table
738 SM1; Böning et al., 2015). The Early Holocene and mid-Holocene were characterized by
739 higher export production compared to the last glacial-interglacial transition. During the Early
740 Holocene, the export production did not show the strong multi centennial-scale variability
741 observed during the Late Holocene. Finally, from ~4 kyr BP to the present, a positive trend
742 towards higher export production with strong multi-centennial scale variability is observed
743 (Fig 3F).

744

745 Oxygen demand as a result of local export production exerted a strong signal in water
746 column denitrification and sedimentary redox conditions in the ETSP-OMZ; however, in the
747 case of several remarkable exceptions the regional signal (i.e. remote factors) dominated the
748 record (Fig. 3). Export production, as inferred by Ni EFs, was strongly coupled with water
749 column denitrification during the ACR ($r=0.69$, $n=13$), Early Holocene ($r=0.70$, $n=35$), and
750 Late Holocene ($r=0.69$, $n=83$), but not during the Early Glacial ($r=0.32$, $n=19$), LGM ($r=0.28$,
751 $n=18$), the H1S ($r=0.24$, $n=65$), and the mid-Holocene ($r=0.27$, $n=35$). These findings suggest
752 that the original $\delta^{15}\text{N}$ signal of the water masses reaching the ETSP during the Early Glacial,
753 LGM, H1S, and mid-Holocene was not significantly modified by the effect of local export
754 production. By contrast, during the ACR, Early Holocene and Late Holocene, oxygen
755 demand as a result of local export production, likely exerted a strong impact on the $\delta^{15}\text{N}$
756 signal. Additionally, export production and benthic oxygenation (indicated by the Re/Mo
757 ratio) were coupled during the Early Holocene ($r=0.57$, $n=35$) and Late Holocene ($r=0.58$, n
758 $=118$), but not during the Early Glacial ($r=0.32$, $n=19$), LGM ($r=0.47$, $n=18$), H1S ($r=0.4$,
759 $n=65$), the ACR ($r=0.07$, $n=13$), and the mid-Holocene ($r=0.32$, $n=61$). These results indicate
760 that during the Early and Late Holocene, export production, water column denitrification, and
761 sediment redox conditions were strongly coupled; the high export production likely exerted a
762 strong influence on the water column denitrification and benthic redox conditions. By
763 contrast, during the LGM, H1S, ACR, and mid-Holocene, remote factors may have
764 controlled water column denitrification and sediment redox conditions.

765

766 **6.3 High latitude processes driving oxygenation changes during glacial times and the** 767 **deglaciation**

768

769 The good match among low $\delta^{15}\text{N}$ values, lack of laminae preservation, low Mo EFs,
770 low Mo/U and high Re/Mo ratios provides very strong evidence of low denitrification in the
771 water column and less reducing conditions in the surface sediments, implying a weaker OMZ
772 during the Early Glacial and the LGM (Fig. 5A and B). These results are in agreement with
773 $\delta^{15}\text{N}$ records along the Central and South American margin between 15°N and 36°S, which
774 suggest weak water column denitrification and thus a weaker OMZ during the glacial periods
775 (Robinson et al., 2007; 2009; Martinez and Robinson, 2010). Reduced water column
776 denitrification during the glacial periods is attributed to reduced upwelling, decreased export
777 productivity, and consequently to a lower oxygen demand along the continental margin of the
778 Americas (Ganeshram et al., 2000). This is in agreement with our record of export production
779 (Fig. 5C), reinforcing the idea of low productivity and thus lower oxygen demand, with a
780 negligible signal on water column denitrification. Additionally to the reduced upwelling, the
781 lower surface temperature during glacial stages increased oxygen solubility, while stronger
782 winds in high-latitude regions enhanced the rate of thermocline ventilation (Galbraith et al.,
783 2004). Moreover, sediment redox metals in sediment cores off Chile (e.g., core ODP-1235,
784 Fig. 1B) indicate relatively high pore-water oxygen concentrations during glacial intervals
785 (Fig. 5D; Muratli et al., 2010; Chase et al., 2015); this implies a weak OMZ in the ETSP
786 during glacial times and consistent with our findings.

787

788 The decoupling between water column denitrification and sediment redox conditions
789 during the ACR periods suggests that an extra-tropical process was responsible for
790 oxygenation of the bottom waters. A possible explanation for the less reducing conditions
791 during the ACR was an increase in flow of the Antarctic Intermediate Water (AAIW), which
792 is characterized by high O_2 values (Fig. 1B). The AAIW is a dominant southern hemisphere
793 water mass that spreads from its formation regions north from the Antarctic Circumpolar
794 Current to at least 20°S into all oceans (Schmidtko and Johnson, 2012); however, it was
795 hypothesized that during the deglaciation the AAIW penetrated much further northward than
796 today (Marchitto et al., 2007, Basak et al., 2010). The increase in AAIW flow was likely
797 produced by an increase in Southern Ocean upwelling during the Termination 1 period as
798 demonstrated by enhanced diatom productivity in the Southern Ocean (Fig. 5E; Anderson et

799 al., 2009). This enhanced upwelling in the Southern Ocean coincided with the deglacial
800 warming in Antarctica and the rise in atmospheric CO₂ (Anderson et al., 2009). Radiogenic
801 isotope compositions of neodymium from a sediment core collected off Baja California also
802 showed an AAIW signal during the H1S and ACR (Fig. 5F; Basak et al., 2010), supporting
803 the hypothesis of an AAIW strengthening during these periods. Our record is consistent with
804 the hypothesis of an increase in AAIW flow: it appears that during the Termination 1 period,
805 the ETSP-OMZ was strong, as evidenced by our $\delta^{15}\text{N}$ record (Fig. 5A) and several other $\delta^{15}\text{N}$
806 records (e.g., Higginson and Altabet, 2004; Martinez et al., 2006; Galbraith et al., 2013;
807 Jaccard and Galbraith, 2013). However, during part of the Termination 1 period, the sediment
808 floor in the ETSP-OMZ was in contact with relatively more oxygenated water, indicating that
809 the OMZ was shallower than at present. The lower boundary of the OMZ was located at a
810 depth of at least 350 meters, taking into account the sea level changes at those time periods
811 and the present position of core G14 (Fig. 1B).

812

813 **6.4 Factors controlling oxygenation and productivity changes in the ETSP during the** 814 **Holocene**

815

816 We hypothesize that the enhanced oxygenation of the ETSP-OMZ during the mid-
817 Holocene (Fig. 5A and B) was produced by an intensification of the equatorial subsurface
818 countercurrents (EUC, SICC and SSCC, Fig. 1A) that brought more oxygenated waters to
819 Western South America. At present the secondary SSCC carries a water mass with low $\delta^{15}\text{N}$
820 ($5.5\pm 0.3\text{‰}$; Rafter et al., 2012), which is very similar to the $\delta^{15}\text{N}$ values during the mid-
821 Holocene ($6\pm 0.8\text{‰}$, Fig. 5A). A potential mechanism that would explain the intensification
822 of the equatorial subsurface countercurrents could be related to a strengthening of the Walker
823 circulation during the Early and mid-Holocene. The Walker circulation strengthening was a
824 result of an enhanced zonal SST gradient across the tropical Pacific from 9 to 5 kyr BP
825 (Koutavas et al., [2006]; see Fig. 1A). Moreover, a more northerly position of the ITCZ in the
826 eastern Pacific during the mid-Holocene (Mollier-Vogel et al., 2013) may have favored more
827 permanent southeast trades and promoted increased upwelling in the Eastern Tropical Pacific
828 (Koutavas et al., 2006). During the mid-Holocene, the Southern westerlies were situated in a
829 poleward position (Lamy et al., 2001; Jenny et al., 2002), suggesting an expanded South
830 Pacific Anticyclone (SPA) and a strengthening of the Hadley circulation, which resulted in
831 strong alongshore winds off Peru. Thus, as a result of a stronger Walker circulation, the
832 subsurface equatorial currents accelerated mainly due to sea level differences in the western

833 and eastern Pacific. Moreover, stronger alongshore coastal winds, as a result of increased
834 trade winds, may also have contributed to the oxygenation of the upper layers of the water
835 column by enhanced vertical mixing, which resulted in a weakening of the OMZ.

836

837 Indirect evidence based on the lithology of multiple sediment cores retrieved off Peru
838 support the hypothesis of a stronger PUC during the Early and mid-Holocene. Multiple
839 sediment cores that contained Holocene sequences retrieved along the Peruvian margin show
840 winnowed sequences and temporal gaps from ~3 to ~8 kyr BP (Reinhardt et al., 2002;
841 Skilbeck et al. 2006; Makou et al., 2010; Schönfeld et al., 2015). For example, sediment cores
842 1229E, 106KL, and 1228D from the central-Peruvian shelf (Fig. 1B), retrieved between 150
843 and 250 meters depth, show low sediment accumulation during the mid-Holocene. By
844 contrast, the sediment cores used in the present work and another core taken at 15°S (Fig. 1B;
845 Chazen et al., 2009), all from deeper depths, do not show large gaps during the mid-
846 Holocene. Currently, the core of the PUC between 9 °S and 15 °S is centered inshore of the
847 shelf break in contact with the sediment floor, whereas south from 15°S the PUC core is
848 detached from the slope (Chaigneau et al., 2013). During the mid-Holocene the PUC was
849 likely more intense than today and eroded sediment sequences in the central and northern part
850 of the Peruvian margin. Thus, the evidence suggests a stronger PUC during the globally
851 warm mid-Holocene probably reinforced by the strengthening of the equatorial
852 undercurrents.

853

854 By contrast, the Late Holocene is characterized by a strong yet temporally variable
855 OMZ. This can be partially explained by a reduction of the SST gradient (Koutavas et al.,
856 2006) and a reduced influence of the equatorial undercurrents. Around 4 kyr BP, the eastern
857 Pacific started to warm while the western Pacific warm pool experienced a cooling of
858 comparable magnitude, marking the transition to a climate regime more typical of present day
859 conditions (Koutavas et al., 2006). The strong centennial-scale variability of productivity and
860 oxygenation during the last 4 kyr may have been the result of more subtle changes in the
861 expansion/contraction of the SPA and the strength of the Walker circulation (Salvatteci et al.,
862 2014b) compared to the changes observed during the mid-Holocene. The position of the
863 Southern Hemisphere westerlies, and thus the southern boundary of the SPA, is thought to be
864 partially controlled by changes in solar forcing, with higher (lower) solar activity producing a
865 poleward (equatorward) shift of the annual mean westerlies (Varma et al., 2011). A SPA
866 expansion during the global warm periods (e.g. MCA and CWP) drove an increase in

867 upwelling off Peru of low oxygen and high nutrient waters, promoting productivity, and
868 finally consuming oxygen in the water column from the decay of organic matter (Salvatteci et
869 al., 2014b). The increasing trend of productivity during the last ~4 kyr probably resulted from
870 an increase in insolation (Fig. 5C). Currently, the productivity off Peru is higher in summer
871 and spring when the water column is more stratified (Gutierrez et al., 2011), thus an increase
872 in spring-summer insolation may have promoted productivity. The observed increase in
873 centennial scale variability in OMZ intensity and export production during the Late Holocene
874 is consistent with other climate reconstructions from the Eastern tropical Pacific indicating a
875 more variable Eastern Tropical Pacific in the Late Holocene (Moy et al., 2002; Koutavas et
876 al., 2006; Conroy et al., 2008; Chazen et al., 2009).

877

878 **6.5 Implications of the present study**

879

880 The combined results of this work and from the literature suggest a weaker OMZ and
881 a less productive Peruvian upwelling ecosystem in a warmer world. While the stronger
882 Walker circulation in the Tropical Pacific during the mid-Holocene is not an ideal analogue
883 to present global warming due to different forcing it can be seen as a potential future
884 scenario. The mid-Holocene (also known as Holocene Climatic Optimum) was a period of
885 high temperature in the northern hemisphere in response to high latitude orbital forcing. This
886 was reflected in the Tropical Pacific in a stronger Walker circulation produced by a strong
887 SST zonal gradient 1.5 °C higher than today (Koutavas et al., 2006). Reservoir ages and
888 coastal SSTs off Peru suggest that the coastal upwelling intensity off Peru was stronger
889 during the mid-Holocene than during the modern La Niña phases (Carré et al., 2012),
890 however the stronger upwelling did not produce higher productivity. Additionally, a stronger
891 Walker circulation during the mid-Holocene probably intensified the equatorial subsurface
892 countercurrents, bringing oxygen-rich waters to intermediate depths in the ETSP. This
893 observation is at odds with climate models that predict that oceanic dissolved oxygen decline
894 will continue in the future (Keeling et al., 2010).

895

896 Increasing evidence suggests that during the past few decades the Walker circulation
897 strengthened (Luo et al., 2012; L'Heureux et al., 2013) and the SPA intensified (Falvey and
898 Garreaud, 2009). Moreover, observational data and paleoceanographic reconstructions
899 suggest a strengthening in wind intensity in eastern boundary upwelling systems (Bakun,
900 1990; Vargas et al., 2007; Gutierrez et al. 2011). While the current environmental

901 configuration in the Peru-Chile Upwelling Ecosystems are ideal for marine productivity, it
902 appears that further warming will drive the Peruvian upwelling ecosystem out of the current
903 “sweet spot” (Bakun and Weeks, 2008), with profound effects on society and economy. The
904 large changes in OMZ intensity at different timescales during the last 25 kyr BP, triggered by
905 both local and remote forcings, suggest that the decrease in oxygen observed during the last
906 ~50 years is not unprecedented when compared to the geological record. Conclusive
907 statements about the response of the biota to future OMZ intensification could be done by
908 evaluating the response of the communities to past changes in oxygenation.

909

910 **7. CONCLUSIONS**

911

912 Water column denitrification and sediment redox conditions show large changes
913 during the last 25 kyr, making the current oxygenation levels in the last 50 years in the ETSP-
914 OMZ not unprecedented. Global cold periods during the LGM (23 to 19 kyr BP) and the LIA
915 (1500 to 1850 AD) are generally associated with a weak OMZ, while warm intervals such as
916 the deglaciation, part of the MCA and the last 100 years are associated with a stronger OMZ.
917 The presence of sulfidic conditions in the sediments, as observed for the last 50 yr, is not a
918 unique feature for the current warm period since it was sporadically observed in the record
919 associated with high export production levels.

920

921 Extra-tropical forcings and equatorial climate variability were the major drivers of
922 the subsurface ventilation and productivity off Peru during the last 25 kyr. Changes in
923 oxygenation in the sediment-water interface and the water column were strongly coupled
924 during the last 25 kyr BP with a remarkable exception during part of the last deglaciation.
925 The results indicate that remote forcings from high latitudes and changes in equatorial
926 dynamics regulated directly or indirectly the intensity and vertical/horizontal extension of the
927 OMZ.

928

929 The weak ETSP-OMZ during the mid-Holocene is not an ideal analogue for present
930 global warming but it can be seen as a potential future scenario. An expanded SPA and a
931 stronger Walker Circulation during the mid-Holocene produced stronger upwelling off Peru
932 but did not favor productivity. Additionally, a stronger Walker circulation during the warm
933 mid-Holocene probably intensified the equatorial undercurrents, bringing oxygen-rich (and
934 hence nutrient-poor) waters to intermediate depths off Peru dampening productivity.

935 Observational data from the last few decade suggest a strengthening of the Walker
936 circulation, an expansion of the SPA and increased alongshore winds off Peru. While the
937 current environmental configuration in the Peru-Chile Upwelling Ecosystems are ideal for
938 marine productivity, further warming may reduce productivity in the Peruvian Upwelling
939 Ecosystem with profound effects on society and economy.

940

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960

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

R. Salvatelli^{1,2*}; D. Gutierrez^{3,4}; A. Sifeddine^{1,5}; L. Ortlieb¹; E. Druffel⁶; M. Boussafir⁷; R. Schneider²

Tables

Table 1. Average and standard deviation of the proxies developed in the composite record separated by time intervals of interest. The current warm period comprises the last 100 years.

	Current period	Warm	Late Holocene	Mid-Holocene	Early Holocene	Antarctic reversal	cold	Heinrich Stadial	1	Last Maximum	Glacial	Early glacial
TOC (%)	6.6	± 1.7	5.8 ± 0.9	5.3 ± 1.1	4.5 ± 0.6	3.7 ± 0.7	3.0 ± 0.4	2.2 ± 0.4	2.2 ± 0.5			
TOC/Al	3.1	± 0.36	1.4 ± 0.49	1.2 ± 0.36	0.9 ± 0.19	0.6 ± 0.12	0.6 ± 0.15	0.4 ± 0.1	0.3 ± 0.1			
HI (mg.HC.g-1 TOC)	472	± 17	427 ± 34	428 ± 26	427 ± 25	400 ± 31	400 ± 38	305 ± 21	300 ± 28			
δ¹⁵N (‰)	8.4	± 0.9	6.4 ± 1.0	5.8 ± 0.7	7.2 ± 0.8	9.2 ± 0.9	9.3 ± 1.2	5.2 ± 0.4	5.0 ± 0.8			
Al (%)	2.1	± 0.8	4.5 ± 1.2	4.6 ± 1.2	4.9 ± 1.0	6.4 ± 0.3	5.5 ± 1.0	5.9 ± 0.5	6.4 ± 0.6			
Nixs (mg/kg)	47.0	± 9.6	60.6 ± 16.2	57.3 ± 10.6	57.3 ± 9.8	41.4 ± 13.3	28.9 ± 5.6	19.8 ± 9.0	12.5 ± 8.3			
Cuxs (mg/kg)	26.5	± 10.2	24.7 ± 6.3	25.1 ± 3.3	23.8 ± 4.8	13.0 ± 4.4	12.9 ± 5.0	11.5 ± 5.3	8.2 ± 6.1			
Moxs (mg/kg)	74.8	± 4.3	43.5 ± 19.7	34.6 ± 5.8	45.8 ± 11.6	16.8 ± 4.1	21.4 ± 7.3	15.1 ± 5.4	21.8 ± 8.6			
Uxs (mg/kg)	nd	± nd	11.1 ± 3.6	10.9 ± 2.2	9.7 ± 2.3	8.8 ± 2.5	5.0 ± 1.7	6.8 ± 1.3	8.3 ± 1.8			
Rexs (ug/Kg)	24.7	± 7.4	39.2 ± 10.4	40.6 ± 9.9	36.5 ± 8.7	28.8 ± 5.7	19.2 ± 3.7	21.0 ± 3.9	21.8 ± 4.0			
Mo/U	nd	± nd	4.3 ± 2.0	3.3 ± 0.7	5.0 ± 1.8	2.0 ± 0.3	4.5 ± 1.5	2.2 ± 0.6	2.7 ± 1.2			
Re/Mo	0.3	± 0.1	1.1 ± 0.5	1.2 ± 0.3	0.9 ± 0.3	1.7 ± 0.2	1.0 ± 0.3	1.5 ± 0.3	1.1 ± 0.3			
EF Ni	8.9	± 1.1	5.9 ± 2.8	5.2 ± 1.4	4.7 ± 1.0	2.6 ± 0.9	2.2 ± 0.6	1.3 ± 0.6	0.8 ± 0.6			
EF Cu	2.8	± 0.5	1.4 ± 0.7	1.4 ± 0.6	1.2 ± 0.4	0.5 ± 0.2	0.6 ± 0.3	0.5 ± 0.3	0.3 ± 0.2			
EF Mo	151.4	± 47.8	45.4 ± 33.3	33.5 ± 16.7	40.3 ± 18.5	10.4 ± 3.0	16.6 ± 8.6	10.4 ± 5.0	14.1 ± 7.0			
EF U	nd	± nd	8.0 ± 4.0	7.6 ± 3.0	6.0 ± 1.8	4.0 ± 1.2	2.8 ± 1.1	3.4 ± 0.9	3.9 ± 1.0			
EF Re	614	± 113	478 ± 153	477 ± 114	391 ± 68	234 ± 57	186 ± 40	187 ± 49	180 ± 42			

Table 2. Pearson coefficient correlation matrix for total organic carbon, $\delta^{15}\text{N}$, authigenic metals in the composite record B14-G10-G14. The asterisks replace values derived from two categories that share the same data (e.g. Re_{xs} and Re/Mo). The probability level was corrected for multiple comparisons by dividing the probability level α ($p < 0.05$) by the number of tests (10) performed (Glantz 2002). Boldface indicate significant values after correcting for multiple comparisons ($p < 0.005$).

	TOC (%)	HI (mg.HC.g ⁻¹ TOC)	$\delta^{15}\text{N}$ (‰)	Al (%)	Nixs (mg/kg)	Cuxs (mg/kg)	Moxs (mg/kg)	Uxs (mg/kg)	Rexs (ug/Kg)	Mo/U	Re/Mo
TOC (%)	1										
HI (mg.HC.g ⁻¹ TOC)	0.68	1									
$\delta^{15}\text{N}$ (‰)	-0.23	0.37	1								
Al (%)	-0.40	-0.63	-0.15	1							
Nixs (mg/kg)	0.90	0.71	-0.14	-0.43	1						
Cuxs (mg/kg)	0.84	0.67	-0.24	-0.56	0.83	1					
Moxs (mg/kg)	0.62	0.57	0.03	-0.60	0.67	0.69	1				
Uxs (mg/kg)	0.71	0.35	-0.45	-0.25	0.65	0.65	0.54	1			
Rexs (ug/Kg)	0.87	0.46	-0.44	-0.15	0.82	0.74	0.54	0.78	1		
Mo/U	0.08	0.41	0.43	-0.46	0.17	0.21	*	*	-0.10	1	
Re/Mo	0.01	-0.31	-0.35	0.54	-0.06	-0.21	*	0.03	*	*	1

Table 3. Pearson coefficient correlation matrix for normalized total organic carbon, HI, $\delta^{15}\text{N}$, and enrichment factors in the composite record B14-G10-G14. Correlations were calculated only in samples where all the proxies were measured (n= 264; see Table SM2). The asterisks replace values derived from two categories that share the same data (e.g. EF Re_{auth} and Re/Mo). The probability level was corrected for multiple comparisons by dividing the probability level α (p<0.05) by the number of tests (9) performed (Glantz 2002). Boldface indicate significant values after correcting for multiple comparisons (p<0.0056).

	TOC/AI	HI (mg.HC.g- 1 TOC)	$\delta^{15}\text{N}$ (‰)	EF Ni	EF Cu	EF Mo	EF U	EF Re	Mo/U	Re/Mo
TOC/AI	1									
HI (mg.HC.g-1 TOC)	0.69	1								
$\delta^{15}\text{N}$ (‰)	-0.06	0.37	1							
EF Ni	0.94	0.71	-0.03	1						
EF Cu	0.93	0.64	-0.06	0.90	1					
EF Mo	0.81	0.54	0.08	0.83	0.85	1				
EF U	0.86	0.50	-0.18	0.80	0.84	0.77	1			
EF Re	0.91	0.64	-0.25	0.89	0.84	0.71	0.83	1		
Mo/U	0.27	0.41	0.43	0.33	0.33	*	*	0.14	1	
Re/Mo	-0.29	-0.31	-0.35	-0.31	-0.40	*	-0.27	*	*	1

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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FIGURES

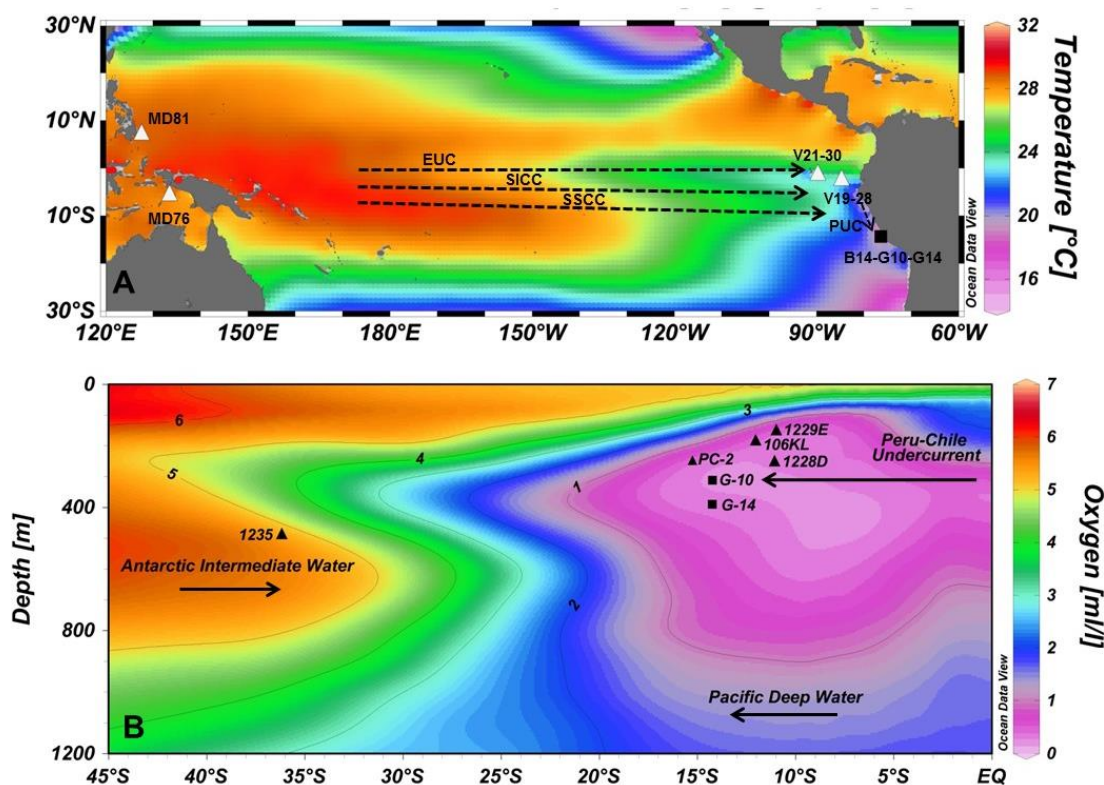


Figure 1. A) Sea surface temperature plot over the Tropical Pacific showing locations of cores (B14, G10, G14) used in this study (black square) and cores from other studies (white triangles V21-30 and V19-28 (Koutavas et al., 2006); MD76 and MD81 (Stott et al., 2004)). Cores V21-30, V19-28, MD76 and MD81 were used by Koutavas et al., (2006) to infer the SST gradient across the Tropical Pacific during the Holocene. Discontinuous lines indicate the main tropical undercurrents: Equatorial undercurrent (EUC), South Intermediate current (SICC) and Southern subsurface countercurrents (SSCC) and the Peru-Chile Undercurrent (PUC). B) Dissolved oxygen content in a meridional transect along 85°W, showing the principal water masses and the position of the cores. Black squares are our cores (G10 and G14), black triangles are cores of published data we discuss in the present study: ODP site 1235 (Muratli et al., 2010); PC-2 (Chazen et al., 2009); ODP 1229E (Contreras et al., 2010); ODP 1228D (Makou et al., 2010); 106KL (Rein et al., 2005).

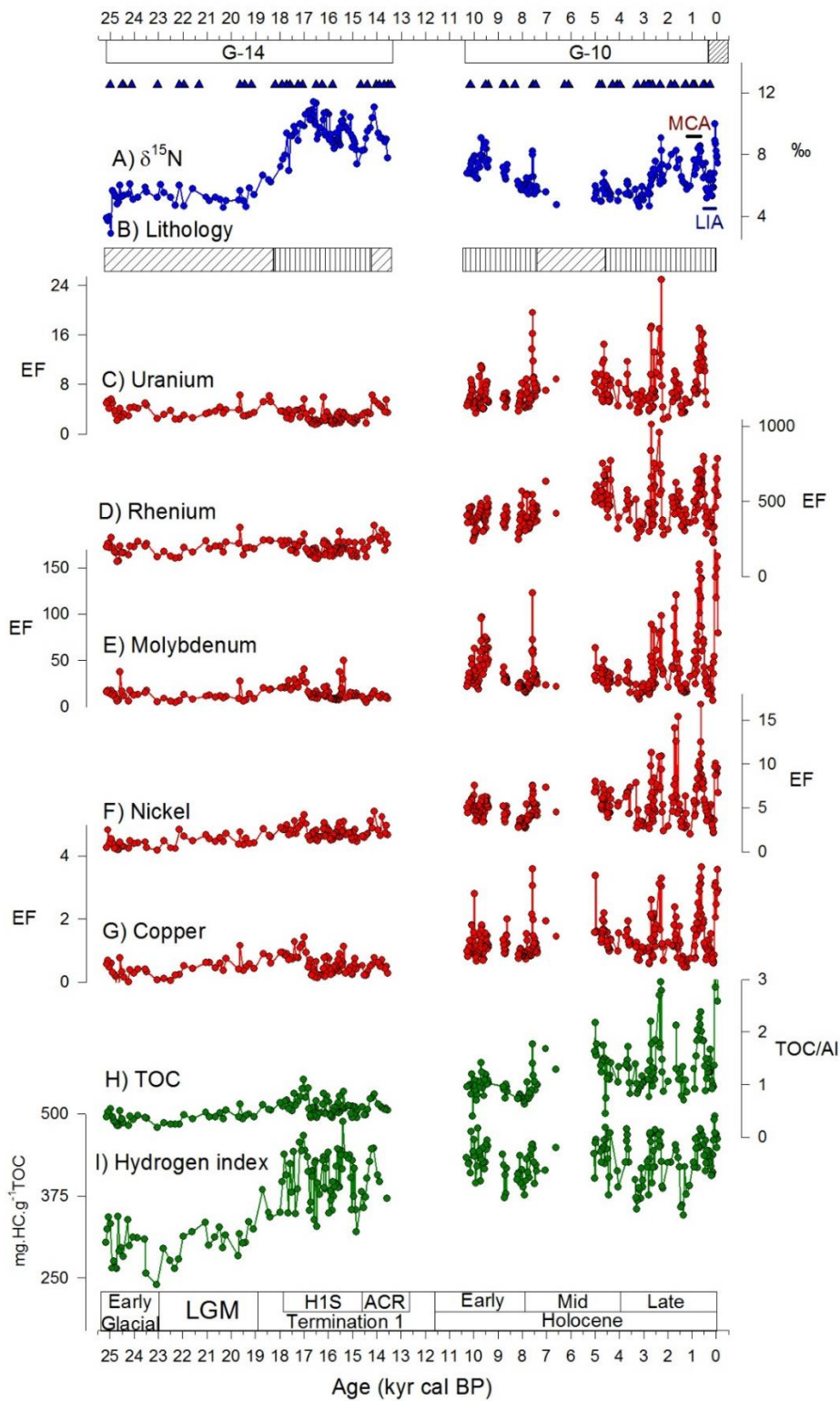


Figure 2. Stacked record assembled using cores B14, G10 and G14 showing proxies for water column denitrification, benthic redox conditions and export production during the last 25 kyr BP. A) $\delta^{15}\text{N}$ as a proxy for water column denitrification, the blue triangles indicate the position of the ^{14}C ages. B) Simplified lithology of the core showing predominantly laminated sequences (vertical stripes) and banded sequences (diagonal stripes); see supplementary material for a detailed description. C) Authigenic Uranium enrichment factor (EF). D) Authigenic Rhenium EF. E) Authigenic Molybdenum EF. F) Authigenic Nickel EF. G) Authigenic Copper EF. H) Total organic carbon (TOC) normalized to Al. I) Hydrogen index as a proxy for organic matter preservation (mg.HC.g⁻¹ TOC). The acronyms used in this figure as follow: Last Glacial Maximum (LGM), Heinrich 1 Stadial (H1S), Antarctic Cold Reversal (ACR), Current Warm period (CWP). The boxes on top indicate the extent of each sediment core, the finely vertically striped box indicate the extent of core B-14.

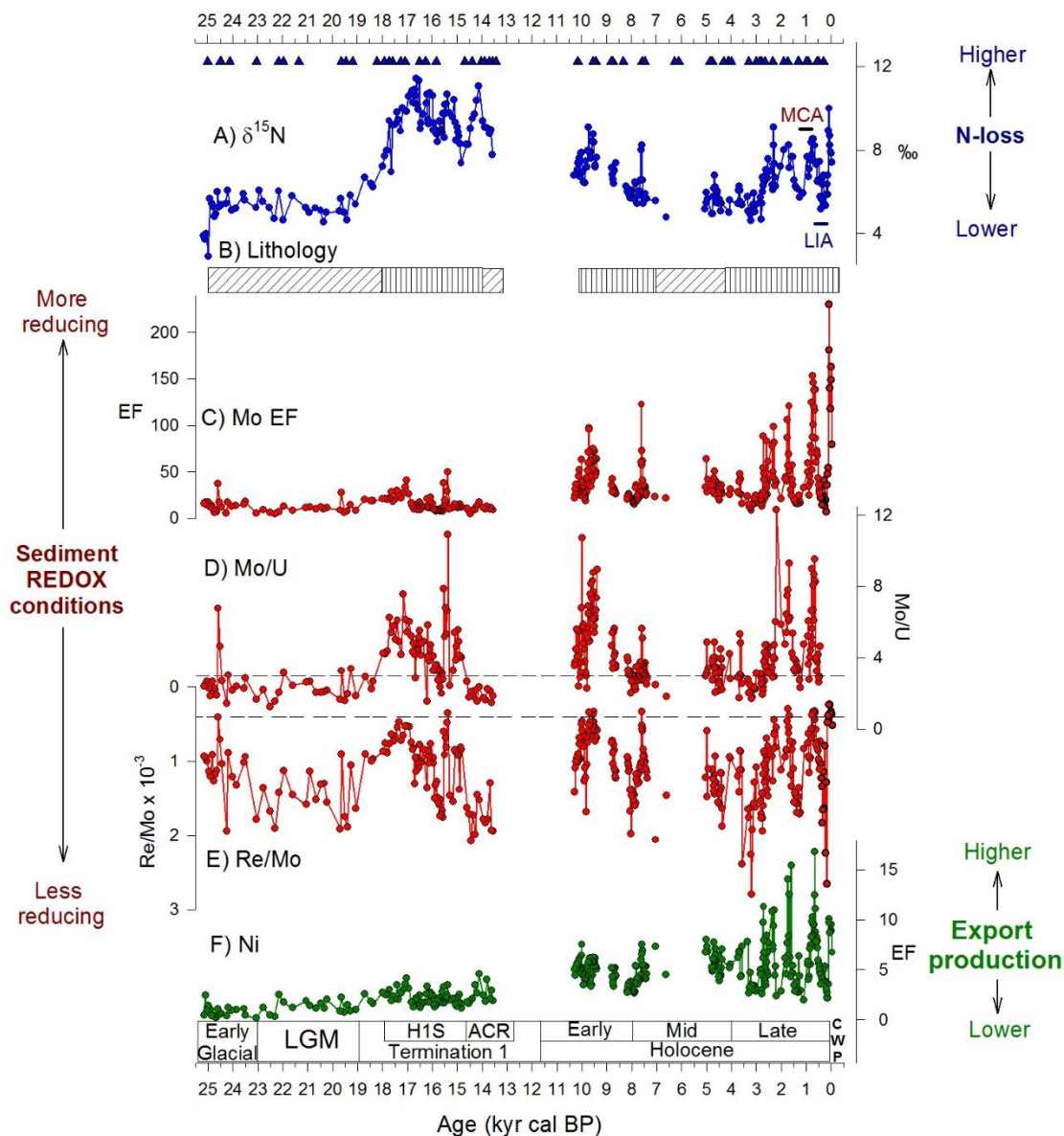


Figure 3. Stacked record assembled using cores B14, G10 and G14 showing proxies for water column denitrification, benthic redox conditions and export production during the last 25 kyr. A) $\delta^{15}\text{N}$ as a proxy for water column denitrification. B) Simplified lithology of the core showing predominantly laminated sequences (vertical stripes) and banded sequences (diagonal stripes); blue triangles indicate the position of the ^{14}C ages, see supplementary material for a detailed description. C) Molybdenum authigenic enrichment factor (EF) as proxy for benthic oxygenation. D) Authigenic Mo/U ratio as a proxy to infer anoxic from suboxic conditions. The discontinuous line indicate the value of 3.2 which correspond the Mo/U weight ratio in seawater, higher values than 3.2 indicate sulfidic conditions. E) Authigenic Re/Mo ratio (y-axis inverted), the horizontal dashed line indicates the value of 0.4×10^{-3} which corresponds to the ratio of the concentration of these metals in the sea-water (Crusius et al., 1996); values higher (equal or lower) than 0.4×10^{-3} indicate suboxic (sulfidic) conditions. F) Nickel EF as a proxy for export production. The acronyms listed as in Figure 2.

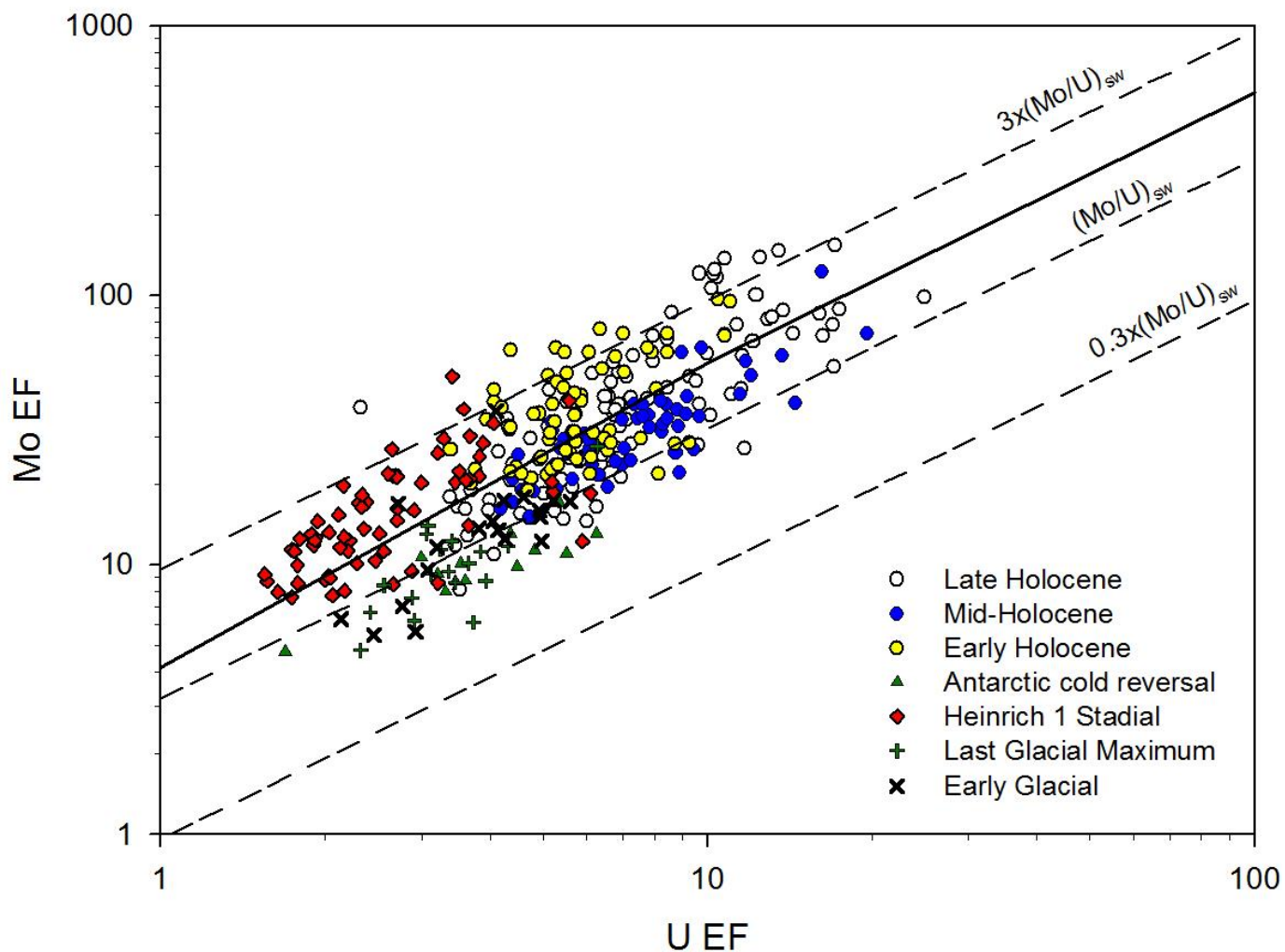


Figure 4. Cross plot of Mo enrichment factors versus U enrichment factors. The dashed lines indicate the relative proportion of Mo and U in seawater (weight ratio of $[\text{Mo}]_{\text{sw}}/[\text{U}]_{\text{sw}} = 3.2$) and to fractions thereof ($0.3x$ and $3x$). The solid line represents the linear regression of all the data set ($r^2 = 0.58$; $n=342$). The symbols indicate the different samples from the different periods of interest. Note the logarithmic scale of both axes.

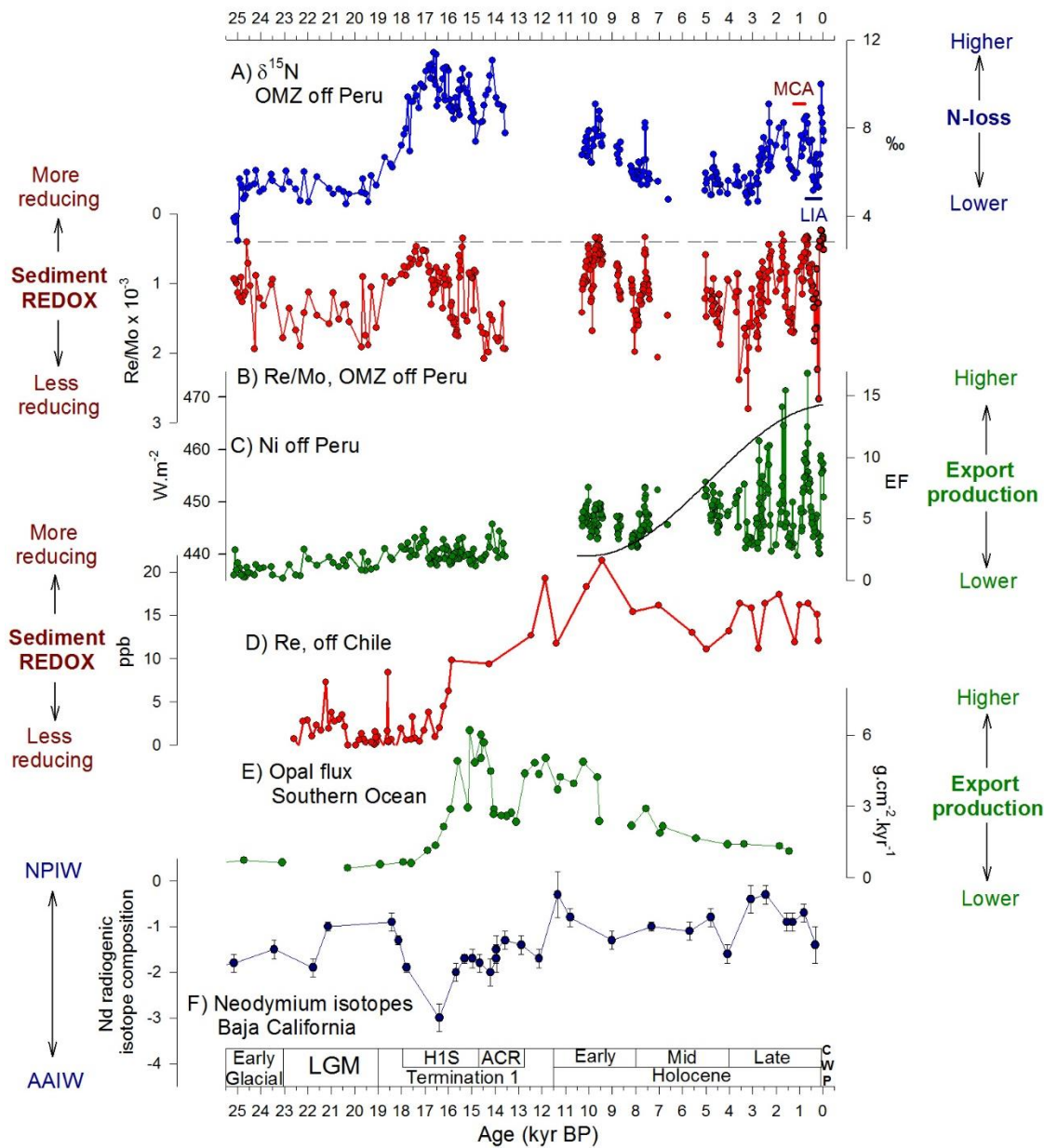


Figure 5. Comparison of OMZ intensity and export production in the Eastern Tropical South Pacific (ETSP) developed in the present study and other selected records from the literature. A) $\delta^{15}\text{N}$ as a proxy for water column denitrification. B) Authigenic Re/Mo ratio (y-axis inverted), the horizontal dashed line indicates the value of 0.4×10^{-3} which corresponds to the ratio of the concentration of these metals in the sea-water (Crusius et al., 1996). C) Export production in the ETSP as indicated by the Nickel EF. The continuous lines indicates the December to February insolation at 15°S (Berger et al., 1978). D) Authigenic Rhenium concentrations from a sediment core off Chile (Muratli et al., 2010), where low values imply better-oxygenated sediments. E) Opal flux from a sediment core taken in the Southern Ocean (Anderson et al., 2009). F) Neodymium radiogenic isotope composition from a sediment core taken in front of Baja California (Basak et al., 2010); indicating water mass variations at the Baja California site: North Pacific Intermediate Water (NPIW) and Antarctic Intermediate Water (AAIW). The acronyms listed as in Figure 2.