- 1 MANUSCRIPT NUMBER: Biogeosciences Discussions 11, 13343-13387, 2014
- 2 TITLE OF THE REVISED VERSION: Records of past mid-depth ventilation:
- 3 Cretaceous Ocean Anoxic Event 2 vs. Pleistocene to Holocene Oxygen Minimum Zones
- 4 Explanation of revisions -
- 5 Associate Editor (Christophe Rabouille), 18 Jan 2015
- 6 I wonder why the title contains reference to the Pleistocene (and not only the Holocene) as
- 7 the OMZ sediments from the Peru margin that you consider in your study are mostly from the
- 8 Holocene, aren't they? The point of your paper is to compare the OAE2 of the Cretaceous
- 9 with present characteristics of the OMZ, and it would be good to show it in your title. If the
- 10 reference to the Pleistocene is made to include the Last Glacial Maximum, then you could
- insert it in the title as well, but you'd better keep it simple.
- reply: Indeed, the majority of evidences for comparing the Cretaceous OAE2 with today's
- 13 OMZ comes from Holocene Peruvian Margin sediments. None-the-less, we refer to Last
- 14 Glacial and Deglaciation records of the last 20 kyr in several parts of the manuscript, in
- particular Figure 3. We also referred to Marine Oxygen Isotope Stage 3 and 11, both beyond
- the Last Glacial Maximum. Therefore, and in order to keep it simple, we decided to change
- 17 the title to "Records of past mid-depth ventilation: Cretaceous Ocean Anoxic Event 2 vs.
- Quaternary Oxygen Minimum Zones". Cretaceous and Quaternary are both Systems in earth's
- 19 history and thus on the same level of hirarchy in chronostratigraphic terms.
- 20 Line 21 of your abstract (page 1), you say that oxygen levels, flux of organic matter and
- benthic life are "well known". Please remove well known. There are controversy on the flux
- deposited and its fate in the sediment, and oxygen levels (at the nanomolar level) are still
- 23 questioned. You could replace by "well studied".
- 24 reply: done -
- Line 24 of abstract replace "were" by "are".
- 26 **reply**: done -
- page 17 line 14-19: a remark was made by reviewer 2 which was not answered in your reply
- on the "20% export flux", and if it applied at the time of OAE2. In your paper, you wrote a
- 29 "20% burial efficiency", and the reviewer was wrong in his remark but please provide more
- arguments in the text why this value was chosen for burial efficiency. Furthermore, when
- 31 dividing burial flux by burial efficiency, you obtain the deposition flux (or rain rate of organic

- carbon), which is different from the export flux. Please change export flux to deposition flux
- 2 (or rain rate).
- 3 reply: We referred to Figure 2 of Flögel et al. (2011) in the first revised version of the
- 4 manuscript, and perhaps this was too brief as explanation. In this Figure, the Holocene burial
- 5 rate of particulate organic carbon in continental margin sediments is plotted versus the rain
- 6 rate of particulate organic carbon at the sites given. The data showed a logarithmic
- 7 relationship, and there is no significant difference between oxygen minimum zones and well-
- 8 ventilated bottom waters. If you extrapolate, for instance a rain rate of 1000 mmol m⁻² yr⁻¹ to
- 9 the regression line, you obtain a corresponding burial rate of 200 mmol m⁻² yr⁻¹, hence about
- 10 20 %. However, Flögel et al. (2011) also provided the equation of the regression curve (burial
- rate = $0.14 * rain rate^{1.11}$) which yields a burial rate of 23 mmol m⁻² yr⁻¹ for a rain rate of 100
- mmol m⁻² yr⁻¹, i.e. 23 %. We therefore used the equation rather than a constant ratio of 0.2,
- and we explained this in the second revised version of the manuscript. The term export flux is
- changed to rain rate as well, because it is denominated in the equation that way.
- page 17 line 19-21: The meaning of the sentence (Therefore, it is conceivable...) is unclear
- to me, and its relation to the previous sentence also. Please clarify the link between "thick
- section of lamination" and "redeposition due to near-bottom turbulence".
- 18 reply: Core SO147-106KL represents ideal conditions. We intended to emphasize with this
- sentence that the other core sites from the Peruvian margin, where lower organic carbon
- accumulation rates prevailed, were probably subjected to winnowing. As we come back to
- 21 core SO147-106KL in the next sentence, this statement is unnecessary and misleading. We
- therefore omitted the sentence in the second revised version of the manuscript.

Reference

- 24 Flögel, S., Wallmann, K., Poulsen, C. J., Zhou, J., Oschlies, A., Voigt, S., Kuhnt, W.:
- 25 Simulating the biogeochemical effects of volcanic CO2 degassing on the oxygen-state of the
- deep ocean during the Cenomanian/Turonian Anoxic Event (OAE2), Earth Planet. Sci. Lett.,
- 27 305, 371-384, doi:10.1016/j.epsl.2011.03.018, 2011.

Records of past mid-depth ventilation: Cretaceous Ocean

2 Anoxic Event 2 vs. Pleistocene to Holocene Quaternary

Oxygen Minimum Zones

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Abstract

Present day oceans are well ventilated except mid-depth oxygen minimum zones (OMZs) 12 13 under high surface water productivity, regions of sluggish circulation, and restricted marginal 14 basins. In the Mesozoic, however, entire oceanic basins transiently became dysoxic or anoxic. 15 The Cretaceous Ocean Anoxic Events (OAEs) were characterised by laminated organic-16 carbon rich shales and low-oxygen indicating trace fossils preserved in the sedimentary record. Yet assessments of the intensity and extent of Cretaceous near-bottom water 17 18 oxygenation have been hampered by deep or long-term diagenesis and the evolution of 19 marine biota serving as oxygen indicators in today's ocean. Sedimentary features similar to 20 those found in Cretaceous strata were observed in deposits underlying Recent OMZs, where 21 bottom-water oxygen levels, the flux of organic matter, and benthic life are well knownstudied. Their implications for constraining past bottom-water oxygenation are 22 23 addressed in this review. We compared OMZ sediments from the Peruvian upwelling with 24 deposits of the late Cenomanian OAE 2 from the NW African shelf. Holocene laminated sediments were are encountered at bottom-water oxygen levels of <7 µmol kg⁻¹ under the 25 Peruvian upwelling and <5 µmol kg⁻¹ in California Borderland basins and the Pakistan 26 Margin. Seasonal to decadal changes of sediment input are necessary to create laminae of 27 28 different composition. However, bottom currents may shape similar textures that are difficult to discern from primary seasonal laminae. The millimetre-sized trace fossil Chondrites was 29

commonly found in Cretaceous strata and Recent oxygen-depleted environments where its diameter increased with oxygen levels from 5 to 45 μmol kg⁻¹. *Chondrites* has not been reported from Peruvian sediments but cm-sized crab burrows appeared around 10 μmol kg⁻¹, which may indicate a minimum oxygen value for bioturbated Cretaceous strata. Organic carbon accumulation rates ranged from 0.7 and 2.8 g C cm⁻² kyr⁻¹ in laminated OAE 2 sections in Tarfaya Basin, Morocco, matching late Holocene accumulation rates of laminated Peruvian sediments under Recent oxygen levels below 5 μmol kg⁻¹. Sediments deposited at >10 μmol kg⁻¹ showed an inverse exponential relationship of bottom-water oxygen levels and organic carbon accumulation depicting enhanced bioirrigation and decomposition of organic matter with increased oxygen supply. In absence of seasonal laminations and under conditions of low burial diagenesis, this relationship may facilitate quantitative estimates of paleo-oxygenation. Similarities and differences between Cretaceous OAEs and late Quaternary OMZs have to be further explored to improve our understanding of sedimentary systems under hypoxic conditions.

1 Introduction

In the present day ocean, most of the water column is well ventilated as a consequence of thermohaline circulation processes that lead to subduction of cold, oxygen rich and dense water masses in high northern and southern latitudes (e.g. Kuhlbrodt et al., 2007). Exceptions are restricted basins, in which the limited exchange with the oxygen rich water masses of the open ocean is not sufficient to counteract oxygen consumption by organic matter respiration such as in the Black Sea (Murray et al., 1989). In the open ocean, strongly oxygen depleted water bodies occur underlying highly productive surface waters such as in the major upwelling areas off the western continental margins of Africa and the Americas or below the monsoon-driven upwelling of the Arabian Sea (Helly and Levin, 2004). In the geological past, regional or global ventilation of the ocean underwent significant changes on different time scales due to a variety of reasons, including changes in atmospheric and ocean circulation, stratification, temperature or tectonic processes. It is, however, difficult to quantify the past spatial extent and intensity of oxygen minima because the oxygen concentration of the water column is not directly recorded in the sediments. As a consequence, derivative proxies have been applied to reconstruct past ocean oxygenation.

A characteristic feature of marine low-oxygen environments on various time scales are black. 1 organic-rich, and laminated sediments (Kemp, 1996; Meyer and Kump, 2008). They are 2 3 known since the late Precambrian (Tucker, 1983). Widespread and contemporaneous 4 occurrences of these deposits in Devonian, Permian, early Jurassic, early and late Cretaceous, 5 and mid-Miocene successions depict periods of sluggish ocean circulation or extensive highly 6 productive seas (Schlanger and Jenkyns, 1976; Buggisch, 1991; Flower and Kennett, 1993; 7 Wignall and Twitchett, 1996; Trabucho-Alexandre et al., 2010). The question whether these 8 laminated sediments were formed due to enhanced primary production or due to restricted 9 ventilation of near-bottom waters has fueled a long-lasting debate (e.g. Calvert, 1987). Yet the 10 discovery of laminated sediments in the Arabian Sea during the International Indian Ocean 11 Expedition in 1965 revealed that this sedimentary facies is confined to OMZs at mid-depth 12 (Schott et al., 1970). Laminated sediments at the southwest African, Peruvian and Californian 13 margin provided further evidence for their association with today's OMZs (van Andel, 1964; 14 Reimers and Suess, 1983; Struck et al., 2002;). In contrast, basinwide stagnation events resulting in the deposition of organic-rich, at least partially laminated sediments were 15 16 recorded during short time intervals with specific environmental settings from the Pliocene to 17 early Holocene in the eastern Mediterranean (sapropels) and in the Sea of Japan (Stein and Stax, 1990; Rohling and Hilgen, 1991). They are, however, not considered potential 18 19 analogues for the extensively occurring black, laminated shales of the Mesozoic including the 20 Cretaceous OAEs (Erbacher et al., 2001). 21 Stable carbon isotope data obtained from Devonian, Toarcian, Aptian and 22 Cenomanian/Turonian successions revealed that the organic-rich beds recorded profound 23 perturbations of the global biogeochemical cycles, of which the Cenomanian/Turonian boundary interval (OAE2) was probably the most extensive event (e.g. Jenkyns et al., 1994; 24 25 Hesselbo et al., 2000; Joachimski et al., 2002; Herrle et al., 2004). Detailed investigations of 26 the geochemistry, microfossil assemblages, and sedimentary structures of both, recent and 27 fossil strata were performed to unravel the interplay of local, regional and global processes 28 driving their formation, and to enforce a mutual understanding of late Quaternary OMZs and 29 Cretaceous OAEs (Thiede and Suess, 1983; Anbar and Rouxel, 2007; Dale et al., 2012; Owens et al., 2013). These studies were complemented by oceanographic, biological and 30 biochemical studies in recent upwelling systems and OMZs. However, this actualistic 31 approach has been hampered by long periods of burial, diagenesis, and evolution of the 32 biosphere since their deposition in Mesozoic times. 33

- 1 Geochemical redox proxies were extensively explored on Cretaceous black shales in order to
- 2 constrain past ocean oxygenation, in particular trace metals (Brumsack, 2006; van Bentum et
- 3 al., 2009; Dale et al., 2012), sulfur isotopes (Hetzel et al., 2009; Owens et al., 2013), and iron
- 4 isotopes (Owens et al., 2012). Some of these proxies have also been measured on surface
- 5 sediments and sediment cores from the Peruvian OMZ, in particular U/Mo ratios (Böning et
- al., 2004, Scholz et al., 2011, 2014a, b). However, only a very few data points are available
- 7 for a regional U/Mo bottom-water oxygen calibration in the Peruvian OMZ (Scholz et al.,
- 8 2011). They strongly differ from corresponding data obtained from other OMZs (McManus et
- 9 al., 2006). This hampers a quantititative reconstruction of past oxygenation with U/Mo ratios
- 10 for the Peruvian OMZ as well as for black shales from Cretaceous of OAE2.
- Besides geochemical redox indicators, there are only few other reliable parameters that are
- sufficiently explored to investigate paleo low-oxygen conditions in the Mesozoic and
- 13 Cenozoic, which are trace fossils, laminations, and organic carbon accumulation rates. Their
- potential, constraints, and implications for an assessment of past water column oxygenation
- are addressed in this review. Particular emphasis is put on the comparison of Holocene OMZ
- sediments from the upwelling area off Peru with deposits of Cretaceous Oceanic Anoxic
- 17 Event 2 from the Moroccan shelf.

2 Material and Methods

- 19 The Peruvian Margin study is based on stratigraphic and sedimentological data from 136
- sediment cores within and below today's OMZ off the western South American continental
- 21 margin. They are located between the Equator and 18°S and were retrieved from water depths
- between 180 and 2200 m (Figure 1). Data of 94 cores were taken from the literature and 42
- 23 new cores recovered during R/V METEOR cruises M77/1 and M77/2 in 2008 were assessed
- 24 as part of this study (Appendix Table A1). The cruises were performed in the framework of
- 25 Collaborative Research Centre (SFB) 754 "Climate Biogeochemistry Interactions in the
- 26 Tropical Ocean", through which supplementary data for the environmental interpretation of
- 27 the sedimentary records are available.
- 28 In particular, oxygen concentrations along the Peruvian continental margin were measured
- during R/V METEOR cruises M77-1, M77-2 (Krahmann, 2012) and M77-3 (Kalvelage et al.,
- 30 2013). We considered 159 CTD stations with a maximum water depth of 1750 m and a
- maximum distance of 175 km to the shore (online supplement M77-1-3 CTD Data.xls).
- 32 Other CTD casts further offshore were not included because they already showed

- significantly elevated oxygen concentrations compared to proximal locations at the same
- 2 latitude. Kalvelage et al. (2013) observed an offset of ~2 µmol/kg between the CTD attached
- 3 optode oxygen sensors and the more sensitive STOX sensors, which are based on a Clark-
- 4 type oxygen sensor, and corrected the optode data by 2 μmol/kg during the cruises M77-3 and
- 5 M77-4. The oxygen data presented in our study were not corrected for a 2 μmol/kg offset
- 6 since the STOX sensors were not deployed during M77-1 and M77-2.
- 7 We considered visual core descriptions, physical property data, in particular dry bulk
- 8 densities, sand content and abundances of biogenic, terrigenous and diagenetic components,
- 9 and organic carbon contents. The chronostratigraphy of the cores was established with
- 10 radiocarbon datings on monospecific samples of planktonic or benthic foraminifera, or bulk
- 11 sedimentary organic carbon.
- The age models of the cores from M77/1 and M77/2 cruises are based on Mollier-Vogel et al.
- 13 (2013). Otherwise, published, conventional radiocarbon ages and new ¹⁴C Accelerator Mass
- 14 Spectrometer (AMS) datings were calibrated using the software "Calib 7.0" (Stuiver and
- Reimer, 1993) and by applying the marine calibration set "Marine 13" (Reimer et al., 2013).
- Reservoir age corrections (ΔR) were carried out by using the Marine Reservoir Correction
- 17 Database (http://calib.qub.ac.uk/marine/). Regionally weighted mean ΔR values rangedfrom
- 18 89 to 338 years for the eastern Pacific off Peru. The uncertainties of the source data ranged
- from ± 31 to ± 82 years (2-sigma). For the pre-Holocene part of the records, the radiocarbon-
- 20 based chronologies were supplemented with planktonic and benthic oxygen isotope curves
- 21 correlated to stacked reference records (e.g. Liesicki and Raymo, 2005) or Antarctic ice cores
- 22 (e.g. EPICA Community Members, 2006). Subrecent sedimentation rates were constrained by
- 23 ²¹⁰Pb excess activity profiles (Reimers and Suess, 1983; Mosch et al., 2012). All ages are
- 24 given in calendar years before 1950 AD (abbreviated as cal. ka.). Organic carbon and bulk
- 25 sediment accumulation rates (g cm⁻² kyr⁻¹) were calculated from linear sedimentation rates
- 26 (cm 10⁻³ years) and bulk dry densities (g cm⁻³) following van Andel et al. (1975).
- 27 The M77/1 and M77/2 cores included in this study were described immediately after opening
- aboard R/V METEOR (Pfannkuche et al., 2011). Two parallel series of volume-defined
- samples were taken in 5 or 10-cm intervals with cut-off syringes. One series of 10-cc samples
- 30 was freeze-dried and physical properties were determined from wet sample volumes and the
- weight loss after drying applying standard protocols and a pore-water density of 1.026 g cm⁻³
- 32 (Boyce, 1976). The other series of 20-cc samples dedicated to isotopic measurements,

microfossil, and sand-fraction examination was washed gently with tap water through a 63 1 2 um sieve within a few hours after sampling. Washing of fresh, wet samples facilitates a better 3 preservation of delicate calcareous microfossils, which otherwise may have been corroded or 4 even dissolved by oxidation products of ferrosulphides and labile organic matter (Schnitker et 5 al., 1980). The residues were dried at 50°C and weighed. For stable oxygen and carbon 6 isotope analyses, about 30 specimens of the planktonic foraminiferal species Globigerinoides 7 ruber (white), Neogloboquadrina dutertrei or 3 to 6 specimens of the benthic species 8 Uvigerina striata, U. peregrina or Globobulimina pacifica were picked from the size fractions 9 250 to 355 μm or >63 μm, respectively. We used these species because they were abundant in the cores studied and incorporate stable oxygen isotopes in equilibrium with the surrounding 10 pore and supernatant bottom waters (e.g. McCorkle et al., 1990). Oxygen and carbon isotopes 11 12 were measured with a Thermo Fisher Scientific 253 Mass Spectrometer coupled to a CARBO KIEL automated carbonate preparation device at GEOMAR, Kiel. The long-term analytical 13 precision (1-sigma) for δ^{18} O and δ^{13} C was better than 0.06 % and 0.03 % on the VPDB scale, 14 respectively, based on more than 1000 measurements of an in-house carbonate standard 15 16 during the respective measurement sessions. Replicate measurements of benthic foraminifera from the same sample showed an external reproducibility of ± 0.1 ‰ for $\delta^{18}O$. For 17 radiocarbon analyses, 33 to 179 specimens of *Planulina limbata* or 229 to 250 specimens of 18 19 Neogloboquadrina dutertrei were picked from the size fraction >63 µm or 5 to 20 mg of ground bulk sediment was prepared. AMS measurements were performed at the Leibniz 20 21 Laboratory for Radiometric Dating and Stable Isotope Research, University of Kiel (CAU) and at Beta Analytic Inc. Dried samples used for physical properties measurements were 22 23 ground with an agate mortar. Aliquot subsamples of 3 to 20 mg were analysed for total carbon 24 and organic carbon content with a Carbon Erba Element Analyzer (NA1500) at GEOMAR, 25 Kiel. The long-term precision was ± 0.6 % of the measured values as revealed by repeated 26 measurements of two internal carbon standards. 27 Since the pioneering work of Einsele and Wiedmann (1975), Cenomanian to Lower 28 Campanian organic-rich marlstones of the Tarfaya Basin in southern Morocco have been 29 studied as a type locality of Cretaceous upwelling-related sediments at the eastern margin of the central North Atlantic (Wiedmann et al., 1978; Leine et al., 1986; Kuhnt et al., 1997, 30 2001, 2005; Kolonic et al., 2005; Aguit et al., 2013). Numerical climate and circulation 31 models of the mid-Cretaceous Atlantic support a prevalence of cool and nutrient-rich 32

- 1 intermediate deep water masses in this area along the NW African margin (Poulsen et al.,
- 2 2001; Topper et al., 2011). The late Cenomanian to early Turonian OAE 2 sediments
- 3 discussed here were examined in outcrop sections during five field expeditions of the Kiel
- 4 Micropaleontology Group in 1997, 1998, 2000, 2003 and 2009. In addition, core material
- 5 from two commercial wells (S13 and S75), and a 350 m deep research well drilled in
- 6 October-December 2009 (Tarfaya SN°4) were considered in this study (Figure 1).
- 7 Analytical methods applied to samples from outcrops and drill cores were detailed in Kuhnt et
- 8 al. (2005) and Aquit et al. (2013). Core sections from the new exploration well Tarfaya SN°4
- 9 were cut lengthwise and described. Line scan measurements and photographs were acquired
- with a Ja CVL 1073 CCD color line scan camera with 3 sensors of 2048 pixels and Dichroic
- 11 RGB beam splitter prism (RGB channels at 630 nm, 535 nm and 450 nm) at the Institute of
- 12 Geosciences, Kiel University. Color measurement in L*a*b* units are from RGB digital
- images. Scanning was performed (resolution of 143 pixel per 70 micron) on the polished
- surface of oriented cores. Intensity of lamination vs. bioturbational homogenization of the
- sediment was estimated using high resolution lightness (L*) measurements for cores of SN°4.
- We calculated a lamination index based on a moving window standard deviation of the
- 17 lightness values, similar to the method previously applied on core S75 (Kuhnt et al., 2005).
- Organic carbon and carbonate contents of SN°4 core samples were measured with a Carbon
- 19 Erba Element Analyzer (NA1500) at Geomar, and with a conventional carbonate bomb at the
- 20 Institute of Geosciences, Kiel University.

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3 Results

3.1 Holocene to Recent organic-rich sedimentation underneath Recent OMZs

- 24 Bioturbation
- 25 Organisms dwelling in sediments below the redox boundary commonly rely on oxygen supply
- 26 from the above near-bottom waters (Savrdaand Bottjer, 1991). They disappear if bottom-
- water oxygenation drops below a certain limit (Rhoads and Morse, 1971; Savrdaet al., 1984).
- 28 Observations from Recent OMZs suggested that deposit-feeding gastropods, in particular
- 29 Astyris permodesta, may temporarily enter dead zones for grazing on fresh organic detritus or
- 30 sulphur bacterial filaments (Levin et al., 1991; Mosch et al., 2012). These gastropods leave

small biodeformational structures on the sea bed, which are, however, usually not preserved (Schäfer, 1956). Sediments from oxygen-depleted environments are therefore characterised by scarcity or absence of ichnofossils (Savrdaand Bottjer, 1987). Only a few ichnogenera are recognisable, in particular the mm-sized Chondrites. Their diameter correlates with oxygenation although food availability or substrate properties also exert an influence (Bromley and Ekdale, 1984; Fu, 1991; Kröncke, 2006). In eastern Pacific hypoxic environments, a covariance of the highest average burrow size and oxygen content of nearbottom water was recognised for an oxygen range of 5 to 45 µmol kg⁻¹ in the San Pedro Basin (Savrdaet al., 1984). This relationship was based on 6 to 10 burrows identified per x-ray image. An assignment to particular ichnotaxa other than Arenicolites was not attempted, even though many ichnogenera have a well constrained range of dimensions (e.g. Wetzel, 2008). The general inverse relationship of burrow diameter and oxygenation has been challenged by sea-floor observations with a photo sledge and shallow multicorer samples taken during R/V METEOR cruise M77/1 (Mosch et al., 2012). Surprisingly, it was not Chondrites, but centimetre-sized open crab burrows that were recognised as first biogenic structures at bottom-water oxygen concentrations approaching 10 µmol kg⁻¹ close to the lower OMZ boundary where endobenthic macrofauna was able to exist. Chondrites burrows have not been reported to date from any of the Peruvian OMZ sediment cores even though the responsible organism, a nematod, most likely pursues chemotrophy at anaerobic conditions (Fu, 1991). Older strata, such as Mesozoic sediments were usually subjected to a high degree of compaction altering the shape and size of burrows (e.g. Gaillard and Jautee, 2006; Gingras et al., 2010). A correct identification of ichnogenera may then not be possible any more. Burrows have been preserved at their genuine dimensions in carbonate-rich sediments (e.g. Savrda and Bottjer, 1986; Ekdale and Bromley, 1991). In particular *Chondrites*-rich layers were reported from Cenomanian/Turonian limestones and marls deposited during OAE 2 in NW Europe (Schönfeld et al., 1991; Hilbrecht and Dahmer, 1994; Rodríguez and Uchmann, 2011). As this ichnogenus is appearently missing from the Peruvian OMZ, bioturbation structures do not offer a detailed comparison between Pleistocene to recent OMZs and Cretaceous OAEs. The only feature in common is the scarcity or absence of bioturbation in both, laminated Cretaceous shales and Holocene to Pleistocene sediments deposited under dysoxic to anoxic conditions below the Peruvian upwelling.

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Laminations

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2 Laminated sediments have been studied in great detail to unravel the processes forming 3 millimetre-scale interbedded sediments with the perspective that alternations between the 4 varves reflect seasonal, annual or decadal environmental variability (von Stackelberg, 1972; 5 Brodie and Kemp, 1994; Kemp, 1996). In the Arabian Sea, laminated sediments were found 6 between 300 and 900 m water depth whereas the OMZ with oxygen concentrations of <23 umol kg⁻¹ impinges the sea floor between 200 and 1200 m depth. Minimum values of 4.5 7 umol kg⁻¹ were reported (Schulz et al., 1996). No benthic macroinvertebrates were observed 8 9 between 300 and 800 m where these low oxygen concentrations prevailed. The laminations 10 form couplets of dark grey organic-rich summer varves and light grey winter varves of terrigenous detritus. Holocene average sedimentation rates were in the range of 0.9 to 1.5 mm 11 yr⁻¹. Winnowing and reworking by slope currents or turbidites was common, which prevented 12 the establishment of continuous long records of annual resolution (Schulz et al., 1996). 13 Instead, cyclic alternations of laminated and bioturbated core sections suggested a spatial 14 variability of the OMZ on longer time scales (von Rad et al., 1995). 15 16 In the California borderland basins the laminae consist of dark lithogenic winter layers and 17 light-coloured, nearly monospecific *Thalassiothrix longissima* diatom layers deposited during spring and early summer (Thunell et al., 1995). In the Soledad Basin off northern Mexico, 18 19 whitish coccolith layers are intercalated as well (van Geen et al., 2003). Average sedimentation rates may exceed 1 mm yr⁻¹, and despite the pronounced seasonal or El Niño 20 21 cyclicity of 3-6 years (Hagadorn, 1996), up to five biogenic sublaminae per year may be 22 preserved (Pike and Kemp, 1997). The regional and intra-basinal distribution of laminations 23 in latest Holocene sediments was confined to bottom-water oxygen concentrations <5 µmol kg⁻¹. In contrast, a decoupling of sediment banding and bottom-water oxygenation has been 24 found at sites with a low primary production or where a less profound seasonality prevailed 25 26 (van Geen et al., 2003). There, alterations of bioturbated glacial and stadial sediments and 27 laminated Holocene and interstadial core sections suggested climatically driven variations in 28 northeastern Pacific OMZ intensity (Behl and Kennett, 1996; Cannariato and Kennett, 1999; 29 Jaccard and Galbraith, 2012). In the Peruvian OMZ, laminated sediments from the Salaverry and Pisco Basins were 30 described in great detail (Kemp, 1990; Wefer et al., 1990). The sediments showed 0.3 to 0.6 31 m thick intervals of laminated and sub-laminated sediments with intercalated homogenous 32

bioturbated units. They are unconformably overlain by sand-rich layers with phosphorite 1 2 pebbles representing periods of erosion due to strong near-bottom currents (Reimers and Suess, 1983; Garrison and Kastner, 1990). In banded core sections, the laminae form 0.3 to 3 4 0.7 mm thick couplets of clay-rich and silt-rich layers probably reflecting depositional 5 variability on seasonal timescales. Nearly monospecific *Skeletonema* or *Chaetoceras* diatom 6 layers of 2 to 10 mm thickness are irregularily intercalated. These diatom ooze layers were 7 often not preserved due to dissolution or grazing. Evidence for the latter is provided by 8 microbioturbation within the laminated intervals and pellet-rich horizons of 5 to 30 mm 9 thickness. These were created by epibenthic, vagile macrofauna during periods of elevated 10 bottom-water oxygenation, which lasted for 8 to 16 years (Brodie and Kemp, 1994). A 11 covariance of laminated core sections with certain climatic conditions was not identifiable 12 whereas pebbly or sand-rich beds preferentially occurred during cold stages suggesting either 13 stronger bottom currents or increased terrigenous sediment supply (Reimers and Suess, 1983; Rein et al., 2005; Mollier-Vogel et al., 2013). On decadal to subdecadal time scales, however, 14 laminations were linked to changes in climate and ecosystem properties in the mid 19th 15 16 century (Gutiérrez et al., 2006). In particular, periodical "regime shifts" in the Peruvian OMZ during the late Holocene were related to the variability of solar irradiance (Agnihotri et al., 17 18 2008). 19 Information on the presence of laminations is available for 74 of 136 sediment cores reported 20 from the western South American Margin between the Equator and 18°S (Appendix Table 21 A1). From those, 36 showed laminated intervals whereas 38 cores were homogenized by bioturbation with the exception of sediment-transport related structures, sand or gravel beds. 22 Laminated sediment sections are confined to a distinct area between 9° and 16°S and were not 23 retrieved from water depths below 600 m. With the exception of two cores from the 24 25 continental shelf, the upper and lower distribution limits of laminated sediments match the outline of today's OMZ as depicted by the 7 µmol kg⁻¹ isoline of bottom-water oxygen 26 concentration. However, most laminated cores were retrieved from areas with bottom-water 27 oxygen values of <5 µmol kg⁻¹ (Figure 2). The distribution limits are not reliably traceable 28 further to the North and South due to sparse data coverage and rarely observed laminated 29 30 sections. Sediment records may go as far back in time as marine oxygen isotope stage 11 and contain several unconformities representing extended times of non-deposition or erosion 31 32 (Rein et al., 2005).

- 1 A reliable stratigraphic record is available for 9 sediment cores with laminated intervals.
- 2 Laminations occurred at any time and water depth during the past 20 kyrs with the exception
- 3 of the 6 to 8 ka time interval (Figure 3). This implies that there was no period of time during
- 4 the late Pleistocene and Holocene, during which the entire OMZ expanded and intensified, or
- 5 contracted and weakened on a regional scale. Some of the shallowest locations showed
- 6 weaker or no laminations during periods of inferred increased El Niño frequency marking
- 7 seasonally decreased productivity and elevated oxygen levels in the bottom waters (Rein et
- 8 al., 2005; Ehlert et al., 2013). Laminated deposits were rarely continuous and did not show a
- 9 time-transgressive pattern as previously suggested (Reimers and Suess, 1983). Sections
- documenting periods of more than 2 kyrs duration of laminated sediment deposition were
- recorded only between 11 and 13°S and at water depths of 184 to 325 m, i.e. in the upper
- 12 OMZ and underneath the most intense upwelling.
- 13 Organic carbon accumulation rates
- 14 Accumulation rates of sedimentary organic carbon have been widely considered as a proxy
- 15 for paleoproductivity reconstructions (Stein and Stax, 1991; Sarnthein et al., 1992; McKay et
- al., 2004). While usually less than 1 % of organic matter exported from the photic zone is
- deposited on the sea floor and preserved in the fossil record under oxic conditions, the burial
- may increase to up to 18 % in low-oxygen environments (Müller and Suess, 1979). The
- 19 preservation of organic substances in OMZ sediments from the Arabian Sea was enhanced at
- 20 oxygen concentrations of <22 μmol kg⁻¹ suggesting a covariance between organic carbon
- accumulation rates and bottom-water oxygenation (Koho et al., 2013). Recent organic carbon
- accumulation rates ranged from 0.01 to 0.4 g C cm⁻² kyr⁻¹ in the Arabian Sea.
- 23 In the Peruvian OMZ, mid- to late Holocene and subrecent organic carbon accumulation rates
- varied substantially between 0.06
- and 6.8 g C cm⁻² kyr⁻¹ with most values between 1 and 3 g C cm⁻² kyr⁻¹ (Appendix Table A2),
- i.e. one magnitude higher than in the Arabian Sea. Dilution by seasonal terrigenous sediment
- input from Pakistan probably accounts for the difference (von Rad et al., 1995).
- 28 The organic carbon data from the Peruvian cores revealed distinct distribution patterns.
- 29 Laminated sediments showed scattered values at bottom-water oxygen <5 μmol kg⁻¹ whereas
- 30 bioturbated sediments depicted a well constrained inverse relationship of organic carbon
- accumulation and bottom-water oxygenation (Figure 4).

3.2 Organic-rich sedimentation during Cretaceous OAE-2 of the Tarfaya Basin

2 Laminations

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3 The laminated intervals in sediments from the Tarfaya Basin as recovered from SN°4 well were usually 2 to 4 m thick organic-rich marlstones with intercalated bioturbated limestones 4 5 of 0.5 to 2 m thickness, the laminations showed a high scatter in lightness (Figure 5), which is depicted by a lamination index based on a moving window standard deviation of high 6 7 resolution lightness data (L*). Intense lamination is indicated by high standard deviations, 8 while standard deviations in homogenous sediments are close to zero. The average 9 thicknesses of individual laminae was extremely variable ranging from sub-millimetre 10 (mainly light layers composed of planktonic foraminiferal tests) to several millimeters 11 (mainly kerogen-rich dark layers). Simple estimates from average sedimentation rates of 4 to 8 cm per thousand years suggest an average time of 25 to 12.5 years to account for the 12 13 deposition of a 1 mm lamina, which points to a control on lamination by depositional or winnowing processes, rather than a control by periodical climatic variations on the formation 14 15 of laminae. 16 Wavelet spectral analyses of the 70 µm resolution linescan data of core SN°4 also do not exhibit clear periodicity patterns. The most prominent periodicities are in the range of 4, 15 17 18 and 30 mm, which would correspond to approximately 100, 400 and 800 years at a sedimentation rate of 4 cm kyr⁻¹ and clearly do not reflect seasonal variability or ENSO-type 19 20 sub-decadal oscillations (3-7 years) (Figure 6). 21 Sediment re-working and re-distribution through small scale erosion and/or winnowing by 22 bottom currents appeared commonly in the deposition of organic-rich sediments during OAE 23 2. Low angle truncations, indicating small scale erosion surfaces occurred frequently in the 24 upper part of the OAE 2 black shales in the Tarfaya Basin (i.e. in black shales at the base of 25 the Turonian within the Amma Fatma outcrop section, Figure 7). 26 Recent depositional environments off NW Africa were distinctly different from those during 27 OAE 2. In the modern upwelling zone off NW Africa, textural upwelling indicators, such as organic-rich, laminated sediments, were virtually absent in shallow shelf sediments directly 28

underlying upwelling cells (Fütterer, 1983). They were winnowed out by strong bottom

currents, sediment particles were transported across the shelf and finally redeposited in deeper

parts of the shelf or on the continental slope. The main depositional center of organic-rich

- 1 material is located today at water depths between 1000 and 2000 m, where fine-grained
- 2 material is accumulating as mid-slope mud lenses (Sarnthein et al., 1982).
- 3 The organic-rich sediments in the Cretaceous Tarfaya Basin also exhibited a range of
- 4 sedimentary features pointing to an important role of re-suspension and lateral advection in
- 5 the depositional processes. However, sedimentological (El Albani et al., 1999) and
- 6 micropaleontological evidences (Wiedmann et al., 1978; Gebhardt et al., 2004, Kuhnt et al.,
- 7 2009) indicated that the main depositional center of organic-rich sediments during OAE 2
- 8 were in the middle to outer shelf part of the Tarfaya Basin in relatively shallow water depths
- 9 between approx. 100 and 300 m. Such a setting would be in general agreement with the
- situation on the Peruvian shelf and upper slope today, where similar high-accumulation areas
- were recognised at depths of less than 300m (Wefer et al., 1990).
- 12 Organic carbon accumulation rates during OAE 2 in the Tarfaya Basin
- Organic matter accumulation rates were calculated in three cores (S13, S75, SN°4) for
- individual cycles based on an orbitally tuned age model (Meyers et al., 2012) for the time
- interval from the onset of OAE 2 (late Cenomanian, upper part of the R. cushmani Zone) to
- the lower Turonian (end of the OAE 2 carbon isotope excursion in the *H. helvetica* Zone).
- 17 This period represents a time span of ~ 800 kyr (Sagemann et al., 2006; Meyers et al., 2012).
- 18 Cores were correlated using density and natural gamma ray logs. We used density/NGR
- minima/maxima for each individual cycle as tie points, and, whenever possible, correlatable
- 20 features within individual cycles. The overall pattern and number of cycles in the studied
- 21 interval revealed that most of the regular density variations mirrored obliquity cycles, i.e. a
- periodicity of 41 kyrs. The local cyclostratigraphic age model is then tied to the GTS2012
- 23 timescale chronology using the new radiometric age of 93.9 Ma for the C/T boundary (top
- 24 cycle 3, FO *Quadrum gartneri*). Based on this age model, we calculated sedimentation rates
- 25 for each individual cycle, dry bulk density from density logging and total organic carbon
- values from individual measurements as well as continuous organic carbon estimates from
- NGR logging and lightness (L*) measurements (Figure 8).

4 Discussion

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4.1 Origin and composition of laminae

- 3 Light laminae in Peruvian upwelling sediments represent diatom blooms, either resulting from
- 4 seasonal variations or deposition during strong La Niña events (Kemp, 1990), whereas in the
- 5 Tarfaya Basin light layers are mainly composed of planktonic foraminiferal tests, phosphate
- 6 or fecal pellets, indicating periods of higher oxygenation of the water column with enhanced
- 7 grazing activity of vagile benthic organisms. These events occurred on decadal-centennial
- 8 timescales as brief interruptions of otherwise continuously dysoxic to anoxic conditions.
- 9 The different marine primary producers in the Cenomanian-Turonian may have influenced the
- stoichiometry and isotope composition of marine organic matter. Whereas Holocene to
- Recent organic-rich sediments in the Peruvian upwelling contain high proportions of diatoms,
- 12 Cretaceous organic-rich sediments are dominated by haptophyte algae preserved as shields of
- coccolithophorids and nannoconids, archaeans, and cyanobacteria as revealed by biomarkers
- 14 (Kuypers et al. 1999; Dumitrescu and Brassell, 2005). It is conceivable that such organisms
- may have induced higher C/P and C/N ratios under high pCO₂ conditions, exceeding the
- Redfield ratio (Sterner and Elser, 2002; Riebesell, 2004; Sterner et al., 2008; Flögel et al.,
- 17 2011; Hessen et al., 2013). As a result, nutrient limitation for marine productivity may have
- been less severe during Cretaceous OAEs, than it was reached under low pCO₂ conditions
- during the last deglaciation and the Holocene.

4.2 Persistence of laminated sediments – dynamics of the OMZ

- 21 The geological record of OAE 2 in the Tarfaya Basin showed a cyclic sedimentation of
- variegated, laminated marlstone beds with low gamma-ray density and high organic carbon
- accumulation rates, which were intercalated with uniformly pale, bioturbated limestones
- showing low organic carbon values. A regular periodicity of cyclic sedimentation in the
- 25 obliquity domain indicated climatic forcing that was different from Late Cretaceous times
- 26 with well-ventilated oceans, when short and long precession, and eccentricity had a stronger
- influence (Gale et al., 1999; Voigt and Schönfeld, 2010). It has been suggested that changes
- 28 in mid-depth ocean circulation during OAE 2 promoted the influence of a high-southern
- 29 latitude climatic signal in the Cretaceous North Atlantic (Meyers et al., 2012).

- 1 In the north-eastern Pacific, we also see alterations of bioturbated sediments deposited during
- 2 the last glacial and stadial climatic intervals with laminated intervals deposited during the
- 3 Holocene and late Pleistocene interstadials (Behl and Kennett, 1996; Cannariato and Kennett,
- 4 1999). Even though these alterations reflect much shorter periodicities than during the mid
- 5 Cretaceous, they were climatically driven by intensified upwelling due to stronger trade winds
- 6 and enhanced nutrient supply through Subantarctic Mode Water, thus again linked to
- 7 processes in the Southern Ocean (Jaccard and Galbraith, 2012, and references therein).
- 8 Off Peru, laminations have neither been strictly linked to climatic periodicities nor were they
- 9 continuously preserved in the fossil record. Numerous discontinuities, their time-transgressive
- 10 nature, and phosphoritic sand layers are evidences for the impact of strong bottom-near
- currents and breaking internal waves (Reimers and Suess, 1983). On the other hand, eddies
- and warm, oblique filaments can facilitate a short-term supply of oxygen to the Peruvian
- OMZ (e.g. Stramma et al., 2013), and large burrowing or grazing organisms may invade the
- dead zone from below (Mosch et al., 2012), thus destroying recently deposited laminae.
- 15 Therefore it is conceivable that a preservation of continuous laminated sediments has rather
- been an exception than the rule in the Peruvian OMZ. This exception was more likely to
- occur in the permanently anoxic centre of the OMZ underneath the most intense upwelling
- 18 cell.

- None-the-less, it has to be emphasized that many of the north-eastern Pacific cores were
- 20 retrieved from marginal basins where a quiet depositional regime prevailed. Furthermore, the
- 21 impact of bottom-near currents and redeposition is also documented in OAE 2 deposits from
- 22 Tarfava outcrop sections. We speculate that if there were a possibility to examine older
- 23 Peruvian OMZ sediments in an outcrop section, many similar features will emerge helping to
- better understand the fragmentations of the stratigraphic record described above.

4.3 Organic carbon accumulation and bottom-water oxygenation

- A large range of chemical, biological and oceanographic factors controlling organic detritus
- 27 flux to the sea bed, decomposition and remineralisation, preservation and finally
- 28 accumulation as refractory substances constitute the complex nature of organic matter
- 29 turnover. Furthermore, organic carbon preservation strongly depends on the local
- 30 circumstances of deposition (Hedges and Keil, 1995; Arndt et al., 2013), thus limiting the
- 31 comparability of settings between regions and oceanic basins. There is an ongoing debate

- 1 whether the proportion of organic matter, which is buried and preserved in marine sediments,
- 2 is dependant on the ambient bottom water oxygenation or not (Dale et al., 2014). The only
- 3 assured perception is that carbon burial does not co-vary with bottom-water oxygenation at
- 4 high sedimentation rates near continental margins (Betts and Holland, 1991; Canfield, 1994).
- 5 At low sedimentation rates, the oxygenated near-surface layer of sediments deposited under
- 6 oxygenated bottom water increases in thickness and faciltates enhanced aerobic
- 7 decomposition, while sediments deposited under low-oxic conditions remain anaerobic and
- 8 decomposition is effected by nitrate and sulphate reduction (Hartnett and Devol, 2003). As a
- 9 consequence, organic carbon burial correlates with oxygen exposure time of particulate
- organic carbon at the sea floor in oxic to suboxic environments, and shows no covaraince in
- dysoxic zones (Hartnett et al. 1998).

4.4 Comparison of organic carbon accumulation rates: Glacial-Holocene

Peruvian upwelling vs. Cretaceous upwelling along the East Atlantic

Margin

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- 15 For a comparison of Cretaceous organic carbon accumulation rates with those of Recent
- OMZs, we considered Cretaceous sections with more than 90% organic rich shales (Kuhnt et
- al., 1990). With reference to Recent OMZ sediments, we assumed a bottom water
- oxygenation <5 µmol kg⁻¹ at sites where fine laminations were preserved. The first estimates
- of TOC accumulation rates of Kuhnt et al. (1990) were based on a duration of 500 kyr for
- 20 OAE 2 and on averaging of a relatively small number of discrete organic carbon
- 21 measurements over the entire interval. These rough estimates resulted in accumulation rates
- between 0.01 g C cm⁻² kyr⁻¹ for deep sea sites and 1.1 g C cm⁻² kyr⁻¹ for NW African shelf
- basins with upwelling conditions, which showed the highest accumulation rates (Kuhnt et al.,
- 24 1990). A re-evaluation of organic carbon accumulation rates in the Tarfaya Basin using an
- orbitally tuned age model and high resolution measurements or continuous organic carbon
- estimates indicated variable carbon accumulation rates, which varied between 0.7 and 2.8 g C
- 27 cm⁻² kyr⁻¹ and thus match the data range of the majority of laminated late Holocene sediments
- 28 from the Peruvian margin presently under bottom-water oxygen levels of <5 µmol kg⁻¹
- 29 (Figure 4).
- 30 The palaeo water depths of the Tarfaya Basin during OAE 2 were slightly shallower than the
- 31 centre of the Peruvian OMZ today. Based on molecular evidences, it was even suggested that

- the Cretaceous OMZ extended into the photic zone (Sinninghe Damsté and Köster, 1998). As
- 2 such, decomposition and remineralisation of organic detritus while sinking to the sea floor
- 3 was less likely (Martin et al., 1987). We therefore have to assume that the deposition rate of
- 4 particulate organic matter was very close to the export flux rate at 150 m water depth
- 5 (Buesseler et al., 2007). An empirical relationship between the rain rate and Holocene burial
- 6 rate of particulate organic carbon has been established by Flögel et al. (2011) for continental
- 7 margin settings:
- 8 Eq. 1: $BUR_{POC} = 0.14 * RR_{POC}^{1.1}$
- 9 (BUR_{POC} = burial rate of particulate organic carbon; RR_{POC} = rain rate of particulate organic
- 10 carbon)
- 11 No significant difference between data from oxygen minimum zones and well-ventilated
- bottom waters is recognised If we assume a burial efficiency of about 20 % (Flögel et al.,
- 13 2011, their Figure 2). , and consider Applying Equation 1 and considering a maximum
- organic carbon accumulation rates of 2.8 g C cm⁻² kyr⁻¹, i.e. approximately 30 g C m⁻² yr⁻¹ to
- bring up to a round figure, the maximum paleo export flux rain rate would be on the order of
- 16 126 150 g C m⁻² yr⁻¹, i.e. about half the productivity of the present day Peruvian upwelling
- 17 provides ranging from 200 to >400 g C m⁻² yr⁻¹ (Wefer et al., 1983). Even though this
- approximation includes many uncertainties, e.g. reliability of early sediment traps, variable
- burial efficiency (Dale et al., 2014), poorly constrained rates of Cretaceous primary
- 20 production, it is reasonable to assume that part of the OAE 2 organic matter was lost during
- 21 early diagenesis.
- 22 It has to be emphasized that Holocene organic carbon accumulation rates in the centre of the
- 23 Peruvian OMZ show a large scatter too, with maximum values of 6.8 g C cm⁻² kyr⁻¹ in core
- 24 SO147-106KL, i.e. rounded up 70 g C m⁻² yr⁻¹. If we likewise apply Equation 1, assume a
- 25 burial efficiency of about 20 %, we obtain an export flux arain rate of 350-270 g C m⁻² yr⁻¹.
- 26 This value is in good agreement with today's productivity of the Peruvian upwelling, and it is
- derived from a core interval, where an unusually thick section of laminations was preserved.
- 28 Therefore, it is conceivable that organic matter deposition at many Peruvian core sites is
- 29 hampered by instantaneous redeposition due to near-bottom turbulences. None-the-less, the
- Recent carbon burial efficiency at 10 cm sediment depth close to the SO147-106KL coring
- 31 site amounts to 62 % of the organic matter arriving at the sea floor (Dale et al., 2014). It is
- thus much higher than burial rate estimates for the late Holocene (Müller and Suess, 1979).

The difference may either originate from a strong inter-annual variability, a subrecent rise in carbon accumulation since 1800 AD (Gutierrez et al., 2009), or for a further remineralisation

3 of organic matter with time in the historical layer below 10 cm sediment depth and beyond.

For the laminated beds of OAE 2 in the Tarfaya Basin, a bottom water oxygenation of less than 5 µmol kg⁻¹ is suggested with reference to the distribution of laminated sediments in Recent oxygen minimum zones worldwide. The question arises whether it is possible to assign a bottom-water oxygen estimate to the intercalated, pale bioturbated limestones from the Tarfaya sections. Indeed, benthic foraminifera from the non-laminated light coloured interval at the base of cycle 0 in core S75 revealed a diverse benthic foraminiferal assemblage dominated by Bolivina species in high abundances. They indicate less dysoxic bottom waters (Kuhnt et al., 2005). The organic carbon accumulation rate was estimated at 1.1 g C cm⁻² kyr⁻¹ over this interval. If we apply the late Holocene relationship of organic carbon accumulation rates and bottom water oxygen for bioturbated sediments, an oxygenation of ca. 38 µmol kg⁻¹ is obtained. Such levels prevail at the Peruvian Margin today either below 800 m water depth, i.e. well below the OMZ, or above 90 m depth in the surface ocean mixed layer. Bolivina dominated faunas live in the centre of the Peruvian OMZ today, with high abundances between 150 and 520 m, and at oxygen concentrations of <2 µmol kg⁻¹ (Mallon, 2012). Between 800 and 900 m depth, the range to which the Cretaceous oxygen approximation points, Bolivina species were rare, accounting for less than 5 % of the living fauna.

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5 Conclusions

Pleistocene to Holocene and late Cenomanian to early Turonian stages are more than 94 million years apart in Earth's history. A direct comparison of their sedimentary record and environmental processes is hampered by burial diagenesis, evolution of marine biota, different continental and ocean configuration, different climate, ocean circulation, and biogeochemical cycles. The late Cenomanian was marked by the onset of OAE 2. Sedimentological, faunistic, and biogeochemical parameters suggested that large parts of the water column were devoid of dissolved oxygen, but the absolute levels are less well constrained. In an actualistic approach, we compared deposits of OAE 2 from the Moroccan shelf close to Tarfaya with deglacial and Holocene OMZ sediments from the upwelling area off Peru and found only a few parameters for a reliable investigation of paleo low-oxygen

- 1 conditions in both records, i.e. trace fossils, laminations, and organic carbon accumulation
- 2 rates.
- 3 The millimetre-sized trace fossil *Chondrites* was common in Cretaceous strata, in particular in
- 4 the beds directly underlying OAE 2 black shales. It was also found in modern oxygen-
- 5 depleted environments, where it is created by a nematod pursuing chemotrophy at anaerobic
- 6 conditions. The burrow diameter increased with oxygen level from 5 to 45 μmol kg⁻¹ in the
- 7 San Pedro Basin, California. However, *Chondrites* has never been reported from Peruvian
- 8 OMZ sediments. The oxygen burrow size relationship is challenged by cm-sized crab
- 9 burrows appearing at oxygen levels around 10 μmol kg⁻¹ below the OMZ already. Crab
- burrows are also common in Cretaceous sediments. Their appearence in OAE 2 sediments
- may therefore indicate that a threshold of approximately 10 μmol kg⁻¹ bottom-water oxygen
- has been exceeded.
- Laminations are a more reliable indicator, but they display only one, very low oxygen level.
- 14 In the Peruvian, northeastern Pacific, and Pakistan OMZs, depositional laminae created by
- seasonal or multi-annual variations in sediment supply or composition were preserved at
- bottom-water oxygen concentrations of less than 5 μmol kg⁻¹. Coherent occurrences of
- 17 laminated beds and biogeochemical indicators for oxygen drawdown in Tarfaya OAE 2
- sediments supported the applicability of this feature for bottom-water oxygen estimates. The
- 19 cyclic pattern of laminated and non-laminated intervals in Tarfaya sections and in sediment
- 20 cores from the eastern Pacific suggested the impact of climatic variations with direct linkages
- 21 to the high-latitude Southern Ocean as source of nutrients and better ventilated intermediate
- 22 waters. This regular cyclic pattern is blurred in Peruvian OMZ sediments by erosion,
- omission and redeposition due to bottom-near currents and breaking internal waves, making
- 24 the preservation of laminated sediments an exception rather than the rule. Redeposition
- 25 features were also observed in Tarfaya outcrop sections and reveal episodic, strong currents
- on the Cretaceous shelf and upper slope as an important process that was likely responsible
- for many observed unconformities in upper Cenomanian and lower Turonian formations.
- Organic carbon accumulation rates of late Holocene sediments off Peru displayed a disjunct
- 29 pattern. They showed a high scatter and a broad abundance maximum between 0.8 und 2.8,
- 30 mode value at 1.3 μmol kg⁻¹, in laminated sediments under a Recent bottom-water
- 31 oxygenation of $<5 \mu mol kg^{-1}$. If we compare the carbon accumulation rates of the Tarfaya
- 32 OAE 2 laminated sediments with late Holocene to Recent ones from the Peruvian OMZ, the

- 1 Cretaceous rates between 0.7 and 2.8 g C cm⁻² kyr⁻¹ match the data range of the majority of
- 2 late Holocene sediments very well. Taking into account the high burial efficiency of organic
- 3 carbon deposited in OMZs, and calculating export deposition fluxes rates from the photic
- 4 zone, the maximum Cretaceous values would account for only half of the present-day export
- 5 production under the Peruvian upwelling. Thermal maturation or the loss of volatile
- 6 hydrocarbons from Tarfaya black shales may well account for this difference. Maximum
- 7 Holocene carbon accumulation rates off Peru compare well to the present-day export
- 8 production. This agreement is, however, valid only for sediments with a continuous,
- 9 laminated record. All other cores exhibiting average carbon accumulation rates have most
- 10 likely been subjected to instant winnowing and redeposition of organic detritus.
- 11 At higher oxygen levels, organic carbon accumulation rates showed an inverse exponential
- 12 relationship with oxygen concentrations. This mirrors the successive bioirrigation and
- concomittant decomposition of organic matter through increasingly better ventilation below
- 14 the Peruvian OMZ. Such a relationship has not been described before. Few available data
- 15 from the Arabian Sea suggested a similar covariance conferring credibility to the pattern
- observed at the Peruvian margin (Koho et al., 2013). The relationship has been used to assign
- a paleo oxygen level to a well constrained, intermittently oxygenated interval at the base of
- cycle 0 (named Plenus Cold Event) in the Tarfaya sections. The estimate of 38 µmol kg⁻¹
- 19 overall disagrees with the composition of the Cretaceous and Recent benthic foraminiferal
- assemblages prevailing at this oxygen level.
- 21 In summary, close similarities and distinct differences between the two periods of low
- 22 oxygenation in the sedimentary record of the Cretaceous OAE2 and the Late Ouaternary
- 23 OMZs were recognised. More data are needed to further constrain the organic carbon
- 24 accumulation oxygen relationship. This emerging paleoproxy has to becomplemented and
- corroborated by other, advanced bottom-water ventilation proxies, e.g. molybdenum isotopes
- or I/Ca ratios in foraminiferal shells in order to achieve more quantitative reconstructions of
- 27 past oxygen levels and their controlling factors.

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1 Tables

Appendix Table A1: Metadata of cores for which information about laminations were available. *: Last Glacial to 12 ka, ** chronostratigraphy based on $\delta^{18}O$ curve, *** chronostratigraphy based on correlation with cores from IODP hole 680A, -: no information available.

		Latitude	Longitude	Depth	Lamina-	Age
Cruise	Core	S	W	(m)	tions	model
M77/1	413	17°47.10'	72°04.44'	2166	no	-
M77/1	414	17°38.60'	71°58.38'	928	no	-
M77/1	415	17°34.39'	71°56.19'	800	no	-
M77/1	417	17°26.02'	71°51.76'	328	yes	-
M77/1	493	10°59.97'	78°44.79'	2020	no	-
M77/1	494	11°0.025'	78°44.80'	2024	no	-
M77/1	495	10°59.96'	78°34.44'	1194	no	-
M77/1	496	11°0.01'	78°34.39'	1192	no	-
M77/1	503	11°0'	78°25.65'	699	no	-
M77/1	504	11°0.01'	78°25.67'	699	no	-
M77/1	505	11°0.01'	78°25.66'	699	no	-
M77/1	506	11°0'	78°21.14'	521	yes	-
M77/1	507	11°0.03'	78°21.13'	520	no	-
M77/1	508	11°0.03'	78°14.19'	377	yes	-
M77/1	509	11°0.03'	78°17.18'	377	yes	-
M77/2	002-6	15°04.75`	75°44.00`	285	yes	-
M77/2	003-2	15°06.21'	75°41.28`	271	yes	yes
M77/2	005-3	12°05.66'	77°40.07`	214	yes	-
M77/2	024-5	11°05.01'	78°00.91'	210	yes	-
M77/2	026-1	10°45.13'	78°28.43'	424	yes	-
M77/2	028-3	09°17.69'	79°53:86'	1104	no	-
M77/2	029-1	09°17.70'	79°37.11'	444	yes	yes

M77/2	029-3	09°17.70'	79°37.11'	433	yes	-
M77/2	045-4	07°59.99'	80°20.51'	359	no	-
M77/2	050-4	08°01.01'	80°30.10'	1013	no	yes
M77/2	052-2	05°29.01'	81°27.00'	1249	no	yes
M77/2	053-2	05°29.02'	81°43.00'	2591	no	-
M77/2	054-1	05°29.00'	81°18.35'	299	no	-
M77/2	056-3	03°44.99'	81°07.25'	350	no	-
M77/2	056-5	03°44.99'	81°07.48'	355	no	yes
M77/2	059-1	03°57.01'	81°19.23'	997	no	yes
M77/2	060-3	03°50.98'	81°15.50'	699	no	-
M77/2	062-1	02°29.98'	81°14.72'	1675	no	-
M77/2	064-3	01°53.49'	81°11.76'	523	no	-
M77/2	065-1	01°57.01'	81°07.23'	204	no	-
M77/2	067-4	01°45.18'	82°37.50'	2080	no	-
AM77/2	069-1	03°16.00'	80°56.86'	338	no	-
M77/2	072-3	02°49.00'	81°00.53'	425	no	-
M77/2	075-1	00°13.00'	80°39.44'	1316	no	-
M77/2	076-4	00°05.45'	80°33.40'	291	no	-
W7706	40	11°15'	77°57'	186	yes	yes
W7706	41	11°20'	78°07'	411	yes	yes
W7706	44	11°24.6'	78°13.8'	580	no	yes
W7706	04	12°58'	76°57'	325	no	yes
W7706	37	13°37'	76°50'	370	yes*	yes
B0405	13	12°00.8'	77°42.64'	185	yes	yes
B0405	6	14°07.9'	76°30.1'	299	yes	yes
IODP112	680A	11°03.90'	78°04.67'	253	yes	yes**
IODP112	686A	13°28.81'	76°53.49'	447	yes	yes***
SO78	158KAL	10°57'	78°06'	237	yes	-
SO78	175KAL	11°03'	78°36'	695	no	-

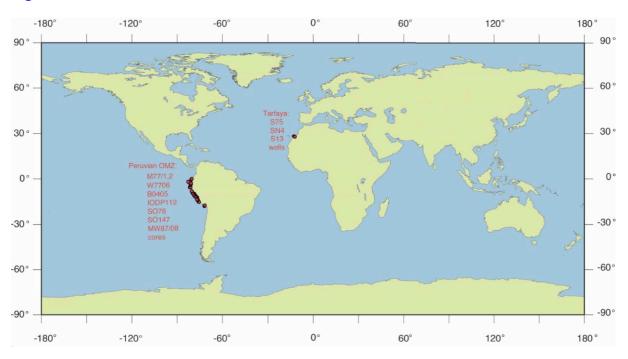
SO78	173KAL-4	11°05.64'	78°01.35'	204	yes	-
SO78	162KAL-5	11°21'	78°	281	yes	-
SO78	162KAL-6	11°21'	78°	283	yes	-
SO78	172KAL	11°30'	78°09.6'	511	yes	-
SO147	34SL	9°39.55'	79°28.43'	702	no	-
SO147	46SL	9°41.43'	78°40.97'	154	yes	-
SO147	41SL	9°51.08'	79°20.31'	587	yes	-
SO147	40SL	9°51.18'	79°20.22'	597	yes	-
SO147	83SL	10°36.5'	78°44'	605	no	-
SO147	80SL	10°40'	78°51.2'	1276	no	-
SO147	97SL	11°16.5'	77°58.4'	219	yes	-
SO147	27KL	11°37'	78°02'	382	no	-
SO147	25SL	11°54.7'	78°	202	yes	-
SO147	118KA	11°56.9'	77°18'	95,8	yes	-
SO147	4SL	11°56'	77°18'	96	no	-
SO147	106KL	12°03.0'	77°39.8'	184	yes	yes
SO147	123KA	12°57.30'	77°00.10'	363	yes	-
SO147	128KA	13°30.9'	76°21'	86	yes	-
SO147	137SL	13°36.4'	76°40.6'	196	yes	-
SO147	136SL	13°36.9'	76°45.9'	282	yes	-
MW87/08	SC2	11°04.21'	-	255	yes	-
MW87/08	SC7	14°56.62'	-	105	no	-
MW87/08	SC3	15°06.16'	-	253	yes	-

- 1 Appendix Table A2. Bottom-water oxygen and organic carbon accumulation rates of
- 2 Quaternary sediment cores from the Peruvian OMZ. BW: bottom water, AR: accumulation
- 3 rate, *average dry bulk density for near-surface sediments at the 12°S transect off Peru, -:
- 4 value not reported.

			Sed.	Dry	4.0		C_{org}		
		BW O ₂	rate	bulk	AR	_	AR (g	Time	
	Depth	(µmol	(cm	density	(g cm ⁻²	C_{org}	cm ⁻²	interval	
Core	(m)	kg ⁻¹)	kyr ⁻¹)	(g/cm ³)		(%)	kyr ⁻¹)	(cal ka)	Data source
W7706-40	186	2.17	-	-	28.00	13.40	3.30	0-0.5	Reimers, Suess (1983)
W7706-04	325	2.22	-	-	9.00	17.30	1.30	0-0.5	Reimers, Suess (1983)
W7706-37	370	2.65	-	-	11.00	13.20	1.60	0-0.5	Reimers, Suess (1983)
W7706-41	411	2.89	-	-	33.00	19.60	6.30	0-0.5	Reimers, Suess (1983)
SO147-106KL	184	2.10	168.8	0.36	60.38	11.25	6.79	1.5-1.9	Wolf (2002)
543MUC52	85	1.10	70	0.5*	35.00	3.50	1.23	recent	Mosch et al. (2012)
449MUC19	319	2.12	50	0.5*	25.00	10.65	2.66	recent	Mosch et al. (2012)
516MUC40	512	2.47	20	0.5*	10.00	6.07	0.61	recent	Mosch et al. (2012)
487MUC39	579	3.69	26	0.5*	13.00	6.48	0.84	recent	Mosch et al. (2012)
459MUC25	697	12.84	81	0.5*	40.50	6.72	2.72	recent	Mosch et al. (2012)
549MUC53	1005	40.34	45	0.5*	22.50	4.00	0.90	recent	Mosch et al. (2012)
M77/2-03-2	271	2.40	39.6	0.19	7.38	4.87	0.36	0.5-1.5	this study
M77/2-29-3	433	2.80	47.67	0.50	23.84	5.77	1.38	10.7-12.6	this study
M77/2-50-4	1013	53.90	23.77	0.50	11.81	3.94	0.46	11.2-14.0	this study
M77/2-52-2	1249	73.20	28.75	0.51	14.58	0.42	0.06	0-3.0	this study

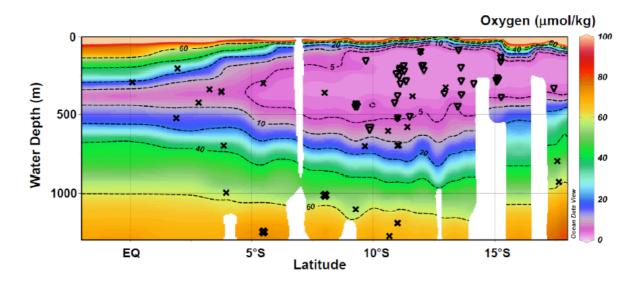
1 Figure captions

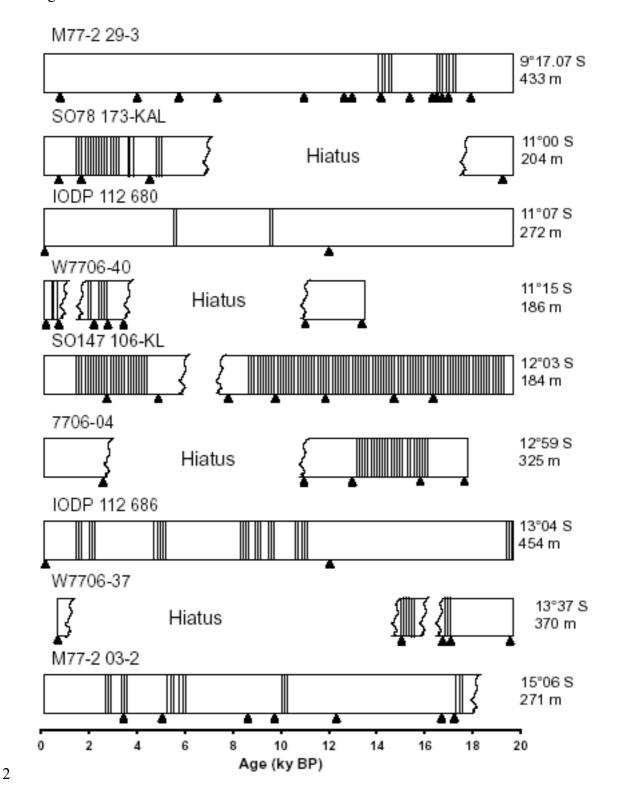
- 2 Figure 1. Location map of the sediment cores and wells studied.
- 3 Figure 2. Oxygen concentrations of a composite section along the Peruvian continental
- 4 margin and locations of sediment cores. Triangles: cores with laminated intervals. Crosses:
- 5 non-laminated cores.
- 6 Figure 3. Distribution of laminated intervals in sediment cores from the Peruvian OMZ.
- 7 Triangles depict age control points. All cores were radiocarbon dated except IODP 112 680
- 8 and 686, which have been dated by graphic correlation of the benthic stable oxygen isotope
- 9 curve with the SPECMAP stack (Imbrie et al., 1984; Wefer et al., 1990). Note that
- laminations were not recorded in sediments deposited between 6 and 8 cal. ka.
- Figure 4. Organic carbon accumulation rates versus bottom-water oxygen. Filled symbols
- indicate laminated sediment cores.
- 13 Figure 5. Onset of OAE2 in Tarfaya well SN°4. Red box indicates transition from
- 14 homogenous to laminated sediments. Note the increase in lightness variability.
- 15 Figure 6. Wavelet power spectrum of lightness values in a laminated portion of Core SN°4
- 16 (Section 41, Segment 1). Morlet wavelet with 6 parameters, the contour levels are chosen so
- that 75%, 50%, 25%, and 5% of the wavelet power is above each level, respectively.
- 18 (Torrence and Compo, 1998).
- 19 Figure 7. Low angle truncations and small scale erosional surfaces indicating sediment
- 20 reworking and re-distribution through small scale erosion and/or winnowing by bottom
- currents. A.-B. Coastal section near Shell/Onhym oil shale mine, lower Turonian; C. Amma
- Fatma coastal section, base of Turonian. Scale: 1 Dirham coin (24 mm diameter)
- Figure 8. Organic carbon accumulation rates estimated from TOC measurements of 2 m
- 24 continuously sampled and homogenized core sections, and density logging in Tarfaya well
- S13. Note the maximum between 94.4 and 93.75 Ma corresponding to the OAE-2 positive
- 26 carbon isotope excursion.

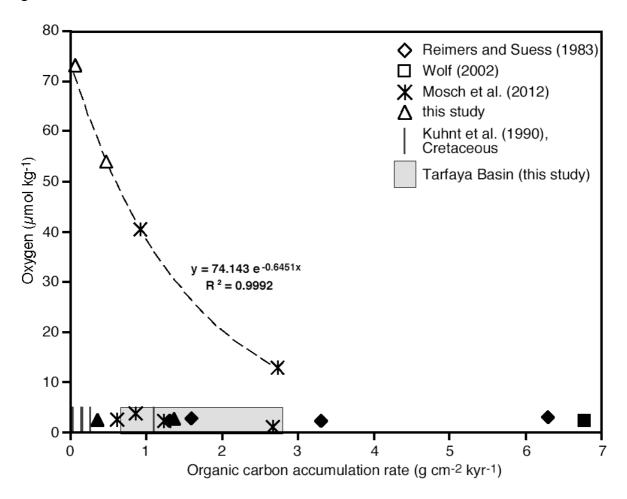


3 Figure 2

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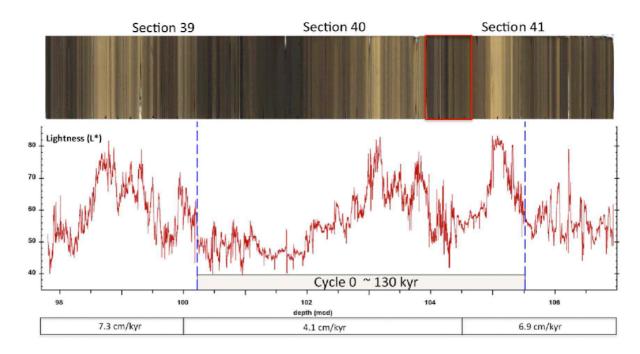


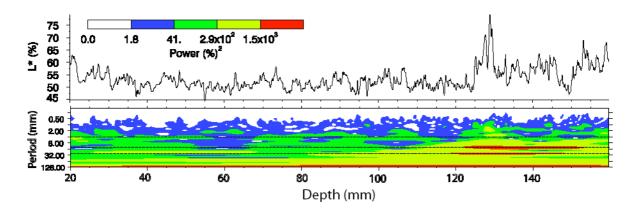




3 Figure 5

2





3 Figure 7

2

