

## ***Interactive comment on “Systematics of past changes in ocean ventilation: a comparison of Cretaceous Ocean Anoxic Event 2 and Pleistocene to Holocene Oxygen Minimum Zones” by J. Schönfeld et al.***

**J. Schönfeld et al.**

jschoenfeld@geomar.de

Received and published: 10 December 2014

Referee 1 noted that the title reflects only partly the contents of the paper

reply: indeed, we did not describe changes in past ocean ventilation but compared records of the late Quaternary Peruvian OMZ and the Cenomanian /Turonian Tarfaya Basin. We changed the title to: “Records of past mid-depth ventilation: Cretaceous Ocean Anoxic Event 2 vs. Pleistocene to Holocene Oxygen Minimum Zones”. The new title is shorter by four words, and we hope it is now more to the point.

C7260

1. The referee found abstract too long and recommended it to be shortened.

reply: we shortened the Abstract from 416 to 388 words in the revised version of the manuscript.

2. Holger Gebhardt asked why the authors did not compare Cretaceous and Quaternary benthic foraminiferal assemblages as they have been considered by many authors to be excellent oxygenation indicators. He asked to explain why foraminiferal assemblages were not considered for the evaluation of past ocean ventilation.

reply: benthic foraminiferal assemblages exhibited different community structures in Jurassic and Early Cretaceous low oxygen assemblages, which were characterized by low population densities and a dominance of textulariids and lagenids. Modern buliminid-boliviniid dominated benthic foraminiferal OMZ assemblages with a typical productivity driven distribution pattern became fully established during the Santonian/Campanian OAE3 (Holbourn and Kuhnt, 1998). Critical turning points in benthic foraminiferal evolution were the Cretaceous OAEs 1 and 2 (Aptian and Cenomanian/Turonian), when rotaliids began to dominate the assemblages in low oxygen environments. These changes may have been related to changes in benthic - pelagic coupling, when diatom-derived phytodetritus became an important source of food for benthic foraminifers in the deep sea. Although morphotypes may be similar in Pleistocene and Cretaceous assemblages, the trophic structure of the faunas were most likely different due to evolutionary changes.

3. The referee questioned that reservoir ages can be determined that exactly as stated, and he suggests to take 90 to 340 years throughout.

reply: The reservoir ages were calculated as regionally weighted mean values by using data entries from the Marine Reservoir Correction Database (<http://calib.qub.ac.uk/marine/>) for the eastern Pacific off Peru. The uncertainties of the source data range from  $\pm 31$  to  $\pm 82$  years (2-sigma). Therefore, it is not a mirror of analytical precision to round up 89 to 90 and 338 to 340 yrs. We are aware of the

C7261

uncertainties of AMS radiocarbon measurements but keep the mean values because they were accurately calculated. This is now specified in the text of the revised version.

4. Referee 1 asked why we have used shallow infaunal *Uvigerina* species for stable isotope analyses and not epifaunal *Cibicidoides* species.

reply: *Cibicidoides* species were rare, *Uvigerina striata*, *U. peregrina* and *Globobulimina pacifica* were abundant throughout the sediment cores from the Peruvian OMZ. We agree that preference should be given to epibenthic foraminiferal species for isotope measurements mirroring bottom water conditions. Despite exceptions caused by bacterial mats (Hoogakker et al., 2010 and references therein), *Uvigerina* and *Globobulimina* species incorporate stable oxygen isotopes in equilibrium with the surrounding pore waters, which are same as in the supernatant bottom water (e.g. McCorkle et al., 1990). We specified this in the text of the revised version.

5. The referee recommended the paragraph between 13349, line 26 and 13350, line 4 to be shifted to the Introduction, and he asked the check again the appropriateness of Poulsen (1998) and Topper et al. (2011) references.

reply: the references were wrong. We inserted the correct citations in the revised version of the manuscript.

6. Referee 1 noted that Chapter 3.1 is not exclusively focusing on the Peruvian OMZ and suggests to change the title accordingly. Furthermore, the subchapter on laminations describes general concepts developed in many parts of the world. He suggests only those parts referring to the modern Peruvian or Cretaceous Moroccan shelf should be presented in the results section.

reply: the referee is right indeed. We therefore changed the title of subchapter 3.1 to "Holocene to Recent organic-rich sedimentation underneath Recent OMZs". The separation of information gained from the Peruvian OMZ from data created in other OMZs is not justified. Our paper is a review paper. Therefore, it has to address the

C7262

subject comprehensively and it has to include all available information and resources, also from other places. This applies in particular to concepts that were developed off California or the Pakistan Margin.

7. Holger Gebhardt suggested to present a location map for all cores analysed including Peru and Morocco in order to underpin the dimension of this study.

reply: we included a location map with the studied sediment cores and wells as new Figure 1 in the revised version of the manuscript.

8. Referee 1 recommended the following technical corrections:

- the succession of cited papers within the text would not follow an obvious rule. They should be in an order according to the journal guidelines.

reply: according to the guidelines for authors, citations can be sorted either according to relevance, in chronological or alphabetical order. We decided to sort them in chronological order as we report the progress of knowledge in places. The citations were re-formatted in the revised version of the manuscript accordingly.

- page 13346, l. 12: Expedition in 1965 revealed. . . in order to distinguish the phrase from a reference.

reply: - done -

- page 13351, l. 1: Kuhnt et al. 2001 is missing in the ref.-list.

reply: - done -

- page 13351, l. 6ff.: Correct spelling is Savrda (see also ref.-list).

reply: - done -

- page 13354, l. 13: Gutierrez et al. 2006 as in ref.-list?

reply: - done -

C7263

- page 13356, l. 11: bioturbated

reply: - done -

- page 13357, l. 18: Gebhardt et al. 2004.

reply: - done -

- page 13358, l. 18: Kemp et al. 1990 or Kemp 1996?

reply: Kemp (1990) is correct.

- page 13361, l. 13: Martin et al. 1987 is missing in ref.-list.

reply: Martin et al. 1987 is now added to the reference list of the revised version..

- page 13362, l. 17: Mallon 2012 as in ref.-list?

reply: yes, corrected in the revised version.

- page 13380, Tab A3 Figure caption: Sections with. . .

reply: - done -

- page 13387, Fig. 7: Please arrange the upper and the lower panel in such a way that the ages are in line with each other in order to make a comparison of both panels easy. Correlation of peaks is rather difficult at the present stage.

reply: both panels have the same x-axis scales in the revised version of Figure 7, which is now Figure 8, done -

- Remark: I would have liked to see a possibility (electronic supplements, link etc.) for an easy access to the complete data set used in this paper.

reply: we will provide all the CTD data of the new Figure 2 and the data of the new Figure 8 as electronic supplements (MS-Excel documents).

Referee #2 (anonymous)

C7264

1. Referee 2 complained that Table A3 listed the data directly from Kuhnt et al., 1990 implying an OAE2 duration of 1.3 million years. This needs to be adjusted according to latest age models. There is also the decision to be taken either to include all the other sections from the Tethys Ocean, and to discuss their implications in full detail including latest results, or to strictly stay with the Moroccan localities.

reply: the accumulation rates in Kuhnt et al (1990) were calculated for the *W. archaeocretacea* foraminifera Zone, with an assumed duration of 1.3 million years (based on the time scale of Haq et al., 1986). This did not imply an OAE-2 duration of 1.3 million years, but it was at this time the only way to make sure, that all sedimentation rates were calculated for approximately the same time interval. High resolution  $\delta^{13}\text{C}$  curves, which define the extent of OAE2 much better than foraminiferal biozones were not available. However, this also means that the accumulation rates provided in Kuhnt et al. (1990) are minimum accumulation rates, since the period of high organic matter accumulation associated with OAE2 (approx. 800 kyr) is shorter than the *W. archaeocretacea* zone (approx 1300 kyr).

Furthermore, the first occurrence of *H. helvetica*, which defines the top of the *W. archaeocretacea* zone is in the Tarfaya sections later than its global first appearance datum (which is close to the FA of *Quadrum gartneri* just above the Cenomanian/Turonian boundary). Similar inconsistent FOs of *H. helvetica* have been recently reported from Tanzania, and the reliability of the FA of *H. helvetica* as a stratigraphic datum is becoming questionable. However,  $\delta^{13}\text{C}$  stratigraphy and the FA of *Quadrum gartneri* are consistent in the Tarfaya basin and the accumulation rates calculated on the basis of these events in addition to cyclostratigraphy (new Figure 8 of the revised version) are thus more reliable.

In the present paper, we only mention the organic carbon accumulation rates from well S13. In order to avoid confusion that may arise from the data of the other sections mentioned in the Kuhnt et al. (1990) paper, we have decided to omit Appendix Table 3 and referred to the original publication where more details can be found.

C7265

2. Referee 2 criticised absence of recent publications on the local and global redox state of the OAE2 ocean which could help our study to justify why it is important to understand these OMZ regions.

reply: we agree, only citing the book edited by Thiede and Suess (1983) is not enough to support our case. The Mesozoic Era is characterized by numerous oceanic anoxic events (OAEs) that are diagnostically expressed by widespread marine organic-carbon burial and coeval carbon-isotope excursions. Amongst the Cretaceous OAEs, the Cenomanian/Turonian boundary interval (OAE2) is probably the most extensive event. It is characterized by a globally recognized, stratigraphically distinct perturbation of the carbon cycle. For instance, redox-sensitive trace metal composition suggests contrasting depositional conditions and paleoceanographic processes in the western Tethys compared to the North Atlantic (Anbar and Rouxel, 2007; Dale et al., 2012). Nevertheless both, the western Tethys and Northern Atlantic sites show redox variations, reaching anoxic/euxinic conditions during OAE2. Furthermore, combined carbon- and sulfur-isotope data have indicated that oxygen-free and hydrogen sulfide-rich waters extended across roughly 5% of the global ocean, compared to a negligible proportion today, but with the likelihood that much broader regions were also oxygen challenged. These conditions must have impacted nutrient availability in the ocean and ultimately the spatial and temporal distribution of marine life across a major climatic perturbation (Owens et al., 2013). Thus, we argue that it is relevant to investigate meso scale processes such as modern and more recent OMZs in order to understand paleo OAEs, and vice versa. We referred to the abovementioned papers in the introduction of the revised manuscript.

3. Referee 2 asked for more discussion on the control of sedimentation rate on organic matter preservation, and he quoted that already Canfield (1994) has emphasized that bottom-water oxygenation is less important. The reviewer understood that sedimentation rates could be very important in the Peruvian OMZ where they also are very high compared to the OAE2 sites. Additionally, Hartnett et al. 1998 should be referenced.

C7266

reply: A large range of chemical, biological and oceanographical factors controlling organic detritus flux to the sea bed, decomposition and remineralisation, preservation and finally accumulation as refractory substances constitute the complex nature of organic matter turnover. Furthermore, organic carbon preservation strongly depends on the local circumstances of deposition (Arndt et al., 2013), thus limiting the comparability of settings between regions and oceanic basins. There is an ongoing debate whether the proportion of organic matter, which is buried and preserved in marine sediments, is dependant on the ambient bottom water oxygenation or not (Dale et al., 2014). The only assured perception is that carbon burial does not co-vary with bottom-water oxygenation at high sedimentation rates near continental margins (Betts and Holland, 1991; Canfield, 1994). At low sedimentation rates, the oxygenated near-surface layer of sediments deposited under oxygenated bottom water increases in thickness and facilitates enhanced aerobic decomposition, while sediments deposited under low-oxic conditions remain anaerobic and decomposition is effected by nitrate and sulphate reduction (Hartnett and Devol, 2003). As a 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 covariation in dysoxic zones (Hartnett et al. 1998). We added this paragraph to the discussion chapter of the revised version.

4. It is unclear to Referee 2 how the "20 % export production" value was obtained, and whether it is justified to apply this to OAE2 settings.

reply: This is certainly a misunderstanding. We meant burial efficiency and not export production here.

5. Referee 2 recognised several blanket statements needing clarification: "As a consequence, a whole suite of proxies have been applied to reconstruct past ocean oxygenation" reference has given to what proxies have been applied exactly. The statement "There are only few reliable parameters that are sufficiently explored to investigate paleo low-oxygen conditions in the Mesozoic and Cenozoic, which are trace fossils, laminations, and organic carbon accumulation rates" seems to exclude many geochemical

C7267

proxies applied with great success.

reply 1: The term “derivative” is more specific than saying “a whole suite of proxies”, which are, by the way, explained in the following paragraphs. This is now amended in the revised version of the manuscript.

reply 2: we agree, many geochemical redox proxies have been applied on Cretaceous black shales. These include redox-sensitive trace metals (Brumsack, 2006; van Bentum et al., 2009; Dale et al., 2012), sulfur isotopes (Hetzl et al., 2009; Owens et al., 2013), and iron isotopes (Owens et al., 2012). Some of these proxies have also been measured on surface sediments from the Peruvian OMZ (Böning et al., 2004, Scholz et al., 2011, 2014a). However, no calibration of these indicators is available for a quantitative reconstruction of past oxygenation of the Peruvian OMZ to date. This also hampers an application to black shales of OAE2. Most promising are U/Mo ratios, and there are first downcore records from the Peruvian OMZ (Scholz et al., 2014b). Nonetheless, only very few data points are available for a regional U/Mo – bottom-water oxygen calibration in the Peruvian OMZ (Scholz et al., 2011). They strongly differ from corresponding data obtained from other OMZs (McManus et al., 2006), which hampers application to black shales from Cretaceous OAEs. A respective paragraph is now added to the revised version of the manuscript.

Minor comments

- Referee 2 requested more information in order to understand why there was an adjustment to the oxygen measurements. What is the detection limit of this method?

reply: This is probably a misunderstanding. We did not correct the data of the CTD sensors. The oxygen concentrations shown in the new Figure 2 are a compilation of all measurements done by CTD attached Seabird oxygen sensors during RS Meteor cruise M77 legs 1-3. Stations from leg 4 were not considered because all CTD-stations from leg 4 were located further offshore. The typical detection limit of the CTD optode sensors is  $\sim 2 \mu\text{mol/kg}$ . In the study of Kalvelage et al. (2013) oxygen concentrations

C7268

determined with the seabird sensor showed an offset of  $\sim 2 \mu\text{mol/kg}$  compared to the concentrations determined with the more sensitive STOX sensors, which are based on Clark-type oxygen sensors, during M77 legs 3 and 4. Hence, the data from the optode sensors were corrected by  $2 \mu\text{mol/kg}$ . Unfortunately no STOX data is available for legs 1 and 2. Thus, we cannot assure that the optode data had the same offset during these legs. Furthermore, we wanted to present a dataset which is comparable to other datasets since the Seabird sensor is more commonly used than the STOX sensors. We changed the text in the methods to avoid further misunderstandings and added the following sentences: “Kalvelage et al. (2013) observed an offset of  $\sim 2 \mu\text{mol/kg}$  between the CTD attached optode oxygen sensors and the more sensitive STOX sensors, which are based on a Clark-type oxygen sensor, and corrected the optode data by  $2 \mu\text{mol/kg}$  during the cruises M77-3 and M77-4. The oxygen data presented in our study were not corrected for a  $2 \mu\text{mol/kg}$  offset since the STOX sensors were not deployed during M77-1 and M77-2 cruises.”

- Page 13353 Line 15 - It seems as though this sentence is putting an oxygen concentration from the modern to encompass all laminations from the late Holocene and subrecent sediments.

reply: this is probably a misunderstanding. Laminations were visible in the entire cores from the respective depths in the California borderland basins, despite the age of the core base. We amended the stratigraphic reach to “latest Holocene” and hope this is now better understandable.

- Figure 4 Increase in lightness scatter? The red box seems to show a decrease? Is the red box in the correct place? Please clarify.

reply: indeed, the red box is in the correct place. We meant lightness variability, which obviously increases although the sediment colour appears to get darker. We amended the wording of the figure caption in the revised version of the manuscript accordingly.

- Page 13364 Line 6: Typo where I think the word should be combined to showed

C7269

reply: - done -

#### References

- Anbar, A.D., Rouxel, O.: Metal Stable Isotopes in Paleoceanography, *Annual Review of Earth and Planetary Sciences*, 35, 717-746, doi: 10.1146/annurev.earth.34.031405.125029, 2007.
- Arndt, S., Jørgensen, B.B., LaRowe, D.E., Middelburg, J.J., Pancost, R.D., Regnier, P.: Quantifying the degradation of organic matter in marine sediments: A review and synthesis. *Earth-Science Reviews*, 123, 53–86, doi:10.1016/j.erscienv.2013.02.008, 2013.
- Betts, J.N., Holland, H.D.: The oxygen content of ocean bottom waters, the burial efficiency of organic carbon, and the regulation of atmospheric oxygen. *Palaeogeography, Palaeoclimatology, Palaeoecology* 97, 5–18, doi:10.1016/0921-8181(91)90123-E, 1991
- Böning, P., Brumsack, H.J., Böttcher, M.E., Schnetger, B., Kriete, C., Kallmeyer, J., Borchers, S.L.: Geochemistry of Peruvian near-surface sediments, *Geochimica et Cosmochimica Acta*, 68, 4429-4451, doi:10.1016/j.gca.2004.04.027, 2004.
- Brumsack, H.J.: The trace metal content of recent organic carbon-rich sediments: Implications for Cretaceous black shale formation, *Palaeogeography, Palaeoclimatology, Palaeoecology*, 232, 344-361, doi:10.1016/j.palaeo.2005.05.011, 2006.
- Canfield, D.E.: Factors influencing organic carbon preservation in marine sediments. *Chemical Geology*, 114, 315-329, doi:10.1016/0009-2541(94)90061-2, 1994.
- Dale, A.W., Meyers, S.R., Aguilera, D.R., Arndt, S., Wallmann, K.: Controls on organic carbon and molybdenum accumulation in Cretaceous marine sediments from the Cenomanian–Turonian interval including Oceanic Anoxic Event 2. *Chemical Geology*, 324-325, 28-45, doi: 10.1016/j.chemgeo.2011.04.014, 2012.

C7270

- Dale, A.W., Meyers, S.R., Aguilera, D.R., Arndt, S., Wallmann, K.: Controls on organic carbon and molybdenum accumulation in Cretaceous marine sediments from the Cenomanian–Turonian interval including Oceanic Anoxic Event 2. *Chemical Geology*, 324-325, 28-45, doi: 10.1016/j.chemgeo.2011.04.014, 2012.
- Dale, A.W., Sommer, S., Lomnitz, U., Montes, I., Treude, T., Gier, J., Hensen, C., Dengler, M., Stolpovsky, K., Bryant, L.D., Wallmann, K.: Organic carbon production, mineralization and preservation on the Peruvian margin. *Biogeosciences Discussions*, 11, 13067-13126, doi:10.5194/bgd-11-13067-2014, 2014.
- Hartnett, H.E., Devol, A.H. Role of a strong oxygen-deficient zone in the preservation and degradation of organic matter: a carbon budget for the continental margin of northwest Mexico and Washington State. *Geochimica et Cosmochimica Acta* 67, 2., 247–264, doi:10.1016/S0016-7037(02)01076-1, 2003.
- Hartnett, H.E., Keil, R.G., Hedges, J.I., Devol, A.H.: Influence of oxygen exposure time on organic carbon preservation in continental margin sediments. *Nature*, 391, 572–574, doi:10.1038/35351, 1998.
- Hetzel, A., Böttcher, M.E., Wortmann, U.G., Brumsack, H.J.: Paleo-redox conditions during OAE 2 reflected in Demerara Rise sediment geochemistry (ODP Leg 207), *Palaeogeography, Palaeoclimatology, Palaeoecology*, 273, 302-328, doi:10.1016/j.palaeo.2008.11.005, 2009.
- Holbourn, A.E.L., Kuhnt, W.: Turonian-Santonian benthic foraminifer assemblages from Site 959D (Côte d'Ivoire-Ghana transform margin, equatorial Atlantic): Indication of a Late Cretaceous oxygen minimum zone, *Proc. ODP Sci. Res.*, 159, 375–387, doi:10.2973/odp.proc.sr.159.038.19981998.
- Hoogakker, B., Elderfield, H., Oliver, K., Crowhurst, S.: Benthic foraminiferal oxygen isotope offsets over the last glacial-interglacial cycle, *Paleoceanography*, vol.25, PA4229, doi:10.1029/2009PA001870, 2010

C7271

Kalvelage, T., Lavik, G., Lam, P., Contreras, S., Arteaga, L., Löscher, C. R., Oschlies, A., Paulmier, A., Stramma, L., Kuypers, M. M. M.: Nitrogen cycling driven by organic matter export in the South Pacific oxygen minimum zone, *Nat. Geosci.* 6, 228-234, doi: 10.1038/ngeo1739, 2013.

Kuhnt, W., Herbin, J.P., Thurow, J., Wiedmann, J.: Distribution of Cenomanian-Turonian Organic Facies in the Western Mediterranean and along the Adjacent Atlantic Margin, in: *Deposition of Organic Facies*, edited by: Huc, A.Y., AAPG Stud. Geol., 30, 133-160, 1990.

McCorkle, D.C., Keigwin, L.D., Corliss, B.H., Emerson, S.R.: The influence of microhabitats on the carbon isotopic composition of deep-sea benthic foraminifera, *Paleoceanography* 5, 2, 161-185, doi: 10.1029/PA005i002p00161, 1990.

McManus, J., Berelson, W.M., Severmann, S., Poulson, R.L., Hammond, D.E., Klinkhammer, G.P., Holm, C.: Molybdenum and uranium geochemistry in continental margin sediments: Paleoproxy potential, *Geochimica et Cosmochimica Acta*, 70, 4643-4662, doi:10.1016/j.gca.2006.06.1564, 2006.

Owens, J.D., Gill, B.C., Jenkyns, H.C., Bates, S.M., Severmann, S., Kuypers, M.M., Woodfine, R.G., Lyons, T.W.: Sulfur isotopes track the global extent and dynamics of euxinia during Cretaceous Oceanic Anoxic Event 2. *PNAS*, 110 (46), 18407-18412, doi:10.1073/pnas.1305304110, 2013.

Owens, J.D., Gill, B.C., Jenkyns, H.C., Bates, S.M., Severmann, S., Kuypers, M.M.M., Woodfine, R.G., Lyons, T.W.: Sulfur isotopes track the global extent and dynamics of euxinia during Cretaceous Oceanic Anoxic Event 2, *PNAS*, 110, 18407-18412, doi:10.1073/pnas.1305304110, 2013.

Owens, J.D., Lyons, T.W., Li, X., Macleod, K.G., Gordon, G., Kuypers, M.M.M., Anbar, A., Kuhnt, W., Severmann, S.: Iron isotope and trace metal records of iron cycling in the proto-North Atlantic during the Cenomanian-Turonian oceanic anoxic event (OAE-

C7272

2), *Paleoceanography*, 27, 1944-9186, doi:10.1029/2012PA002328, 2012.

Scholz, F., Hensen, C., Noffke, A., Rhode, A., Wallmann, K.: Early diagenesis of redox-sensitive trace metals in the Peru upwelling area – response to ENSO-related oxygen fluctuations in the water column, *Geochimica Cosmochimica Acta*, 22, 7247-7276, 2011.

Scholz, F., McManus, J., Mix, A.C., Hensen, C., Schneider, R.: The impact of ocean deoxygenation on iron release from continental margin sediments, *Nature Geoscience*, 7, 433–437, doi:10.1038/ngeo2162, 2014b.

Scholz, F., Severmann, S., McManus, J., Hensen, C.: Beyond the Black Sea paradigm: The sedimentary fingerprint of an open-marine iron shuttle, *Geochimica et Cosmochimica Acta*, 127, 368-380, doi:10.1016/j.gca.2013.11.041, 2014a

Thiede, J., Suess, E. (eds.): *Coastal Upwelling: Its sediment record*, Part B: *Sedimentary Records of Ancient Coastal Upwelling*, NATO Conference Series IV: Mar. Sci., Vol. 10b, 610 p., 1983.

van Bentum, E.C., Hetzel, A., Brumsack, H.J., Forster, A., Reichart, G.J., Sinninghe Damsté, J.S.: Reconstruction of water column anoxia in the equatorial Atlantic during the Cenomanian–Turonian oceanic anoxic event using biomarker and trace metal proxies, *Palaeogeography, Palaeoclimatology, Palaeoecology*, 280, 489-498, doi:10.1016/j.palaeo.2009.07.003, 2009.

---

Interactive comment on Biogeosciences Discuss., 11, 13343, 2014.

C7273