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Biogeosciences Discussions

Interactive comment on "Redox sensitive elements in foraminifera from the Peruvian oxygen minimum zone" *by* N. Glock et al.

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We appreciate the effort the reviewer put into our manuscript to improve our manuscript. Below we comment in detail the points of major revision.

The recommended minor revisions in grammar and technical details in the supplement have been followed and are not discussed further here, except two points which need a bit closer attention:

The reviewer criticized several times, when we wrote about Mn settling down to the seafloor (in the supplement: page 7969, line 15 and 19,page 7972, line 24; page 7973, line1). He made a suggestion to correct this to "MnO2 is precipitated insitu at surface sediments". We think the reviewer has conditions in mind with high Mn concentra-

tions in the deeper pore-waters due to reduction of Mn oxides at the oxycline. In this case usually dissolved Mn diffuses towards the sediment surface and precipitates in the presence of oxygen (Burdige, 1993). This does not happen in the Peruvian OMZ because even in the deeper pore waters Mn is present only in trace amounts (Scholz et al., 2011). Since most of the Mn oxides from the continental input are already reduced in the water column, the only Mn which arrives at the seafloor below the OMZ are rests of these Mn oxides or dissolved Mn through diffusion out of the OMZ.

The second point regards a comment of the reviewer about the accumulations in chambers of U. peregrina. on page 7964, line 11. He wrote: "How do you know they are "muddy", could they also be organic, like protoplasm of the lining as they are rich in S an P?" We doubt that these accumulations are rests of protoplasm or the lining because they optically differ from protoplasm and the lining would be located at the inner wall surfaces and much thinner (about 1 um). Nevertheless, the reviewer is right that these accumulations probably do not consist out of mud. Thus other possibilities are now discussed in the revised version of the paper, page 14 line 11-20.

In the following the major points will be discussed. Each of the comments was addressed separately.

Anonymus Referee #2 (AR)

AR: 1. The manuscript contains interesting data, however, the current form is not well organized and the focus of the paper is not clear. Question is: Is there enough field date to conclude whether Mn/Ca and/or Fe/Ca ratios can be used in paleoreconstructions or should the main focus of the study concentrate on the comparison of different measuring and cleaning techniques? I suggest the authors should re-examine and re-evaluate the scope of the study and formulate the title/introduction/discussion accordingly. Also, one topic should be discussed only once to avoid unnecessary repetition.

Reply: We thoroughly thought about the focus of the paper. Of course, the data set presented does not provide a comprehensive base for proxy calibration or complete

validation. Nevertheless we assured the quality of the data by the comparison of the different analytical techniques and the preanalyses with EMP. Interpretations are on preliminary level due to the limited data set of this initial study and worth to be discussed as the promising impetus for future studies. The methodic studies are important preparatory work for this study and the sense of these has to be implied into the manuscript. In the revised manuscript we want to assure that the results about the proxy identification are only a contribution and not a complete validification of a proxy. The dataset is limited due to the elaborateness of the pre-analyses and the available pore water data and number of B. spissa specimens. The new title already tries to describe focus of our study: "EMP and SIMS studies on Mn/Ca and Fe/Ca systematics in benthic foraminifera from the Peruvian OMZ: A contribution to the identification of potential redox proxies and the impact of cleaning protocols". Abstract, introduction, discussion and conclusions have also been rewritten in major parts to clear the focus of the paper: We wanted to test the possibility to use Mn/Ca and Fe/Ca ratios in benthic foraminifera with microanalytical techniques as a possible proxy for redox-conditions by comparison with available pore water data. Due to the problem of possible contamination, thorough preanalyses were necessary which are discussed in detail. The dataset is limited may be rated as base for the still pending detailed calibration. We also tried to avoid unnecessary repetition in the revised version of the manuscript.

AR: 2. The authors should also re-examine all their tables and figures. Are all the tables really necessary (e.g. tables 2-5), what can be deleted and what can be put into the appendix? Figures should be above all readable, and also neat and informative. At the moment I find figures 1-8 not very attractive and the scales are not legible in figures 2 and 3. To give more space for the scales, the secondary electron images could be made smaller and the elemental maps larger? Also, authors should carefully consider if all figures are really necessary (e.g. Figure 9). Finally, tables and figures should be referred to in a chronological order (not the case now).

Reply: The former tables 2-4 and figure 9 were moved into the appendix. Former table

5 (table 2 in the revised manuscript) contains the Fe/Ca and Mn/Ca ratios determined with ICP-MS. This data is important for the discussion in this manuscript and has neither been changed nor moved. The scales at all elemental maps have been changed to make them more readable and attractive. As the reviewer suggested, the SE images in figures 2 and 3 have been made smaller and the elemental maps larger. All tables and figures are referred in a chronological order now.

AR: 3. I also have a problem with the trend lines and accompanied R2 values, which are reported in Figure 10. The R2-values and the trend-lines are based on averages, thus excluding the scatter (error-bars) in the real date. If all data would be used instead of the averages the trends would not be visible at all. So the R2 is misleading. I also find it very tedious, if not impossible, to figure out how many measurements were really carried out in this study? And how many measurements the error bars in figures 10 and 12 represent. What is the n-number?

Reply: The reviewer is right. The trend-lines in former figure 10 (figure 9 in the revised manuscript) were based on averages. For the new trend lines given in this figure all data was used. Although the R2 became worse the trends are still slightly visible. Furthermore, the n-number has been given in this figure to show how many SIMS measurements have been done on a single average datapoint. For visualization we also put plots of all data points into the appendix (fig. A1).

AR: 4. Figures 11 and 13 seem out of scope of this study. The foraminifera were collected from top 1 cm of sediment, so it is not necessary to discuss/present the Fe-pore water profiles down to 20 cm depth in sediment. In stead, the real miss-match between the Fe/Ca in foram vs. pore water Fe/Ca may be more appropriate to plot.

Reply: Former figures 11 and 13 which were showing the downcore Fe pore-water profiles have been deleted in the revised manuscript. The real miss-match between the Fe/Ca in foram vs. pore water Fe/Ca is now plotted in figure 10b. Furthermore the whole discussion about Fe in pore water was shortened to avoid unnecessary

repetition of the already published data.

AR: 5. Some other smaller comments: Diagenesis discussion (sections 4.1 and 4.2.) All discussion regarding uncleaned vs. cleaner specimens (regardless of foram species) should be done in one section to avoid unnecessary repetition. Reply: Discussion sections 4.1 and 4.2 and the corresponding result sections 3.1 and 3.2 have been tightened to one section (4.1 and 3.1 respectively in the revised manuscript).

AR: 6. p. 7968 line 7. On average, how large proportion of the foraminiferal test is covered in pores? 1-3% or more? If measuring (trace) metal in foraminiferal calcite with LAICP- MS, I doubt that the pores make such a big difference, or the "pore error" would be smaller than inter-specimens variability from the same site.

Reply: The "pore error" is much bigger than the reviewer assumes. Porosities of 20% or more are not unusual (Bé. 1968, Glock et al., 2011). Furthermore the relative Fe count rates (EMP) are 2-4 times higher in the contaminated areas and the Ca count rates are slightly lower at the contaminated areas. Thus the "pore error" might be significant. This is now discussed in detail in section 4.1 in the revised manuscript (page 15, line 1-7).

AR: 6. The discussion regarding the miss-match of Fe/Ca ratios in forams and pore water data (Section 4.3.) How stable is the Peruvian OMZ through time/seasons? In the Arabian sea OMZ the lower boundary is relatively stable through time and only the upper part shows seasonal fluctuates (Cowie and Levin, 2009). Thus, how plausible is it that such and anoxic intrusion occurred prior to sampling?

Reply: The environmental conditions in the Peruvian OMZ are strongly influenced by El-Nino events. Periodic shifts in the upper OMZ boundary are well known and not all oxygenated episodes are restricted to El-Nino (Guitierrez et al., 2008). The input of organic matter is much lower during El-Nino even below the lower OMZ boundary (Levin et al., 2002). This can cause higher oxygen levels even in deeper water levels below the OMZ and may cause a shift to anoxic conditions after El-Nino like events

when the input of organic matter raises again. This is discussed in detail in the revised manuscript section 4.2.2 (page 17, line 12-28).

AR: 7. Were any of the analysed foraminifera identified as living (e.g. Rose Bengal stained)? If not, the specimens measured here could be relatively old. Is the sediment bioturbated? What are the sedimentation rates like?

Reply: None of the analysed foraminifera were stained. Nevertheless the fauna in this region is very restricted and bioturbation should be limited to the surface sediments except in water depths from 640-740 m (Mosch et al., submitted). Together with the sedimentation rates (Mosch et al.; submitted) we assume the maximum age of the top cm in the sediments from 12-50 years. This is referred in detail in section 2.2 (page 7, line 8-15).

AR: 8. page 7971 line 8. What do the authors mean with a long phase of oxygenation? How long is long? Bolivinids are know to be very opportunistic (e.g. Hess et al. 2005, Langezaal et al. 2006) and can reproduce offspring quickly. The life span of foraminiferal species is estimated to vary from a month to few years (Murray 1991), during which a foraminifer can produce hundreds of offspring. Thus species with shorter longevity and large offspring, like Bolivinids, can become overrepresented in the dead assemblage. This part of the discussion should be omitted. It is too speculative.

Reply: The reviewer is right. This part of the discussion indeed was too speculative and we deleted it completely in the revised manuscript.

AR: 9. p. 7970 line 25. I do not agree that you can conclude from your data whether B. spissa needs trace amounts of oxygen to live or not. B. spissa is known to accumulate nitrate (Glud et al. 2009), and is a potential denitrifier.

Reply: In the first version we already wrote that B. spissa either needs trace amounts of oxygen to survive or enough nitrate for denitrification, since nitrate is usually depleted, too when pore waters turn anoxic. Nevertheless, we outlined this in more detail to avoid

misunderstandings (section 4.2.2, page 16, line 9-13).

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