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Interactive comment on “Imbalanced nutrients as triggers for black shale formation in a shallow shelf setting during the OAE 2 (Wunstorf, Germany)” by M. Blumenberg and F. Wiese

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Reply to referee comment of Dr. Ohkouchi

Referee

This paper reports analytical results of OAE-2 black shales collected at Wunstorf, north Germany. Together with carbon isotopic composition of carbonate published before, they reported bulk properties including $\delta^{15}\text{N}$ and a series of hopanoids. I think OAE includes essence of biogeochemical processes on Earth and many piece is still missing. This manuscript is well written and data reported here are original. Interpretation of the data, especially for the final section of the manuscript is important and intriguing. I

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recommend the manuscript is acceptable for publication in Biogeosciences after minor revision. Below I describe some comments;

Referee comment: A previous study with SEM-EDS (Ohkouchi *et al.* 2003) suggested that organic matter in the OAE black shale exists mainly as micrometer scale organic “chunks” rather than spreading over the surface of clay minerals. Prof. Andrew Aplin at Newcastle University recently got a similar result. Therefore, There are more data to support the author’s view that protective mechanisms of the organic matter on clay mineral surfaces does not affect effectively in the black shale.

Reply: We thank the referee for this comment and will add a respective sentence in the discussion (under section “5.2 Triggers for high organic carbon accumulation”). Moreover, we also will add the reference “Ohkouchi, N., Kuroda, J., Okada, M., and Tokuyama, H., 2003. Why Cretaceous black shales have high C/N ratios: Implications from SEM-EDX observations for Livello Bonarelli black shales at the Cenomanian-Turonian boundary. *Frontier Research on Earth Evolution* 1, 239-241”.

Referee comment: To my knowledge, sedimentary phosphorus in Cretaceous black shale is mainly associated with calcium phosphate, bone/teeth of organisms (Please see Kuroda *et al.* 2005 *GCA* 69, 1479-). Did the authors check this in their samples? If this is the case, how it affects the author’s thoughts on biogeochemical cycles during OAE-2?

Reply: Concerning the occurrence of phosphorus, Kuroda *et al.* (2005) suggested that the phosphorus enrichment in parts of the Livello Bonarelli might be interpreted to result from bone fossils. We did not measure the P content in our samples, but data from other works contribute to this subject. In extension to Kuroda *et al.* (2005) Mort *et al.* (2007) reported a peak occurrence of authigenic and organic phosphorus for the OAE 2 of the Western Interior Seaway (Pueblo), England (Eastbourne), Spain (Manilva) and Italy (Furlo) (see Mort *et al.*

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p. 483, Fig 1). This indicates that the P peak is an interbasinal phenomenon. Especially relevant to our model is the occurrence of a P peak at Pueblo and in the middle of the OAE 2-CIE from the Seewen Formation of the Helvetic Shelf (Switzerland), where no BS are developed. The Seewen Formation consists of calcareous nannofossil oozes with c-dinocysts and planktonic foraminifera (see Westermann *et al.* 2010, Fig. 4), and it represents basically an identical N-limited biosedimentary system like the Brochterbeck Formation or the white limestone beds intercalated with the BS layers (Hesseltal Formation; see our Fig. 2). This strongly supports our model that in these N-limited distal shelf settings excess phosphorus – deriving from the increased continental weathering in the course of the LIP volcanism – could not be transferred into biomass due to a low degree of N fixation. Instead, it by-passed the shelf into areas, where (cyano)bacterial N-fixation occurred (which then fueled productivity; see our Fig. 11) or was stored in the sediment as authigenic phosphate.

Referee comment: Based on the model results (of modern ocean), denitrification and N₂-fixation are regulated internally (Deutsch *et al.* 2007, *Nature*, 445, 163-). Do the authors think it the case during the OAE-2?

Reply: Yes, we propose exactly a similar mechanism for the OAE 2 situation, where enhanced anoxia (and denitrification) and phosphorus excess through riverine input should have promoted N₂ fixation. This relationship is explained under section 5.2 (page 5392, line 7ff.) and we added the interesting study by Deutsch *et al.* (2007) as further support of this linkage.

Referee comment: I cannot find van Bentum *et al.* 2012 in the list of references. Please check the list carefully.

Reply: The referee must have overlooked it, but “van Bentum *et al.* 2012” paper is included in the MS (under B). Anyway, we will check the list carefully before resubmission of the corrected MS.

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