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Biogeosciences Discussions

Interactive comment on "An importance of diazotrophic cyanobacteria as a primary producer during Cretaceous Oceanic Anoxic Event 2" *by* N. Ohkouchi et al.

Anonymous Referee #2

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General Comments

This paper presents data that furthers our understanding of the marine environmental conditions during the Cretaceous OAE-2. While confirming that the well-preserved organic matter deposited during this period has a low d15N as compared to the modern ocean, I don't believe that their main conclusion that N2-fixing cyanobacteria were the dominant photoautotrophs is substantiated. I recommend the paper be extensively revised to 1) include other likely interpretations consistent with the evidence presented and drawing upon modern analogues and 2) be more thoroughly synthesized with prior studies of this time period to provide as coherent a view as possible of the marine

environmental conditions at that time.

Specific Comments

It should be acknowledged that it is a considerable technical challenge to isolate sedimentary porphyrins for identification and stable isotope analysis. These compounds are mainly derived from chlorophylls and since the tetrapyrrol ring remains intact, they retain the N isotope composition of their precursor molecules and thus the d15N of the photoautotrophs that produced them. Sachs and Repeta (1999) used this approach to show that the bulk N in OM-rich Pleistocene sapropel layers in the Mediterranean retain their original N isotopic composition whereas intervening OM-poor layers suffered from diagenetic enrichment. Preservation of original d15N signatures in the bulk N of OM-rich sediments has found to be a general phenomenon. Analysis of porphyrin isotopic composition in OM-poor sediments would be an important means to overcome the problems of diagenetic alteration but so far their concentration appears to be too low for isotopic analysis.

The measured geoporhyrin d15N of -3.4 per mil does appear to confirm a low d15N for photoautotrophs during OAE 2. I am concerned, though, that this values is for only one sample of the OM-rich sequence. At a minimum, 3 to 4 determinations are needed for confirmation. The text is also not clear as to the stratigraphic position of the sample analyzed (GCB-17) and this datum should be plotted on Fig. 1 for direct comparison to the bulk OM d15N values. The authors do point out that from culture studies, chlorophyll N is lower than the organism's bulk d15N by about 5 per mil (Fig. 5) explaining the biochemical pathway that apparently gives rise to this difference. Sachs and Repeta (1999), observed such an offset in both water column samples and in the sapropel layers. However the offset seen in this paper is only 2 per mil. It is not clear why this is not noted and discussed by the authors as it puts a question mark on this approach for these much older sediments. If this one sample is representative, either the sediments have a experienced a 'reverse' diagenetic effect on d15N values or the geoporphyrins extracted do not record the d15N of coeval photoautotrophs.

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Either way, the data are nevertheless consistent with low d15N values for OAE-2 (as compared to the modern ocean) as well as literature values for similar paleo-environments. However by itself, this observation does not conclusively point toward N2 fixing organisms as both the dominant photoautotrophs and direct source of the preserved OM. The authors need to consider in their discussion at least two other possibilities; 1) DIN utilization in surface waters was not complete leading to isotopic fractionation and low d15N for sinking OM as found in today's HNLC regions and/or 2) the average d15N of DIN (NO3- and/or NH4+) was low as compared to today and this signal was imprinted on sinking OM. Fe limitation of primary production is implied by #1, a global ocean N cycle rather different from today is implied by #2. In the latter case, it must be recognized that in the absence of water column denitrification (where partial removal of NO3- results in 15N enrichment of the remainder) the average global marine d15N values would be the same as the weighted average of the sources. Other possible loss terms (sediment denitrification or OM burial) do not significantly affect the d15N of the N remaining in the system. Since N2 fixation is one way or the other, the source of combined N to the biosphere, the average d15N without water column denitrification has to be 0 to -2 per mil. N2 fixation thus does not have to be the proximal source of N for OM low in d15N since without water column denitrification the NO3- or NH4+ taken up by photoautotrophs would on average have these low values.

This scenario is found in both the modern Mediterranean and Black Seas. In the former, oligotrophic conditions due to lagoonal conditions maintains high O2 throughout the water column. In the latter, estuarine circulation produces euxinic conditions and anoxia below the thermocline. Suboxic conditions promoting partial denitrification are absent except as a thin layer between the oxic and anoxic zones. I would argue that the Cretaceous OAE's as well as the Pleistocene Mediterranean sapropels are likely most analogous to the modern Black Sea and one should examine carefully that environment to beginning understanding what these ancient environments might have looked like.

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Identifying molecular biomarkers as employed here is another common approach to determining the sources of sedimentary OM that complement the isotopic determination. However the chlorophyll precursor for the geoporphyrins isolated are not specific to cyanobacteria (let alone N2 fixers) so their molecular identification does not per se support the paper's conclusions.

Other points:

1) There should more discussion of prior literature for this time period and current understanding of the climatological and environmental setting of the study site. A map showing this paper's study site as well as those previously examined with respect to estimated paleo-continental configuration would be useful.

2) It should be pointed out that the d15N of newly fixed N is not likely to have changed in the remote past given the size of the atmospheric N2 reservoir and its long turnover time.

3) there is bit too much methodological detail presented on pgs. 578-579 that likely can be cited from prior literature.

4) there is background material on pgs 580-581 that is better placed in the Introduction
5) pg. 580, section 3.1; there should be discussion of the form of N found in the high ?15N portion of the sedimentary sequence shown in Fig. 1. Also %N or %Corg data should be plotted in Fig. 1.

6) pg. 582, lines 2 to 6; again this in background material better suited for the Introduction; lines 7 to 24, the point of this discussion is not clear since assignment of Chl a, b, c, or d to the geoporphyrin isolated does not make a unique identification as to the algal source.

7) pg. 587, lines 15 & 16; this statement implies knowledge of the d15N of NO3- or NH4+ at that time. This assumption needs to be stated explicitly. As discussed above, the d15N of Cretaceous DIN was not necessarily the same as in today's open ocean.

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8) pg. 589 top, the extra amount of Fe needed by N2 fixers has been revised downward see Kustka et al. (2003) Journal of Phycology, 39, 12-25.

9) English grammar and usage are shaky at points and the paper needs a thorough going over in this respect.

References

Kustka, A., et al. (2003), A revised estimate of the iron use efficiency of nitrogen fixation, with special reference to the marine cyanobacterium Trichodesmium spp. (Cyanophyta), Journal of Phycology, 39, 12-25.

Sachs, J. P., and D. J. Repeta (1999), Oligotrophy and nitrogen fixation during Eastern Mediterranean sapropel events, Science, 286, 2485-2488.

Interactive comment on Biogeosciences Discuss., 3, 575, 2006.