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Biogeosciences Discussions

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3, S605–S609, 2006

Interactive Comment

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

N. Ohkouchi et al.

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Reply to the comments from Referee #2

First of all, I acknowledge the reviewer to provide thorough review and insightful comments of our paper. Below I will reply these comments.

General comments (S538) 1) Include other likely interpretations consistent with the evidence presented and drawing upon modern analogues

I think that the reviewer's major concern is that the reconstructed nitrogen isotopic composition of the phototrophic cell (+1 per mil) cannot be an evidence strong enough to support diazotrophy but can be explained by other oceanographic processes. I think

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that the reviewer is theoretically correct. However, the advantage of cyanobacteria hypothesis over others is that it has been supported by some other (but not perfect) evidence like 2-methylhopanoids and SEM observation as I described in the paper. Anyway, I agree that I should mention the point in the paper. In the revised ms, we added the following phrase and partially tone down our assertion; "..., although we should note that the value (+1 per mil) cannot perfectly rule out other possibilities like reduced nitrate utilization or 15N-depleted nitrate in the surface ocean due to the modified ocean nitrogen cycle during the OAE." (p. 15, line 21-23).

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.

The aim of this short paper is to report novel evidence based on a brand-new technique for supporting my previous paper (Ohkouchi et al., 1997, Ancient Biomolecules). As described in this paper, partly based on the bulk-sediment d15N evidence, several scientists including myself have concluded that the major primary producer during the Cretaceous OAEs is cyanobacteria. However, their assertion has been strongly criticized in the point that the d15N value of bulk sediments is not a reliable proxy because it can alter during the diagenesis. This criticism was a major driving force for me to work on the compound-specific nitrogen isotopic composition of geoporphyrins. One of my students (Y. Kashiyama, second author of this paper) recently established more sophisticated analytical method, worked more samples from Bonarelli black shales, and confirmed the data reported in this paper. He is currently preparing a full-paper for reporting/interpreting the d15N of geoporphyrins from the Cretaceous black shales. In that paper, we will discuss them with referring prior works of Cretaceous OAEs more extensively.

Specific comments First paragraph We are aware of Sachs and Repeta (1999) determined N isotopes of chlorophylls purified from Mediterranean sapropels. In 3.3 and Conclusion sections of our original ms, we have already cited the paper and mention about Mediterranean sapropel. I agree with the reviewer in the point that OM-poor sed-

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iments, as a counter part of OM-rich sediments, would provide important information on the paleoceanographic changes. Currently, we are making an effort to reduce the amount needed for isotopic analyses of N by modifying the EA/IRMS system. For a moment, our improved system can determine the N isotopic ratio with the sample size as small as 500 ngN (the lower limit of the commercial system is ˜30 gN). We still have potential for making progress to further reduce the lower limit, which will realize the deterrmination of N isotopes of porphyrins in the OM-poor sediments in near future.

Second paragraph (S539) We have recently worked more samples from Bonarelli black shales. The nitrogen isotopic compositions of major porphyrins from these samples are in the same range (-3 to -5 per mil) as that presented in this ms. This work has just finished and one of the coauthors (Y. Kashiyama) is preparing another manuscript for reporting/discussing them. The stratigraphic position of our porphyrin sample was indicated in the revised Fig. 1. As the reviewer pointed out, the N isotope difference between porphyrin and bulk OM are 2 per mil which is lower than that found in Mediterranean sapropel reported by Sachs and Repeta (1999). Bulk sedimentary OM is a mixture of OM derived from various sources and the relative contribution of these sources should be different from one sediment to another. The sediments worked by Sachs and Repeta have sedimentation rate of ca. 3-10 cm/kyr, whereas the sediments we worked have sedimentation rate of ˜0.13 cm/kyr (after compaction; Ohkouchi et al., 1999, Geology), more than an order of magnitude smaller than the former. It means that the sedimentological setting of our sediments should have been quite different from the one observed by Sachs and Repeta (1999). For example, Mediterranean sediments may contain more terrestrial organic matter or have 10 times more chance to be "contaminated" by clay-ammonium. Based on these considerations, we do not think it a serious point.

Third paragraph (S540) As I mentioned above, in the revised ms, we added the following phrase and partially done down our assertion; "..., although we should note that the value (+1 per mil) cannot perfectly rule out other possibilities like reduced nitrate utilization or 15N-depleted nitrate in the surface ocean due to the modified ocean nitrogen cycle during the OAE." (p. 15, line 21-23).

Fourth paragraph (S541) At this moment, unfortunately, organic geochemists do not know any source-specific molecules for cyanobacteria. Even 2-methylhopanoids are produced by about half species of cyanobacteria, whereas the other half produces normal hopanoids which are also produced by other prokaryotes (Summons et al., 1999, Nature).

Other points 1) Paleocontinental configuration in 94 Ma has been published in many other papers. In the revised ms, we refer these papers for readers to easily access them (p. 5, line 9-11). 2) We inserted a sentence "When interpreting this value, our assumption is that the nitrogen isotopic composition of newly fixed nitrogen have not changed significantly in the remote past given the size of atmospheric N2 reservoir and its long turnover rate." (p. 15, line 17-19) 3) The analytical protocol of geoporphyrins is very much different from that of chlorophylls. I am afraid that some readers need (at least rough) information on the analytical protocols (Actually, I have been asked many times). Therefore, in the revised ms, I reduced the volume of analytical protocol description, but remain some bit for helping such readers (p. 5-6). 4) Following the reviewer's suggestion, the section was placed in the Introduction (p. 2-3). 5) In the revised ms, I clarified that one sample (d15N = +3.0) is not included in the statistics (p 7, line 14). In the revised Fig. 1, contents of total nitrogen and TOC were plotted. 6) I tried to put the portion to Introduction, but it does not fit very well. I remain it where it was. I omitted "...not only they are strongly source-specific but also..." and change the phrase simply to "...because they contain four nitrogen atoms in a single molecule" (p. 9, line 17). 7) I think above discussion and revision cover this comment. 8) In the revised ms, we mention the results of Kustka et al. (2003) and substantially toned down the discussion that the lack of iron controls the bloom of diazotrophic cyanobacteria (p. 17, bottom). 9) I made an effort to revise our English, although I am not confident with

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the results...

Reply to the comments from Referee #3

I acknowledge the reviewer to provide very positive comments of our paper. As the reviewer suggested, we know that the weakness of the paper is that this paper only reports the nitrogen isotopic composition of geoporphyrins. Some other supporting evidence such as lipid biomarkers will be reported in a coming full-paper which is currently prepared by the second author of this paper (Kashiyama et al., in prep.)

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

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