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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 #3

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This short manuscript reports and discusses the N-isotope chemostratigraphy through the Livello Bonarelli black shale deposited during the Cretaceous OAE2. The data are compared to relationships between N-isotopes in pigments, total organic nitrogen and the various physiologies of N-assimilation.

The key observations made are the presence of a positive to negative swing on the d 15N values for bulk nitrogen in sediments of the black shale horizon compared to the underlying unit. An individual porphyrin that can be traced to an origin from chlorophyll-a, and a combined porphyrin fraction were shown to have d15N values of about -3.5 per mil which is in the range of photoautotrophs which fix their N from dinitrogen as

opposed to assimilating nitrate. Other studies of from Mesozoic OAE intervals report enhanced abundances of 2-methylhopanoids (purported biomarkers for cyanobacteria) and isorenieratene derivatives, which are well-established biomarkers for green sulfur bacteria and, in turn, proxies for photic zone euxinia. Thus, the authors hypothesize that diazotrophic cyanobacteria were major primary producers during the OAE2.

The strength and importance of the paper lies in the techniques developed for N-isotopic measurements on individual compounds (Kashiyama et al. 2006 submitted). While not totally new (see Chicarelli et al. 1993 and Sachs and Repeta, 1999), the impressive technical advances made by Ohkouchi's team make it feasible using LC-MS methods to purify and identify a range of porphyrins and to measure their C- and N-isotopic compositions on manageable (ie tiny) amounts of individual compound. This is important because, as the authors well know, measurements of bulk N are notoriously troublesome because ammonium attached to clays can lead to erroneous results and interpretations of N-isotopic data.

The main weakness of the paper is the selective focus on nitrogen. It would have been interesting, and technically very simple, to have measured the abundances of some key biomarkers in the same samples, to report how they fluctuated with the N-isotopic data. It would have added a lot of weight to (or perhaps disproved) the hypothesis presented. But, perhaps this data is saved for a more complete report on these samples?

In summary, the impact of this paper is likely to come from the technical approach that opens opportunities for more detailed studies of the isotopic compositions of porphyrins. Together with other recent papers on biomarker aspects of Mesozoic OAE's, a compelling case is being built for their being characterized by photosynthetic communities that are radically different to those found in most regions of today's oceans. I personally think there are strong similarities in the progressions of numerous isotopic and biomarker parameters through all the major Phanerozoic OAE's and that these speak to oceanic anoxia being a recurring phenomenon related to biological extinction events.

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