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PHYSIOLOGY OF PHOTOAUTOTROPHS AND PALEOENVIRONMENT DURING THE CRETACEOUS OCEAN ANOXIC EVENTS BASED ON NITROGEN AND CARBON ISOTOPE ANALYSES OF INDIVIDUAL SEDIMENTARY PORPHYRINS

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Sedimentary porphyrins are tetrapyrrole molecules with alkyl chains derived from chlorophylls, heme, and other biomolecules (e.g., Treibs, 1936; Baker and Louda, 1986; Callot and Ocampo, 2000). In particular, structures of deoxophylloerythroetioporphyrin (DPEP) and its analogues strongly suggest them to be originated from chloropigments. Thus, stable isotopic compositions of nitrogen and carbon of these porphyrins should directly reflect those of the chloropigments (e.g., Hayes et al., 1987; Chicarelli et al., 1993). We analysed nitrogen and carbon isotopes of various individual porphyrins extracted from sequential samples from the Livello Bonarelli black shale (uppermost Cenomanian, Italy) to elucidate the physiology of photoautotrophs and paleoenvironment during the Cretaceous OAE.

Based on the isotopic relationship between tetrapyrrole portion of chlorophylls and cells of the photoautotroph (the former 4.8‰ depleted in ^{15}N and 1.8‰ enriched in ^{13}C relative to the latter; Ohkouchi et al., 2006; Ohkouchi et al., in prep.), nitrogen isotopic compositions of the entire photoautotrophic community is estimated to be -2 to 0‰ based on $\delta^{15}N$ of Ni DPEP (-6.6 to -4.8‰) and Cu DPEP (-5.7 to -5.1‰). These values strongly suggest that the nitrogen assimilated during phototrophic primary production was largely supplied *via* N_2-fixation. Meanwhile, carbon isotopic compositions of Ni DPEP (-20.5 to -17.9‰) and Cu DPEP (-20.1 to -16.3‰) suggest that of the entire photoautotrophic community being approximately -22 to -18‰. Thus, the estimated isotopic fractionation associated with carbon fixation in the Bonarelli paleoenvironment was strikingly small (-15 to -13‰) compared to those of the simulated *ordinary* photoautotrophic community in each paleoenvironments, namely, -20 to -14‰ and -23 to -20‰, respectively. The result suggests rapid growth rates for these photoautotrophs in an intense bloom conditions that perhaps had associated active transport of carbon substrates and/or a significant rate of β-carboxylation. Therefore, both nitrogen and carbon isotopic signatures of the porphyrins suggest considerable contribution of diazotrophic cyanobacteria in the primary production.

Moreover, all samples from the Livello Bonarelli black shale contain trace amounts of porphyrins with more than 34 carbon atoms that should have derived from

bacteriochlorophylls *c*, *d*, and *e* of the obligate anaerobic photoautotroph, green sulfur bacteria. It thus suggests presence of reduced, anaerobic water mass within the photic zone (0<200m) in a strongly stratified water column. In fact, the dominance of diazotrophic cyanobacteria in primary production should be an inevitable consequence of water column stratification due to diminished supply of dissolved inorganic nitrogen to the surface water.

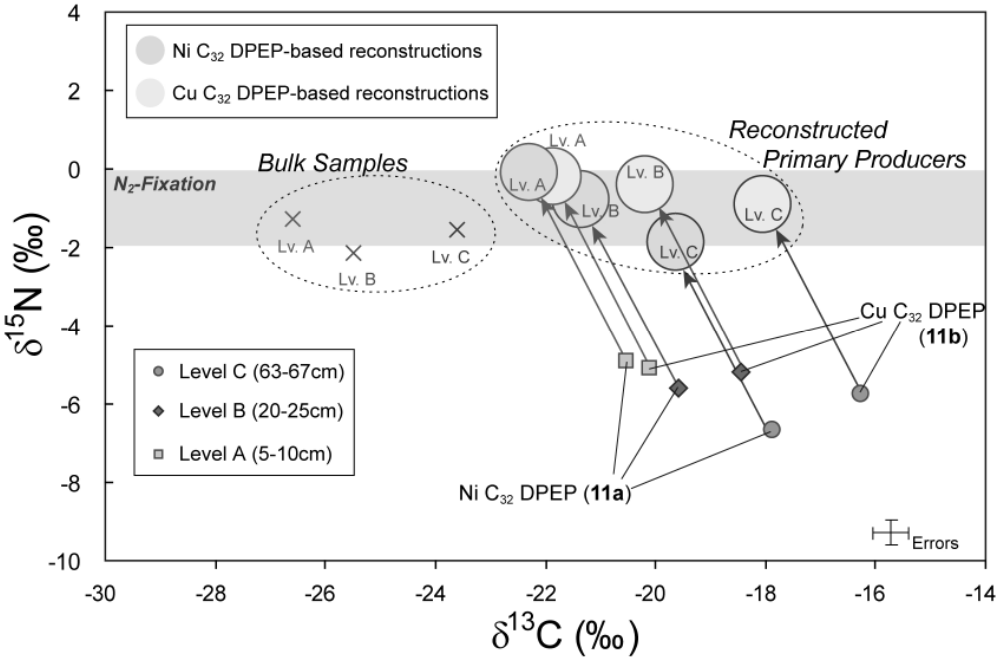

Figure 1. Reconstructed $\delta^{15}N$ and $\delta^{13}C$ values of photoautotrophic cells from the Livello Bonarelli black shale. Circles indicate approximate ranges of mean isotopic compositions for the photoautotrophic community reconstructed from by Ni and Cu C_{32} DPEPs for each stratigraphic level. $\delta^{15}N$ for diazotrophic photoautotrophs is expected to be -2 to 0‰. Isotopic compositions of bulk organic matters are plotted as well.

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