Nitrogen and carbon isotopic analyses on sedimentary porphyrins of organic-rich shales from Miocene and mid-Cretaceous

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Sedimentary porphyrins are derived from chloropigments of the past phototrophs and ubiquitously found in organic-rich sediments. They carry information on stable isotopic compositions of N as well as C of the photosynthetic organisms in the geological past. We have improved a method for the precise determinations of N and C isotopic compositions of these porphyrins. It includes (1) an efficient method for isolation and purification of intact metalloporphyrins by HPLC and (2) an EA/IRMS system allowing determination of N and C isotopic compositions with a few μgN or μgC. By applying the method, we have analyzed the isotopic compositions of porphyrins from Miocene sediments of a marginal, semi-enclosed rift basin of the paleo-Japan Sea (Onnagawa Formation). The N isotopic composition of common, chlorophyll-derived sedimentary porphyrins (i.e., those of oxygenic photoautotrophs) ranges from -7 to -4‰ and indicates that the N_2 fixation was a major process for N assimilation. This suggests the dominance of diazotrophic cyanobacteria in the photosynthetic primary production during the formation of these "diatomaceous" organic-rich sediments. On the other hand, statistically significant differences were found in the isotopic compositions of various porphyrins. For example, C_{33} 15,17-cycloheptanoDPEP was 0.9 ± 0.7‰ and 2.3 ± 0.5‰ depleted in ^{15}N and ^{13}C, respectively, relative to C_{32} DPEP among 6 samples, indicating distinct sources for these two common sedimentary porphyrins. C_{30} 17-nor-DPEP was 0.7 ± 0.4‰ (6 samples) enriched in ^{13}C relative to C_{32} DPEP suggesting different source between them. However, its absolute N isotopic composition (-5.1 ± 1.8‰ among 6 samples) suggesting an origin of diazotrophs apparently conflicts with the previous view that C_{30} 17-nor-DPEP is derived from chlorophyll *c* of eukariotic algae. We have also been analyzing black shales of the Cretaceous Ocean Anoxic Events collected from central Italy. Our preliminary results of dual isotopic analyses of sedimentary porphyrins suggest critical role of the diazotrophic photoautotrophs in the photosynthetic primary production during the events.