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Reconstruction of the past biogeochemical cycles based on compound-specific N and C isotopic analyses of sedimentary porphyrins

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Porphyrins are thought to have derived from biomolecules such as chlorophylls and heme, among which deoxophyllo-erythroetioporphyrins (DPEP) and its analogues are structurally related to chloropigments. These compounds thus preserve stable isotopic compositions of N and C of phototrophs of the past environment. We have developed methods for precise determinations of N and C isotopic compositions of individual sedimentary porphyrins and maleimides, which include isolation and purification of individual alkylporphyrins and porphyrin acids by dual-step HPLC preparation (Kashiyama et al., 2007a). We have analyzed various alkylporphyrins and porphyrin acids from organic-rich Miocene sediments of the paleo-Japan Sea (Onnagawa Formation) as well as Cretaceous black shales (Livello Selli and Livello Bonarelli, Italy) deposited in the western Tethys during the Ocean Anoxic Events (OAEs). The N isotopic composition of DPEP, which should have derived in chlorophylls in general, ranged from -6.9 to -3.6‰(n=7) in the Miocene shale and -6.6 to -3.9‰ (n=5) in the OAE black shales, indicating that the N_2 fixation was a major process for N assimilation hence the dominance of diazotrophic cyanobacteria in primary production in these paleo-oceans. Furthermore, DPEP were relatively enriched in ^{13}C in both environments(-17.9to -15.6‰ in the Miocene shale and -20.5 to-17.9‰ in the OAE black shales), which suggests relatively small carbon isotopic fractionation during photosynthesis and supports significant contribution of cyanobacteria-derived chloropigments. We also determined isotopic compositions of *source-specific* porphyrins such as 17-nor-DPEP (derived from chlorophyll-*c*), 8-nor-DPEP (possibly derived from divinylchlorophylls; Kashiyama et al., 2007b) as well as DPEP with extended alkyl side chains and their equivalents among porphyrin acids (derived from bacteriochlorophyll *c*, *d*, and *e*; analyzed as maleimides). The latter two porphyrins had variable and rather unique isotopic compositions compared to DPEP. Such an approach should allow reconstruction of community structures of phototrophs and associated biogeochemical processes associated with the photosynthesis in the past oceans.

Kashiyam Y., Kitazato H. and Ohkouchi N. (2007a), Journal of Chromatograpgy A 1138 73-83.
Kashiyam Y., Shiro M., Tada R. and Ohkouchi N. (2007b), Chemistry Letters, in press.