Nitrogen and carbon isotopic analyses on sedimentary porphyrins: a novel proxy for the paleo-photoautotrophs

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The photosynthetic organisms in the marine environment intimately links between physicochemical conditions of the surface ocean and the marine ecosystem, so that it should be a key to understand the dynamics of geological events such as the mass extinction occurred in the ocean. The information of such oceanic photoautoptophs in the past is, however, relatively poor mainly due to incompleteness of fossil records. Sedimentary porphyrins (i.e., geoporphyrins), tetrapyrrole molecules with various alkyl chains, are organic compounds derived from chloropigments of the past photosynthetic organisms and ubiquitous among organic-rich sediments. These homologues are promising biomarkers because (1) all photosynthetic organisms synthesize chloropigments as antenna pigments, and their derivatives, sedimentary porphyrins, are diagenetically stable and preserved even in sedimentary rocks as old as the Precambrian, (2) the chemical structure of sedimentary porphyrins reflect the structural features of original chloropigments so that higher taxonomic information is preserved, and, more importantly, (3) sedimentary porphyrins contain both nitrogen and carbon in their structures so that isotopic compositions of nitrogen as well as carbon of the photosynthetic organisms in the geological past can be reconstructed. Thus, they are useful proxies for nitrogen cycle in the paleo-surface-ocean.

Recently, we have established an improved method for nitrogen and carbon isotopic analyses of sedimentary porphyrins. The method includes (1) efficient isolation and purification of sedimentary porphyrins by a preparative technique of high performance liquid chromatography and (2) isotopic measurement with an improved system of continuous flow elemental analyzer/isotopic ratio mass spectrometer. Thus, a practical efficiency can be achieved for the applications of multi-isotopic analysis of sedimentary porphyrins to the paleoenvironmental studies.

We applied this novel method to Miocene sediments of a marginal rift basin of the Sea of Japan (Onnagawa Formation, northeast Japan). The nitrogen isotopic compositions of the major sedimentary porphyrins (-7 ~-4 per mil) suggest that the nitrogen fixation was a major nitrogen assimilation process for the photosynthetic organisms. Together with the information on the porphyrin structure, we conclude the dominance of diazotrophic cyanobacteria as photoautotrophs during the formation of 'diatomaceous' organic-rich sediments. On the other hand, the carbon isotopic compositions of these porphyrins (-15 ~-19 per mil) perhaps indicates high growth rates for these organisms, possibly growth under blooming states. Only sedimentary porphyrins can provide such dual isotopic signals directly related to the biochemical processes of the past photosynthetic organisms. These results demonstrate the significance of sedimentary porphyrins as an excellent paleoenvironmental proxy (it is a multi-proxy itself!). This novel proxy is particularly worthy to apply it to the studies of the critical boundaries such as the Cretaceous Ocean Anoxic Events when unusual surface oceanic environment are invoked, or studies of the early history of phototropic organisms in the Precambrian time when limited information has been presented so far.