Porphyrins: a diagnostic biomarkers in early Earth

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In modern natural environments, porphyrins, organic compounds with a tetrapyrrole structure, are synthesized mainly as nucleus of chloropigments. Some of them survive post-depositional thermal degradation processes, and have been found even in petroleum and Precambrian sedimentary rocks. The porphyrins are also synthesized by non-O2-evolving photosynthetic bacteria, suggesting them to be potentially useful for tracing biogeochemical processes at the time close to the origin of life. Since oceanic euphotic zone should have been anaerobic during the Archaean, the porphyrins should be biomarkers useful for paleoceanographic studies in such old sediments. In this study to confidently interpret the isotopic signatures recorded in porphyrins from geological samples, we investigated carbon and nitrogen isotopic compositions of porphyrin nucleus of several chloropigments including bacteriochlorophylls a and e collected from a modern anoxic lake, Lake Kaiike, Japan.

Lake Kaiike is a saline meromictic lake with a O2/H2S interface around 5 m depth throughout the year. At the O2/H2S interface, a dense population of various microbes such as purple sulfur bacteria, green sulfur bacteria, and cyanobacteria form a bacterial plate. In this study, chlorophyll a (Chl a), bacteriochlorophyll a (BChl a) and e (BChl e) in suspended particulate matter and benthic microbial mats from the lake were isolated and purified by normal-phase and reverse-phase HPLC. Subsequently, the isotopic compositions of carbon and nitrogen were determined by an on-line system of elemental analyzer / isotope-ratio mass spectrometry.

In the bacterial plate, the BChl a related to the purple sulfur bacteria is 9 per mil enriched in 13C relative to BChls e related to the green sulfur bacteria. It could reflect that the purple sulfur bacteria assimilate CO2 through Calvin cycle, whereas the green sulfur bacteria through reverse TCA cycle. The carbon isotopic compositions of BChl a little changed with the depth of the water column. By contrast, the BChls e at 8 m depth are 1-2 per mil and those from bacterial mats are 6 per mil depleted in 13C relative to those in the bacterial plate. It suggests that the green sulfur bacteria inhabit the deep anoxic water and bacterial mats and synthesize BChls e by using regenerated CO2. Nitrogen isotopic compositions of BChl a and BChls e are around -7 and -1 per mil, respectively. Taking the isotopic fractionation between biomass and chloropigments into account, we conclude that dinitrogen was enzymatically fixed by the green sulfur bacteria but not by purple sulfur bacterial and cyaobacteria. In our samples, phaeopigments which are formed by the loss of Mg2+ ion from the chloropigments. Nitrogen isotopic compositions of these phaeopigments are equivalent to those of source chloropigments, suggesting that the isotopic fractionation associated with the loss of Mg2+ ion is negligible.

We have also determined the carbon isotopic ratio of porphyrin rings in these chloropigments after hydrolysis of the purified pigments. The porphyrin rings are enriched in 13C by 0.5-3 per mil relative to the whole chloropigments. It may be reflected by the isotopic difference between direct precursors of prophyrins and isoprenoid side-chain, namely glycine and acetyl-CoA, respectively.