Heme: The distribution and dynamics of a ubiquitous iron-tetrapyrrole molecule

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Hemes are Fe(II)-tetrapyrrole complexes that catalyze various electron transfer and redox reactions. They are essential for biological systems, and are possessed by all life forms. Because heme-iron represents as much as 40% of the iron pool in phytoplankton (Gledhill, 2007), hemes in the biomass likely comprise a major fraction in the bioavailable-iron pool which limits primary productivity in over 30% of the world oceans (Moore et al., 2013). They are also expected to be found in the sediments, either as allochthonous compounds deposited from the water column or synthesized in situ by the benthic and subsurface microorganisms. It is noteworthy that etioporphyrin III preserved in various sedimentary rocks, which is supposedly derived from heme, has a highly distinct carbon and nitrogen isotopic compositions ($\delta^{13}C$, $\delta^{15}N$) with respect to other chlorophyll-derived porphyrins in Cretaceous black shales (Ohkouchi et al., unpub. results). As such, hemes are ubiquitous in any environment where life exists, but little is known on their distribution and dynamics in natural environments.

Here, we established a new analytical method to quantify, isolate, and purify heme *b*, a major homolog of hemes, from various environmental samples. Detection of picomole levels of heme *b* is achieved with a photodiode-array detector connected to HPLC, which covers the heme *b* concentration range in particulate (> 0.7 μm; 0.15 nmol L^{-1}) and dissolved organic matter (> 3000 Da; ~0.006 nmol L^{-1}) in the coastal seawater of Tokyo Bay, as well as that in the surface sediments of the Japan Sea (~0.03 $\mu g\ g^{-1}$ dry weight). Importantly, concentration of heme *b* in the dissolved phase was contrastingly low with respect to that in the particulate phase of the coastal seawater, which imply that hemes may constitute a major fraction of the regenerated iron in the ocean. The $\delta^{13}C$ and $\delta^{15}N$ values of heme *b* isolated and purified from various environmental samples are determined with our modified EA/IRMS (Ogawa et al., 2010). These isotopic values will be compared with those of chlorophylls and amino acids, which will reveal the sources of hemes in natural environments and the isotopic fractionation associated with their biosynthesis. Our new analytical approach will provide first detailed insights into the ubiquitous iron-tetrapyrrole molecule playing an essential role in biogeochemical cycle.

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