

TREIBS' SCHEME RE-EVALUATED WITH NITROGEN AND CARBON ISOTOPIC COMPOSITIONS OF SEDIMENTARY PORPHYRINS

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Metallo-alkyl-porphyrins, tetrapyrrole structures of chloropigments and hemes are long preserved in the sediments and sedimentary rock. Over 70 years ago, Alfred Treibs observed deoxyphylloerythroetioporphyrin (DPEP) and related compounds in petroleum, oil shales, and coals and proposed the sedimentary porphyrins to be derived from chlorophylls or hemes. It is still one of the logical grounds that the petroleum originates from maturation of sedimentary organic matter rather than produced through inorganic processes. Treibs also proposed a transformation pathway for the conversion of chlorophyll to DPEP with a series of biological and chemical reactions. Later, based on the distribution of various chlorin/porphyrin species in the sediments and their carbon isotopic composition, several studies confirmed the Treibs' scheme with some modification (Baker and Louda, 1986; Keely et al., 1990; Hayes et al., 1990; Callot and Ocampo, 2000).

We have recently developed a method for isolating/purifying the sedimentary porphyrins for determining both nitrogen and carbon isotopic compositions of these porphyrins (Kashiyama et al., 2007). We applied the method and determined both carbon and nitrogen isotopic compositions of various porphyrins from Cretaceous black shales deposited in the west Tethys associated with Oceanic Anoxic Events and Miocene black shales distributed in north Japan. These isotopic compositions exhibited unexpectedly wide range of distribution. For example, in the Miocene black shales, both carbon and nitrogen isotopic compositions of C₃₂ DPEP are substantially different between nickel- and vanadyl-chelated C₃₂ DPEPs (Fig. 1a and 1b, respectively). Furthermore, in the Cretaceous black shales, the isotopic compositions of C₃₂ DPEP are also substantially different between nickel- and copper-chelated C₃₂ DPEPs. Together with the distinct distribution of chemical species among Ni(II), V=O(II), and Cu(II) porphyrins in these sediments, the metal insertion process may occur in the early stage (rather than the latest stage) of the transformation pathway (Ohkouchi et al., 2005) at least some portion of the porphyrins, which discriminates the source chloropigments.

In the Cretaceous black shales, we observed abundant Ni C₃₂ etioporphyrin (Fig. 1c) that is substantially enriched in ¹⁵N relative to other porphyrins including Ni C₃₂ DPEP. It

suggests that the C₃₂ etioporphyrin to be derived mainly from hemes rather than chloropigments. In the presentation, we will further discuss the source and transformation pathways of chlorophylls to porphyrins based on dual isotopic compositions.

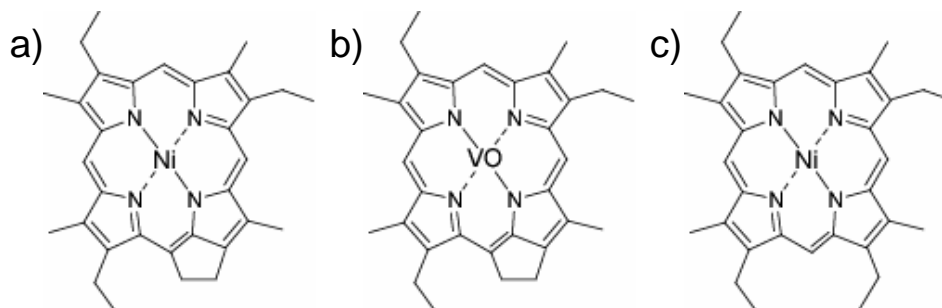


Figure 1. Chemical structures of a) Ni and b) VO-chelated C₃₂ DPEPs and c) Ni C₃₂ etioporphyrin

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