

**ALKYL-PORPHYRIN DIVERSITY AND VARIABILITY RESULTING FROM  
LARGE-SCALE OCEANIC REDOX CHANGES DURING THE CRETACEOUS  
OCEANIC ANOXIC EVENT II**

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Geoporphyrins and chlorins are biomarkers that result from the transformation of tetrapyrroles including chlorophylls, bacteriochlorophylls and haems. The transformation reactions are initiated in the water column and sediments during early diagenesis and are dependent on a range of variables including, but not limited to, water column redox state, burial conditions (e.g. Eh and pH), and time. Geoporphyrins and chlorins can retain structural characteristics that allow unambiguous assignment to specific precursor structures and source organisms, making their utility in paleoenvironmental studies extraordinary where such information is preserved. Oceanic Anoxic Event II (OAE II, Cenomanian-Turonian Boundary, 93.5 Ma) is characterized by large scale changes in oceanic redox state, recorded by quasi-global deposition of organic matter-rich "black shales" and biomarker evidence for photic zone euxinia. This study utilized very well preserved sediments from ODP Leg 207, Demerara Rise to assess the diversity and variability in the tetrapyrrole record through OAE II. Identification and structural assignment of tetrapyrroles in this study were achieved by a combination of high-performance-liquid-chromatography (HPLC)/diode-array-detection (DAD) and liquid chromatography-mass spectrometry (LC-MS<sup>n</sup>) on acetone extracts. The tetrapyrrole distributions are characterized by unusually high abundances of a C<sub>33</sub> bicycloalkanoporphyrin in both metallo and free-base (metal free) forms (Figure 1). The C<sub>33</sub> bicycloalkanoporphyrin is most likely derived from rearrangement of chlorophyll *a*. Together with other geochemical and sedimentary evidence, the results suggest that a high proportion of the extractable geoporphyrins derive from cyanobacteria and/or calcareous nannoplankton. Stratigraphic variations in geoporphyrin distributions through OAE II are significant, but relate almost exclusively to the abundances and relative proportions of metallated (vanadyl and nickel) vs. free-base porphyrins. Free-base porphyrins are in very high abundance (coupled with very low metallo-porphyrin abundance) during the height of the anoxic event. The greater proportion of free-base porphyrins is associated with more extensive reducing conditions in the water column that are characteristic of the apex of OAE II, consistent with metal ion limitation during OAE-II. The limited extent of metallation of

the porphyrins is not the result of changes in sedimentary Eh-pH conditions, as is typically invoked to account for metalloporphyrin distributions. Rather, it is the result of a substantially lower local inventory of vanadate and Ni(II) in the water column. The limited metal ion availability for complexing with tetrapyrroles presumably resulted from metals being stripped from the water column at the onset of the OAE., The results suggest that metallation of tetrapyrroles is controlled by water column metal availability, as in addition to controls that may relate to the Eh-pH conditions of the early diagenetic environment.

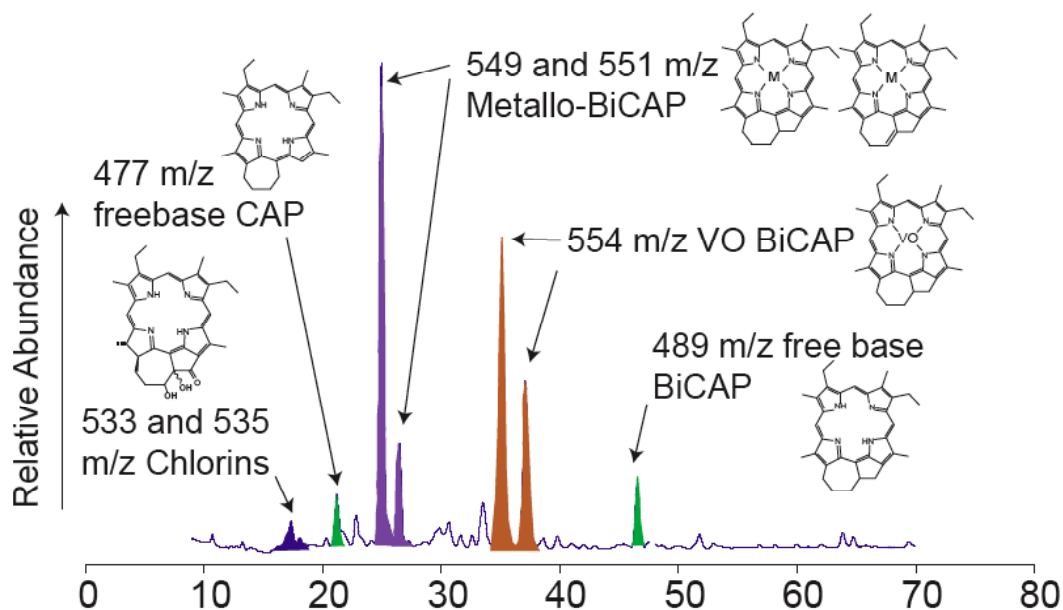


Figure 1. HPLC chromatogram showing typical distribution of tetrapyrroles in Cretaceous “black shales” from Demerara Rise. Complexing metal and structural identifications were performed by diode array detection (DAD) and multi-stage mass spectrometry ( $MS^n$ ) respectively.