P420-TH

ALKYLSULFUR CHLOROPHYLL DERIVATIVES: LABORATORY PREPARATION OF THE NOVEL SEDIMENTARY SPECIES

Matthew D. PICKERING[1] and Brendan J. KEELY[1]

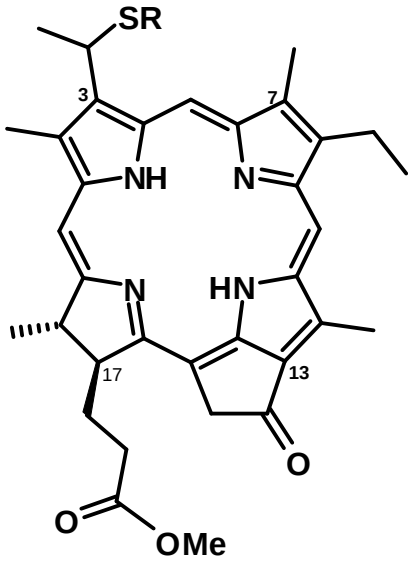
1. Department of Chemistry, University of York, Heslington, York, YO10 5DD.

The incorporation of sulfur into functionalised organic molecules, sulfurisation, is a widespread mechanism for the preservation of sedimentary organic matter, reported to operate extensively in anoxic depositional environments during early diagenesis. Reduced sulfur species react with functionalised molecules leading to the formation of both low molecular weight organosulfur compounds and, following sulfur crosslinking, macromolecular resins reticulated by catenated sulfur-sulfur bonds.

Sulfur-bound forms of many different compound classes have been recognised among sedimentary constituents (for a review see Sinninghe Damsté and de Leeuw, 1990). The occurrence of sulfur-bound porphyrins in mature sediment provides strong evidence for the involvement of chlorophyll in sulfurisation reactions (Schaeffer and Ocampo, 1993). Until recently, however, evidence has been lacking from younger sediments. The identification of a suite of novel sulfur-bound chlorophyll derivatives in immature Antarctic lake sediment provides proof that sulfurisation of chlorophyll operates during early diagenesis (Squier et al. 2004). Furthermore, the depth profiles of sulfur-bound chlorophyll derivatives and free chlorophylls were shown to differ, providing different accounts of the paleoenvironment. To validate further the analytical data collected by Squier et al. (2004), and to aid the identification of similar components in future studies, we have prepared a series of synthetic standards of alkylsulfur chlorins.

Standards of the five structures observed in the sedimentary species, with alkyl groups ranging from methylS to pentylS at position C-3[1] on the macrocycle (Fig. 1), were prepared from the chlorophyll *a* derivative pyrophaeophorbide *a*. High performance liquid chromatography (HPLC), with photodiode array detection, was used to record the online UV/vis spectra and atmospheric pressure chemical ionisation-liquid chromatography multistage tandem mass spectrometry (APCI-LC-MS^n), up to a maximum of six stages of mass analysis (MS^6), was performed on each of the standards. The standards show identical retention times, UV/vis and MS fragmentation behaviour to the sedimentary species. Mass spectral analysis reveals the favoured loss of the alkylsulfur group as a radical, confirming this as a diagnostic feature of the spectra.

The work carried out will allow routine identification of these components in future studies from their online UV/vis and mass spectral data obtained during APCI-LC-MS^n analysis. During the course of developing the method to prepare the alkylsulfur chlorophyll derivatives, valuable insight has been gained into the factors and environments conducive to their formation in the geosphere and the significance of their occurrence.



R= methyl, ethyl, propyl, butyl, pentyl

Figure 1. Structures of -alkylsulfur chlorophyll standards.

REFERENCES

Schaeffer P., Ocampo R., Callot H.J., Albrecht P. (1993) Extraction of bound porphyrins from sulfur-rich sediments and their use for the reconstruction of paleoenvironments. *Nature*, **364**, 133-136.

Sinninghe Damsté J.S. and de Leeuw J.W. (1990) Analysis, structure and geochemical significance of organically-bound sulfur in the geosphere: State of the art and future research. *Organic Geochemistry*, **16**, 1077-1101.

Squier A.H., Hodgson D.A., Keely B.J. (2004) Structures and profiles of novel sulfur-linked chlorophyll derivatives in an Antarctic lake sediment. *Organic Geochemistry*, **35**, 1309-1318.