

Mechanisms of natural sulphurization and its role in the preservation of sedimentary organic matter

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Organo-sulphur compounds are often abundant in sediments and crude oils deposited under anoxic conditions, especially in evaporitic environments. The latter are, indeed, favourable for the growth of microorganisms (e.g. sulphate reducers, photosynthetic sulphur bacteria) which are implied in the formation of reduced inorganic sulphur species such as hydrogen sulphide, elemental sulphur or related polysulphides. These species are able to react with decaying biological organic matter to form organo-sulphur components of low molecular weight and, to a much greater extent, macromolecules build-up of low molecular weight functionalized sub-units cross-linked with sulphur or polysulphide bridges.

Structural characterization of low and high molecular weight organo-sulphur constituents has largely contributed during the last decade to unravel their mode of formation in the subsurface (e.g. Adam *et al.*, 1993 and references therein). Moreover, simulation experiments carried out with various reference constituents have led to a more detailed understanding of the chemical mechanisms underlying the incorporation reactions of sulphur into sedimentary organic matter.

Structural characterization of sedimentary organo-sulphur components

Low molecular weight organo-sulphur components usually occur in sediments and petroleum as complex mixtures. Structural characterization of individual molecules can be achieved after separation by high performance liquid chromatography and identification by nuclear magnetic resonance or synthesis. The precise location of the sulphur atom in biologically derived molecules can thus, in many cases, give information on the reacting precursors. Recent examples obtained on novel polyprenoid sulphides (Poinsot *et al.*, 1998) and thiosteranes (Behrens *et al.*, 1997) illustrate the importance of a full detailed structural characterization and show that hypotheses based on mass spectral data alone can be misleading.

Sulphur-rich macromolecules, which occur

currently in sediments and petroleum, have mostly been studied by selective chemical degradation (e.g. reductive cleavage of C-S or S-S bonds, eventually using labelled reagents), leading to low molecular weight components which can then be structurally characterized in the usual way. These studies have again shown that the sulphur is mostly located at positions which are functionalized in the precursor biological molecules. It is particularly significant that the fractions obtained by desulphurization of sulphur-rich macromolecules are often enriched in carotenoids or other long-chain polyisoprenoid derivatives, indicating that functionalities such as double bonds are important in the sulphurization of sedimentary organic matter (Adam *et al.*, 1993). Moreover, this shows that sulphurization of polyunsaturated components and their incorporation into macromolecular entities play a key role in the selective preservation of these sensitive molecules, and must occur during early diagenesis when the latter are still present (e.g. in the water column and/or at the recent sediment stage), a hypothesis confirmed by the common occurrence of fragile polysulphide bridges in the macromolecules from thermally immature sediments (Schaeffer *et al.*, 1995).

Furthermore, the use of labelled (deuteriated) cleaving reagents gives information on the number of sulphur linkages by which hydrocarbon subunits are attached to the macromolecules, as well as on the positions of attachment.

Structural characterization of the biological markers obtained by cleavage of the macromolecules, along with carbon isotope measurements carried out on individual compounds give clues on their origin and their geochemical significance. These features will be illustrated, in particular, in the case of molecular markers such as hopanoids, steroids, carotenoids and regular polycyclic terpenoids.

Mechanisms of sulphur incorporation

Two main avenues are now being pursued for the elucidation of the chemical reaction mechanisms

which are responsible for the formation of sedimentary organo-sulphur compounds. One is the characterization of labile sulphurization intermediates occurring in recent sulphur-rich environments. The other is the set-up of laboratory simulation experiments in which organic standards, such as alkenes, ketones and aldehydes, are reacted with various reduced sulphur species under relatively mild conditions comparable to those occurring in actual environments (e.g. Schouten *et al.*, 1993).

These two approaches have, in particular, recently highlighted the key role played by thioketones and thioaldehydes in the reductive sulphurization of the corresponding carbonyl functions. The sulphurization of alkenes has also been investigated under varying conditions; there is the possibility that some of these reactions may be triggered by light under appropriate conditions (Adam *et al.*, 1998).

References

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