

## Preservation of sedimentary organic matter through natural sulphurisation: An overview

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Preservation of organic matter (OM) in sediments has been and still is a major topic of research in earth sciences because it significantly affects the global biogeochemical cycles and because it is of prime importance for the formation of fossil fuels. Both the influence of oxygen on OM preservation as well as the actual mechanisms of preservation (e.g. condensation, selective preservation, sorptive preservation, natural sulphurisation) have been studied and debated in the last decade. The reaction of reduced inorganic sulphur species with OM during the early stages of diagenesis is an important mechanism to transform labile low-molecular-weight OM into an insoluble form (i.e. kerogen), especially in the marine realm. The developments in this area over the last decade will be discussed.

Studies of immature kerogens over the last years have demonstrated that they can contain high levels of organic sulphur, which may reach almost 20 wt.% and occur much more widespread than previously assumed. Kerogens with an atomic  $S_{org}/C$  ratio of  $>0.04$  have been designated as special kerogen types (Orr, 1986) and occur as Type I-S, Type II-S as well as Type III-S, depending on their atomic H/C and O/C ratios. Recognition of these kerogen types is very important from a petroleum geochemistry point of view since they will generate petroleum at a significantly lower thermal stress than corresponding sulphur-poor kerogen types, due to the presence of relatively weak S-S and C-S bonds. The relatively early loss of sulphur from these kerogens during maturation may have caused the underestimation of the occurrence of sulphur-rich kerogens.

How are sulphur-rich kerogens formed? It has been well established that the sulphur in sulphur-rich kerogens is predominantly of diagenetic and not of biogenic origin. In anoxic sediments reduced inorganic sulphur species are formed by sulphate reducing bacteria and, depending on the availability of iron species, this sulphur is capable of reaction with functionalised groups in OM. This reaction may occur in an intramolecular fashion, leading to

formation of low-molecular-weight sulphur compounds, or in an intermolecular fashion, generating sulphur-rich macromolecular aggregates including kerogen. The timing of this reaction has been studied mainly by the formation of low-molecular-weight sulphur compounds, which are relatively easy to analyse. This reaction is almost completed within the upper 10 m of the sediment. A recent study of the sediments of the Cariaco Basin, where it was possible to monitor this reaction by both the increase in concentration of a tricyclic triterpenoid sulphide and the decrease in the concentration of its precursor indicated that the reaction was completed within 10 ka (Werne and Sinninghe Damsté, unpublished results). This is in good agreement with a recent study of a small lake in Antarctica, where the concentration of sulphur-rich macromolecular aggregates steadily increased in sediments of up to 5 ka (Kok *et al.*, unpublished results). However, it should be realised that the reaction rate of sulphurisation of OM, like that of iron minerals resulting in formation of iron sulphides (Raiswell and Canfield, 1996), strongly depends on the substrate. For example, it is known that some very reactive alkenes may even become sulphurised in an euxinic water column on a very short time scale (Hartgers *et al.*, 1997). Therefore, it is difficult to say that iron out competes OM for reaction with sulphide, although it is generally observed that in iron-poor sediments (e.g. carbonates) sulphurisation of OM plays a more important role, suggesting that large amounts of reactive iron inhibit the formation of sulphur-rich OM. Further confirmation of the early diagenetic formation of organic sulphur is coming from laboratory studies in which at relatively mild conditions and short time scales natural sulphurisation has been successfully simulated.

What kind of OM is prone to natural sulphurisation? Most of the work done up to now has concentrated on sulphurisation of lipids. Substantial evidence exists to demonstrate that functionalised lipids may become sulphurised, leading to formation



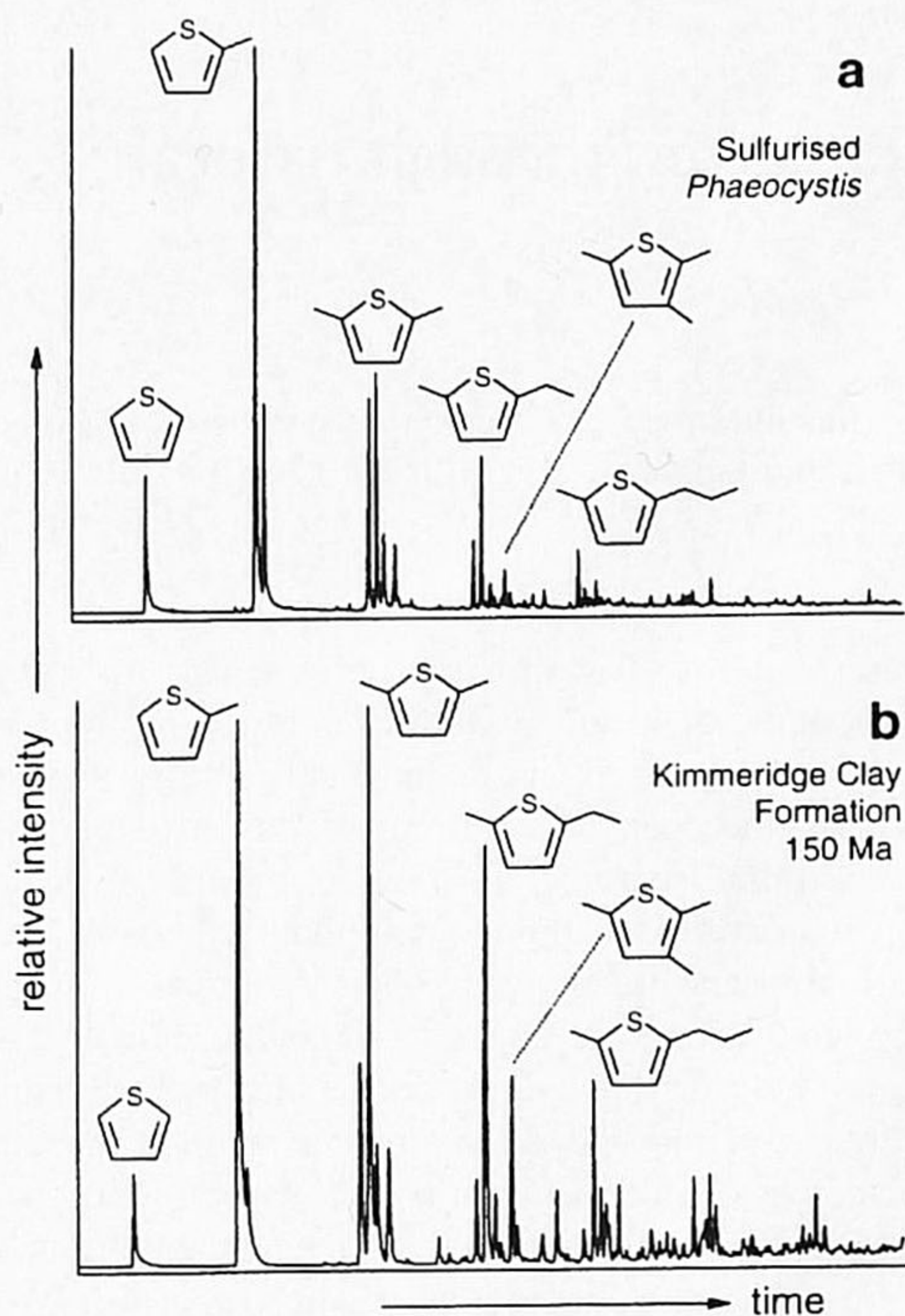


FIG. 1. Partial accurate mass chromatograms of  $m/z$  84 + 97 + 98 + 111 + 112 + 125 + 126 + 139 + 140 + 153 + 154 of the flash pyrolysates of (a) sulfurised *Phaeocystis*, and (b) the kerogen of the Jurassic Kimmeridge Clay Formation showing the distributions of the  $C_0$ - $C_6$  alkylated thiophenes. These components represent the most abundant compound class of both pyrolysates. These results can be explained as follows: during sulphurisation carbohydrate skeletons (i.e. predominantly  $C_5$ - $C_7$  linear alkanes) react through their functional groups with reduced inorganic sulphur species, generating a sulphur cross-linked insoluble macromolecular network of carbohydrate skeletons. Upon pyrolysis thermodynamically stable products (i.e. alkylthiophenes) with  $C_5$ - $C_7$  skeletons are formed.

of low-molecular-weight sulphur compounds and sulphur-rich macromolecular aggregates. This work is mainly based on sulphur-selective chemical degradation work of macromolecular fractions of sediments. It has recently also been demonstrated experimentally that functionalised lipids (from the alga *Nannochloropsis salina*) may become incorporated into the kerogen fraction through sulphurisation

(Gelin *et al.*, 1998). No evidence could be obtained for sulphurisation of the aliphatic biopolymer (alganaen), although there are indications that this may also occur (Sinninghe Damsté *et al.*, 1993). Recently, it has become clear that also carbohydrates are prone to sulphurisation (Sinninghe Damsté *et al.*, 1998). Carbohydrate carbon forms a large fraction of the OM of the OM-rich upper Jurassic Kimmeridge Clay Formation. This is evident from both changes in the molecular composition of the insoluble OM (an increasing contribution of low-molecular-weight linear alkylthiophenes in their flash pyrolysates) and from  $\delta^{13}C_{TOC}$  shifts of 6‰ with varying carbohydrate carbon contents. Furthermore, experiments simulating the natural sulphurisation of the carbohydrate-rich alga *Phaeocystis* spp. demonstrated that sulphurisation can indeed lead to a substantial preservation of carbohydrates with a molecular fingerprint similar to that of the Kimmeridge Clay and many other Recent and ancient marine  $C_{org}$ -rich sediments (Fig. 1). In this way an important fraction of the labile OM may escape from mineralisation and becomes preserved in the sedimentary record.

## Conclusions

Natural sulphurisation is an important pathway for the preservation of OM, especially in marine sediments. Natural sulphurisation is an early diagenetic process and may occur with both lipids and carbohydrates. It results in the formation of sulphur-rich kerogens which generate petroleum at a lower thermal stress than sulphur-poor kerogens.

## References

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