

HOW INORGANIC SULFUR IS TRANSFER INTO ORGANIC MATTER AT EARLY DIAGENESIS: EVIDENCES FROM AN IMMATURE SULFUR-RICH OIL IN HYPERSALINE ENVIRONMENTS BY ESI FT-ICR MS

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Carbon cycle and sulfur cycle are both important parts of global biogeochemical cycle, and they interact in several ways. An example for these interactions is the reactions between inorganic sulfides and organic matter in hypersaline sediments, namely, the sulfurization of organic matter. Although there have already been studies on sulfurization of organic matter, most of them are based on GC-amenable compounds (Damsté et al., 1989). To systematically understand the sulfurization reactions, here, a Solarix XR 9.4T Fourier transform mass spectrometry (FT-ICR MS) coupled with electrospray (ESI) was used to examine an immature sulfur-rich crude oil from the Jiangnan Basin of PR China.

FT-ICR MS analysis reveals the wide occurrences of organic sulfur compounds (OSCs) and non-sulfur polar compounds in the oil sample. We have found extensive similarities in molecular structures and distributional characteristics between the OSCs detected and some non-sulfur compounds in the oil sample. First, such similarities are well-indicated by the double bond equivalent (DBE) in that the lowest DBE values of most OSCs are higher than those of their non-sulfur counterparts by 1. For example, pyridine-containing non-sulfur compounds (N1) have a lowest DBE of 4, i.e., alkyl-pyridines, while pyridine-containing OSCs (N1S1) have a lowest DBE of 5. Such an increase in DBE can be attributed to the addition of one sulfur ring in OSCs. Besides, we have found some other similarities in distributional characteristics between OSCs and their non-sulfur counterparts. For example, alkyl-indoles and alkyl-carbazoles are abundant in pyrrole-containing non-sulfur compounds, interestingly, alkyl-thieno-indoles and alkyl-thieno-carbazoles are also abundant in pyrrole-containing OSCs. Such similarities may suggest that there are genetic relationships between OSCs and some non-sulfur compounds.

The occurrences of C₄₀ OSCs can well illuminate such genetic relationships. Apart from the existence of sulfur atoms, these C₄₀ OSCs have similar molecular structures with carotenoids. We speculate that these C₄₀ OSCs may derive from the sulfurization of carotenoids. In the FT-ICR mass spectrum, C₄₀ OSCs detected can contain up to 5 sulfur atoms, indicating that most functional groups of carotenoids can react with inorganic sulfides. Besides, though C₄₀ OSCs are of various DBE, those C₄₀ OSCs containing thiolane rings and cyclohexane rings are of the highest abundance. The high abundance of these saturated C₄₀ OSCs indicate that double bonds of carotenoids are preferentially sulfurized or reduced rather than preserved. C₄₀ OSCs with higher DBEs can derive from the condensation of these saturated C₄₀ OSCs at late diagenesis when temperature increased. The highest DBE of C₄₀ OSCs containing 1, 2 and 3 sulfur atoms are 11, 14 and 17, respectively, indicating that their cyclic structures can all be transformed to aromatic rings, i.e., thiophene and benzene rings. Moreover, such similarities are found not only between carotane and C₄₀ OSCs, but also between some other non-sulfur polar compounds and OSCs. For example, both fatty acids and sulfur-containing fatty acids have a similar even-over-odd carbon number predominance. We speculate that they both derive from

polyunsaturated fatty acids (PUFAs). PUFAs are common constituents of phytoplankton and zooplankton, and they mostly contain even numbers of carbon atoms. At early diagenesis, these PUFAs can either be reduced to saturated fatty acids or be partly sulfurized to sulfur-containing fatty acids, and the two species thus have a similar even-over-odd carbon number predominance.

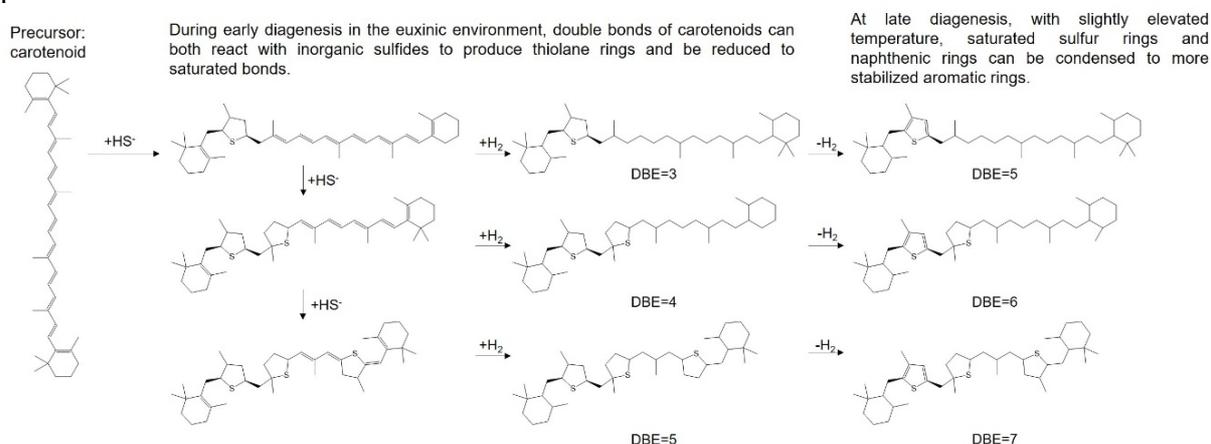


Figure 1 Formation pathways of the C₄₀ OSCs detected in the oil sample.

Despite the similarities exhibited above, some OSCs have different distributional characteristics from non-sulfur compounds. C₂₈ alkyl-phenol is of the highest abundance among its homologs, while such abundance is not found in alkyl-thiolano-phenols. We speculate C₂₈ alkyl-phenol mainly derives from tocopherols. There are no double bond or hydroxyl group in tocopherols. Therefore, tocopherols cannot be sulfurized at diagenesis, and have no contributions to alkyl-thiolano-phenols. Such differences are also found between neutral nitrogen compounds and their corresponding OSCs.

Conclusively, when organic matter is preserved in a euxinic environment, only those contain functional groups can react with inorganic sulfides. The type and number of functional groups of organic compounds are the key factor controlling their sulfurization process. The formation of thiolane rings can transform reactive functional groups to more stable cyclic structures, and they can also be further condensed to thiophene rings when temperature increases at late diagenesis. The interactions between carbon cycle and sulfur cycle here significantly enhance the preservation of functionalized organic matter.

References

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