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**Structural and stable carbon isotope studies of lipids in immature sulphur-rich sediments.**

Schouten, Stefan

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## Summary

The work described in this thesis aims to decipher the biogeochemical information contained in sulphur-rich organic matter present in immature sediments. Previous studies have shown that investigations of sulphur-containing biomarkers in such sediments are highly worthwhile for reconstruction of palaeoenvironments, because organic sulphur compounds (OSC) reflect functionalized biochemicals which would have otherwise been recycled. The first part of the thesis (Chapters 2-6) describes the results of the action of several chemical reagents on geomacromolecules present in sulphur-rich sediments. These results showed that the methods used have the potential of revealing information on sulphur-bound carbon skeletons in polar and asphaltene fractions. The second part (Chapters 7-9) describes the results of simulation reactions concerning natural sulphurization and the reactivity of hydropolysulphides towards several functionalized lipids. In this way a better reconstruction of palaeobiochemicals from their sedimentary sulphurized counterparts was achieved. The third part of the thesis (Chapters 10-12) reports on the occurrence and distribution of several novel compounds present in sulphur-rich sediments which were characterized by comparison with authentic standards and by spectroscopic methods. The final part (Chapters 13-17) describes the distribution and stable carbon isotopic compositions of free and sulphur-bound carbon skeletons in immature sediments from two basins of the Monterey Formation. Through this many aspects of the biogeochemistry of lipids in sulphur-rich organic matter of immature sediments have become clear.

Chapter 1 summarizes the importance of lipids in organisms and their presence in sediments. Sulphurized lipids are discussed in detail since research has shown that it is possible to reconstruct palaeobiochemicals from their sulphurized counterparts. Compound specific isotope analysis is also discussed since this recently developed technique has revealed valuable information on lipids in sediments.

Chapter 2 deals with the application of a novel desulphurizing agent, nickel boride, for the chemical degradation of sulphur-rich macromolecules in sediments. This agent has several advantages over the commonly used Raney Nickel; higher yields are obtained in desulphurizing asphaltene fractions and deuteration of released carbon skeletons is easily achieved using deuteriated chemicals. The method was tested using standards and applied on the polar and asphaltene fractions of the Vena del Gesso sediment and the Rozel Point oil. Chapter 3 describes a novel chemical degradation method using superheated methyl iodide, which selectively cleaves acyclic sulphide moieties in sulphur-rich

geomacromolecules. The method was tested using model compounds. Acyclic sulphides are cleaved and released as alkyl iodides which are transformed into methylthioethers. The application of this method on the polar and asphaltene fraction of the Rozel Point oil showed that substantial amounts of, among others, steroidal methylthioethers are released. In Chapter 4 the sequential use of methyl lithium/methyl iodide (MeLi/Mel), a reagent cleaving polysulphide bonds only, and Raney nickel or nickel boride, reagents cleaving all carbon-sulphur bonds, on several polar fractions of sediments and oils was shown to be useful for determination of the mode of occurrence of carbon skeletons. The relative amount of polysulphide-linkages of carbon skeletons can vary significantly due to differences in the number of sulphur-linkages per carbon skeleton and the timing of the sulphurization of the palaeobiochemical. Sulphoxides may also form a substantial part of the OSC in polar fractions (Chapter 5). XANES-analyses revealed that in some sediments up to 50% of sulphide-bonds are oxidized to sulphoxides. Through reduction of these polar fractions with  $\text{LiAlH}_4$  the low-molecular-weight sulphoxides are converted to their sulphide counterparts and could thus be analyzed qualitatively and quantitatively. Significant differences in the degree of oxidation of structurally different cyclic sulphides were observed. In Chapter 6 a sulphur-rich bitumen was separated by gel permeation chromatography (GPC). Desulphurization of the polar fractions of the bitumen and its GPC-fractions with deuterated nickel boride revealed increasing amounts of deuterium atoms in carbon skeletons released in GPC-fractions of increasing molecular weight. This indicates that the degree of sulphur cross-linking is a controlling factor in determining the molecular-size distribution of sulphur-rich geomacromolecules.

The origin of organic sulphur compounds is discussed in the next part of this thesis. Using a previously developed simulation method of natural sulphurization the reactivity of ketones and aldehydes was investigated (Chapter 7). They reacted surprisingly well, whereby the ketone or aldehyde was reduced and substituted with a (poly)sulphide-moiety through an as yet unknown mechanism. It is suggested that this reaction can play an important role in the formation of organic sulphur compounds during early diagenesis. Multi-functionalized lipids were also subjected to the hydrosulphurization reaction (Chapter 8). For instance, from squalene very specific reaction products were formed, indicating that both inter- and intramolecular reactions take place. Thiophenes were generated by thermal treatment of a polysulphidic polymer indicating that thiophenes may be formed from sulphur-rich polymers upon diagenesis. In combination with previously obtained results it is suggested that the hydrosulphurization reaction mimics natural sulphurization, though several differences are noted. To investigate the effect of sulphurization on the stable carbon isotopic composition of lipids, the

hydrosulphurization reaction products were analyzed. The isotopic compositions of the OSC were compared with the isotopic compositions of the OSC at different stages of the reaction (Chapter 9). This reaction whereby the carbon skeletons are identical carbon skeletons. This effect could not be observed. The effect is much smaller due to the fact that the reaction is not quantitatively sulphurized. The differences in the isotopic composition of sulphur-bound lipids with respect to the differences rather than due to the differences in the isotopic composition of the OSC.

The following chapter discusses the occurrence of sulphur-bound lipids in a number of sedimentary basins. A family of sulphur-steroids was identified in sulphur-rich sediments and their occurrence during desulphurization and sulphurization was investigated. The occurrence with other diagenetic products are derived from the initial products thereof, during diagenesis. The products originate from microbial activity. Several algal species. A novel steroidal hydrocarbon and desulphurized steroidal hydrocarbon using an authentic standard. The isotopic composition is similar to that of other steroidal hydrocarbons. The precursor sterol, ocellular sterol, indicating that they may be derived from the same compound is probably the same. Chapter 12 a novel sulphur-steroid (1,10-bis(methylthio)chroman)-butane, is identified. The carbon skeleton; 1,10-bis(methylthio)chroman skeleton, proved to be a novel occurrence points to a novel occurrence in samples of sedimentary basins. It may be unique for certain depositional basins.

The final part of the thesis describes the occurrence of sulphur-bound lipids in sedimentary basins of the North Sea. It describes a detailed investigation of the formation of sulphur-bound lipids taken at different stages of the formation. The compounds were qualitatively and quantitatively analyzed.

hydrosulphurization reaction was performed on 1-decene. The carbon isotopic compositions of the OSC formed and the substrate were determined at progressive stages of the reaction (Chapter 9). A strong fractionation effect was observed for this reaction whereby the OSC became depleted in  $^{13}\text{C}$  relative to the substrate. This effect could not be deduced from free and sulphur-bound compounds with identical carbon skeletons in sediments indicating that either the fractionation effect is much smaller during natural sulphurization or that functionalized lipids are quantitatively sulphurized. Differences in carbon isotopic compositions of free and sulphur-bound lipids with identical carbon skeletons are thus due to source differences rather than diagenetic effects.

The following chapters describe the identification of several free and sulphur-bound lipids in a number of immature sulphur-rich sediments. In Chapter 10 a novel family of sulphur-steroids, 3,7-epithio-5 $\beta$ -steranes, is described in several sulphur-rich sediments and petroleum. Their structures were determined by desulphurization and spectroscopic techniques. Their structure and their co-occurrence with other diagenetic products of  $\Delta^7$ -sterols suggest that these steroids are derived from the incorporation of sulphur into  $\Delta^7$  5 $\beta$ -sterols, or diagenetic products thereof, during early diagenesis. The  $\Delta^7$ -5 $\beta$ -sterols are suggested to originate from microbial reduction of  $\Delta^{5,7}$ -sterols which are biosynthesized by several algal species. A novel sterane, 27-nor-24-methylcholestane, was identified in hydrocarbon and desulphurized polar fractions of several immature sediments using an authentic standard (Chapter 11). Its stable carbon isotopic composition is similar to that of other steranes which are derived from algae. Its alleged precursor sterol, ocellasterol, is present in certain dinoflagellate and diatom species indicating that they may have acted as the source for this compound. The compound is probably biosynthetically related to 24-nor-methylcholestane. In Chapter 12 a novel sulphur-compound, (1,4-bis(2',5',5',8a'-tetramethylhexahydrothiochroman)-butane, is reported which possesses a unique bicyclic triterpenoid carbon skeleton; 1,10-bis(2',2',6'-trimethylcyclohexyl)-3,8-dimethyldodecane. Its carbon skeleton, proven by synthesis of an authentic standard, and mode of occurrence points to a novel enzymatic cyclization product of squalene. Its occurrence in samples of different formations and ages indicates that it may not be unique for certain depositional environments and/or time spans.

The final part of this thesis describes the analyses of samples from two sedimentary basins of the Monterey Formation (California, USA). First, Chapter 13 describes a detailed investigation of 13 outcrop samples from the Monterey Formation taken at Naples Beach. Free hydrocarbons and organic sulphur compounds were qualitatively and quantitatively analyzed. Substantial variations

in the concentrations of some compounds were observed and are probably due to subtle variations in the palaeoenvironment. Overall, it was concluded that the composition of the biota did not change qualitatively during the deposition of the Monterey Formation 20-6 Ma ago. Subsequent base and acid hydrolysis of two selected kerogens of this set of samples released substantial amounts of fatty acids, dicarboxyl acids, hydroxy fatty acids and alcohols (Chapter 14). Several specific lipids indicate the presence of methanogenic and methylotrophic bacteria in the depositional environment, thus revealing that a methane cycle may have been operational. Furthermore, lipids originating from terrestrial input and input of diatoms were observed.

The application of compound specific isotope analysis on lipids present in immature sulphur-rich sediments proved to be a powerful tool in the reconstruction of palaeoenvironments. For instance, the stable carbon isotopic compositions of cholestane and sulphur-bound pentakishomohopane change in different ways during deposition of the sediments of the Monterey Formation (Chapter 15). Cholestane has a constant  $^{13}\text{C}$ -content indicating stable conditions for algae living in the upper part of the photic zone whilst the sulphur-bound  $\text{C}_{35}$  hopane, probably derived from cyanobacteria, becomes more depleted in  $^{13}\text{C}$  during deposition of the younger sediments. This phenomenon is attributed to the Miocene climatic change resulting in an influx of cold,  $\text{CO}_2$ -rich waters into the bottom part of the photic zone. In Chapter 16 carbon isotopic data of other compounds present in these sediments are reported. They show for instance that free *n*-alkanes are terrestrially derived in contrast to the sulphur-bound *n*-alkanes. The sulphur-bound  $\text{C}_{25}$  highly branched isoprenoid compound derived from diatoms is relatively enriched in  $^{13}\text{C}$  and comparable in  $^{13}\text{C}$ -content to the kerogen indicating that diatoms may be the dominant source for the kerogen. Other isotopic data are more difficult to interpret due to the unknown origin of some compounds. To recognize lateral variations in the depositional environment of the Monterey Formation, outcrop samples from a basin different from that of Naples Beach were also examined (Chapter 17). Similar differences in stable carbon isotopic compositions of cholestane and the  $\text{C}_{35}$  hopane were observed indicating that they do not depend on regional variations. The amount of terrestrial input, determined by the free *n*-alkanes, is much lower suggesting that there was less fluvial and/or aeolian input. The distributions and stable carbon isotopic composition of the highly branched carbon skeletons are quite different than those observed for those compounds in the Naples Beach section which may be due to the presence of different species of diatoms in the two basins.

In summary, the development of new methods to characterize sulphur-rich geomacromolecules have led to an improved understanding on their structure.

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