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The Origin of Organic Sulphur Compounds and Their Impact on the Paleoenvironmental Record

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Ilya Kutuzov, Yoav O. Rosenberg, Andrew Bishop, and Alon Amrani

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Abstract

Over the past three decades, significant scientific progress has been achieved in the field of sedimentary organic sulphur compounds (OSC). Advances include structural identification, formation pathways, sulphur and carbon isotopic signatures of OSC, and their significance with respect to the paleoenvironmental record. The scope of the present review covers these efforts and highlights future directions in the field.

Initially, we review the marine sulphur cycle and its coupling to the carbon cycle from modern sediments to thermally immature sedimentary rocks. Microbial sulphate reduction (MSR) is a central process in providing reduced sulphur (e.g., HS^-) which reacts abiotically with organic matter, on a very rapid (geological) timescale ($<10,000$ years), leading to its preservation. The S isotopic fractionation during MSR is significant, which subsequently leads to sedimentary OSC with very distinctive $\delta^{34}\text{S}$ signature from that of biochemical OSC. Evaluating S isotope values on bulk fractions (e.g., kerogen), as well as individual OSC, can shed light on their formation pathways, the relative contributions of biochemically derived and abiotic sulphur, and competition with inorganic S pathways (e.g., organic S incorporation versus pyrite formation). New reservoirs of OSC (volatile, dissolved, and particulate), some of which comprise biochemically sourced sulphur, have been recently identified. Their role in the S cycle with respect to sedimentary OM is an ongoing research question.

We further discuss the progress made on specific groups of OSC as paleoenvironmental indicators. For each group, we first briefly highlight their significance as biomarkers. Then, we discuss aspects related to their sulphurization sites, rates and extent of sulphurization, preservation, and biases of the geological record resulting from the sulphurization process. New frontiers, both on the analytical level and in terms of our conceptual view of the sulphur cycle, are also highlighted.

1 Introduction

Sedimentary organic sulphur compounds (OSCs) are a ubiquitous class of compounds, which directly reflect the prevailing mechanisms of organic matter (OM) preservation, thereby recording the paleoenvironmental signature (Sinninghe Damsté and De Leeuw 1990; Werne et al. 2004). Thousands of sedimentary OSC, some with assumed biomarker carbon skeletons, were identified during the 1980s

(Sinninghe Damsté and De Leeuw 1990) and in the following decades (Adam et al. 1991; Kohnen et al. 1993; Schaeffer et al. 1993, 1995, 2006; Sinninghe Damsté and Rijpstra 1993; Vairavamurthy et al. 1994; Poinot et al. 1997; Sinninghe Damsté et al. 1999; Squier et al. 2003; van Dongen et al. 2006; Junium et al. 2011). Some sulphurized compounds are linked to a precursor biomarker, but many are still of unknown affinity (e.g., Poinot et al. 1998; Pancost et al. 2001). Most of these OSCs result from secondary incorporation of sulphur into the OM during early diagenesis (“sulphurization”). This process imparts a substantial overprint on the resulting molecular signature, with consequences for paleoenvironmental interpretation (Kohnen et al. 1991a, 1992; Sinninghe Damsté et al. 1995; Koopmans et al. 1997; Köster et al. 1997; Kok et al. 2000a). Since the landmark review by Sinninghe Damsté and De Leeuw (1990), several other papers have discussed specific aspects of sedimentary OSC (Aizenshtat et al. 1995; Anderson and Pratt 1995; Aizenshtat and Amrani 2004a, b; Werne et al. 2004; Amrani 2014; Greenwood et al. 2015).

This review considers the biogeochemistry of sedimentary OSC, their formation pathways, and their effect on the biomarker distributions in young sediments and immature sedimentary rocks, focusing on advances documented since Sinninghe Damsté and De Leeuw (1990).


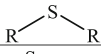
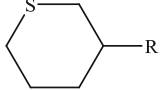
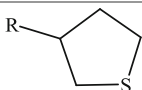
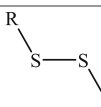
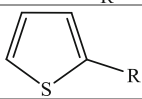
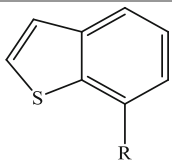
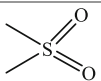
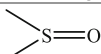
The term *sediments* is used synonymously when its age is not important for the discussion. When it is, we use the term *young sediments* for recent or modern systems (i.e., mainly not older than Holocene, 10,000 years), in which the sediments were not necessarily lithified and sulphurization processes are still active (see Sect. 3.3), and the term *immature sedimentary rocks* when dealing with older sediments that were lithified, but were not matured thermally (at least not extensively). The linkages of the marine sulphur and organic carbon cycles are discussed, which is essential to understanding the information that OSCs convey. This synthesis includes the more “traditional” view of sulphur incorporation, leading to the formation of sulphurized biomarkers, but highlights recent work suggesting possible new sources of sedimentary OSC. We then survey the progress made in identifying sulphurized biomarkers and how they affect paleoenvironmental records. Though the use of OSC as proxies for maturation and other thermochemical processes is extensive and important, it is beyond the scope of the current review and will only be discussed briefly.

2 Nomenclature, Methods, and Instrumentation for the Characterization of Sedimentary Organic Sulphur Compounds

2.1 Nomenclature and Chemical and Thermal Treatment for the Analysis of Organic S

Sedimentary OSCs comprise thousands of structures that can be found either in insoluble (e.g., protokerogen, kerogen) or soluble (polar and nonpolar) fractions of the OM. Table 1 summarizes the nomenclature and structures of the main sulphur moieties. Organic matter is often operationally divided into different fractions:

Table 1 Common sulphur moieties in sedimentary organic matter. R represents H or alkyl group

Compound class	Structure
Thiol (mercaptan)	
Sulphide (thioether)	
Thiane	
Thiolane (tetrahydrothiophene)	
Disulphide or polysulphide	
Aromatic S (thiophene)	
Fused aromatic S (benzothiophene)	
Sulphone	
Sulphoxide	

kerogen (insoluble in organic solvents) and the soluble fractions, e.g., asphaltenes (polar and macromolecular fraction), saturates (apolar), aromatics (slightly polar), and nitrogen, sulphur, and oxygen compounds (polar), with the saturate and aromatic fractions containing OSC amenable to gas chromatography (GC). These fractions might be considered to form a continuum, with decreasing size, heteroatom content, and polarity (Tissot 1984; Orr 1986). The preservation and distribution of these fractions highly depends on sulphurization at the molecular level, as well as on oxygen and nitrogen cross-linking (Koopmans et al. 1996a; Putschew et al. 1998; Farrimond et al. 2003; Amrani et al. 2007; McKee and Hatcher 2010). For example, pyrolysates of the asphaltene and kerogen fractions from an Upper Jurassic carbonate source rock exhibit striking similarities, except that the asphaltene has a lower OSC content. This suggests that the asphaltene differs from the kerogen primarily in terms of the number and nature of intermolecular linkages (van Kaam-Peters and Sinnighe Damsté 1997).

Several different analytical approaches can be used to effectively characterize sedimentary OSC constituents, including various preparative methods to make the

OSC amenable for measurement. For example, chemical or thermal degradation methods need to be applied to macromolecular and polar fractions, cleaving either C-S or S-S bonds, in order to release compounds bound by sulphur linkages. The common approaches for the study of OSC are presented in Table 2. This is not an exhaustive list, but provides a comprehensive overview of the most commonly applied approaches. Care needs to be taken as to which methods are applied, as some methods may mask original sulphur signatures.

2.2 Instrumentation for the Analysis of Organic S

Once OSCs are liberated from the macrostructure (e.g., asphaltene, kerogen), using chemical or thermal methods, their concentration, structural, and isotopic analysis requires liquid chromatography and other analytical techniques, some of which are specific for S compounds (Table 2). In young sediments and immature sedimentary rocks, many of the OSC are not thermally stable, especially those moieties with S-S bonds (Table 1). Because of their high reactivity, it is important to note that they can thermally react upon GC analysis, either in the injection port or on the column, and generate *artificial* OSC (Krein 1993; Schouten et al. 1994). Therefore, the characterization of OSC in young sediments should be performed with caution, preferably with the application of appropriate chemical degradation methods (e.g., MeLi/MeI, Table 2).

The most common separation and detection technique for sedimentary OSC is GC with a sulphur-specific detector, such as flame photometric detector (FPD) or sulphur chemiluminescence detector (SCD). Identification of the various OSCs, and quantification of lower abundance species, is typically performed by gas chromatography-mass spectrometry (GC-MS), with interrogation of the characteristic mass fragment ions for each of the major compound groups (e.g., Sinninghe Damsté and De Leeuw 1990). Other techniques and instruments (e.g., X-ray absorption near edge structure, Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS)) are used for elemental analysis, determination of sulphur functionality distribution, and mass spectrometry of non-GC-amenable components, such as the kerogen, asphaltene, and polar fractions (Table 2).

2.3 Sulphur and Carbon Isotope Analysis

Since isotope chemistry is essential in understanding the geochemical processes discussed here, some basic definitions are given.

The *isotopic value* of a certain element is defined as:

$$\delta^H X = \left[\left(\frac{{}^H X / {}^L X}{\text{sample}} \right) / \left(\frac{{}^H X / {}^L X}{\text{standard}} \right) - 1 \right] \quad (1)$$

where X is the element (e.g., S) and the superscript H and L denote the fraction of the heavy and light isotopes, respectively (e.g., ^{34}S and ^{32}S or ^{13}C and ^{12}C). The ratio

Table 2 Summary of common approaches and methods for the characterization of sulphur-bearing OM

Approach	Chemical consideration	Method(s) or instruments	Comments	Refs ^b
Chemical cleavage^a	Selective for S-S and S-H bonds	MeLi/MeI	Cleaves S-S bonds and methylates the S attached to carbon (MeLi/MeI) or reduces it to the thiol (LiAlH ₄)	[1, 2]
		LiAlH ₄		
	Any S-S and C-S bonds for solvent-soluble OM (polar, asphaltene)	Raney nickel	Open cyclic structures. Hydrogenation step may be required following Raney Ni. Ni boride is better for less soluble fractions and allows deuteration	[3, 4]
		Nickel boride		
	Any S-S and C-S bonds for non-soluble OM (kerogen)	Li/EtNH ₂	Labelling with deuterium is possible	[5–7]
		Ni(0)cene/LiAlH ₄		
Thermal cleavage^a	Nonselective	Flash pyrolysis	High temperature (~610 °C) and short time pyrolysis (~10 s), online coupling to GC. Products do not preserve their original carbon skeleton	[8, 9]
	Nonselective	Closed system hydrous/anhydrous pyrolysis	Medium temperatures (~160–360 °C), keeping some of the biomarkers intact for a later <i>offline</i> GC analysis A more time-consuming approach and the maximum yield of the biomarkers vary significantly with pyrolysis temperature. Useful for laboratory simulations of maturation	[10–14]

(continued)

Table 2 (continued)

Approach	Chemical consideration	Method(s) or instruments	Comments	Refs ^b
	Nonselective	Hydro (H ₂)-pyrolysis	Thermal cleavage under H ₂ pressure maximizes the fraction of GC-amenable products for offline analysis, while structural rearrangement of biomarker species is minimal The effect of the catalyst used ((NH ₄) ₂ MoO ₂ S ₂) on the compound-specific $\delta^{34}\text{S}$ values is not yet known	[15–18]
Isotopic analysis	Bulk OM	Isotope-ratio mass spectrometry (IRMS)	Most common is elemental analyzer coupled with IRMS. Kerogen must be isolated offline from other sulphur and mineral phases For a precise quartet sulphur isotope analysis, fluorination to SF ₆ is needed	[19, 20]
	Compound-specific isotopic analysis	GC-IRMS GC/MC-ICPMS	Measured on apolar volatile compounds. S isotope analysis is achieved by a GC coupled with multicollector inductively coupled plasma mass spectrometry (GC/MC-ICPMS). Often liquid chromatography is needed before isotope analysis	[21, 22]
Elemental analysis	High-resolution mass determination, providing molecular elemental composition	Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS)	Solid-phase extraction technique for water-soluble compounds (DOM) should precede the FT-ICR MS analysis	[23–25]

(continued)

Table 2 (continued)

Approach	Chemical consideration	Method(s) or instruments	Comments	Refs ^b
Nondestructive	Identification of S functionalities	X-ray absorption near edge structure (XANES)	May be applied to solid samples including kerogen. No chemical pretreatment needed. Relative crude abundance of S moieties such as thiophenes, sulphonic acids, sulphoxides, and sulphonates	[26, 27]

^aCleavage is followed by gas chromatography (GC) coupled with specific S detectors (flame photometric detector (FPD), sulphur chemiluminescence detector (SCD)) or mass spectrometer (MS, see characterized fragments in Table 1)

^bReferences: 1. Eliel et al. (1976); 2. Kohnen et al. (1991b); 3. Sinninghe Damsté et al. (1988); 4. Sinninghe Damsté et al. (1994); 5. Hofmann et al. (1992); 6. Hartgers et al. (1997); 7. Richnow et al. (1992); 8. Eglinton et al. (1992); 9. Goñi and Eglinton (1994); 10–14. Koopmans et al. (1995, 1996a, b, 1997, 1998); 15. Love et al. (1997); 16. Lockhart et al. (2008); 17. Murray et al. (1998); 18. Grotheer et al. (2017); 19. Giesemann et al. (1994); 20. Grassineau (2006); 21. Amrani et al. (2009); 22. Hayes et al. (1990); 23. Dittmar et al. (2008); 24. Ksionzek et al. (2016); 25. Pohlabein and Dittmar (2015); 26. Vairavamurthy et al. (1994); 27. Sarret et al. (2002)

between these two isotopes in a sample is normalized to an internationally accepted standard (e.g., Vienna Canyon Diablo Troilite (V-CDT) in the case of sulphur). The $\delta^H X$ notation is a relative scale, expressed as a per-mil (‰) deviation of the sample from that of the standard. Negative values of $\delta^H X$ imply that the element in the sample is “lighter” compared to the internationally defined standard, while positive values are considered to be “heavier.”

For a given reaction, the *isotopic fractionation* generated by it is defined as:

$$\varepsilon_{A \rightarrow B} = (\delta^H X_B - 1,000) / (\delta^H X_A - 1,000) - 1 \quad (2)$$

where the subscripts A and B denote the reagent (e.g., SO_4^{2-}) and product (e.g., H_2S), respectively, for a given reaction (e.g., sulphate reduction). The most common methods for sulphur ($^{34}\text{S}/^{32}\text{S}$) and carbon ($^{13}\text{C}/^{12}\text{C}$) isotope analysis are described in Table 2.

3 The Marine Sulphur Cycle and Its Impact on Organic Matter

3.1 The Link Between the Sulphur and Organic Carbon Cycles

Sulphur, with its multiple oxidation states (from -2 to $+6$), participates in many biochemical processes in conjugation with the carbon cycle, such as biosynthesis of proteins, and as electron donor/acceptor for respiration (Sievert et al. 2007). Hence,

these two elements mutually affect the fate of each other through their biogeochemical cycles. Figure 1 conceptually illustrates the coupling between sulphur and organic carbon in the marine system. Sulphate (SO_4^{2-} , oxidation state S^{6+}) is the most stable form of sulphur in the ocean today. It participates in two major biochemical processes, which eventually reduce it into H_2S , namely, *assimilatory sulphate reduction* (point # 1a, Fig. 1) and *dissimilatory sulphate reduction* (point # 2, Fig. 1).

Assimilatory sulphate reduction (ASR) is the metabolic pathway employed by organisms to incorporate SO_4^{2-} into constituents of the living cell. In this process, sulphate is enzymatically reduced first to sulphite and then to H_2S , whereupon the sulphide can be incorporated into, e.g., the amino acids cysteine and methionine (Schiff 1980). Each reaction step requires ATP, and thus it is an energy-consuming process (Takahashi et al. 2011). This is a fundamental biochemical process, given sulphur's essential requirement for life. Quantitatively, sulphur constitutes on average about 1% of the dry mass of living organisms (Shen and Buick 2004; Sievert et al. 2007), with a Redfield ratio similar to phosphorus ($\text{C}_{124}\text{N}_{16}\text{P}_1\text{S}_{1.3}\text{K}_{1.7}$) in many marine phytoplanktons (Ho et al. 2003). Because in this pathway sulphur is biologically incorporated into functional molecules needed by living organisms (e.g., as the amino acid cysteine, point #1b in Fig. 1), it is termed a *biotic sulphurization* pathway.

Dissimilatory sulphate reduction is a fundamentally different type of process. In many environments on Earth, such as below the water-sediment interface of aquatic systems, oxygen becomes depleted. Important groups of bacteria and archaea, known as *microbial sulphate reducers* (MSR), are capable of using SO_4^{2-} as the electron acceptor for respiration. This ubiquitous process of anaerobic environments is termed *dissimilatory sulphate reduction* since the reduced sulphur species (typically H_2S) is released back into the environment (point # 2 in Fig. 1; Rabus et al. 2006). The dissimilatory sulphate reduction process utilizes organic matter as the electron donor and is an energy-yielding metabolic process. It has a critical effect on both the carbon and sulphur cycles. Studies on young sediments suggest that this process can remineralize up to ~80 to 90% of initially buried organic carbon (Kasten and Jørgensen 2000 and references therein). However, the H_2S produced will rapidly react with available iron to form pyrite (point #7, Fig. 1) or be available to react with the remaining dead OM via *abiotic sulphurization* (points # 8–10, Fig. 1), thus fostering OM preservation.

Pyrite is usually the major sink for reduced sulphur species in the geological record, with sedimentary OSC being the second largest sink (Bernier and Raiswell 1983; Bernier 1984; Werne et al. 2004). In some cases (e.g., carbonate depositional environments) such as in the Ghareb Formation, limited iron availability leads to sedimentary OSC becoming the major sink (Minster et al. 1992; Alsenz et al. 2015). It has also been suggested that sulphurization of OM can even compete with pyrite formation, despite the presence of Fe (Urban et al. 1999; Filley et al. 2002; Shawar et al. 2018). Thus, understanding the interplay between organic carbon, reduced sulphur, and iron in a sedimentary sequence is essential to paleoenvironmental interpretation. Like OSC, the formation of pyrite also depends on the supply of

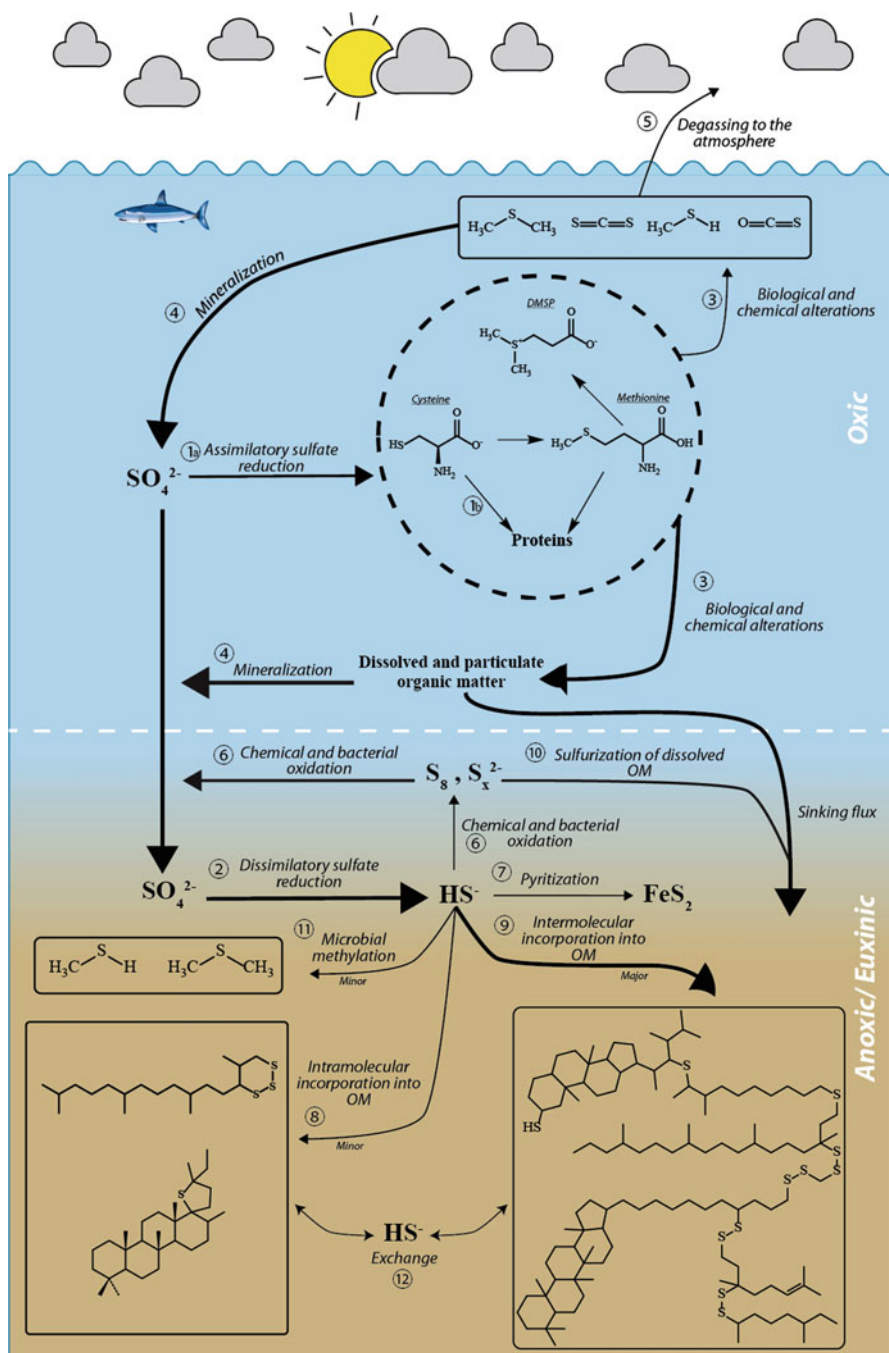


Fig. 1 (continued)

labile OM (Schoonen 2004), and clear correlations between pyritic S and total organic carbon (TOC) have been demonstrated (Berner and Raiswell 1983; Berner 1984). Accordingly, cross plots and ternary diagrams using bulk elemental concentrations (i.e., total S, Fe, and organic C) can be applied to elucidate the oxidation state of young and ancient environments (Dean and Arthur 1989; Morse and Emeis 1992; Leventhal 1995).

3.1.1 Isotopic Evidence for the Abiotic Sulphurization Pathway of Sedimentary Organic Matter

The assimilatory and dissimilatory sulphate reduction pathways have distinctive isotopic fractionations for sulphur ($\epsilon_{\text{Assimilatory}} = -1$ to -3‰ (Kaplan and Rittenberg 1964), $\epsilon_{\text{Dissimilatory}} = -20$ to -75‰ (see summary table in Brunner and Bernasconi 2005; Sim et al. 2011)). The very light $\delta^{34}\text{S}$ generated by the dissimilatory pathways recorded in pyrite was suggested as evidence that microbial sulphate reducers are one of the most ancient forms of life on Earth, dated back to 3.47 Ga (Shen and Buick 2004). Similarly, the large isotopic difference between the assimilatory and dissimilatory pathways is a powerful evidence for the significance of the abiotic sulphurization in sedimentary OM (Amrani 2014).

Abiotic sulphurization, based on isotopic mass balance consideration, is estimated to account for at least 75–90% of total sedimentary organic sulphur (Anderson and Pratt 1995; Werne et al. 2004). Biosynthetic OSCs are generally biologically and chemically labile, typically being remineralized quickly (points # 3–4, Fig. 1). In contrast, secondary OSCs from abiotic sulphurization are more stable and less accessible to microbial degradation (Sinninghe Damsté and De Leeuw 1990; Grice et al. 1998). Therefore, it is expected that in the course of diagenesis, the fraction of secondary sulphur will increase over that of primary biosynthetic, through both the degradation of biosynthetic compounds and also via the incorporation of inorganic S species (Aizenshtat et al. 1983; Mossman et al. 1991).

The pathways and the role of abiotic sulphurization on the OM are discussed in more detail below. However, new studies on sulphur of biotic origin raise new questions on the role of biotic sulphurization in the sedimentary record and are addressed in more detail in Sect. 3.5.



Fig. 1 A conceptual drawing of the marine sulphur cycle and its coupling to the organic carbon cycle. Annotated numbers showing important pathways as discussed in the text: Assimilatory sulphate reduction pathway, introducing OSC of biogenic origin (1), while dissimilatory sulphate reduction generates reduced sulphur species (2). The biotic OSC are labile and undergo biological and chemical alteration (3), some of which can be further remineralized back to SO_4^{2-} (4), degassed to the atmosphere as volatile OSC (5), or sink to the sediment. The assimilatory reduced sulphur (e.g., HS^-) can be oxidized (6) and can react with iron to precipitate pyrite (7) or with OM leading to different pathways of secondary sulphurization (7–11) and OM preservation. Exchange of S between these different fractions of OSC (free and bound) is possible during diagenesis (12)

3.2 Mechanism of Abiotic Sulphurization

Abiotic sulphurization pathway requires three main biogeochemical conditions (Werne et al. 2004; Amrani 2014): (1) presence of reduced S species, (2) low concentration of metal ions, and (3) supply of reactive organic compounds. While H_2S is supplied by the MSR, subsequent biological and chemical oxidation processes produce elemental S and S_x^{2-} (point # 6, Fig. 1). Polysulphide anions are stronger nucleophiles and thus react faster with organic compounds than $\text{H}_2\text{S}/\text{HS}^-$ (LaLonde et al. 1987; Loch et al. 2002; Amrani and Aizenshtat 2004c; Wu et al. 2006). The presence of reduced sulphur species (HS^- , S_x^{2-}) thereby facilitates sulphur incorporation into OM, while metal ions forming insoluble sulphides, especially Fe (II), compete with OM for the available sulphur. When metal ions are in low concentrations (e.g., carbonate environments) sulphur incorporation into OM is often favored. In some settings, sulphurization of OM may compete with pyrite formation despite the presence of Fe (Urban et al. 1999; Filley et al. 2002). More specifically, it was suggested that in OM-rich and Fe-poor environments, iron species can be scavenged by organic compounds to form Fe-organic complexes, thus limiting the formation of pyrite and enhancing the formation of OSC (Shawar et al. 2018). Finally, not all OM may react with the available reduced sulphur species. Rather, a supply of organic compounds with appropriate functional groups (e.g., conjugated double bonds, carbonyl groups), which can react with reduced sulphur species, is required.

The potential and rate of a given biomarker to undergo abiotic sulphurization strongly depends on the reactivity of the organic precursor, with the carbonyl functionality and conjugated double bond systems being the most reactive (Schouten et al. 1994; Adam et al. 2000; Kok et al. 2000a; Amrani and Aizenshtat 2004a). Prior to sulphurization, early diagenetic changes (point # 3, Fig. 1) can increase the sulphurization potential of some compounds by altering less reactive functionalities (e.g., isolated double bonds, alcohols) to more labile moieties, such as carbonyl groups and conjugated double bonds (Grossi et al. 1998; Rontani et al. 1999; Schaeffer et al. 2006; Blumenberg et al. 2010). Inorganic reduced S species (e.g., HS^- , S_x^{2-}) attack the functional sites of organic precursors via nucleophilic, electrophilic, or radical mechanisms, generating an initial C-S bond (Amrani 2014). Some of these initially formed C-S bonds and S-S bonds subsequently undergo continuous exchange with the surrounding inorganic reduced sulphur pool (Amrani et al. 2006). The specific chemical mechanisms for sulphurization are still a matter of debate and are beyond the scope of this review. The interested reader is referred to other reviews that summarized previous works, under variable chemical and physical conditions, that attempted to simulate sulphurization in the laboratory (Krein 1993; Werne et al. 2004; Amrani 2014).

Abiotic sulphurization can proceed via two general pathways, *intramolecular* and *intermolecular* sulphurization which lead to free OSC and bound OSC products, respectively (Sinninghe Damsté and De Leeuw 1990). An intramolecular S cyclic structure is formed if the S-bound can create another S-C bond on the same molecule (point # 8, Fig. 1). Common S moieties that form by the intramolecular pathway are

thianes, thiolanes, thiophenes, benzothiophenes, and dibenzothiophenes (Table 1, Fig. 4; Krein 1993). In this context, aromatic compounds are usually indicative of OM which is more thermally mature (Krein and Aizenshtat 1995; Rosenberg et al. 2017). Intermolecular C-S and S-S cross-linkages may occur when a second bond on the same molecule cannot be formed (e.g., the next reactive site is too far or does not exist), enabling the S functionality to react with a second molecule (point # 9, Fig. 1). These compounds can form monosulphidic (C-S-C), disulphidic (C-S-S-C), or polysulphidic (C-S_x-C) bonds (Werne et al. 2004). Successive intermolecular sulphurization cross-links more and more compounds into a macromolecules, which eventually contributes to the formation of kerogen. It is important to note that cross-linking of organic compounds is not limited to sulphur bridges. Oxygen, and possibly nitrogen, also may play a role in the cross-linking of organic compounds and thus the preservation of OM in sediments (Koopmans et al. 1996a; Putschew et al. 1998; Farrimond et al. 2003; Amrani et al. 2007; McKee and Hatcher 2010).

The intramolecular sulphurization pathway creates OSC that, if not further bound into the macromolecule, may be found in the free, apolar fraction of petroleum and bitumen. The number of suitable functional groups of a given precursor will affect its sulphurization pathway (i.e., intermolecular, intramolecular, or both) and the mode of occurrence in an immature sedimentary rock (i.e., in the macromolecules or as a free OSC) (Kohnen et al. 1992). At early stages of diagenesis, different chemical alterations can take place leading to multiple routes of S addition (Schaeffer et al. 2006; Amrani 2014). Thus the occurrence of OSC with a given carbon skeleton in different fractions of the OM (free OSC and bound OSC) does not necessarily imply that these were two distinguished biological precursors. Moreover, it is important to note that through the diagenetic process, there may be interaction between free OSC and bound OSC fractions (point # 12, Fig. 1; Amrani et al. 2006).

Following the discussion above, OM is operationally divided into three pools: (1) free (GC-amenable) hydrocarbons that were not sulphurized; (2) free (GC-amenable) OSC that derive from intramolecular sulphurization and were not further cross-linked into the macromolecular structure, hereafter termed “free OSC”; and (3) S-bound (i.e. cross-linked) – compounds that were sulphurized intermolecularly into the macrostructure of the organic matter hereafter termed “bound OSC.”

3.3 Timing of Abiotic Sulphurization

Timescales of 60–10,000 years have been reported for the sulphurization of different compounds within the sediment column (Wakeham et al. 1995; Urban et al. 1999; Kok et al. 2000a, b; Werne et al. 2000; Farrimond et al. 2003; Sinninghe Damsté et al. 2007). This reflects the fact that below the water-sediment interface, the environment becomes rapidly anoxic when burrowing macrofauna are absent (Werne et al. 2004). In extreme cases, extensive parts of the water column can be anoxic or even euxinic (e.g., Black Sea, Cariaco Basin; Wakeham et al. 2007; Raven et al. 2016), where the chemocline of O₂ is very shallow and H₂S is detected below

it. In such settings, abiotic sulphurization may occur within the water column as the organic particles sink through it, on a timescale of days (Raven et al. 2016). Such rapid sulphurization rates are supported by laboratory experiments, with reaction times ranging from minutes to weeks for different functionalities (Amrani and Aizenshtat 2004a).

When sulphurization rate is considered at the molecular level, additional complexity arises, thus affording further insight into the process and its paleoenvironmental significance. Since sulphurization depends (among other factors) on the reactivity of the precursor, different precursors will undergo sulphurization at different rates. For example, in young sediments of Ace Lake (Antarctica), Kok et al. (2000a) found that only steroid biomarkers were extensively sulphurized. Further into the diagenetic process (i.e., deeper sediments), other classes of biomarkers (e.g., isoprenoids, hopanoids) can be found primarily in a sulphurized form or even exclusively in the S-bound OSC fraction (e.g., the dinosteranes; Kohnen et al. 1992). The sulphurization process may continue deeper in the sediments, sulphurizing other, less reactive classes of organic compounds, fueled by other biogeochemical processes. For example, deeper in the sediments, where SO_4^{2-} becomes depleted, a consortium of anaerobic methane-oxidizing bacteria and sulphate-reducing bacteria (AOM-SR) can produce significant amounts of H_2S (Kasten and Jørgensen 2000). The AOM-SR microbial consortium is constrained to a narrow depth interval at the sulphate-methane transition zone, but the overall effect is that the H_2S maxima is located between the zones of MSR and AOM-SR. Recently, Quijada et al. (2016) showed in the Cariaco Basin that the maximum of OM sulphurization is associated with this maxima of H_2S concentration between the MSR and AOM-SR zones.

3.3.1 Sulphur Isotope Considerations

In most young sediments, the $\delta^{34}\text{S}$ of all bulk phases (H_2S , SO_4^{2-} , pyrite, kerogen) increases with depth (Fig. 2) as a result of the MSR process acting in a closed system for sulphate (e.g., Werne et al. 2003). Both OSC and pyrite respond to this effect, but there is a S isotope difference between them, with an average discrepancy of 10‰ globally (Anderson and Pratt 1995). Several scenarios have been suggested to explain this phenomenon (see detailed discussion in Anderson and Pratt 1995; Amrani 2014). One such scenario is the potentially different timing of sulphurization for Fe and organic compounds. Indeed, reactive iron species are likely to outcompete organic compounds for reduced S species (Gransch and Poshtuma 1974; Hartgers et al. 1997), thereby taking the most ^{34}S -depleted fraction from the MSR according to the Rayleigh distillation model. However, several studies have shown that during early diagenesis, OSC may form simultaneously with Fe sulphurization or even outcompete it (Bates et al. 1995; Brückert and Pratt 1996; Urban et al. 1999; Filley et al. 2002; Werne et al. 2003; Riedinger et al. 2017). The variability in S isotopes as a result of the different timing of sulphurization and/or reactive S species may be recorded by specific OSC, whereas bulk S phases such as pyrite and kerogen average it out (Amrani 2014). Compound-specific sulphur isotope analysis (CSSIA) data may unravel this process (Amrani et al. 2009).

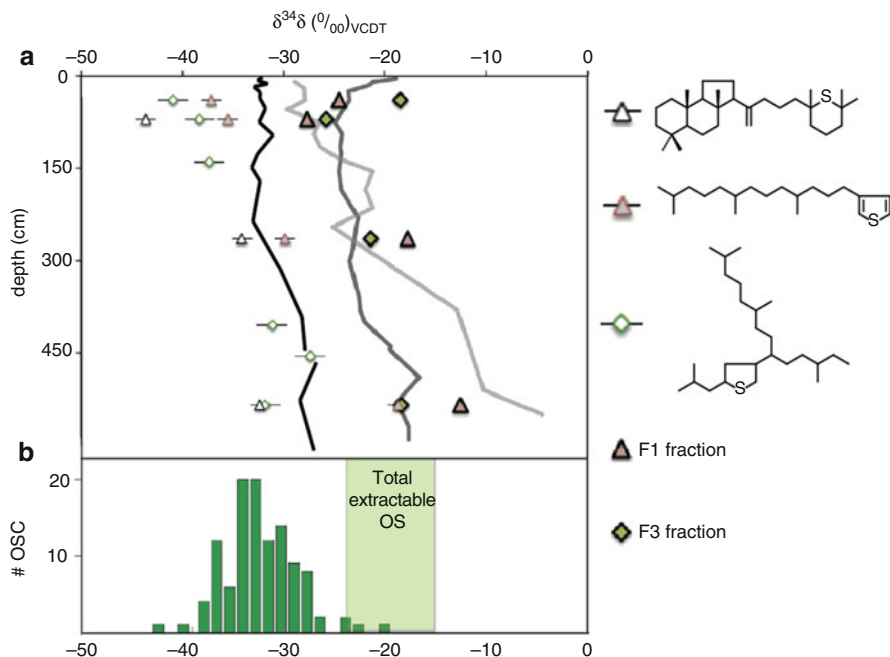


Fig. 2 Early sulphurization in the Cariaco Basin sediments. Sulphur isotopic values of inorganic compounds, extractable OM fractions, and individual OSC. (Panel **a**) Porewater sulphide (light gray line), residual OS (dark gray line), and pyrite S (black line). Symbols with thick outlines indicate $\delta^{34}\text{S}$ values of bulk extractable OM fractions F1 (apolar, triangles) and F3 (polar, diamonds). Open symbols indicate $\delta^{34}\text{S}$ values of individual GC-amenable compounds in these fractions – tri-terpenoid thiane in F1 (open triangles), C_{20} isoprenoid in F1 (shaded triangles), and HBI thiolanes in F3 (diamonds). (Panel **b**) Histogram of all compound-specific measurements from Cariaco Basin sediment extracts, including both assigned and unidentified compounds. The shaded area represents the range of $\delta^{34}\text{S}$ measured for total extractable OS. (Modified from Raven et al. (2015) and Werne et al. (2003))

Raven et al. (2015) used CSSIA in young sediments from the Cariaco Basin. Large S isotopic variability between the different OSC was observed (up to 23‰). Moreover, they have shown an intriguing phenomenon where some specific OSCs were ^{34}S -depleted relative to pyrite, while the bulk organic S was ^{34}S -enriched compared to pyrite (Fig. 2). Raven et al. (2015) explained their observations by different sulphurization mechanisms, either kinetic or equilibrium effects that are associated with ^{34}S depletion or enrichment of the OSC, respectively (Amrani and Aizenshtat 2004a; Amrani et al. 2008). They further suggested that the kerogen is ^{34}S -enriched relative to the measured individual OSC because there is a significant contribution of ^{34}S -enriched organic sulphur from the overlying water body (Raven et al. 2016).

In another recent CSSIA study on the immature Ghareb Formation, a wide range of $\delta^{34}\text{S}$ values (up to 14‰) of individual OSC has also been observed

(Shawar et al. 2015). However, all of the measured OSC were ^{34}S -enriched relative to the coexisting pyrite throughout the studied section (~350 m). The bigger variability in $\delta^{34}\text{S}$ of OSC of the young Cariaco sediments (23‰) compared to the immature Ghareb Formation (14‰, Late Cretaceous) might reflect S isotope exchange and homogenization with inorganic S species and other diagenetic processes during later stages (Amrani et al. 2006; Rosenberg et al. 2017). It is also possible that some of the most reactive organic compounds in the Cariaco Basin may react with reduced S species shallower within the sediments than the reaction of S with Fe species to form Fe sulphides (Shawar et al. 2018). The timing of sulphurization in the Rayleigh distillation sequence probably dictates the $\delta^{34}\text{S}$ of both pyrite and OSC. Formation of pyrite later than OSC may be the result of faster reaction kinetics of some organic compounds with reduced S, very high abundances of organic matter, or some hindrance to Fe sulphide formation as was suggested by Shawar et al. (2018). More detailed CSSIA studies from young sediments to mature rocks are needed to answer such questions.

3.4 Sulphurization as OM Preservation Mechanism

An important geochemical consequence of the sulphurization process is better preservation of the OM record. Because most components of living OM are chemically and biologically labile (e.g., proteins and carbohydrates), the preserved fraction in the sedimentary record is not necessarily representative of the original input. Upon diagenesis, more refractory compounds are preferentially preserved, and the initial distribution between terrestrial and marine input (see review by Arndt et al. 2013), or between plankton and heterotroph populations (Wakeham et al. 1997), can be distorted. Since sulphurization quenches reactive OM sites and binds biomolecules into macromolecules, it makes the organic matter less susceptible to microbial consumption (Kohnen et al. 1992; Werne et al. 2004). Sulphurization of biologically labile carbohydrates is another example of the important preservation role of sulphurization in euxinic environments (Kok et al. 2000b; van Dongen et al. 2006).

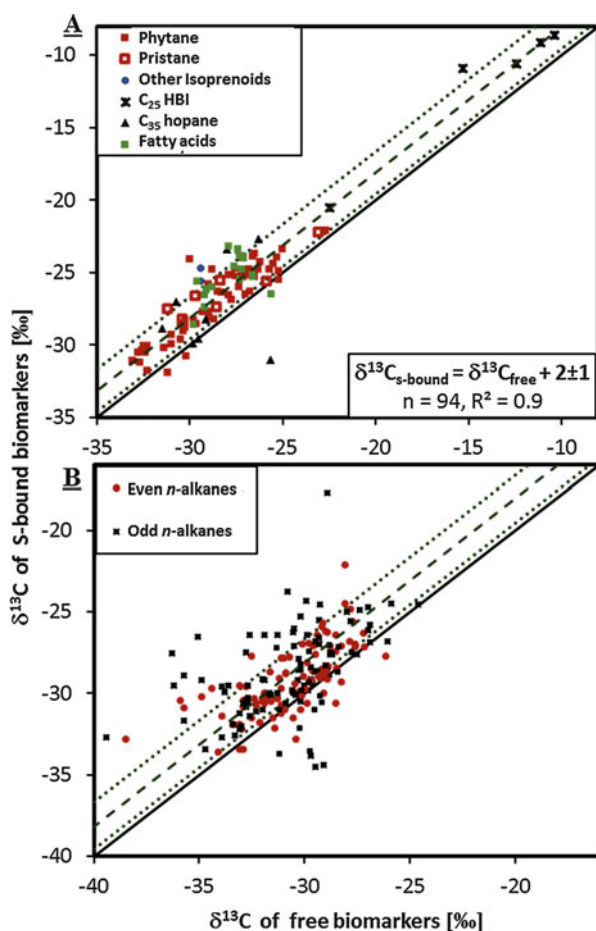
Indeed, many sedimentary rocks exhibit a strong correlation between bulk organic carbon and organic S, indicating that the fate of these elements is connected. Examples for such $\text{TOC-S}_{\text{organic}}$ correlation have been reported in the Monterey Formation (Zaback and Pratt 1992), the Kimmeridge Clay Formation (Lallier-Vergès et al. 1997), and the Ghareb Formation (Meilijson et al. 2015). Marine kerogens with atomic S-C ratios greater than ~0.04 are recognized as a unique type (type II-S, Orr 1986), reflecting the importance that S plays in preserving organic matter in such sedimentary rocks.

Another possible characteristic of preservation via sulphurization, notable at the molecular level, is suggested by compound-specific ^{13}C isotope studies. Through a compilation of literature data, Rosenberg et al. (2018) have found a consistent difference between the $\delta^{13}\text{C}$ of S-bound and free HC, where the former are heavier by $2 \pm 1\text{‰}$ on average (Fig. 3). The difference in $\delta^{13}\text{C}$ between these two fractions is rather constant, regardless of the type of the biomarkers (i.e., *n*-alkanes,

isoprenoids, HBIs, hopanes), the source of the compounds (e.g., marine vs. terrestrial, autotrophic vs. heterotrophic), the age of the rock (~235 to 5 Ma), the range of $\delta^{13}\text{C}$ (from ~ -30 to -10‰), and the prevailing paleoenvironment of each data point depicted in Fig. 3. The different mechanisms suggested to account for this difference include (A) kinetic isotope effects of the reactions involved in the sulphurization process (Schouten et al. 1995b) and (B) different sources of the original precursors of the biomarkers in the free HC and S-bound fraction having different $\delta^{13}\text{C}$ values (Kohnen et al. 1992; Grice et al. 1996).

Rosenberg et al. (2018) have suggested that a broader diagenetic process, such as the degradation of OM, may be responsible for the constant difference. As the free compound is more prone to degradation compared to its S-bound counterpart, it is possible that the $\delta^{13}\text{C}$ of the S-bound biomarker better represents the original $\delta^{13}\text{C}$ signature. Such preservation of the $\delta^{13}\text{C}$ record has significant geochemical

Fig. 3 $\delta^{13}\text{C}$ of S-bound biomarkers vs. $\delta^{13}\text{C}$ of free biomarkers for isoprenoid-based skeletons and fatty acids (a) and *n*-alkanes (b). Data was compiled from 17 different studies (e.g., Forster et al. 2008; Grice et al. 1996, 1998; Hefter et al. 1995; Kohnen et al. 1992; Putschew et al. 1995; Schouten et al. 1997, 2001, 1995b; Sinninghe Damsté et al. 2007, 2008). The complete list of references and more details can be found in Rosenberg et al. (2018). Bold black line is the 1:1 agreement line. The fine line and the two dashed lines are the best fit and the 1 stdev envelope after adjusting the slope to unity in plot A (i.e., reflecting a $2 \pm 1\%$ constant difference between the two axes)



implications, as carbon isotopes are often used for precursor identification and paleo- $p\text{CO}_2$ estimations (Sinninghe Damsté et al. 2008; Pagani 2014).

3.5 Other Possible Sources for Sedimentary Organic Sulphur

3.5.1 Volatile Organic Sulphur Compounds (VOSC) as a Possible Source to Sedimentary Organic Sulphur

In the photic zone of the ocean, some of the biogenic OSC are chemically or biologically altered and become volatile (hence, VOSC, point # 5, Fig. 1) such as methanethiol (MT), dimethyl sulphide (DMS), carbonyl sulphide (COS), and carbon disulphide (CS_2) (Liss et al. 1997). These VOSC are typically present in the surface ocean at low concentrations, in the range of 10^{-12} to 10^{-8} M (Mopper and Kieber 2002). Despite their low concentration, VOSC play a major role in the global sulphur cycle as they transfer sulphur from the ocean to the continents (Bates et al. 1992; Lomans et al. 2002; Lana et al. 2011). The most abundant oceanic VOSC is DMS that has been suggested to affect the Earth's radiative balance and cloud formation (Charlson et al. 1987; Levasseur 2013). DMS is produced by the enzymatic cleavage of dimethylsulphoniopropionate (DMSP) which is biosynthesized by phytoplankton in vast amounts as an osmoregulator as well as for several other suggested functions (Stefels et al. 2007).

At the present time, ocean-derived DMS is the primary source of sulphur to the atmosphere (Bates et al. 1992; Gondwe et al. 2003), yet only a small fraction of VOSC produced in the ocean is released to the atmosphere. A complex set of reactions in the ocean can oxidize VOSC back to sulphate (point # 5, Fig. 1), or they can be consumed as sources of sulphur and carbon by microbial populations (Kiene and Linn 2000; Simó et al. 2009). Alternatively, VOSC can react with DOM or metals to form complexes and be deposited with the sediment (Stefels et al. 2007), where they may provide another source of S that participates in the formation of sedimentary OSC. The magnitude of this flux is as yet unknown.

Under anoxic conditions (e.g., stratified water body or sediment), VOSC can also be formed in situ (as opposed to transfer from the surface water) via different formation pathways (Lomans et al. 2002; Higgins et al. 2006). For example, DMS can be formed by microbial reduction of dimethyl sulphoxide (DMSO) and sequential methylation of H_2S (evolved from MSR) by enzymatic activity carried out by a variety of microorganisms, possibly including methanogens (Stets et al. 2004; Zhuang et al. 2017 and references therein).

Several studies provide isotopic evidence for the dissimilatory sulphur source of VOSC in anoxic environments. For example, Oduro et al. (2013) have shown that VOSC in stratified freshwater of Fayetteville Green Lake (NY, USA) are ^{34}S -depleted, down to about -30‰ , close to the coexisting H_2S $\delta^{34}\text{S}$ value. These authors suggested a combination of biological and abiotic processes in the formation of VOSC that involved reactive sulphur species evolved from MSR and methyl groups of lignin components. In a compound-specific sulphur isotope study, DMS in the hypolimnion (during summer) of the freshwater Lake Kinneret (Israel) was ^{34}S -depleted, similar to the coexisting H_2S (Sela-Adler et al. 2016). When the lake

was mixed (winter), DMS was ^{34}S -enriched, similar to DMSP and coexisting sulphate as also observed in oxic oceanic basins (Oduro et al. 2012; Amrani et al. 2013). In the sediment of Lake Kinneret, DMS has mixed sources between dissimilatory S (^{34}S -depleted, e.g., methylation of H_2S) and assimilatory S (^{34}S -enriched) from the degradation of detrital OSC (Sela-Adler et al. 2016). Kiene (1988) was the first to identify this pool of “DMS” and suggested that the precursors could be sulphonium compounds or DMS that were absorbed to sediment particles and could only be released by a strong base treatment. This “base-hydrolyzable” DMS fraction is two to three orders of magnitude more concentrated (10–200 $\mu\text{mol/kg}$ sediment) than the dissolved DMSP and DMS. Therefore, this fraction represents a significant quantity of S that might also contribute to CH_4 formation (by demethylation) in anoxic sediments (Kiene 1996). This is a widespread phenomenon, occurring in sediments from all over the world, including diverse settings such as freshwater lakes, salt marshes, subtidal, intertidal, carbonate, and across a range of water depths (Kiene 1988, 1996; Kiene and Service 1991; Sela-Adler et al. 2016; Zhuang et al. 2017). Vairavamurthy et al. (1997) have noted a similar phenomenon in marsh sediments from Shelter Island (NY, USA), since their “base-hydrolyzable” 3-mercaptopropionate (3-MPA) is another DMSP degradation product. Since such “base-hydrolyzable” fractions of OSC are associated with the sediment, they are protected from biodegradation and can escape mineralization at the very early stages of diagenesis (Kiene 1996). Vairavamurthy et al. (1997) estimated the age of the “base-hydrolyzable” 3-MPA to be 90 years, well into the timing of abiotic sulphurization of OM. Therefore, this “base-hydrolyzable” OSC, once released from its association with sediment particles, might react with other organic compounds to form secondary sulphur compounds (i.e., part of protokerogen or humic substances) that could be preserved through diagenesis. It has been shown that compounds such as thiols act as good nucleophiles for sulphurization and formation of other OSCs (Amrani et al. 2008). Hypothetically, it is therefore conceivable that some sulphurized biomarkers might carry sulphur from this source; that is, they will have an assimilatory heavy $\delta^{34}\text{S}$ value. Combined compound-specific sulphur and carbon isotope determination for these “sediment-bound” OSC and sulphurized biomarkers in young sediment may reveal the significance of this process.

3.5.2 Refractory Biotic Organic Sulphur Compounds in the Ocean Possible Abiotic Sulphurization of Dissolved and Particulate Organic Matter

When organic compounds (e.g., DOM) enter sulphidic water, abiotic sulphurization can occur, potentially adding to the particulate sulphur that reaches the sediment. Sulphurization experiments of DOM (e.g., humic acids) with H_2S have shown incorporation into DOM, accompanied by oxidation of H_2S (Heitmann and Blodau 2006). However, these experiments were conducted at $\text{pH} = 6$ and thus may not be applicable to marine environments. In a recent study, Pohlabein et al. (2017) have carried out laboratory experiments to study the sulphurization of DOM with HS^- and S under anaerobic conditions. They found that sulphurization was nonselective for the chemical properties of the DOM precursors, such as saturation, aromaticity,

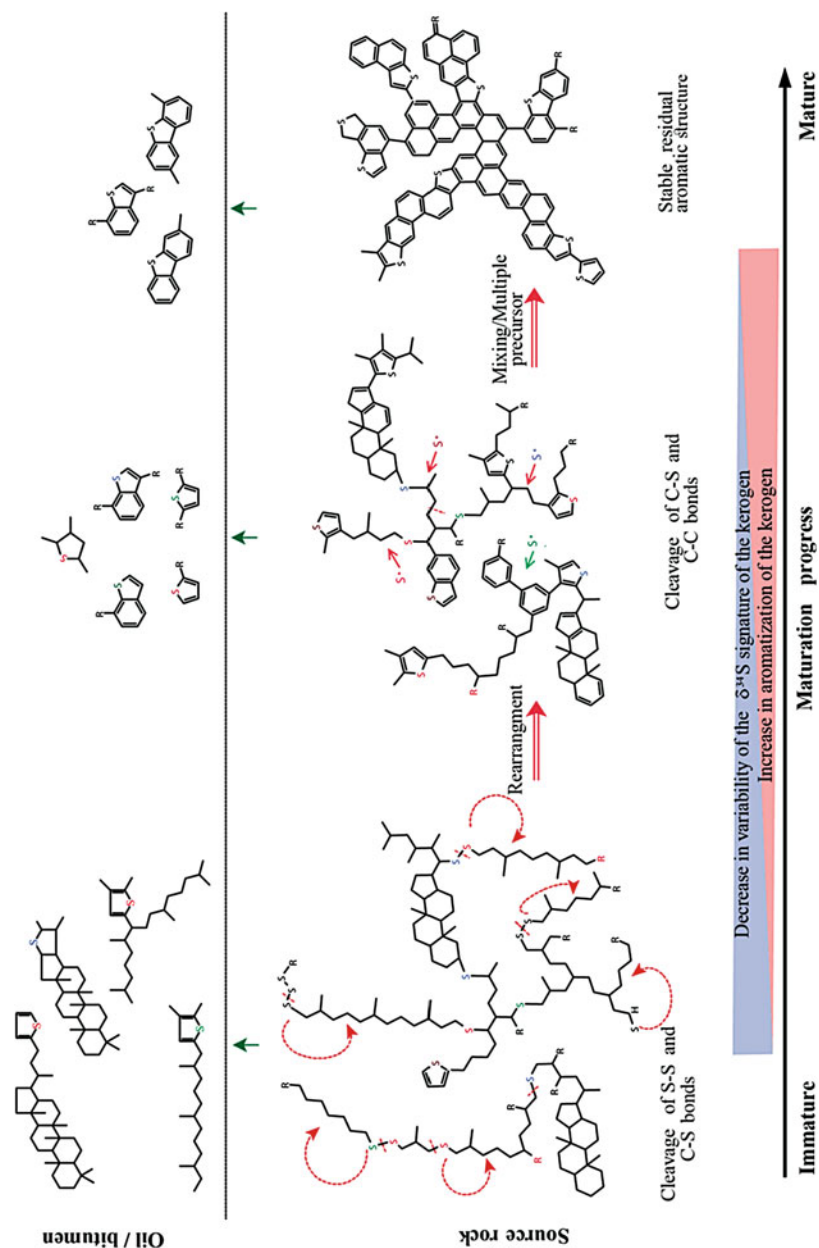


Fig. 4 (continued)

and degree of oxidation or heteroatom content (e.g., nitrogen). The authors concluded that sulphurization of DOM under anaerobic conditions is likely to be a major source of DOS in the open ocean. Using isotopic mass balance models, Raven et al. (2016) argued that abiotic sulphurization, in the water column of the Cariaco Basin, was responsible for 50% of the total organic sulphur found in the young sediment. However, rapid exchange of S isotopes between organic and reactive sulphur can commence even at moderate temperature, and thus the contribution of abiotic S from the water column may not be readily determined (point # 12, Fig. 1; Amrani et al. 2006). It is possible that refractory OSC may not participate in such organic-inorganic S isotope exchange, but further studies are needed to address this.

3.6 The Formation and Structural Modifications of Sedimentary OSC During Catagenesis

The discussion so far has dealt with the different pathways whereby OM and S are transferred from young sediments and into the geological record. With burial and increase of thermal stress on the sediments, the chemistry of OSC evolves further. Though the effects of thermal maturation (catagenesis) are beyond the scope of this review, some aspects are described here briefly to provide a more complete view of the S cycle. There is no definitive and clear line which separates diagenesis from catagenesis. Rather, they should be considered as a continuum, ranging between the realms of biochemical processes and temperature-driven reactions. The S-S and C-S bonds that were generated as a result of the sulphurization of the OM are weak relative to C-C bonds. This can lead to their further rearrangement to more stable bonds (i.e., aromatic) in the macromolecular structure, cleavage at relatively low thermal stress, and to the formation of radicals that further destabilize the OM (Tannenbaum and Aizenshtat 1985; Orr 1986; Baskin and Peters 1992; Martin 1993; Krein and Aizenshtat 1994; Koopmans et al. 1998; Lewan 1998; Aizenshtat and Amrani 2004a). Thus, apparently “thermally immature” sedimentary rocks may already have been altered to some degree by catagenetic processes (Siedenberg et al. 2018). In such cases, some of the “free” OSC may be different from those of the initial, low-temperature sulphurization products, with the formation of compounds such as alkylthiophenes rather than organic sulphides and polysulphides. With increasing maturation, the kerogen continues to rearrange into thermally more stable configurations, expressed as an increase in cyclization and aromatization of the kerogen, as well as the eventual generation of petroleum fluids (Fig. 4; Sinninghe



Fig. 4 A conceptual figure of kerogen maturation. The different colors of the S atoms represent different $\delta^{34}\text{S}$ values (i.e., high variability in $\delta^{34}\text{S}$). There is no sharp transition from the diagenetic to the catagenetic processes: they should rather be thought of as continuum, where the later becomes dominant as the transfer of organic carbon from the macromolecular structure to the free HC liquids increases. With thermal maturation, the kerogen continues to undergo rearrangement and structural changes. This is reflected by an increase in the aromatization and decrease in the variability of $\delta^{34}\text{S}$ values (represented by only black S atoms) of the OSC generated as oil and bitumen constituents

Damsté and De Leeuw 1990; Krein and Aizenshtat 1995). This gradual process is reflected by decreasing variability of $\delta^{34}\text{S}$ among the different OSC generated from the kerogen with progressive maturation (Rosenberg et al. 2017).

4 Application of Organic Sulphur Compounds in Paleoenvironmental Research

In the following sections, nine groups of biomarkers and their sulphurized derivatives are discussed. Studies in which these groups have been characterized in terms of their sulphurized fraction (free or bound OSC) are summarized in Table 3. For each group, we first briefly highlight their significance as biomarkers. Then, we discuss aspects related to their sulphurization sites, rates and extent of sulphurization, preservation, and biases of the geological record resulting from the sulphurization process. Where possible we discuss the potential benefit gained by quantifying sulphurized biomarkers in paleoenvironmental studies.

4.1 *n*-Alkanes

The distribution of *n*-alkanes is considered to be a marker of the relative input of marine vs. terrestrial organic matter into the depositional basin (Wakeham et al. 1995; Grice et al. 1996; Gelin et al. 1997; Hartgers et al. 1997; Peters et al. 2005). Their distribution and source is often represented by indices such as the carbon preference index (CPI) and odd-to-even predominance (OEP), which is occasionally used also for thermal maturity assessment (Peters et al. 2005). Under conditions where sulphurization takes place, *n*-alkanes occur as both free and S-bound compounds. However, the occurrence of *n*-alkane carbon skeletons as S-bound compounds might bear extra insight, not revealed by the free HC. The content of S-bound *n*-alkanes may greatly exceed (up to 90%) the content of their free-form counterparts (Fig. 5). Moreover, distributions of free and S-bound *n*-alkanes may be considerably different from one another (Fig. 5), leading to significant differences in the CPI and OEP indices (by a factor of 1.5–8) for a given sample (Koopmans et al. 1996a; Schouten et al. 1997, 2001; van Kaam-Peters and Sinninghe Damsté 1997; van Kaam-Peters et al. 1998). Strong even-over-odd carbon number predominance of the *n*-alkanes released by desulphurization was observed, in contrast to the OEP of the free *n*-alkanes fraction (Schaeffer et al. 1995; Koopmans et al. 1996a; van Kaam-Peters et al. 1998). Schaeffer et al. (1995) noted that the even-over-odd distribution of bound *n*-alkanes is widespread in evaporitic sediments, but did not identify the responsible mechanism. Schouten et al. (2001) suggested that different distributions of *n*-alkanes in the free and S-bound fractions of the Monterey Formation represent a predominant origin from terrestrial and marine sources in each of these fractions,

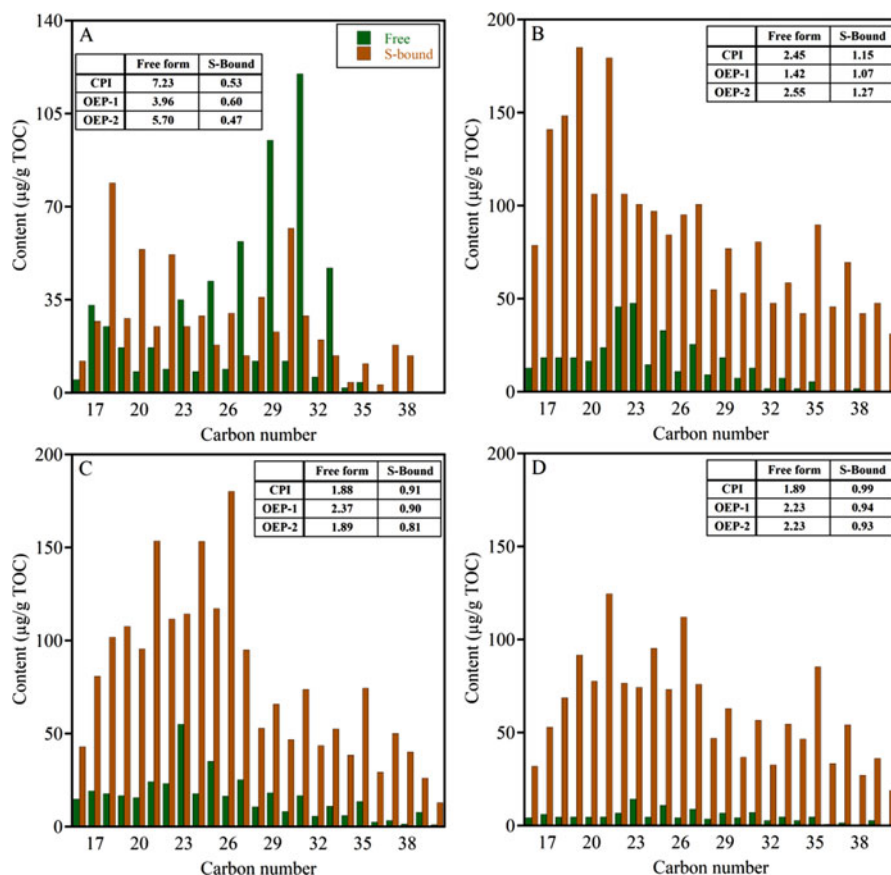


Fig. 5 Free and S-bound *n*-alkane contents ($\mu\text{g/g TOC}$) of several sulphur-rich sedimentary rocks, showing how their distribution and CPI and OEP indices differ dramatically between the two fractions. Data is from (a) Vena del Gesso marl (Koopmans et al. 1996a), (b) Calcaires en plaquettes (van Kaam-Peters and Sinninghe Damsté 1997), (c, d) Calcaires en plaquettes, layers M and DU, respectively (van Kaam-Peters et al. 1998)

respectively. No mechanism to explain the selective preservation of marine and terrestrial *n*-alkanes in the two fractions was suggested by the authors. It might be that terrestrial OM, which travels longer to the sulphurization regime, is then less reactive (Arndt et al. 2013) and therefore less prone to sulphurization.

Linear fatty acids are thought to be one of the sources of *n*-alkanes in sedimentary OM (e.g., Hartgers et al. 2000). Sulphur-bound $\text{C}_{16}\text{--C}_{26}$ linear fatty acids predominated by C_{18} were identified in the Messinian age Tripoli Unit rocks of the Lorca Basin, SE Spain (Russell et al. 2000). The most abundant isomers were those with sulphur substitution at carbon atom 9. This points to an early sulphurization of

Table 3 Summary of main applications of the biomarker families discussed in the text and aspects of their sulphurization as revealed by different studies cited here

Biomarker group	Main applications as biomarkers and aspects of their sulphurization	References
<i>n-Alkanes</i>	<i>n</i> -Alkane distribution is a signature of OM origin. Distribution of free and S-bound may vary significantly (Fig. 5). For the application of proxies, such as CPI and OEP, both fractions should be considered	[1–4]
<i>Long-chain C₃₇–C₃₉ alkenes and alkenones</i>	C ₃₇ –C ₃₉ alkenones and their derivatives indicate input of calcareous nanoplankton material. In addition C ₃₇ unsaturated alkenones are used for reconstruction of ancient sea surface temperatures (SST) and paleo- <i>p</i> CO ₂ . The effect of sulphurization on the SST proxy is minimal, but if all alkenones are sulphurized, SST determination is not applicable	[5–8]
<i>Phytol-derived and phytol-related isoprenoids</i>	Sulphurization of phytane and pristane can be significant. Under S-rich conditions, sulphurization of phytane seems to be favored over pristane. This selective sulphurization creates a bias which might limit the use of the Pr/Ph ratio under S-rich conditions (Fig. 6). Free OSC compounds such as the C ₂₀ isoprenoid thiophenes can be highly abundant at moderate thermal maturation. Their distribution is used as a marker for paleosalinity	[2, 4, 5, 9–20]
<i>Highly branched isoprenoids (HBIs)</i>	HBI occurrence indicates diatom OM input, with an age constrain (U. Turonian–present day). Also, they may act as a marker for nutrient abundance during deposition (i.e., upwelling conditions). HBIs are known to undergo rapid sulphurization in young sediments, both inter- and intramolecularly	[5, 12, 15, 21–30]
<i>Steroids</i>	The distribution of the sterane groups is used to determine the origin of OM. Steroids are known to undergo rapid sulphurization in the early stages of diagenesis. The sulphurized form occurs mainly as free OSC. Preferential sulphurization of C ₂₇ steroid derivatives is common and may introduce bias if only the free hydrocarbon fraction is analyzed. 4-Methylsteroids (dinosterane) can be found in large abundance in the S-bound fraction	[7, 31–36]
<i>Hopanoids</i>	Indicator of OM input from bacterial origin, redox conditions of the water column, and assessment of the extent of diagenesis in immature samples. Also, they may be applied for paleo-reconstruction of dissolved CO ₂ concentration. Sulphurization is relatively rapid and preferential for C ₃₅ hopanoids. This can introduce a bias if only the free hydrocarbon fraction is analyzed for both redox and maturity proxies	[1, 37–39]
<i>Carotenoids</i>	Isorenieratene and chlorobactane are exclusively synthesized by green sulphur bacteria and are therefore specific indicators of photic zone euxinia. They are easily degraded and	[1, 3–5, 34, 39–47]

	therefore rarely observed as free compounds. They usually are present in the sulphurized forms with the majority being in the S-bound OSC fraction. Main limitation of use is because β -isorenieratane can be formed by diagenetic aromatization of β -carotene (regardless of anoxic conditions). Degradation of isorenieratene as a result of thermal maturation may result in the formation of aromatic OSCs	
<i>Porphyryns</i>	Used as a marker for the source of OM input. Their preservation is enhanced by sulphurization, with the majority being in the S-bound OSC fraction. In addition, sulphur derivatives of bacteriochlorophyll <i>c</i> and <i>d</i> are indicators of photic zone anoxia	[7, 48–51]
<i>Polyprenoid sulphides</i>	C ₃₀ tetraacyclic polyprenoid sulphides are an indicator of lacustrine depositional environments. They require sulphur-rich conditions to form, under which they will mostly occur in the free OSC fraction. They have a unique source or specific path of sulphurization that is not yet known	[38, 52–55]

References: 1. Grice et al. (1998); 2. Koopmans et al. (1996a); 3. van Kaam-Peters et al. (1998); 4. van Kaam-Peters and Sinninghe Damsté (1997); 5. Wakeham et al. (1995); 6. Brassell and Dumitrescu (2004); 7. Schaeffer et al. (1995); 8. Koopmans et al. (1998); 9. van Dongen et al. (2006); 10. Fukushima et al. (1992); 11. Barakat and Rullkötter (1995); 12. Hartgers et al. (1997); 13. Koopmans et al. (1995); 14. Sinninghe Damsté et al. (1989); 15. Adam et al. (2000); 16. Eglinton et al. (1994); 17. Grimalt et al. (1993); 19. Naaß and Pancost (2014); 20. Putschew et al. (1996); 21. Grossi et al. (2004); 22. Schouten et al. (1995a); 23. Sinninghe Damsté et al. (2007); 24. Volkman et al. (1994); 25. Xavier et al. (1997); 26. Kohnen et al. (1990); 27. Russell et al. (2000); 28. Sinninghe Damsté and Rijpstra (1993); 29. Bechtel et al. (2013); 30. Belt et al. (2017); 31. Adam et al. (1991); 32. Schouten et al. (1998a); 33. Sinninghe Damsté et al. (1999); 34. Kok et al. (2000a); 35. Bayona et al. (2002); 36. Dellwig et al. (1998); 37. Köster et al. (1997); 38. Schaeffer et al. (2006); 39. Sinninghe Damsté et al. (1995); 40. Koopmans et al. (1996b); 41. Sinninghe Damsté and Koopmans (1997); 42. Hebing et al. (2006); 43. French et al. (2015); 44. Kohnen et al. (1991b); 45. Kenig et al. (1995); 46. Kolonic et al. (2002); 47. Broeks et al. (2005); 48. Squier et al. (2003); 49. Squier et al. (2004); 50. Pickering and Keely (2013); 51. Junium et al. (2011); 52. Poinot et al. (1998); 53. Holba et al. (2003); 54. Adam et al. (2009); 55. Cabrera et al. (2002)

octadeca-9,12-dienoic acid and/or octadec-9-enoic acid, which are major lipid constituents of algae. Therefore sulphurization can preferentially preserve the unsaturated fatty acids and may cause a major bias of the original compositions of fatty acids (Russell et al. 2000).

The different abundance of specific *n*-alkanes in the free and S-bound fractions may lead to inaccurate assessments of the source of organic matter and thermal maturity, if only free HC are measured. Such bias can be overcome by measuring both free and S-bound *n*-alkane distributions in sediments deposited in a S-rich environment.

4.2 Long-Chain C₃₇–C₃₉ Alkenes and Alkenones

Long-chain C₃₇–C₃₉ alkenones are biosynthetic products of the alga *Emiliania huxleyi* and other members of the Prymnesiophyceae (Brassell 1993). The C₃₇ alkenones, mainly the di- and triunsaturated compounds, are used as valuable proxies for sea surface temperatures (SST) and paleobarometer for atmospheric *p*CO₂ (Brassell et al. 1986a; Brassell 1993; Wakeham 2002). The presence of C₃₇–C₃₉ alkenones in sediments is also used as a marker for input of calcareous nanophytoplankton material (coccolithophore), as was shown, for example, for sediment of the oceanic anoxic event 3 (87.3–84.6 Ma, Wagner et al. 2004). Long-chain C₃₇–C₃₉ alkenes and alkenones (di- and triunsaturated methyl and ethyl ketones) were observed in young sediments (<7,000 years) as those of the Black Sea (Wakeham et al. 1991, 1995) and many ancient sediments ranging in age from Pliocene to lower Aptian (~120.5 Ma) (see Table 3 for references; Brassell and Dumitrescu 2004 and references therein). Under oxic marine conditions, where sulphurization plays a minor role, the application of this SST proxy is age-limited to ~270 ky BP or younger sediments, as *Emiliania huxleyi* only evolved during that period (Thierstein et al. 1977; Volkman et al. 1995; Sawada et al. 1996). However, there is a continuous effort to extend the applicable time range of alkenones based SST proxy to ancient sediments (see a review of Brassell and Dumitrescu 2004 for the occurrence of different alkenones in the geological record).

Under anoxic-sulphidic (euxinic) conditions, both alkenes and alkenones are known to react with reduced S species and evolve into C₃₇–C₃₈ alkylthiolanes or to macromolecular S-bound forms (Schaeffer et al. 1995; Koopmans et al. 1996a, 1997). However, compared with older sedimentary rocks, in which all the C₃₇–C₃₈ alkenes and alkenones were S-bound, in the young sediments of the Black Sea, these compounds were found exclusively in the free HC fraction (Wakeham et al. 1995). These authors suggested that time spans greater than ~7,000 years may be needed for the formation of such OSC.

Koopmans et al. (1996a, 1997) found that alkenones may occur as macromolecular S-bound and O-bound components in varying proportions. Despite variations in their abundance in the macromolecular structure, the relative amounts of di- and triunsaturated ketones, which are used for the SST proxy, were unaffected. This indicates that there is no selectivity for the reactions of different alkenones with

reduced S species. Hence, if free di- and triunsaturated ketones occur in sediments from S-rich environments, they can be used for the SST proxy. When all of the long-chain C_{37} – C_{39} alkenes and alkenones are sulphurized, the determination of SST is impossible, even after desulphurization treatment, because the original unsaturations disappear (Brassell 1993).

4.3 Phytol-Derived and Phytol-Related Isoprenoids

Sulphurized isoprenoids are one of the most abundant sedimentary OSC groups (Sinninghe Damsté and De Leeuw 1990). The most abundant carbon numbers of linear sulphurized isoprenoids are C_{20} (phytane-derived) and C_{19} (pristane-derived), but other examples of C_{15} to C_{40} carbon skeletons are known as well (Krein 1993; Pancost et al. 2001). Pristane (Pr) and phytane (Ph) are ubiquitous isoprenoids in sediments as they are diagenetic products of phytol which is part of chlorophyll *a* (Eglinton et al. 1964). Pristane and phytane carbon skeletons can also derive from pristenes (zooplankton) and archaeol (archaea species), respectively (Kuypers et al. 2001). The pristane to phytane ratio (Pr/Ph) is often used as an indicator of the redox state of the depositional environment with $Pr/Ph < 1$ indicating anoxia (Didyk et al. 1978). In addition, Pr/Ph ratio was suggested to be lithology related when used in conjunction with the ratio of dibenzothiophene to phenanthrene (Hughes et al. 1995).

Under S-rich conditions, the carbon skeletons of these isoprenoids can be found both as free and S-bound compounds with varying distributions among these fractions. Chemical cleavage treatment of the macromolecular fractions in young sediments and immature sedimentary rocks has shown the preferential sulphurization of phytane at carbon atoms 1–4 and 17 with 1 and 3 being the most dominant by far (Fig. 6 please note legend to the figure for details on the numbering of carbon atoms; Kohnen et al. 1993; Adam et al. 2000). Sulphurized phytane was suggested to derive mainly from phytenal or (to lesser extent) phytadiene, early diagenetic products of phytol (Krein and Aizenshtat 1994; Adam et al. 2000; Schouten et al. 2001; Amrani and Aizenshtat 2004c).

Different diagenetic processes occurring within the sediment lead to preferential preservation of phytane over pristane in the S-bound fraction (Fig. 7a; Kohnen et al. 1991a; Wakeham et al. 1995). Pristane is the diagenetic product of phytol formed under oxic conditions by loss of a carbon atom as a result of decarboxylation. Under reducing conditions, phytol is hydrogenated via a series of steps to form phytane (Didyk et al. 1978). Thus the Pr/Ph ratio is used for paleo-reconstruction of the redox conditions during deposition with $Pr/Ph < 1$ indicating anoxia (Didyk et al. 1978). It is logical to assume that under euxinic conditions, phytol will tend to undergo sulphurization rather than oxygenation and will thus be preserved as S-bound phytane. The selective preservation of phytane over pristane leads to a remarkable difference in the Pr/Ph ratio between the free and S-bound fractions in several basins (Fig. 8b). This difference in the Pr/Ph ratios between the free and S-bound fractions can thus give rise to contradicting interpretations as shown in Fig. 8b for the Black Sea and for

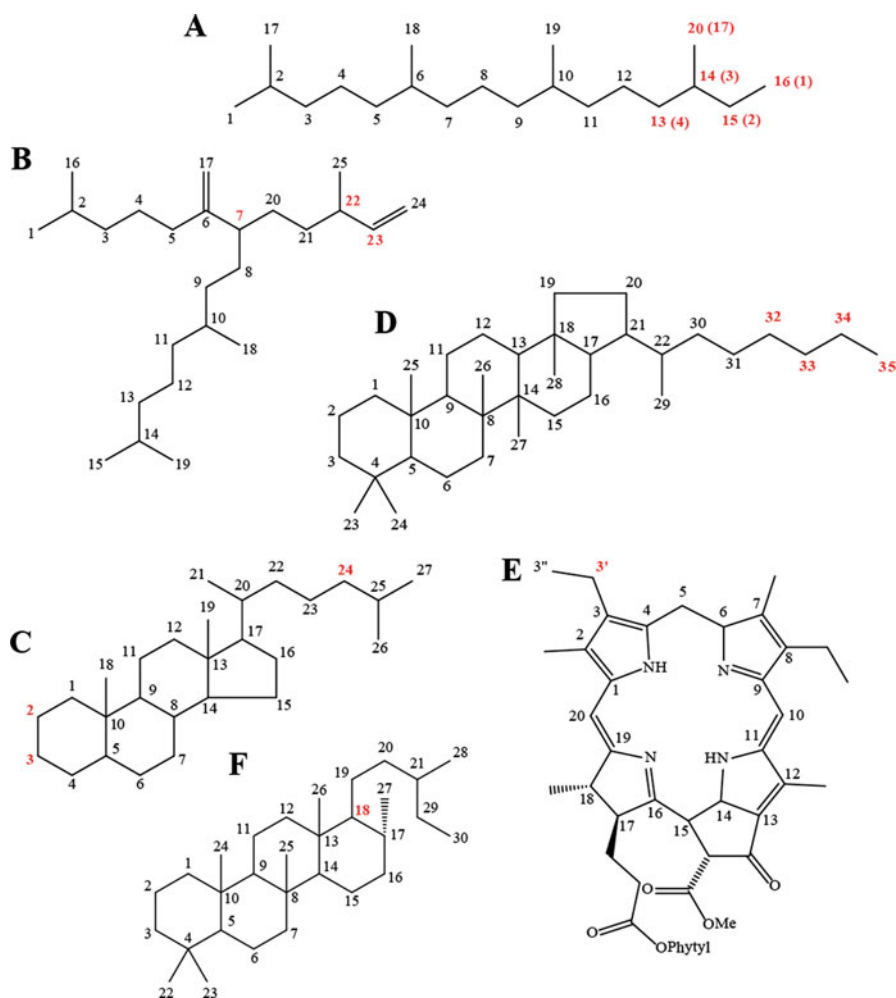


Fig. 6 Examples of carbon skeleton structure of biomarkers representing the main groups discussed in Sect. 4 with the main sulphurization sites are marked in red: (a) Phytane, sulphurization sites are after Kohnen et al. (1993) (site numbering is in respect to IUPAC numbering of phytane. For numbering in respect to phytol, the sulphurization sites are 1–4 and 17 respectively, as presented in parentheses). (b) $C_{25:2}$ HBI. Structure and sulphurization sites are after Hartgers et al. (1997) and Sinnighe Damsté et al. (2007). (c) C_{27} sterane. Structure and sulphurization sites are after Adam et al. (1991), Schouten et al. (1998), and Adam et al. (2000). (d) C_{35} hopane. Structure and sulphurization sites are after Schoell et al. (1994) and Ourisson et al. (1984). (e) Chlorophyll *a* derivative: methyl pyropheophorbide *a*. Structure and sulphurization sites are after Pickering and Keely (2008). (f) C_{30} tetracyclic terpane. Structure and sulphurization sites are after Holba et al. (2003). It is important to note the sulphurization sites are the most common ones that reported in the literature. Other sulphurization positions were identified as well, and they are usually directly related to previous locations of functional groups such as double bonds, carbonyls, and hydroxyls in specific biomarkers. See more details about the sulphurization mechanisms in Sect. 3.2 and references therein. A more specific example for sulphurization pathways is given in Fig. 7 for phytol

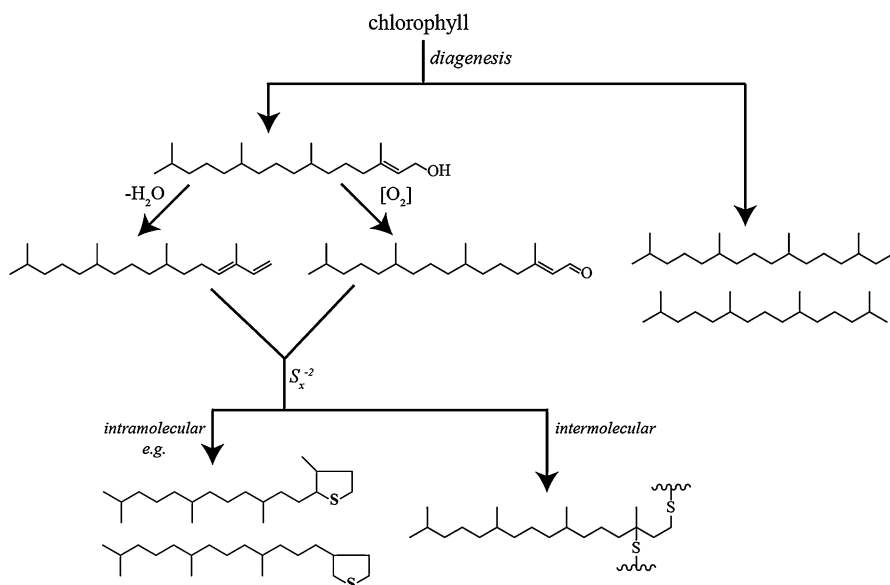


Fig. 7 General scheme for the diagenesis of the phytol side chain in sediments. Formation of OSCs with a phytol carbon skeleton is shown in the left pathway. Formation of pristane and phytane is shown in the right pathway. (Modified after Schouten et al. (2001) and Krein and Aizenshtat (1994))

Messinian sediments from Sicily. Therefore, under anoxic-sulphidic conditions, the analysis of free pristane and phytane only may be misleading, unless both free and S-bound fractions are considered. However, some very S-rich sediments still show close correspondence of Pr/Ph ratios between free and S-bound fractions, such as in Calcaires en plaquettes and the Ghareb Formations (Fig. 8). Under S-poor conditions, such as those in the Green River Formation, the extent of pristane and phytane sulphurization is still significant (Fig. 8), yet there is no apparent preferential preservation of phytane over pristane in the S-bound fraction, and Pr/Ph ratios in the free and S-bound fractions are very similar (Koopmans et al. 1999).

The most abundant group of isoprenoid thiophenes in paleoenvironmental studies has a phytane carbon skeleton (i.e., C₂₀ isoprenoid thiophenes). Compounds of this group were first isolated and identified in immature sedimentary rocks recovered during the Deep Sea Drilling Project (DSDP) in the apolar fraction of organic-rich sediments (Brassell et al. 1986b). This group has seven main isomers (Fig. 9) which were observed in young sediments and immature sedimentary rocks of various depositional settings (see Table 3 for references). The most abundant ones are thiophenes I and II (Fig. 9). These thiophenes are not formed during low-temperature laboratory sulphurization experiments with phytanal or phytadienes (Krein and Aizenshtat 1994; Schouten et al. 1994; Amrani and Aizenshtat 2004c). During low-temperature thermal alteration of S cross-linked macromolecules, thiophenes I and II are formed rapidly and efficiently (Krein and Aizenshtat 1994; Schouten et al. 1994; Amrani and Aizenshtat 2004b). Therefore, it has been suggested that they

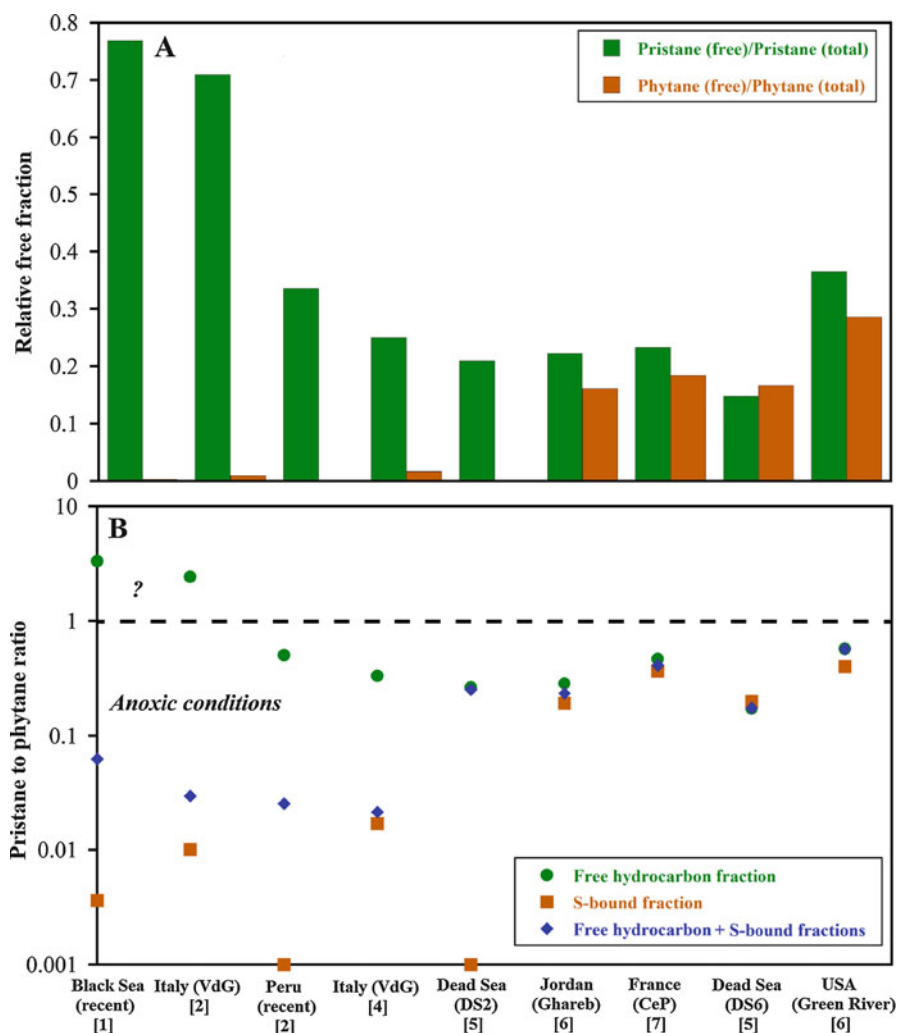


Fig. 8 (a) Relative abundance of free phytane and pristane, (b) Pr/Ph ratio calculated for the free fraction only, the S-bound fraction only, and the sum of the two fractions for different sediments. All sediments, except the Green River shale, are considered to be sulphur-rich. The dashed horizontal line in panel (b) marks the top value for anoxic conditions considered by the Pr/Ph ratio (Peters et al. 2005). Note how this ratio differs between the free and S-bound fractions (panel b) if these biomarkers have different abundance between these fractions (panel a). In some sulphur-rich environments, the relative abundance between the free and S-bound fractions is very similar, leading to very similar Pr/Ph ratios. Numbers in brackets refer to [1] Wakeham et al. (1995) (unit I 0–2.5 cm), [2] Kohnen et al. (1991a) (VgS-4a), [3] Kohnen et al. (1991b) (Peru upwelling), [4] Koopmans et al. (1996a) (VdG), [5] Grice et al. (1998) (DS-2), [6] Koopmans et al. (1999) (Ghareb and Green river Fm.), [7] van Kaam-Peters and Sinninghe Damsté (1997) (Cep fm)

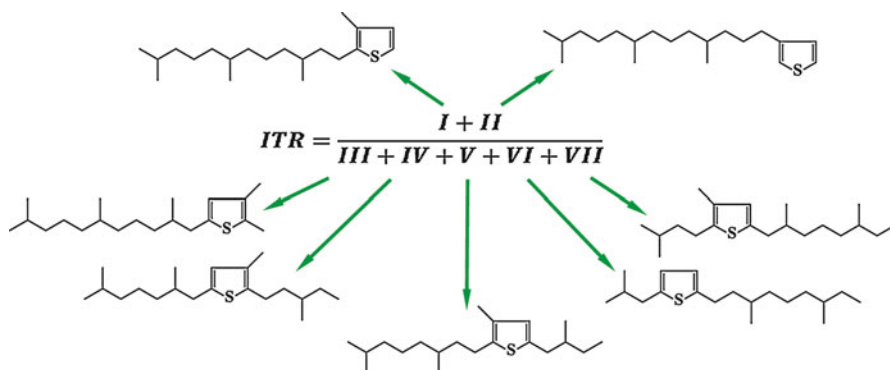


Fig. 9 The isoprenoid thiophene ratio (ITR) after Sinninghe Damsté et al. (1989) and De Leeuw and Sinninghe Damsté (1990). Structures of the various thiophenes implemented in this parameter are shown

arise primarily during early thermal maturation and not as a result of early diagenetic intramolecular sulphurization (Krein and Aizenshtat 1994; Amrani and Aizenshtat 2004b). The origin of specific thiophenic isomers is related to the C-S bonding position in the phytane carbon skeleton, which in turn depends on the functionality of the precursor molecule (Krein and Aizenshtat 1994).

The distribution of isoprenoid thiophene isomers appears to depend on the salinity of the depositional environment (Sinninghe Damsté et al. 1989; Barakat and Rullkötter 1995). Under normal, non-hypersaline conditions, the most abundant photosynthetic microbes have chlorophyll with phytol as a side chain. The sulphurization of phytol diagenetic products (e.g., phytenal), followed by thermal alteration, leads to the formation of compounds I and II (Fig. 9). Under hypersaline conditions, archaeal populations thrive, which produce polyunsaturated phytenols. Sulphurization of these compounds yields isoprenoid mid-chain thiophenes (Sinninghe Damsté et al. 1989; Barakat and Rullkötter 1995; Schwark et al. 1998; Rontani and Volkman 2003). Hence, the distribution of the C_{20} isoprenoid thiophenes was proposed as a proxy for paleo-salinity (referred as the “Isoprenoid Thiophene Ratio,” ITR; Fig. 9), with $ITR < 0.5$ considered to be indicative of a hypersaline paleoenvironment (Sinninghe Damsté et al. 1989; De Leeuw and Sinninghe Damsté 1990; Barakat and Rullkötter 1995).

Several studies have noted that the ITR proxy is not always applicable. Schwark et al. (1998) studied the Solnhofen carbonates (Upper Jurassic, Germany), deposited under stratified water column conditions. They observed low ITR values (< 0.08) which were inconsistent with other markers of salinity such as the Pr/Ph ratio or the methylchromane signature (MTTC ratio). The authors suggested that the ITR might preferentially represent the salinity in deep sections of the stratified water column or it might be impacted by sedimentary diagenetic alteration.

Hartgers et al. (1997) worked on solar salt ponds of La Trinitat and observed ITR >10 despite the high salinity of the ponds ($70\text{--}100\text{ g}\cdot\text{L}^{-1}$). These authors explained the high ITR value to be a result of low abundance of compound III (Fig. 9) in their study. This isomer is abundant in immature sedimentary rocks deposited in hypersaline paleoenvironments, but probably forms only at later stages of diagenesis and therefore is not detected in young, active evaporate settings. A similar issue is observed in young hypersaline environments from Pétrola Saladar in Spain with ITR >0.5 , in which only compounds I, II, and III (Fig. 9) were observed (Schreiber et al. (2001)). The ITR value reached a hypersaline value (<0.5) only after pyrolysis of the samples ($350\text{ }^{\circ}\text{C}$), consistent with the observation that this ratio is not always applicable to immature organic-rich sedimentary rocks.

In immature sedimentary rocks, the C_{20} isoprenoidal thiolanes probably represent earlier diagenetic products relative to their thiophene analogues. Thus, consideration of both thiolane and thiophene C_{20} isoprenoids may give a better representation of their precursors. An improved index that contains the thiolane- C_{20} isomers (ITTR) was suggested by Barakat and Rullkötter (1995). The modified ratio provides the same classification of hypersalinity as ITR, but in one case, ITTR values suggested higher salinity in agreement with the chromane distribution (Rontani and Volkman 2003).

4.4 Highly Branched Isoprenoids (HBIs) and Their Sulphur-Containing Derivatives

Highly branched isoprenoids (HBIs) are a common group of biomarkers derived from four genera of the marine primary producers diatoms (Volkman et al. 1994; Belt et al. 2000, 2017; Grossi et al. 2004; Sinninghe Damsté et al. 2007). Therefore, HBIs are useful biomarkers indicative of high nutrient levels (upwelling systems) due to the high Si consumption of diatoms (Wagner et al. 2004). Their occurrence in marine sediments is limited to the geological period from the Upper Turonian ($\sim 90\text{ Ma}$) to the present (Wakeham et al. 1995; Köster et al. 1998; Sinninghe Damsté et al. 2004).

HBI alkenes are prone to abiotic sulphurization (Fig. 6b) and the formation of free sulphurized HBI such as HBI thiophenes as well as thiolanes and macromolecular S-bound HBI (Kenig et al. 1995; Xavier et al. 1997; Belt et al. 2000; Sinninghe Damsté et al. 2007). Sulphurization of HBI depends on the number and positions of double bonds within the alkene structure, with a minimum of two double bonds in the precursor required to promote this process (Belt et al. 2000). Higher numbers of double bonds significantly increase the reactivity and therefore the chances for sulphurization. Hartgers et al. (1997) noted that under hypersaline conditions, C_{20} HBI-derived thiophenes were formed by preferential sulphurization of C_{20} HBI dienes and polyenes, leaving behind non-sulphurized C_{20} HBI with only one double bond. This is in agreement with laboratory and theoretical work, which shows that the reactivity of alkenes to sulphurization increases with the number of conjugated double bonds (LaLonde et al. 1987).

Wakeham et al. (1995) observed high concentrations of free C_{25} HBI alkenes just below the water-sediment interface in the Black Sea, which rapidly decreased in the

upper 5 cm of the sediment column. C_{25} HBI derivatives were only found below 25 cm in the desulphurized polar fractions. To bridge the gap between their removal from the free HC fraction at shallow depth and their appearance as S-bound HBI significantly deeper in the sediment, the authors suggested the HBI alkenes might be sequestered in fractions not analyzed such as the asphaltenes and protokerogen or alternatively that they were biodegraded. The important implication of this study is that intermolecular sulphurization of HBI alkenes occurs during very early diagenesis (<7,000 years) in the upper sediment column and leads to preservation of the HBI carbon skeletons in the S-bound OSC fraction. Similar results were reported by Werne et al. (2000) for the Cariaco Basin and Sinninghe Damsté et al. (2007) for the Ellis Fjord in Antarctica. Sinninghe Damsté et al. (2007) estimated that complete sulphurization of C_{25} HBI diene would be achieved within 500 years, following a first-order reaction with a rate constant of $1.3 \cdot 10^{-2} \text{ years}^{-1}$.

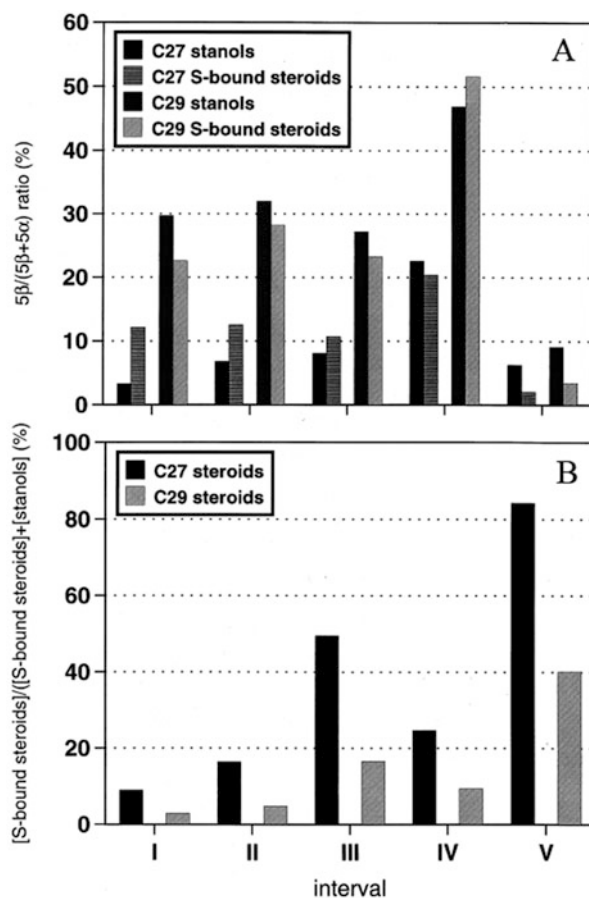
4.5 Steroids

Steroids occur widely in algae and vascular plants and thus are ubiquitous in most depositional environments (Huang and Meinschein 1979). They are commonly used as tools for oil-source rock and oil-oil correlation, as well as proxies for the origin of OM inputs. The sterane carbon number distribution, i.e., the relative amounts of C_{27} , C_{28} , and C_{29} steranes, is the most commonly applied sterane proxy, as it reflects the origin of OM from primary production to the sediment (Huang and Meinschein 1979). During diagenesis, steroids undergo various structural modifications including removal of the hydroxyl group (Mackenzie et al. 1982), the formation of steradienes, and oxidation of sterols to stenones and stanones. Both of these diagenetic products are prone to sulphurization.

The sulphurization of steroids is a relatively rapid process which has been shown to occur within the very early stages of diagenesis (Kok et al. 2000). The C-S bond position in macromolecularly bound steroids is mainly at C_2 and C_3 in the A-ring (Fig. 10; Adam et al. 1991; Kohnen et al. 1991b, 1993; Kok et al. 2000a). In some low molecular weight S-containing steroids, the C-S bond is located at the 3-alkyl side chain of the 3-alkylsteroids (Schouten et al. 1998b) or at the D-ring and at the side chain of regular steroids (Schmid 1986; Behrens et al. 1997; Peng et al. 1998).

Kok et al. (2000a) have estimated steroid sulphurization to be completed in 1,000–3,000 years in the upper sediments of Ace Lake in Antarctica, based on assumed rates of sedimentation and age of the sediment core studied. The authors noted that C_{27} stanols are preferentially sulphurized compared with C_{29} stanols which remain abundant in their free form (Fig. 10). The possibility of a sulphurization bias toward C_{27} relative to C_{29} sterols has also been mentioned by Wang et al. (2004), in a study based on young sediment cores from a salt lake. However, the authors noted that the evidence for such a bias is not conclusive. Desulphurized fractions of samples from the Messinian (Sicily) exhibit a dominance of the C_{27} sterane homologues, while in the free fraction, no steranes were detected (Schaeffer et al. 1995). This observation indicates preferential sulphurization and preservation of C_{27} steranes, as had been suggested by the other studies. The

Fig. 10 The preferential sulphurization of C_{27} stanols over C_{29} stanols. (Panel a) $5\beta/ (5\alpha+5\beta)$ ratio (in %) for C_{27} and C_{29} stanols and S-bound steroids. (Panel b) $[S\text{-bound steroid}]/([S\text{-bound steroid}] + [\text{stanol}])$ ratio (in %) for C_{27} and C_{29} steroids for five different core sections representing $\sim 1,250$ year in Ace Lake sediments (Kok et al. 2000)



mechanism behind this preferential sulphurization (and thus preservation) of C_{27} steranes is still unknown, but it may provide a bias in using the sterane carbon number distributions to assess OM source input. This can be overcome by examining both free and S-bound sterol derivatives.

A more taxon-specific biomarker steroid group are the 4-methylsteroids (dinosteranes), which are derived from certain primary producers such as dinoflagellates (Summons et al. 1987) and prymnesiophyte algae (Volkman et al. 1990). Schaeffer et al. (1995) noted that these compounds were found exclusively in the S-bound fraction of Messinian sediments from Sicily.

4.6 Hopanoids

Hopanoids are ubiquitous compounds in organic-rich sediments, where they are among the most diagnostic biomarkers for bacterial input (Ourisson et al. 1984). Homohopanes in sedimentary environments are thought to result from the

degradation, under relatively oxic conditions, of the labile side chain of C_{35} -hopanepolyols leading to smaller homologues (Peters and Moldowan 1991). Thus C_{35} homohopane is expected to be best preserved under anoxic conditions giving rise to elevated values of the ratio $C_{35}/\Sigma(C_{31}-C_{35})$ (the “ C_{35} homohopane index”) used as an indicator of anoxic depositional settings (Peters and Moldowan 1991).

Hopanoids can undergo sulphurization at carbon atom 4 in the side chain (Fig. 6d) forming S-containing products which are abundant in sedimentary rocks. In fact, a C_{35} hopane containing a thiophene ring was the first reported OSC with a carbon skeleton clearly linked to that of a biological precursor (Valisolalao et al. 1984). Since then, many other S-containing hopanoids (thiolanes, thiophenes, and S-bound) have been reported and grouped into different series (Table 3; Sinninghe Damsté et al. 1995, 2014; Schaeffer et al. 2006).

Richnow et al. (1992) investigated the macromolecular structure of a S-rich oil (resins and asphaltenes) and its presumed source kerogen (Monterey Formation, California) by sequential chemical degradation. They showed that the macromolecularly bound hopanoids were cross-linked by both S and O bonds, with a significantly different distribution of hopanoid species relative to free hydrocarbons in the extractable fraction. Farimond et al. (2003) studied the incorporation of hopanoids into the macromolecular (bound OSC) fraction in young sediments of a freshwater lake (Priest Pot) and an anoxic-sulphidic fjord (Framvaren). They concluded that this process is very rapid (<350 years) and extensive (22–86% of the total hopanoids were incorporated). They further showed that cross-linking bonds of hopanoids by S were 15%, while S and O bonding (at the same molecule) was ~40%, and the rest were bound exclusively with O (ether bonds, ~47%). Despite this, a positive correlation was found between the bound hopanoid fraction and the total S in the sediment (Farimond et al. 2003). Sinninghe Damsté et al. (1995) studied the C_{35} hopanepolyol derivatives in the Upper Cretaceous organic-rich limestone of Jurf ed Darawish in Jordan. The S-bound form made up 50–80% of the total hopanoids preserved in the sediment with preferential sulphurization of the C_{35} $17\alpha,21\beta(H)$ -homohopanes. Similar observation of C_{35} homohopane preferential sulphurization (Fig. 11) of both free and bound OSC forms was later described in marls and limestones of different depositional environments and ages (Köster et al. 1997; Grice et al. 1998; Schaeffer et al. 2006). Schaeffer et al. (2006) found that some thermally stable hopane derivatives (e.g., $17\alpha,21\beta$ -hopanes) can also be directly biosynthesized. This finding implies that the ratios of $\alpha\beta$ -/ $\beta\beta$ -hopanes used to evaluate the maturity of sedimentary organic matter can be biased in some settings.

The C_{35} homohopanes possess the most intact carbon skeleton derived from bacteriohopanepolyols. The predominance of sulphurized C_{35} hopanoids can therefore be explained by the reaction of reduced S species with the homohopane side chain during the earliest stages of diagenesis (Köster et al. 1997). Other sulphurized hopanoids are far less common at that diagenetic stage and therefore less represented in the S-bound fraction.

Köster et al. (1997) noted that the distribution of various sulphurized hopane derivatives may indicate the extent of diagenesis. In a study of samples from the Hauptdolomit, Calcaires en Plaquettes, and Ghareb Formations, which are traditionally defined as immature sedimentary rocks, they were able to distinguish subclasses

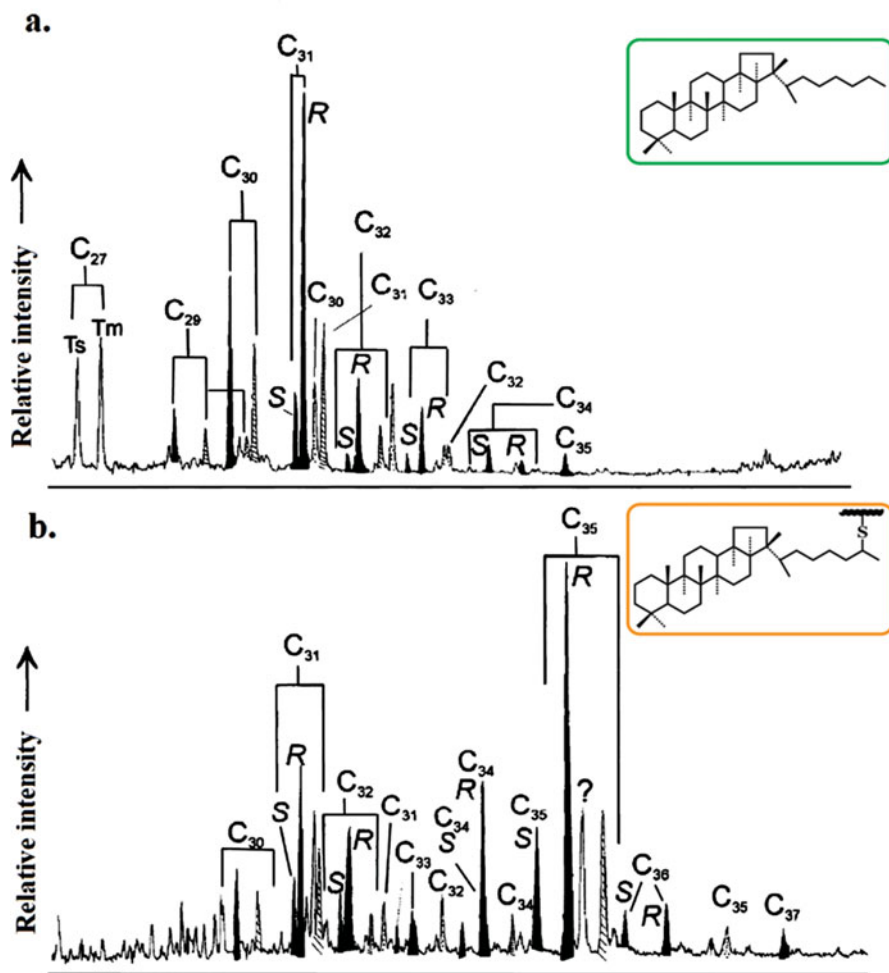


Fig. 11 The bias of C₃₅ hopane sulphurization: (a) Chromatogram of the free hopanes showing C₃₁ predominance. (b) Chromatogram of the S-bound sulphurized hopanes showing distinctive C₃₅ predominance; both are from a sample of the Permian Kupferschiefer Formation, considered to be a type II kerogen. (Modified from Grice et al. (1996))

of maturity based on the distribution of sulphurized hopane derivatives. The thermally most mature sample had the highest content of C₃₅ hopanoid thiophenes, while the least mature samples comprised mostly hopanoid sulphides (Köster et al. 1997). This finding is in accordance with the release of macromolecular S-bound C₃₅ hopanoids and its cyclization to thiophenes upon the early stages of thermal maturation (Fig. 4).

The carbon isotopic ratio of S-bound C₃₅ hopanes has been demonstrated to be useful in paleoclimate reconstructions (Schoell et al. 1994). Changes in $\delta^{13}\text{C}$ (−29.5

to -32.5‰) throughout the Middle to Late Miocene section of the Monterey Formation have been observed. It has been proposed that the distinct $\delta^{13}\text{C}$ signature of the S-bound C_{35} hopanes (compared with C_{27} sterane and bulk kerogen values) reflects changes at the base of the photic zone. This conclusion assumes that this hopane represents the photosynthetic cyanobacteria which live deeper in the photic zone compared with eukaryotic photosynthetic organisms that synthesize steroids. More specifically it has been pointed out that changing water temperature led to a change of dissolved CO_2 concentration that in turn led to a change in the $\delta^{13}\text{C}$ of the hopanes. This hypothesis was supported by the available $\delta^{18}\text{O}$ record for the Pacific Ocean in the relevant timeframe. Sulphurization and thus preservation of the C_{35} hopanes and their presumed original $\delta^{13}\text{C}$ values played a key role in the paleoenvironmental interpretation.

4.7 Carotenoids

Carotenoids are tetraterpenoid pigments (C_{40}) which are widespread in living organisms such as algae, bacteria, and higher plants. The most common members of this group are β -carotene, which is biosynthesized by marine and terrestrial plants, and fucoxanthin which often occurs in planktonic organisms such as diatoms and dinoflagellates (Hebting et al. 2006). The multiple sites of unsaturation in the carotenoids are prone to oxidation, hydrogenation, and other diagenetic reactions. Therefore a low concentration of oxygen and available inorganic S species in the water column and/or sediment are crucial for carotenoid preservation in the geological record (Sinninghe Damsté and Koopmans 1997).

Carotenoids can readily react with reduced S species (e.g., H_2S and polysulphides) at various sites of double bonds in their carbon skeletons (Hebting et al. 2006; French et al. 2015). They usually form bound OSC structures, which increases their stability and resistance to degradation in the sediment. Hebting et al. (2006) studied samples from Lake Cadagno (Switzerland) and suggested that reduced S species can reduce (hydrogenate) the double bonds of the carotenoids, leading to increased preservation in an anoxic water column (Fig. 12). However, their quantitative data indicates that this pathway is minor and sulphurization outcompetes the hydrogenation pathway. Under such conditions, most, if not all preserved carotenoids, are S-bound in the macromolecular fraction (Kohnen et al. 1992). Via cleavage of S-bonds, and release of monomeric compounds, double bonds can be reduced as has been shown in several pyrolysis experiments (Krein and Aizenshtat 1995). This thermal alteration pathway could be another route for the reduction of double bonds during the later stages of diagenesis. Note that both preservation pathways (i.e., sulphurization or double bond reduction) are mediated by reduced S species (Hebting et al. 2006).

Because of their large carbon skeleton structure and multiple C-S binding sites, carotenoids are often not GC-amenable, even after selective S-S cleavage (e.g., MeLi/MeI). This has probably limited studies on their abundance and sulphurization pathways in many young sediments. One of the rare examples of carotenoid GC

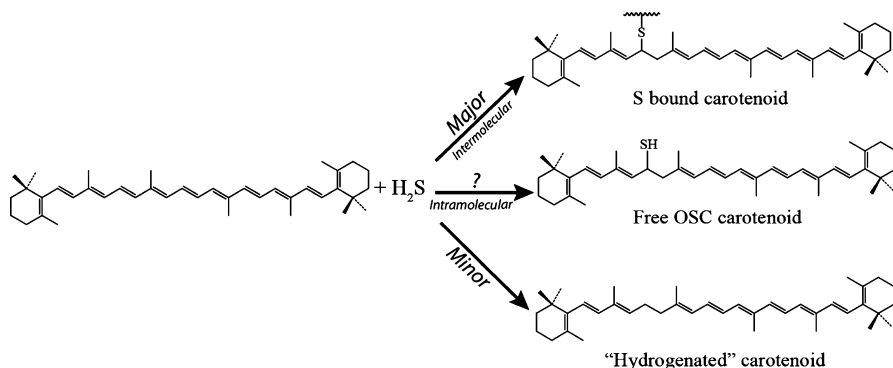


Fig. 12 Reduction (“hydrogenation”) and sulphurization products obtained by reaction of H_2S with β -carotene in aqueous medium (Modified after Hebting et al. (2006)). Other double bond positions can also be sulphurized or hydrogenated as well as multiple sulphurization/hydrogenation positions

analysis is documented by Grice et al. (1998), who identify linear thiophenes and thianes with large carbon skeletons (C_{40}) in the sediments of the Sdom Formation (Miocene, Dead Sea, Israel). The carbon skeletons and $\delta^{13}\text{C}$ values of these OSCs are similar to those of the co-occurring lycopane, which led the authors to conclude that the C_{40} OSC originated from this carotenoid.

Two important carotenoid biomarkers are isorenieratene and chlorobactene. These two carotenoids are exclusively biosynthesized by the brown and green strains of green sulphur bacteria (GSB, *Chlorobiaceae*), respectively (Ohkouchi et al. 2015). These photoautotrophic bacteria use reduced S as an electron donor in photosynthesis and require relatively low light intensities. Thus, the presence of these compounds indicates photic zone euxinia (PZE, Schaeffer et al. 1995; Grice et al. 1996; Koopmans et al. 1996b; Kolonic et al. 2002; French et al. 2015).

The use of sulphurized isorenieratene and chlorobactane derivatives to assess PZE has been exemplified by Wagner et al. (2004), who studied the S-bound profile through the oceanic anoxic event 3 (OAE-3, Coniacian-Santonian, ODP site 959). They observed short-term fluctuations in the S-bound isorenieratene and chlorobactane concentrations during OAE-3, which they attributed to penetration of the chemocline into the photic zone (Fig. 13). The increase of chlorobactane concentration was suggested as an indicator for chemocline rise to very shallow (~15 m) depths during OAE-3. The presence of S-bound chlorobactane and isorenieratene was limited to a specific nannofossil zone, indicating that PZE was confined to a restricted time interval of the OAE-3.

However, a potential concern regarding the use of isorenieratene as a PZE proxy was raised by Koopmans et al. (1996b) who demonstrated that aryl isoprenoids and β -isorenieratene can be formed by diagenetic aromatization of β -carotene. In addition, during diagenesis, sequential cyclization and sulphurization of isorenieratene may lead to formation of aromatic OSC such as benzothiophenes (Koopmans et al. 1996b). The distinct $\delta^{13}\text{C}$ values of β -isorenieratene can help verify the origin of

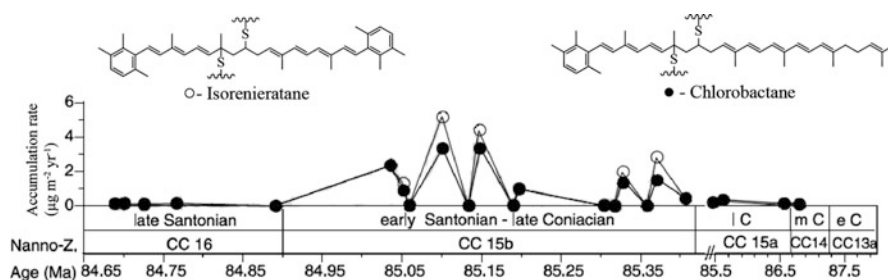


Fig. 13 Time series of accumulation rate of biomarkers indicative of PZE, isorenieratane, and chlorobactane, during the OAE-3 of Late Cretaceous (87.3–84.6 Ma) in the Deep Ivorian Basin (eastern equatorial Atlantic, ODP site 959). Both biomarkers are derived from photosynthetic green sulphur bacteria. Fluctuation in their abundance suggests variation of the chemocline position relative to the photic zone and repetitive penetration of sulphidic conditions into the lower photic zone (Modified from Wagner et al. (2004)). Location of the sulphurization sites is from Koopmans et al. (1996b), but sulphurization in other positions, as well as multiple sulphurization positions, can occur too

these compounds and allow their use as PZE indicators in cases where no genuine β -isorenieratane survived.

4.8 Porphyrins

Porphyrins are compounds of the chlorin group. Among the most common types of porphyrins are the ubiquitous chlorophylls, which occur in all green plants and photosynthetic bacteria. Their presence is a marker of the photoautotrophic primary producer community. During diagenesis, chlorophyll *a* is converted to other stable forms of porphyrins, for example, bicycloalkanoporphyrins (BiCAPs) which are often found in calcareous, OM-rich sediments that are deposited under reducing conditions (Junium et al. 2011).

Sulphur-containing porphyrins have been identified in young sediments of a coastal lake in Antarctica (Squier et al. 2003, 2004), in immature sedimentary rocks of the Messinian of Sicily (Schaeffer et al. 1995), and in laboratory experiments involving the reaction of porphyrins with reduced inorganic S species (Pickering and Keely 2008, 2011, 2013).

Porphyrins may undergo sulphurization by several mechanisms which may lead to their preservation in sediments (Squier et al. 2003; Pickering and Keely 2013). An example for such process is the enhanced preservation of BiCAP. This occurs under euxinic conditions by reduction at carbon atom 3 through reaction with S species as was demonstrated under laboratory and natural conditions (Fig. 6e; Mawson and Keely 2008; Junium et al. 2011).

In sediment extracts from the Messinian of Sicily, the amount of S-bound porphyrins was seven times larger than the amount of their free analogues (Schaeffer et al. 1995). The authors determined that the S-bound porphyrins were dominated by

BiCAPs from a diatom source. The free porphyrins were of a different type and therefore may indicate different environmental conditions in the basin during deposition and diagenesis or perhaps different sources of porphyrins.

The presence of S derivatives of bacteriochlorophyll *c* and *d* is of paleoenvironmental significance since they are a clear marker for anaerobic GSB (*Chlorobiaceae*) activity in the depositional environment and therefore indicate PZE. The detection of these S derivatives suggests that the process of sulphurization can be significant for the preservation of porphyrins (Squier et al. 2004).

4.9 Polyprenoid Sulphides

Polyprenoid sulphides are a group of OSC that possess di-, tri-, tetra-, or pentacyclic carbon skeletons (Fig. 6f shows a tetracyclic structure). Members of this group occur in sediments from a wide range of depositional environments with anoxic conditions including upwelling environments, shallow continental platforms, hypersaline environments, and lagoon sub-basins (Schaeffer et al. 2006; Adam et al. 2009). Polyprenoid sulphides are present in some sediments where no other sulphurized biomarkers (e.g., with linear, sterane, or hopane carbon skeletons) were detected (Poinsot et al. 1998). This observation suggests a unique precursor with high reactivity or a specific path of S incorporation. Moreover, the detection of polyprenoid sulphides in young sediments (<1,000 years) suggests their formation takes place during the earliest stages of diagenesis or even within the water column (Poinsot et al. 1997, 1998).

Polyprenoid sulphides may share a common and specific biological origin with that of the predominant pentacyclic C₃₀ sulphides (Poinsot et al. 1998) and are probably related to the C₃₀ tetracyclic polyprenoids (TPP, Holba et al. 2000). However, the biological lipid precursor of the TPPs is unknown, and based on carbon isotopic studies, it has been suggested that they originate from oxygenic photosynthetic organisms (algae, cyanobacteria) or heterotrophic organisms thriving on algal/cyanobacterial biomass in the oxic part of the water column (Poinsot et al. 1998). This hypothesis of nonmarine algal precursor for TPP was later supported by Holba et al. (2003) who studied a large set of oils which covers lacustrine, terrigenous, and marine source origins. The authors found the presence of high TPP occurrence in oils from fresh to brackish water, algal-rich, lacustrine depositional environments while oils from marine origin were TPP poor. Furthermore, by examining the sterane and hopane distributions in conjunction with TPP, the authors concluded the source of TPP is likely from nonmarine algae, possibly Chlorophyta.

4.10 Carbohydrates

Although carbohydrates are not considered as biomarkers, their preservation in a given environment may give rise to important paleoenvironmental information. Carbohydrates such as polysaccharides and gels comprise a large part of living

biomass. Because these compounds are very labile, they are normally biologically consumed and less preserved in the sedimentary OM record (Arndt et al. 2013). Sulphurization, however, can preserve carbohydrates as part of the macromolecular S-bound fraction as was shown by Kok et al. (2000b). One of the unique signatures of carbohydrates in sedimentary organic matter is their enrichment in ^{13}C (up to 16‰) relative to lipids of a given organism (van Dongen et al. 2006). Van Kaam-Peters et al. (1998) hypothesized that short-chain alkylthiophenes ($\text{C}_1\text{--C}_3$, Kimmeridge Clay Formation (KCF)) were the diagenetic products of S incorporation into monosaccharides based on their higher $\delta^{13}\text{C}$ values relative to *n*-alkanes from the same algal source. Similar conclusions were drawn for the origin of small amounts of $\text{C}_1\text{--C}_3$ alkylthiophenes isolated from pyrolysates of laboratory sulphurization experiments on the algae *Nannochloropsis salina* (Gelin et al. 1998). The reaction of reduced S species with polysaccharides of mucilage origin in the Northern Adriatic Sea was reported by Ciglenečki et al. (2000). The authors also conducted laboratory sulphurization experiments on polysaccharides of bacterial and algal origin, all of which led to the formation of sulphurized polysaccharides. Other sulphurization experiments of algal material and glucose carried out by Kok et al. (2000b) gave rise to S-rich macromolecular material that yielded short-chain alkylthiophenes and other OSCs upon pyrolysis.

The contribution of carbohydrates preserved through sulphurization to the total organic carbon (TOC) of organic-rich sedimentary rocks may, under certain conditions, be significant. van Dongen et al. (2006) worked on the Blackstone Band of the Kimmeridge Clay Formation, where total organic carbon is enriched in ^{13}C relatively to other strata within the Formation. The authors suggested that this might be the result of preservation of sulphurized carbohydrates, which they estimate to account for up to ~90% of the OM in the section of the Blackstone Band richest in total organic carbon. Thus, S incorporation into carbohydrates may preserve a substantial amount of them under euxinic conditions as S-rich macromolecular matter with a ^{13}C -enriched isotopic signature.

5 Summary

This contribution highlights the significant advances achieved by numerous studies on several fundamental aspects of OSC and their role as paleoenvironmental indicators. Among these aspects are the following:

1. Sulphurization is a rapid process (<10,000 years), occurring during the earliest stages of diagenesis. In some cases, sulphurization in the water column can occur within days, even before deposition takes place in the sediment. It is a continuous process, with reactions ongoing deeper in the sediment following diagenetic modifications of the original precursor compounds. Accordingly, sulphurization of less reactive compounds can take place during these later stages after most reactive compounds have already been sulphurized. Sulphurization occurs at specific positions within the carbon skeleton, typically at locations of original

functional groups (i.e., hopanoids are sulphurized via the original hopane polyol side chain), resulting in distinct structural and S isotopic compositions which are different from any original biosynthetic OSC species. The major pathway for sulphurization is via intermolecular linkage, leading to the formation of S cross-linked macromolecules.

2. Recent studies suggest that in some settings, sulphurization of organic matter may compete with iron sulphide (e.g., pyrite) formation. This contrasts with the original presumed sulphur diagenesis scheme, whereby OM sulphurization does not commence until available iron is effectively exhausted. Moreover, compound-specific sulphur isotopic studies suggest that some OSC may form rapidly, resulting in their S isotope signature being lighter than that of the coexisting pyrite. This large S isotope variance between individual OSC, and between bulk fractions (e.g., kerogen), may suggest different sulphurization rates and mechanisms. The sulphur isotopic record of OSC between modern sediments and immature rocks may be changed over the course of diagenesis due to isotopic exchange processes with the reduced inorganic S pool.
3. The contribution of biosynthetic S to the sedimentary organic S pool might be larger than previously thought. Possible reservoirs may include refractory dissolved and particulate organic S, as well as volatile organic S compounds that were adsorbed to inorganic particles. Their interactions with other organic compounds and/or with other sources of reduced sulphur species (i.e., dissimilatory S) can further contribute to their preservation in the sedimentary record.
4. Sulphurization leads to notable preservation of compounds otherwise susceptible to biodegradation and mineralization. Examples include the preservation of carbohydrates, carotenoids, and porphyrins in S-rich sediments as part of the S-bound fraction. The distribution of biomarkers (e.g., Pr/Ph) between the free and S-bound fractions may bias paleoenvironmental interpretations if only the free HC fraction is analyzed. Biomarker analysis for the purpose of paleoenvironmental research should independently examine both the free and S-bound biomarker fractions, as the similarities and contrasts between these pools provide another dimension to the preserved environmental signal. Carbon isotope data may also be biased in a similar manner. A consistent difference is found between the $\delta^{13}\text{C}$ signatures of S-bound and free HC, where the former is heavier by $2 \pm 1\text{‰}$ on average. This may suggest different sources for the original precursors of the biomarkers in the free HC and S-bound fraction and/or a preservation effect of the original $\delta^{13}\text{C}$ values of the biomarkers in the S-bound fraction.

5.1 Future Directions

The analytical developments of the 1980s, primarily GC-MS, fueled the tremendous progress of sedimentary OSC research at that time. Likewise, recent analytical developments in the last decade provide new opportunities to further develop our understanding of the sulphur cycle and its significance with regard to geochemical process in recent and ancient sulphur-rich marine environments. For example, Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS) is

increasingly being used for the analysis of OSC fractions (e.g., O and N functionalized compounds, aqueous dissolved species and molecules with weights in excess of 1000 Daltons), which were not previously amenable to characterization. It is likely that these new data types will reveal mechanisms previously unrecognized, further developing our models of the sedimentary sulphur cycle. Already, sulphur isotope analysis of organic matter in terms of individual compounds (e.g., nonpolar, volatile), specific fractions (e.g., polar, kerogen), and with consideration of all four stable isotopes is changing the way we understand the timing of OM sulphurization and the mechanisms and relationship with other sulphurized species (e.g., pyrite). Not only will these new data enable improved S proxies and potentially provide new proxies for paleoenvironmental research, but inevitably will lead to our better understanding of the sulphur and carbon cycles.

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