Organosulfur Compounds: Molecular and Isotopic Evolution from Biota to Oil and Gas

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Annu. Rev. Earth Planet. Sci. 2014. 42:733–68

The *Annual Review of Earth and Planetary Sciences* is online at earth.annualreviews.org

This article's doi:
10.1146/annurev-earth-050212-124126

Keywords

sulfur cycle, compound-specific sulfur isotope analysis, sedimentary organic matter, organic-inorganic interactions, thermochemical sulfate reduction

Abstract

Organosulfur compounds (OSCs) play important roles in the formation, preservation, and thermal degradation of sedimentary organic matter and the associated petroleum generation. Improved analytical techniques for S isotope analysis have recently enhanced our understanding of the mechanisms for OSC formation and maturation and their associated S isotope distributions. The close interaction of OSCs with inorganic S species throughout their formation and maturation affects their $^{34}S/^{32}S$ isotopic ratio ($\delta^{34}S$), forming specific signatures for distinct sources and processes. Ultimately, thermal maturation homogenizes the $\delta^{34}S$ values of different fractions and individual compounds. Reservoir processes such as thermochemical sulfate reduction (TSR) introduce exogenous and isotopically distinct S into hydrocarbons and can significantly change the $\delta^{34}S$ of petroleum or kerogen. Specific OSCs react at different rates and thus can be used to evaluate the extent of processes such as TSR. This article reviews factors that affect the $^{34}S/^{32}S$ isotopic distribution of OSCs along pathways of formation, diagenesis, and thermal alteration.

1. INTRODUCTION

Organic sulfur is the second most abundant reduced S fraction, after pyrite, in sedimentary rocks (Anderson & Pratt 1995). In some specific locations, such as the Monterey (Miocene, United States) and Ghareb (Maastrichtian, Israel and Jordan) Formations, organic S represents the major S fraction (Werne et al. 2004). Organosulfur compounds (OSCs) have a fundamental impact on the formation, preservation, and thermal degradation of sedimentary organic matter, including petroleum reservoir processes (Amrani et al. 2008b, Baskin & Peters 1992, de Leeuw & Sinninghe Damsté 1990, Koopmans et al. 1996a, Lewan 1998, Orr 1986, Tannenbaum & Aizenshtat 1985).

Organic S is increasingly used as a tracer of geochemical processes in a wide variety of research applications. These applications include the study of source rock–oil and oil-oil correlations (Amrani et al. 2005a, Cai et al. 2009b, Orr 1986), organic matter maturation (Kelemen et al. 2010, Radke et al. 1986), thermochemical processes in petroleum reservoirs (Amrani et al. 2012a, Hanin et al. 2002, Wei et al. 2012), paleosalinity indicators (Barakat & Rullkötter 1997, Sinninghe Damsté et al. 1989b), biomarker preservation (Adam et al. 1993, Grice et al. 2003, Kohnen et al. 1991a, Koopmans et al. 1996a), early microbe metabolism in ancient oceans (Bontognali et al. 2012), and ocean-atmosphere linkages (Amrani et al. 2012b, 2013; Oduro et al. 2012).

S isotopes are very useful in studying redox conditions and the early metabolism of ancient microbes in past environments (Canfield et al. 2000, Claypool et al. 1980, Fike et al. 2006, Halevy et al. 2012). There is a strong S isotope correlation between organic and inorganic S species, which suggests a continuous interaction between them during formation and diagenetic alteration of OSCs (Anderson & Pratt 1995, Cai et al. 2009a, Engel & Zumberge 2007). In the past two decades, an improved understanding of the fates of OSCs and their associated S isotope distributions has been established (Aizenshtat & Amrani 2004a, Werne et al. 2004). New developments for S isotope analysis promise to further advance this field (Amrani et al. 2009, King et al. 2014, Oduro et al. 2011, Paris et al. 2013). This review focuses on the formation, stabilization, and S isotope imprint of OSCs in marine depositional environments and petroleum reservoirs. Possible controlling factors and potential uses as paleoenvironmental proxies are also discussed.

1.1. Nomenclature of Organosulfur Compounds and Sulfur Isotopes

Organic S normally occurs as a complex mixture of hundreds of individual S-containing organic molecules and macromolecules with many structures and stabilities, formed by multiple mechanisms at different stages in the evolution of sedimentary organic matter. These OSCs interact continuously with inorganic S species. **Table 1** presents the main organic and inorganic S structures and their oxidation states and nomenclature.

1.1.1. Sulfur isotope terminology. Sulfur has four stable isotopes: ^{32}S (95.02%), ^{33}S (0.75%), ^{34}S (4.21%), and ^{36}S (0.02%) (Ding et al. 2001, McNamara & Thode 1950). This review deals mainly with changes in the ratio of the most abundant isotopes, ^{34}S and ^{32}S, as measured against the international standard V-CDT (Vienna Canyon Diablo Troilite):

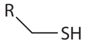
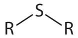
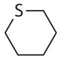
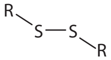
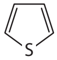
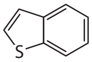
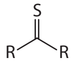
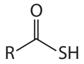
$$\delta^{34}S = (R_{\text{sample}} - R_{\text{standard}})/R_{\text{standard}}, \tag{1}$$

where R is the $^{34}S/^{32}S$ isotope ratio. The $^{34}S/^{32}S$ changes in natural samples are small, and therefore $\delta^{34}S$ is usually expressed in per mill (‰) units, i.e., multiplied by 1,000.

Mass differences between isotopes lead to differences in chemical and physical properties and result in slight differences in reaction rates, bond stability, and boiling points. These different properties underlie the repartition of isotopes during thermodynamic or kinetic transformations. When the ratio between the heavy isotope (^{34}S) and the light isotope (^{32}S) differs between two

Table 1 Sulfur compounds

Erratum

Compound name	Formula/structure	Oxidation state
Inorganic sulfur species		
Sulfate	SO_4^{2-}	+6
Sulfite	SO_3^{2-}	+4
Tetrathionate	$S_4O_6^{2-}$	+2.5
Thiosulfate	$S_2O_3^{2-}$	+2
Elemental sulfur	$S_8(S^0)$	0
Polysulfide anions	S_x^{2-}, HS_x^-	−0.25 to −1
Hydrogen sulfide and bisulfide	H_2S, HS^-	−2
Common minerals		
Anhydrite	$CaSO_4$	+6
Gypsum	$CaSO_4 \bullet 2H_2O$	+6
Iron sulfide	FeS	−2
Pyrite	FeS_2	−1
Oxygenated organic sulfur compounds		
Sulfoxide	R–S(O)–R	0
Sulfone	$R{-}S(O)_2{-}R$	+2
Sulfonate	$R{-}SO_3^-$	+4
Sulfate ester (organosulfate)	$R{-}O{-}SO_3^-$	+6
Sulfate ester (dialkyl sulfate)	$R{-}OS(O_2)O{-}R$	+6
Reduced organic sulfur compounds		
Thiol (mercaptane)		−2
Sulfide (thioether)		−2
Thiane		−2
Thiolane (tetrahydrothiophene)		−2
Disulfide and polysulfide		−2
Aromatic S (thiophene)		−2
Condensed aromatic S (polynuclear thiophene)		−2
Thiaketone		−2
Thioester		−2

Abbreviation: R, alkyl group or aromatic ring substances, such as the initial reactant (A) and the final product (B) in a reaction, the difference is termed isotope fractionation and is expressed approximately as

$$\Delta^{34}S_{A\text{-}B} = \delta^{34}S_A - \delta^{34}S_B, \tag{2}$$

or accurately as

$$\varepsilon = (\delta^{34}S_B - 1{,}000)/(\delta^{34}S_A - 1{,}000) - 1. \tag{3}$$

Both equations are expressed in per mill units.

1.1.2. Sulfur isotope analytical methods. S isotope analysis of organic matter became more common in the past two decades as a result of the development of elemental analysis coupled to isotope ratio mass spectrometry (EA-IRMS) (Giesemann et al. 1994). In this method, solid or liquid organic and inorganic S samples are oxidized to SO_2, and the ratio between $^{34}SO_2$ and $^{32}SO_2$ is subsequently measured. Conversion to SF_6 of S samples followed by IRMS analysis has been used to examine all four stable isotopes of S (Oduro et al. 2011). This method is very precise because it avoids the continuous oxidization/reduction and separation of the combustion products (e.g., H_2O, CO_2) and the need for ^{18}O or ^{17}O corrections in the isotopic ratio of SO_2. However, the advantage in precision comes at the price of much longer runs and a tedious multistep offline conversion and purification of S samples to SF_6 (Oduro et al. 2011). Both types of analysis are restricted to bulk materials, or to compounds or fractions that can be purified offline in milligram quantities (tens of micrograms of S).

Amrani et al. (2009) developed instrumentation and methods capable of measuring $\delta^{34}S$ values in individual compounds at the subnanogram level. The system employs chromatographic separation by gas chromatography (GC) and subsequent $^{34}S/^{32}S$ ratio measurements by multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS). This method requires a sample size approximately 10^4-fold smaller than that required for standard EA-IRMS. It therefore enables precise and accurate $\delta^{34}S$ analysis of trace compounds in petroleum (Amrani et al. 2012a) and can also be implemented on trace gases (Amrani et al. 2012b, 2013; Said-Ahmad & Amrani 2013) and sedimentary organic sulfur (Raven et al. 2013). MC-ICP-MS is also useful for the ^{34}S and ^{33}S analysis of S minerals in both aqueous solution and solid matrices (when coupled to laser ablation) with greater precision and accuracy than EA-IRMS and with much higher sensitivity (Craddock et al. 2008, Paris et al. 2013). A promising technique using secondary ion mass spectrometry (SIMS) is emerging; this technique enables spatial S isotope analysis in solid organic and inorganic samples such as Archean kerogen, pyrobitumen, and pyrite (Bontognali et al. 2012, King et al. 2014).

1.2. The Biologically Induced Sedimentary Sulfur Cycle

Figure 1 presents the sedimentary S cycle in organic-rich environments. The biogenic reduction of sulfate follows two biosynthetic pathways: (*a*) assimilatory incorporation of S (**Figure 1*a***) into cell constituents (e.g., cysteine) with small S isotope fractionation (−1‰ to −3‰) (Kaplan & Rittenberg 1964) and (*b*) dissimilatory processes (**Figure 1*b***) that use sulfate as a terminal electron acceptor for the oxidation of organic matter by bacteria and archaea in oxygen-poor environments (Berner 1982, Goldhaber & Kaplan 1974, Jørgensen 1982) according to the following simplified equation:

$$CH_4 + SO_4{}^{2-} = CO_3{}^{2-} + H_2S + H_2O. \tag{4}$$

This process is termed microbial sulfate reduction (MSR) or dissimilatory sulfate reduction, and it fuels the cycling of S in sediments (Canfield et al. 2010, Jørgensen 1982). Theoretical modeling

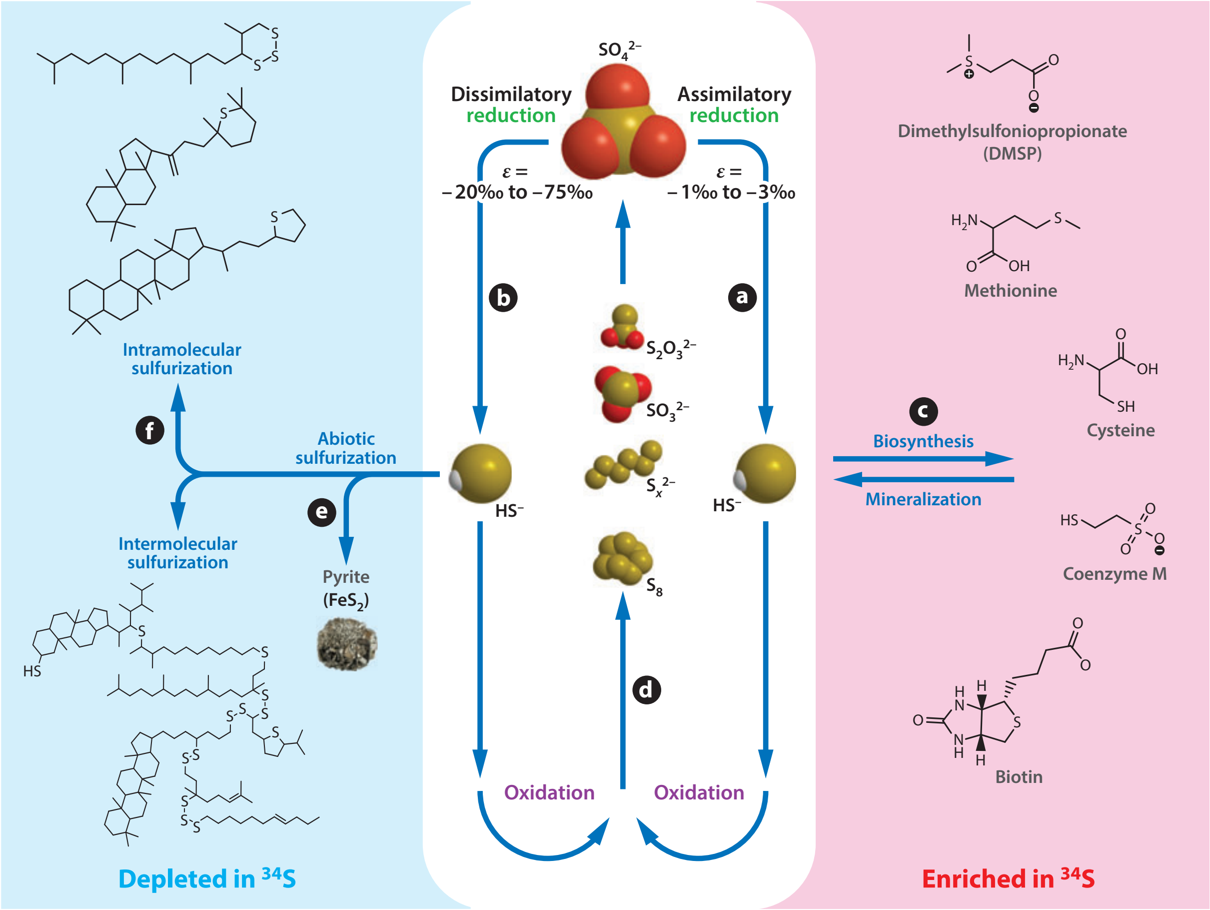


Figure 1

The sedimentary sulfur cycle in organic-rich and oxygen-depleted environments during diagenesis. (*a*) Assimilatory sulfate reduction and biosynthesis of biological sulfur species with small S isotope fractionation (−1‰ to −3‰) relative to the source sulfate. (*b*) Dissimilatory sulfate reduction, used by sulfate-reducing microorganisms to obtain energy through anaerobic respiration using sulfate as a terminal electron acceptor to form H_2S with large S isotope fractionation (−20‰ to −75‰). (*c*) Formation of biosynthetic compounds with the S isotope signature of assimilatory sulfate reduction. (*d*) H_2S from the mineralization of biosynthetic sulfur compounds and from biotic and abiotic oxidation of the products of dissimilatory sulfate reduction forms other reduced S species such as polysulfides (S_x^{2-}) and sulfite (SO_3^{2-}). (*e*) H_2S and S_x^{2-} react with iron to form iron sulfide (FeS) and eventually pyrite (FeS_2) depleted in ^{34}S, reflecting the pore-water H_2S derived from dissimilatory sulfate reduction. (*f*) Reduced S species (mainly H_2S and S_x^{2-}) react with organic matter to form organosulfur compounds (i.e., sulfurization) intramolecularly or intermolecularly. The former produces monomeric sulfur compounds, and the latter forms C–S and S–S cross-linked macromolecules.

and environmental studies have suggested that MSR is associated with large S isotope fractionation (i.e., H_2S is ^{34}S depleted), as much as −70‰ to −75‰ (Brunner & Bernasconi 2005, Canfield et al. 2010, Wortmann et al. 2001). However, experiments with pure MSR cultures did not show sulfate-sulfide fractionations greater than −47‰ (Canfield 2001, Detmers et al. 2001, Fry et al. 1988, Kaplan et al. 1963, Peterson 1999). Larger fractionations, often measured in nature, have been attributed to microbial S disproportionation and extracellular or abiotic oxidative recycling of S (Canfield & Teske 1996, Canfield & Thamdrup 1994). This S oxidative recycling model was used to track the evolution and progressive oxygenation of Earth's surface environment (Canfield &

Teske 1996, Johnston et al. 2005, Parnell et al. 2010). More recently, Sim et al. (2011) reported results from a pure culture of MSR that show a direct fractionation between sulfate and sulfide that reached 66‰. Therefore, a similar magnitude of S isotope fractionation in nature may not necessarily imply S disproportionation metabolism (Brunner & Bernasconi 2005, Sim et al. 2011).

Because biosynthetic S compounds come from assimilatory processes, they are ^{34}S enriched compared with S compounds derived from dissimilatory processes (**Figure 1*c***). The δ^{34}S values of different biosynthetic chemical species from different organisms (e.g., seaweeds, algae) can vary significantly depending on food web dynamics. Biochemical S isotopic values are usually similar to source S (usually sulfate) values (Fry et al. 1987, Sullivan & Moncreiff 1990). However, a difference of several per mill was recorded between individual biochemical compounds, which suggests that S isotope fractionation differs among specific metabolic pathways (Tanz & Schmidt 2010, Tcherkez & Tea 2013). Biosynthetic S compounds such as amino acids are chemically labile and are readily mineralized by microorganisms; thus, they have little chance of surviving diagenesis (Tissot & Welte 1984).

Hydrogen sulfide is microbially or abiotically (e.g., by MnO_2) reoxidized back to sulfate through a variety of S species with intermediate oxidation states (**Figure 1*d***). These S-containing oxidized products are distributed between solid (elemental S, FeS) and solvated forms with oxidation states ranging from −2 (HS^-) to +4 (SO_3^{2-}) (Goldhaber 2004, Zhang & Millero 1993). Hydrogen sulfide and other reduced S species in sediments react with metals, especially iron, to form the iron sulfides mackinawite (FeS), greigite (Fe_3S_4), and the most stable and common sedimentary sulfide mineral pyrite (FeS_2) (**Figure 1*e***) (Goldhaber & Kaplan 1974, Rickard & Luther 2007). Reduced S species can also react with organic compounds to form OSCs (**Figure 1*f***) (Sinninghe Damsté & de Leeuw 1990). Recent and ancient sediments show that sulfides (mostly pyrite) are commonly depleted in ^{34}S by −45‰ to −71‰ relative to seawater sulfate (Canfield & Teske 1996). Sulfate anion mostly precipitates in sediments as gypsum or anhydrite ($CaSO_4$) and is usually the most ^{34}S-enriched S fraction (as much as 89‰; Böttcher et al. 2006). The formation and precipitation of S minerals are thought to involve small fractionation, up to 1.6‰ for sulfates and 1‰ for pyrite (Butler et al. 2004, Price & Shieh 1979, Raab & Spiro 1991, Worden et al. 1997). Thus, the S isotope composition of minerals in marine sediments may be representative of the sulfide and sulfate of the sediment pore water (Canfield et al. 2000, Fike et al. 2006) if the minerals are not altered by secondary processes (Machel 2001).

2. FORMATION OF ORGANOSULFUR COMPOUNDS DURING EARLY DIAGENESIS

Given that biosynthetic organic S occurs in chemically labile forms (e.g., amino acids), it is expected that the percentage of S in organic matter will decrease during the course of diagenesis (Tissot & Welte 1984). However, in most cases, the S content in organic matter increases; it is usually higher than the original biomass S content (∼0.5–1 wt%) and can reach 14 wt% in some oils (Orr 1986). For example, organic matter (kerogen) in the Peru Margin sediments shows a marked increase in the S/C ratio, from 0.03 to 0.15, with depth (**Figure 2**) (Mossmann et al. 1991).

Furthermore, similar δ^{34}S values between organic matter and pore-water inorganic reduced S species were observed in many recent, immature sediments as well as in mature sediments in various depositional settings; these similarities suggest a common source (Aizenshtat et al. 1983, Anderson & Pratt 1995, Canfield et al. 1998, Dinur et al. 1980, Francois 1987, Mossmann et al. 1991, Passier et al. 1999, Werne et al. 2003, Zaback & Pratt 1992). A good example of this trend was observed in the Cariaco Basin sediments (Venezuela), where organic and reduced forms of S are closely related (**Figure 3*a*,*b***) (Werne et al. 2003). The ultimate source of ^{34}S-depleted S is

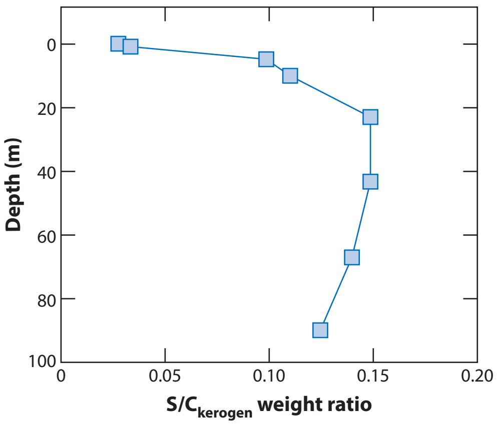


Figure 2

Sulfurization of organic matter in Peru Margin sediments characterized by high primary productivity and organic-rich siliceous shelf sediments from the Miocene. Using data from core 680, S/C weight ratios are plotted against depth below the seafloor. Adapted from Mossmann et al. (1991) with permission.

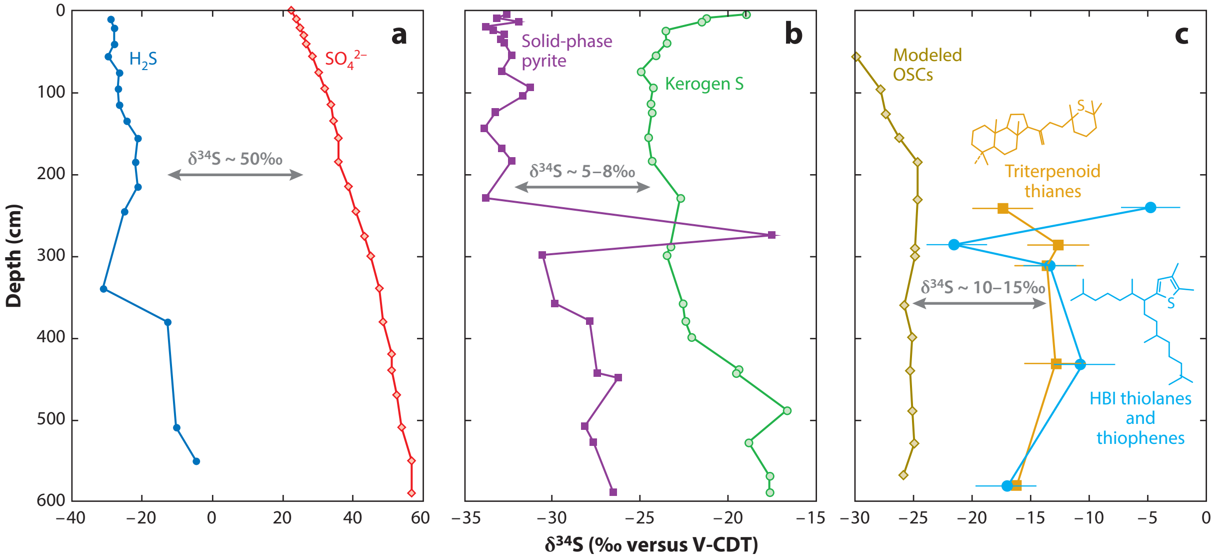


Figure 3

Depth profiles of the S isotope composition in Cariaco Basin sediments (Venezuela). (*a*) Pore-water sulfate and sulfide profile, showing the large fractionation associated with microorganism sulfate reduction (MSR) and the gradual ^{34}S enrichment of both H_2S and SO_4^{2-} with depth. Adapted from Werne et al. (2003) with permission. (*b*) Solid-phase pyrite and kerogen S profile, showing the fractionation between these two forms of reduced S species, both of which originate from MSR-derived H_2S. (*c*) S isotopic composition of specific organosulfur compounds (OSCs). These extracted compounds [triterpenoid thianes and highly branched isoprenoid (HBI) thiophenes and thiolanes] are ^{34}S enriched relative to bulk kerogen S, pyrite, and a model based on the addition of pore-water H_2S to organic molecules without fractionation. Panels *b* and *c* adapted from Werne et al. (2008) with permission. Abbreviation: V-CDT, Vienna Canyon Diablo Troilite.

inorganic reduced S species formed by sulfate-reducing microorganisms (Kaplan & Rittenberg 1964). This strongly suggests that abiotic diagenetic processes are responsible for the secondary enrichment of organic matter by the addition of inorganic reduced S species, a process termed sulfurization or vulcanization (see **Figure 1*f***) (Sinninghe Damsté & de Leeuw 1990).

Further compelling evidence for sulfurization at the molecular level arose with the discovery of the unambiguous link between OSCs and biological precursor molecules or biomarkers (Brassell et al. 1986, Payzant et al. 1988, Schmid et al. 1987, Sinninghe Damsté et al. 1986, Valisolalao et al. 1984). The S atoms in these molecules are located in specific positions, where they replace functional groups such as double bonds or hydroxyl groups. These compounds are structurally distinct from biosynthetic S compounds (**Figures 1*f*** and **3*c***). Since these early discoveries, OSCs derived from precursors representing almost every known biochemical compound class have been identified (see reviews by Krein 1993, Sinninghe Damsté & de Leeuw 1990, Werne et al. 2004). The greatest portion of sedimentary OSCs resides in macromolecular and polar fractions of organic matter (Sinninghe Damsté et al. 1989a), including kerogen, asphaltene, and pyrobitumen (Ho et al. 1974, Nelson et al. 1995, Riboulleau et al. 2000, Walters et al. 2011).

Analytical pyrolysis combined with gas chromatography–mass spectrometry (GC-MS) analysis was one of the first methods used to investigate the structure of the macromolecular fraction (Eglinton et al. 1992, Sinninghe Damsté et al. 1990). Chemical desulfurization using Raney Ni provided information about the original carbon skeletons of the sulfurized hydrocarbons (Grice et al. 1998, Kohnen et al. 1991a, Sinninghe Damsté et al. 1988). The wide variety of released compounds and their relative dominances suggested rapid and selective incorporation of S but could not pinpoint specific sites at which S was incorporated. Selective chemical degradation (e.g., MeLi/MeI) and nondestructive spectrometric techniques such as X-ray absorption near edge structure (XANES) revealed the (poly)sulfide cross-linked polymeric structure of these fractions (Adam et al. 1992, Kohnen et al. 1993, Riboulleau et al. 2000, Vairavamurthy et al. 1995). In many of the compounds in these fractions, S is cross-linked to multiple carbon positions that likely represent multiple functional sites on the precursor structures (Adam et al. 2000, Koopmans et al. 1996b). All major biomarker classes are represented (Adam et al. 1993; Filley et al. 2002; Kohnen et al. 1991b, 1993; Putschew et al. 1998; Schaeffer et al. 1995). In many macromolecular fractions and in kerogen, cross-linking of both O and S is common (Riboulleau et al. 2000, Schaeffer-Reiss et al. 1998, Vandenbroucke & Largeau 2007).

2.1. Sulfurization Conditions and Mechanisms

Three major conditions are required for sulfurization of organic matter. First, reactive reduced S species must be available. This typically implies reducing conditions and MSR activity. Second, concentrations of free metal ions, especially iron, must be low. Iron rapidly scavenges reduced S species more quickly than they can react with organic matter (Berner & Westrich 1985, Hartgers et al. 1997), although simultaneous formation of organic S and iron sulfide may be possible (Filley et al. 2002, Urban et al. 1999). Third, organic compounds with functional sites that are receptive to the addition of inorganic S species must be present.

2.1.1. Reduced sulfur species and their reactivity for sulfurization. Although HS^- is the most abundant reduced S species, polysulfides (S_x^{2-}) have been demonstrated theoretically and experimentally to be the strongest nucleophiles (Lalonde et al. 1987, Loch et al. 2002, Vairavamurthy & Mopper 1989, Wu et al. 2006). Polysulfides regenerate through oxidation of HS^- at the interface between oxic and anoxic water, through oxidation of HS^- with iron or dissolved organic matter, or through reaction of HS^- with S_8 (Ferdelman et al. 1991, Filley et al.

2002, Heitmann & Blodau 2006, Luther & Church 1988). Therefore, despite having lower concentrations than HS^-, polysulfides were suggested to be another important species involved in diagenetic S enrichment of organic matter (Aizenshtat et al. 1983; Francois 1987; Mossmann et al. 1991; Vairavamurthy et al. 1992, 1995; Werne et al. 2008).

The most abundant S_x^{2-} species under marine conditions are S_4^{2-}, S_5^{2-}, and S_6^{2-}; concentrations of hydropolysulfide HS_x are minor (Kamyshny et al. 2004). Polysulfide anions are in equilibrium with HS^-, S, and FeS (Fossing & Jørgensen 1990). The distribution of these species depends on the pH and degree of S_8 saturation (Kamyshny et al. 2004, Kamyshny et al. 2008). Elemental S is a poor nucleophile with low solubility, which makes it an unlikely candidate for reaction with organic matter under diagenetic marine conditions—i.e., slightly basic to neutral pH and low temperature (Krein 1993)—though a recent study may challenge this view (Said-Ahmad 2012). Thiosulfate and sulfite, despite their lower concentrations and nucleophilicity, can be considered as sulfurization agents in oxic-anoxic interfacial zones, and they form sulfonates (Vairavamurthy et al. 1994).

2.1.2. Mechanisms of sulfurization.

Two principal routes for sulfurization (**Figure 1*f***) have been proposed (Sinninghe Damsté et al. 1989c): intermolecular addition, which forms macromolecules via sulfide or polysulfide bridges (e.g., Adam et al. 1993, Kohnen 1991b, Riboulleau et al. 2000), and intramolecular addition (e.g., Schaeffer et al. 2006, Werne et al. 2003), in which the S incorporated into the organic molecule is rearranged to form a ring, usually the thermodynamically favorable thiolane (**Figure 1*f***). An intramolecular mechanism requires at least two functionalities (e.g., double bonds) in the precursor molecule.

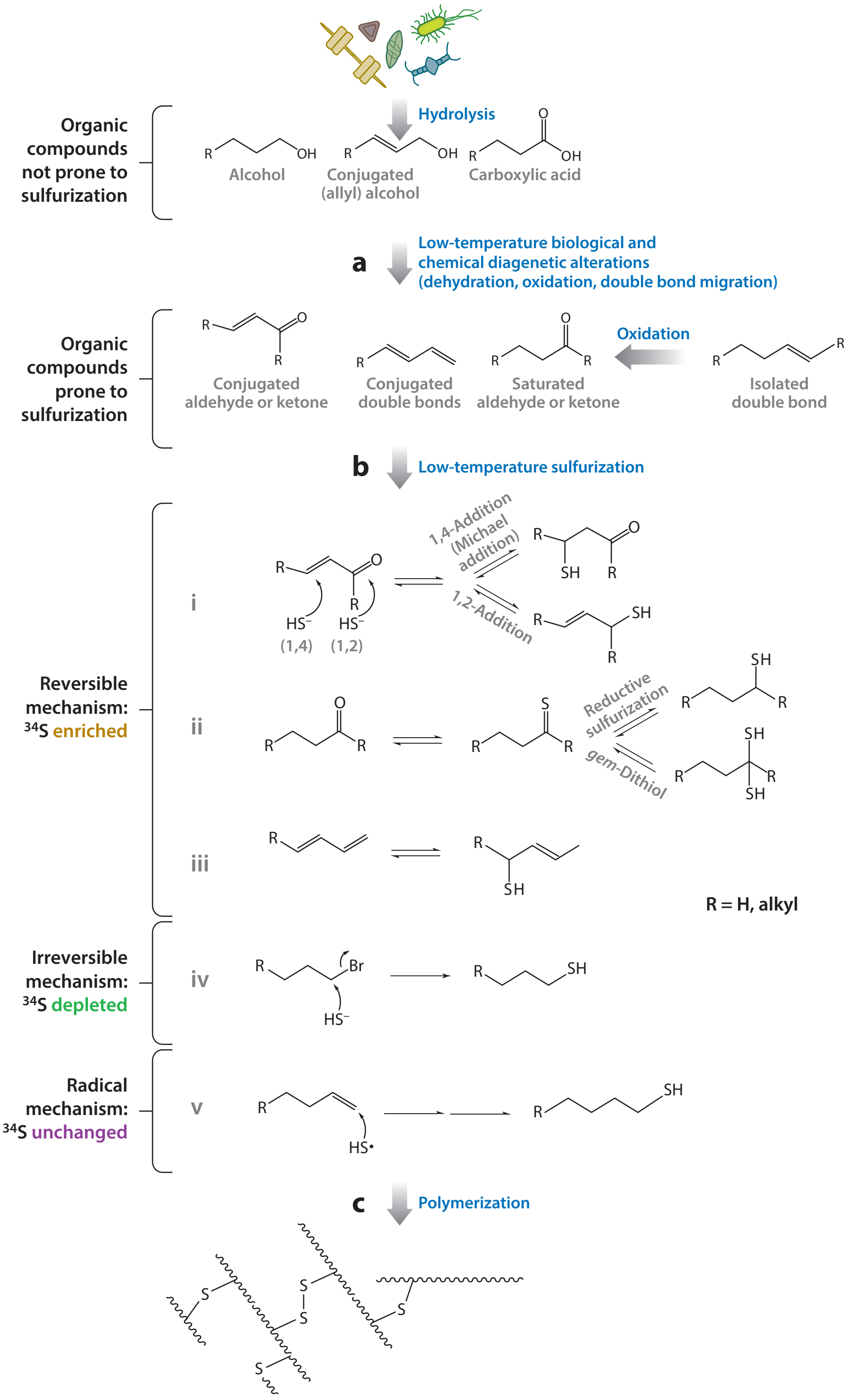
Sulfur addition to organic matter can proceed through electrophilic, nucleophilic, and radical mechanisms. The mechanism depends on reaction conditions, including the medium (e.g., organic or water), pH, and temperature (Krein 1993). Electrophilic addition occurs mostly under highly acidic conditions, when protons are readily available (Smith & March 2001). Nucleophilic substitution is the dominant mechanism under neutral to basic pH and is therefore the most common mechanism in marine environments (Aizenshtat et al. 1995). The radical mechanism is dominant at higher temperatures (i.e., thermal maturation), though several recent studies suggest it can occur at relatively low temperatures as well (Hebting et al. 2003, 2006; Perlinger et al. 2002; Pickering & Keely 2012; Said-Ahmad 2012).

The sulfurization mechanism is highly sensitive to the reaction conditions. Very basic or acidic conditions can initiate reactions such as aromatization and formation of thiophenes that usually occur during thermal maturation, even at ambient temperatures (Fukushima et al. 1992, Krein & Aizenshtat 1993, Lalonde et al. 1987). Warming to a temperature considered mild, such as 50–100°C, can also change the mechanism as well as the distribution of reactants and products (Amrani et al. 2006b). Using organic solvents as the reaction medium to simulate natural sulfurization can change the distribution and reactivity of both inorganic S species and organic compounds (Amrani & Aizenshtat 2004c).

2.1.3. The organic substrate for inorganic sulfur addition.

Figure 4 summarizes some important sulfurization mechanisms. Carbonyl groups have been shown both theoretically and experimentally to be the strongest acceptors for HS^-/S_x^{2-} addition (Amrani & Aizenshtat 2004a, Krein & Aizenshtat 1993, Lalonde et al. 1987, Schouten et al. 1994). Numerous field studies have suggested that carbonyls are important organic substrates for sulfurization (Adam et al. 2000, Schaeffer et al. 2006).

The reaction of S species with aldehydes is considerably faster than with ketones. Double bonds conjugated to aldehydes and ketones further increase their reactivity, and the reaction time


Hydrolysis
Organic compounds not prone to sulfurization
Alcohol
Conjugated (allyl) alcohol
Carboxylic acid
a
Low-temperature biological and chemical diagenetic alterations (dehydration, oxidation, double bond migration)
Organic compounds prone to sulfurization
Conjugated aldehyde or ketone
Conjugated double bonds
Saturated aldehyde or ketone
Oxidation
Isolated double bond
b
Low-temperature sulfurization
i
1,4-Addition (Michael addition)
1,2-Addition
(1,4)
(1,2)
ii
Reductive sulfurization
gem-Dithiol
iii
R = H, alkyl
Reversible mechanism: ^{34}S enriched
iv
Irreversible mechanism: ^{34}S depleted
v
Radical mechanism: ^{34}S unchanged
c
Polymerization

in laboratory experiments can range from minutes to days (Amrani & Aizenshtat 2004c, Amrani et al. 2007, Krein & Aizenshtat 1993, Schneckenburger et al. 1998, Schouten et al. 1994).

Organohalogens react readily with S nucleophiles, although the significance of this process to the geosphere is unknown (Amrani & Aizenshtat 2004a, Loch et al. 2002, Wu et al. 2006). The ocean is the primary source of natural organohalogens, and many marine organisms produce such compounds (Gribble 2003).

The reaction of nonactivated (or isolated) double bonds with HS^- or S_x^{2-} was suggested as an important pathway for the sulfurization of organic matter in the geosphere (Sinninghe Damsté et al. 1989c, Schouten et al. 1994). Laboratory experiments in the presence of polar organic solvents have shown that double bonds can react on a reasonable timescale (de Graaf et al. 1995, Schouten et al. 1994). However, the reaction of H_2S in water with an isolated double bond site requires electrophilic catalysis, such as with concentrated sulfuric acid, and elevated temperatures (Smith & March 2001), which are not likely to be found in marine environments. In experiments that used water with no organic solvents, the reaction of isolated double bonds and HS^-/S_x^{2-} did not produce detectable OSCs at low temperatures, even after months (Amrani & Aizenshtat 2004a, Hebting et al. 2003, Krein & Aizenshtat 1994, Said-Ahmad 2012).

2.2. Diagenetic Alterations Before Sulfur Incorporation

Despite the low reactivity of isolated double bonds and alcohol functionalities toward direct sulfurization under low-temperature marine conditions, many such biosynthetic precursors were suggested for OSCs that were identified in the geosphere (Russell et al. 2000; Sinninghe Damsté et al. 1989c, 2007; Werne et al. 2000). The close association of organic compounds, surface-active particles (such as clay minerals), and S species may activate double bonds and allow their sulfurization by mechanisms other than nucleophilic addition, such as electrophilic or radical mechanisms. The apparent sulfurization of isolated double bonds and alcohols in natural environments may also implicate diagenetic alterations of organic matter prior to sulfurization (Blumenberg et al. 2010),

←

Figure 4

(*a*) Diagenetic transformations prior to sulfurization of molecules not reactive with reduced S species. These transformations, which include biotic and abiotic oxidation, double bond migration, and dehydration, transform these molecules to be prone to sulfurization. The reactivity of an isolated double bond to sulfurization is questionable, but it can be oxidized or migrate toward other double bonds in the molecule and thereby become more reactive. (*b*) The main mechanisms for S incorporation into specific functional groups and their S isotope effects. For convenience, HS^- represents all reduced S nucleophiles, especially S_x^{2-}. (*i*) The reaction with a double bond conjugated to a carbonyl system proceeds via two reversible routes: 1,4-addition (Michael addition) on the conjugated double bond or 1,2-addition directly on the carbonyl carbon (Adam et al. 2000, Lalonde et al. 1987). (*ii*) The reversible addition of HS^- or S_x^{2-} to carbonyl groups under aqueous conditions can proceed via two mechanisms: a reductive sulfurization route or the *gem*-dithiol route, both with thioketone or imine as the intermediate (Amrani et al. 2007, Krein & Aizenshtat 1994, Schneckenburger et al. 1998). (*iii*) Conjugated double bonds are reactive and may react in a 1,4-addition; extended double bond conjugation further increases the organic molecule's reactivity. Because these mechanisms are usually reversible, ^{34}S enrichment is expected, in the range of 4‰ to 8‰ (Amrani et al. 2008a). (*iv*) Haloalkanes usually react irreversibly in an SN_2 nucleophilic substitution reaction, which yields organosulfur compounds that are depleted in ^{34}S relative to HS^-/S_x^{2-}. (*v*) Double bonds can react via a free radical mechanism that does not fractionate the $^{34}S/^{32}S$ isotope ratio. (*c*) Polymerization to form C–S and S–S cross-linked macromolecules. There is no apparent S isotope effect in the formation of macromolecules (intermolecular mechanism) compared with the formation of individual OSCs (intramolecular mechanism).

such as dehydration of alcohols, double bond migration, and oxidation (**Figure 4*a***). Schaeffer et al. (2006) suggested double bond or alcohol oxidation to conjugated double bond systems and to ketones for numerous hopanoid precursors prior to sulfurization. Conjugation to other double bond(s) or to an electron withdrawal group such as carbonyl group can activate double bonds to a nucleophilic attack (Lalonde et al. 1987). Biodegradation and abiotic oxidation (e.g., photochemical or via metals) of alcohols and double bonds are important pathways for the formation of aldehydes and ketones (Grossi et al. 1998, Rontani et al. 1999). Temporal variations of the chemical environment between oxic and anoxic conditions, as occur in the upper centimeters of bacterial mats between day and night (Revsbech & Ward 1984), can increase the formation of reactive organic compounds such as conjugated aldehydes and their subsequent reaction with HS^- or S_x^{2-} (Amrani & Aizenshtat 2004b).

2.3. Sulfurization as an Organic Matter Preservation Mechanism

The sulfurization process quenches functionalized molecules that are very reactive and would otherwise be mineralized rapidly by microorganisms (Sinninghe Damsté & de Leeuw 1990). Sulfurization of these functional sites during early diagenesis and the formation of macromolecules thus enhance organic matter preservation (Grice et al. 1998). The carbon skeleton of OSCs may remain well preserved during organic matter diagenesis and early catagenesis (Koopmans et al. 1996a). Sulfurization can also reduce double bonds and thus increase the potential for molecule preservation (Hebting et al. 2006, Pickering & Keely 2012).

Sulfurization of labile cell material, such as carbohydrates, has been suggested to significantly increase total organic carbon preservation (Hartgers et al. 1997, Kok et al. 2000, Sinninghe Damsté et al. 1998b, van Dongen et al. 2003, Van Kaam-Peters et al. 1998). Examples of this process were reported in the Kimmeridgian Clay Formation (Upper Jurassic, United Kingdom) and the Cariaco Basin (Aycard et al. 2003, van Dongen et al. 2006). The generation of (poly)sulfide cross-linked carbohydrate skeletons and the ^{13}C enrichment relative to alkyl moieties were strong indications that this process had occurred (Riboulleau et al. 2000, Van Kaam-Peters et al. 1998). Sulfurization results in a better representation of the chemically labile cell material of the depositional environment. However, it also causes a selective sequestration of the original sedimentary organic matter. Variations in the distribution and relative abundance of biomarkers in sediments are of crucial importance for paleoenvironment reconstruction or as an organic matter maturity-level indicator (Peters et al. 2005). Thus, selective preservation by S incorporation introduces a bias in the distribution of biomarkers that are used for paleoenvironmental reconstruction (Kohnen et al. 1991a). Examples of such a bias can be found in the ratios of pristane/phytane and $C_{35}/\Sigma(C_{31}-C_{35})$ hopanes, which are commonly used to assess the paleoredox conditions of the depositional environment (Peters et al. 2005). Alternatively, this phenomenon can be explained by diagenetic sulfurization and preservation mechanisms of phytol and the bacteriohopanepolyol side chain (Köster et al. 1997, Sinninghe Damsté et al. 1995). Precursors that are related to phytane and hopane skeletons are prone to sulfurization, and significant quantities are sequestered during diagenesis (Adam et al. 2000, Koopmans et al. 1999). Desulfurization (e.g., by Raney Ni treatment) releases S-bound hydrocarbons and may allow for better quantification of these compounds (Kohnen et al. 1991a).

3. CONTROLS ON THE Δ^{34}S OF ORGANOSULFUR COMPOUNDS DURING DIAGENESIS

Both OSCs and pyrite form from dissimilatory MSR-derived S during early diagenesis. However, OSCs are ^{34}S enriched by up to 30‰ relative to coexisting pyrite, with a global average of approximately 10‰ (Anderson & Pratt 1995). In a compound-specific S isotope study, Werne et al. (2008) found that highly branched isoprenoid (HBI) thiolane and thiophene compounds and triterpenoid thianes (TTs) are ^{34}S enriched by ~10–15‰ relative to pyrite in samples from sediments of the Cariaco Basin (Venezuela) (**Figure 3*b*,*c***). Interestingly, these compounds are also ^{34}S enriched relative to co-occurring kerogen S by ~3–6‰. This illustrates possible temporal variability as well as the importance of multiple chemical pathways involved in S incorporation into organic matter and other diagenetic processes (Aizenshtat & Amrani 2004a, Werne et al. 2008). Specific OSCs may record this S isotope variability, whereas bulk S phases such as pyrite and kerogen average such differences. Some of the factors that affect the δ^{34}S of OSCs are summarized below.

3.1. Biosynthetic and Secondary Organosulfur Compounds

There are two isotopically distinct sources of sedimentary organic S: the original ^{34}S-enriched biosynthetic S and the ^{34}S-depleted S from the secondary sulfurization of organic matter (Bruchert & Pratt 1996, Canfield et al. 1998, Passier et al. 1999). However, isotopic mass balance calculations show that at least 75–90% of sedimentary organic S is not the original biosynthetic S but is instead the result of early diagenesis sulfurization processes (Anderson & Pratt 1995). Moreover, S in biomolecules is easily mineralized and then either consumed by microorganisms or released to the surrounding water where it is diluted with the external dissimilatory pool (**Figure 1**). Thus, its high δ^{34}S signature will be diluted, and its proportion, at least in cases of intense sulfurization, should be minor. As the sulfurization increases, the δ^{34}S of organic S becomes ^{34}S depleted because MSR-derived S is incorporated (Aizenshtat et al. 1983). However, this trend is only observed in the upper centimeters of sediments; there is ^{34}S enrichment of organic matter with depth with an almost constant gap between pyrite and bulk organic S (see **Figure 5**) (Mossmann et al. 1991, Werne et al. 2003). This suggests that there are additional factors that control the δ^{34}S of organic S during diagenesis.

3.2. Timing and Type of Sulfur Species Involved in Organosulfur Compound Formation

Sulfurization of organic matter is a very rapid process on geological timescales (Werne et al. 2004). Sulfurization of organic matter younger than 100 years was reported in lacustrine sediments (Urban et al. 1999). In the Cariaco Basin sediments, ^{14}C studies have shown that the timescales of sulfurization for HBI compounds and malabaricatriene are 100 years and 10,000 years, respectively (Werne et al. 2000). Other studies have indicated that HBI compounds are sulfurized on timescales of hundreds of years (Sinninghe Damsté et al. 2007, Wakeham et al. 1995). Kok et al. (2000) found that steroids in Ace Lake sediments (Antarctica) were sulfurized on timescales of 1,000–3,000 years.

The large differences in sulfurization rates of individual organic compounds correspond to their different reactivities, as shown experimentally (Amrani & Aizenshtat 2004a, Schouten et al. 1994). For example, laboratory experiments show that phytenal is sulfurized in a matter of hours to days, whereas phytadiene is sulfurized over weeks to months under the same conditions (Amrani & Aizenshtat 2004a,c). These differences in reactivities and timing of formation of OSCs can significantly affect their δ^{34}S values. This is because inorganic S becomes ^{34}S enriched with depth as a result of sulfate consumption by MSR (**Figure 3*a***). OSCs that formed later should therefore be enriched in ^{34}S relative to those that formed earlier while still in the upper part of the sediment (**Figure 5**).

Certain types of S species may be ^{34}S enriched as a result of bacterial oxidation and equilibrium fractionation. Mossmann et al. (1991) suggested that S_x^{2-} and S_8 are isotopically heavier than pyrite because they are formed by the oxidation of sulfide diffusing across the sediment-water interface,

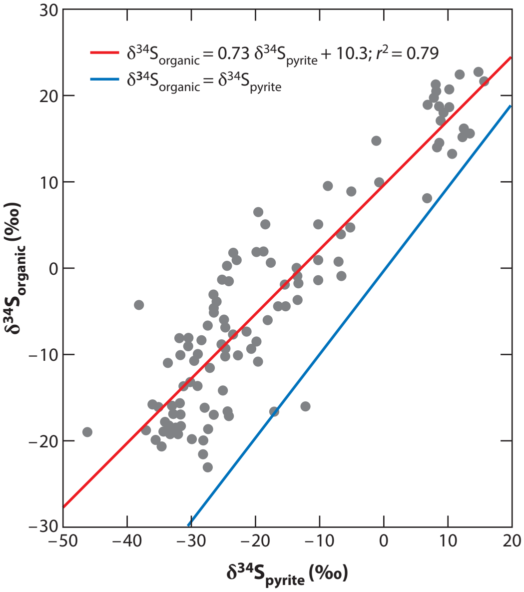


Figure 5

The $\delta^{34}S$ relationship between organic sulfur and coexisting pyrite in S-rich environments around the globe. Despite their common S source (reduced S species derived from microbial sulfate reduction), organic S is enriched in ^{34}S by 10‰ on average compared with coexisting pyrite. Adapted with permission from Anderson & Pratt (1995). Copyright 1995 American Chemical Society.

whereas pyrite is precipitated from pore-water HS^- within the sediment. Sulfide diffusing across the sediment-water interface is isotopically heavier than pore-water sulfides within the surface sediment (Chanton et al. 1987). Amrani et al. (2006a) have shown that aqueous S_x^{2-} species are ^{34}S enriched by between ~3‰ and 6‰ at equilibrium compared with coexisting HS^-. A positive correlation between the S_x^{2-} chain length and its degree of ^{34}S enrichment was observed (Amrani et al. 2006a). Other, more oxygeneted S species (e.g., polythionates) may have up to 19‰ ^{34}S enrichment relative to HS^- (Kaplan & Rittenberg 1964), but their role as sulfurization agents is questionable (Anderson & Pratt 1995).

3.3. Fractionation During Sulfur Incorporation into Organic Matter

Amrani & Aizenshtat (2004b) showed that the incorporation of S_x^{2-} into carbonyl functional groups (aldehydes and ketones) fractionates S isotopes by up to +5‰. Bisulfide (HS^-) and methanethiol addition to saturate carbonyl compounds can produce fractionation of up to +8‰ and +5.4‰, respectively (Amrani et al. 2008a). The addition of SO_3^{2-} to carbonyl compounds at equilibrium in the formation of sulfonates can produce even higher fractionation (+10‰ to 20‰) (Sheppard & Bourns 1954). Reversible mechanisms enrich OSCs in ^{34}S, whereas irreversible, kinetically controlled reactions, such as those that involve the addition of S to haloalkanes, deplete OSCs in ^{34}S, an observation also supported by quantum mechanics calculations (Amrani et al. 2008a). Free radical mechanisms produce no apparent S isotope fractionation, as demonstrated by the reaction of benzylthiol with aldehydes (Said-Ahmad 2012). At elevated temperatures (≥200°C), S isotope fractionation is small, probably because free radical mechanisms dominate the incorporation of S into organic matter (Amrani et al. 2006b, 2011).

Equlibrium-controlled fractionation (4‰ to 8‰) may explain nearly all of the δ^{34}S differences between pyrite and kerogen S during diagenesis in some locations—for example, the Cariaco basin (**Figure 3*b***) (Werne et al. 2003). However, compound-specific studies of the Cariaco Basin show that the δ^{34}S differences of individual OSCs varied significantly from that of the bulk kerogen S (Werne et al. 2008). Recently, Raven et al. (2013) showed much larger variations in the δ^{34}S values of individual OSCs in the Cariaco Basin; some were even ^{34}S depleted relative to pyrite. These large δ^{34}S variations, as well as those recorded at other sites where the fractionation between kerogen and pyrite is large (e.g., 30‰ at the Ghareb Formation), show that other processes were probably more dominant.

The magnitude of S isotope fractionation during the formation of OSCs depends on the mechanism of S incorporation and the original functionality of the organic molecule (Amrani et al. 2008a). Compound-specific S isotope studies may thus reveal specific S incorporation pathways and provide more reliable information about precursor-product relationships at the molecular level (Raven et al. 2013, Werne et al. 2008).

3.4. Isotopic Mixing Between Organic and Inorganic Sulfur

When isotopes exchange among chemical substrates, the substrates' relative abundance and chemical structures remain unchanged but their isotopic composition changes with time. Most OSCs formed by diagenetic processes are bonded to macromolecules through C–S and S–S bridges that are susceptible to significant structural changes under mild thermal alteration (Adam et al. 1993, Kohnen et al. 1991b, Sinninghe Damsté et al. 1989a). Therefore, in this review, the term isotope mixing is used to reflect S isotope changes that result both from S isotope exchange reactions and from processes that add S to or remove S from OSCs and co-occurring reduced inorganic S species.

Bottrell et al. (2009) studied an organic-rich sediment in a Scottish fjord and reported that δ^{34}S values of organic S declined with depth, from −2.8‰ to −11‰, decreasing toward the lower inorganic S values (−30‰), without a net addition or loss of OS. This suggests that S isotope mixing occurs during the very early stages of diagenesis.

Rapid isotopic mixing rates (which authors have termed isotope exchange) for sulfide and polysulfide bonds were reported between organic and inorganic S species by using ^{35}S as a tracer (Douglas et al. 1949, Fedoseev 1990, Yamada et al. 2003, Zielinski & Kanska 1993). In a stable S isotope study, Amrani et al. (2006b) showed that rapid isotopic mixing occurred between synthesized S–S cross-linked macromolecules and inorganic S species (S, HS^-, S_x^{2-}; H_2S) at temperatures between 25°C and 200°C within hours (**Figure 6*c***). In contrast, isotopic mixing did not occur between dibenzothiophenes (aromatic S) or hexadecanethiol (C–SH) and $HS^-_{(aq)}$ under the same conditions (Amrani et al. 2006b). Allyl thiol, however, readily underwent isotope mixing with $HS^-_{(aq)}$ (Hebting et al. 2003).

The activation energy for the isotope mixing reaction of organic polysulfides is small (calculated at 8.3 kJ/mol) due to facile cleavage of the S–S bonds and the formation of free radicals that increase isotope mixing rates (Yamada et al. 2003). Méhay et al. (2009) showed that iron sulfide can induce S isotope mixing of nonaromatic C–S bonds at low temperatures. Laboratory experiments with thiolanes, iron sulfide, and H_2S in aqueous solution at 70°C formed 1,2-dithiane and eventually a monosulfide thiolane. This process can facilitate isotope mixing with bacterially produced H_2S in relatively low-temperature environments such as shallow oil reservoirs (Méhay et al. 2009). Therefore, the early δ^{34}S imprint of OSCs in the upper parts of the sediment can gradually change via mixing with the ^{34}S-enriched inorganic reduced S pool in the lower parts of the sediment. This

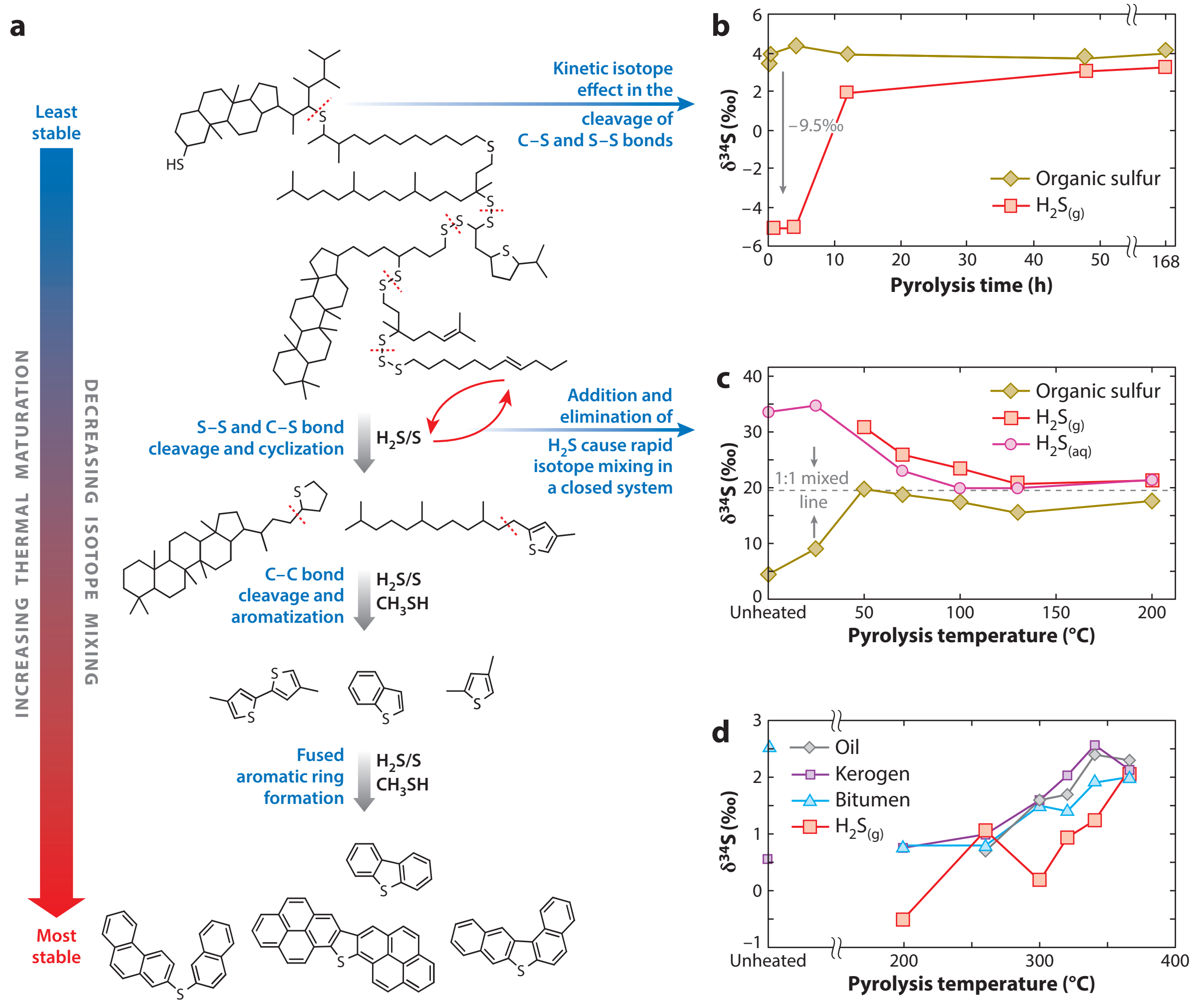


Figure 6

The general thermal maturation scheme of organosulfur compounds and its effect on the distribution of S isotopes. (*a*) The structural changes of organosulfur compounds during thermal maturation from the thermally unstable S–S and C–S bonds, which rapidly mix isotopes, to the most thermally stable fused aromatic structures, which have very slow isotope mixing rates. (*b*) Pyrolysis (N_2 atmosphere) experiments at 200°C in a glass ampoule of polysulfide cross-linked polymer (3.5‰, simulating an immature kerogen) exhibit −9.5‰ fractionation during the early release of H_2S from the polymer. As the pyrolysis time increases, the fractionation between the polymer and H_2S decreases as a result of isotope mixing between the two. Adapted from Amrani et al. (2005b) with permission. (*c*) Isotope mixing experiments between polysulfide cross-linked polymer and $(NH_4)_2S_x$ (1:1 sulfur molar ratio) for 48 h at different temperatures. Adapted from Amrani et al. (2006b) with permission. Even at low pyrolysis temperatures (25–70°C), mixing rates are significant. At higher temperatures (130–200°C), complete isotope mixing is reached within a few hours. (*d*) Hydrous pyrolysis experiments on a sulfur-rich oil shale from the Ghareb Formation, Israel. Adapted from Amrani et al. (2005a) with permission. There is ^{34}S enrichment of all organic fractions relative to the unheated kerogen by up to 2‰. This ^{34}S enrichment is caused by the release of ^{34}S-depleted S, which is released as H_2S or reacts with iron to form secondary pyrite.

process continues until thermally stable OSCs form; these require higher activation energy for isotope mixing.

4. THERMAL MATURATION OF ORGANOSULFUR COMPOUNDS

4.1. A Mechanistic View

The conventional view of products from the thermal maturation of organic matter is the sequence kerogen → bitumen → oil (Baskin & Peters 1992, Lewan 1985, Tissot & Welte 1984). Thermally unstable S–S bonds in protokerogen and immature kerogen are replaced by C–S and aromatic S in bitumen and immature oil, and then by fused aromatic structures (e.g. dibenzothiophenes) in mature oil and pyrobitumen in overmature oil (Aizenshtat et al. 1995, Kelemen et al. 2010, Nelson et al. 1995, Sinninghe Damsté & de Leeuw 1990). Each of these stages is accompanied by a net loss of S, mostly as H_2S (Amrani et al. 2005a, Koopmans et al. 1998, Orr 1986, Tannenbaum & Aizenshtat 1985). The relatively weak S–S and C–S bonds increase the rate of petroleum formation from S-rich kerogens (Baskin & Peters 1992, Orr 1986, Tannenbaum & Aizenshtat 1985). Moreover, the thermal cleavage of these bonds forms S radicals, which reduce the stability of hydrocarbons (Martin 1993), leading to early generation of petroleum (Lewan 1998). The S radicals can also act as hydrogen extractors, resulting in aromatization and oxidation of organic matter in the presence of water (Aizenshtat et al. 1995, Said-Ahmad et al. 2013).

4.2. Early Thermal Maturation: Formation of Alkyl Thiophenes

At the early thermal alteration stage, the macromolecular structure breaks apart and induces OSCs to undergo intramolecular structural changes from the weaker cross-linked C–S and S–S bonds to form thiolane, thiane, and thiophene rings (**Figure 6*a***) (Krein & Aizenshtat 1995, Sinninghe Damsté et al. 1989d). Long-chain alkyl thiophenes can be formed, with surprisingly high stability, well into the oil window (Koopmans et al. 1995, 1998). Thiolanes can form at temperatures as low as 50°C and alkyl thiophenes at 160°C in laboratory experiments (Amrani et al. 2006b, Krein & Aizenshtat 1995). At these early thermal stages, the specific locations of C–S bonds are still preserved, and the thiolane or thiophene rings are formed with minimal C–C bond cleavage and thus preserve information about their biomarker precursor (Koopmans et al. 1995). For example, a molecular paleosalinity indicator was suggested based on the ratio of terminal to mid-chain C_{20} isoprenoid thiophenes (termed ITR; Barakat & Rullkötter 1997, Sinninghe Damsté et al. 1989b). The main precursor for the terminal thiophenes is chlorophyll *a*–derived phytol. The precursors for mid-chain ITR structures include Δ2,6-phytadienol and geranylgeraniol, which are products of photosynthetic S bacteria and archaea common in hypersaline environments.

4.3. Progression of Thermal Alteration: Formation of Thermally Stable Organosulfur Compounds

At increasing levels of thermal maturity, the C–C bonds cleave at higher rates and release short (C_4 to C_{10}) alkyl thiophenes with less similarity to their biochemical precursors (Eglinton et al. 1992, Sinninghe Damsté et al. 1989a). Flash pyrolysis GC-MS studies showed that short thiophenes are released from both macromolecular structures and free molecules at the β position to the thiophene (Eglinton et al. 1992). Short thiophenes are classified in categories that represent their hydrocarbon precursor, i.e., *n*-alkane, isoprenoid, branched, and steroid (Sinninghe Damsté et al. 1989a). Although this analytical approach does provide insights to the macromolecular structure in many samples (Luckge et al. 2002; Sinninghe Damsté et al. 1993, 1998a), it does not necessarily represent the natural maturation process. In geologic basins, the slow heating rate and the close interaction between the organic and inorganic S species may induce secondary reactions (Aizenshtat & Amrani 2004b). The S species that are released from the cleavage of (poly)sulfide bonds back-react with the organic matter to form new OSCs, including thermally labile volatile S compounds and H_2S (Krein & Aizenshtat 1995). Hydrogen sulfide can react with alkanes to form thiols, thiophenes, and benzothiophenes (Nguyen et al. 2013). Despite the thermally unstable nature of labile OSCs (e.g., methanethiol, dimethyl sulfide), the establishment of a steady state between H_2S and volatile OSCs has been verified by high-temperature pyrolysis experiments (Amrani et al. 2008b, Zhang et al. 2008). The dynamic formation and degradation of OSCs at high temperatures gradually erase the specific S locations and isotopic signatures that were carried from early diagenesis (**Figure 6**). The rearrangement of thermally altered OSCs and the thermal incorporation and stabilization of S into hydrocarbons create thermally stable compounds such as benzothiophenes and dibenzothiophenes (Sinninghe Damsté & de Leeuw 1990, Aizenshtat et al. 1995) that are less susceptible to isotopic mixing (Amrani et al. 2006b).

4.4. Formation of Benzothiophenes and Dibenzothiophenes

The formation pathways of benzothiophenes (BTs) and dibenzothiophenes (DBTs) and other fused thiophenic systems in the geosphere are not well understood (Aizenshtat et al. 1995). Cyclization and aromatization of polyunsaturated alkylthiophenes, both as free OSCs or bound to macromolecular structures, were suggested as a pathway for the formation of BTs (Eglinton et al. 1990, Schmid et al. 1987). Low-temperature pyrolysis (200°C) of a polysulfide cross-linked polymer from a polyunsaturated compound (citral) yielded dimethyl BTs, among other products, which supports the above mechanism (Amrani et al. 2006b). However, the wide distribution of BTs and DBTs in petroleum from locations around the globe (Ho et al. 1974) and their clear relationship with the thermal maturity of organic matter (Radke 1988) suggest more widely distributed precursors. Thermally labile OSCs undergoing sequential maturation were suggested as possible precursors for BTs and DBTs (Sinninghe Damsté & de Leeuw 1990). Indeed, pyrolysis experiments (up to 360°C) of *n*-alkanes or immature petroleum in the presence of elemental S or H_2S produced BTs and DBTs (Amrani et al. 2011, Kowalewski et al. 2010, Nguyen et al. 2013). Asif et al. (2009) showed that DBTs have product-precursor relationships with biphenyls that occur in sediments and crude oils and are produced during low-temperature (200–300°C) laboratory experiments. They suggested that a catalytic reaction of biphenyls and S that adsorbed on carbonaceous surfaces could explain the widespread occurrence of DBTs in sediments and crude oils.

4.4.1. Application of benzothiophenes and dibenzothiophenes as a maturity parameter.

Ho et al. (1974) successfully classified oils from different sources and geological ages (Cambrian to Pliocene) using the benzothiophene-to-dibenzothiophene ratio (BDR). The thermal stability of DBTs is greater than that of BTs; therefore, DBTs are more abundant at the higher stages of thermal maturity (Radke et al. 1991, Santamaria-Orozco et al. 1998). Similarly, specific methylated isomers of both BTs and DBTs have different thermal stabilities. For example, 1-methyl DBT (1-MeDBT) is less stable than 4-MeDBT, and its abundance therefore decreases in relation to increased thermal maturation and vitrinite reflectance (Radke 1988, Radke et al. 1986). Theses methylated isomers of DBT (4-MeDBT/1-MeDBT, i.e., the MDR index) were therefore suggested as sensitive maturation indicators (Radke et al. 1986, Radke & Willsch 1994). Other parameters that include ratios of different isomers have been suggested, such as dimethyl DBT (DMDBT) and trimethyl DBT (TMDBT) indices (Chakhmakhchev & Suzuki 1995, Chakhmakhchev et al. 1997) and the C_3-BT index (C_3-BTI) for lower thermal maturity levels (Santamaria-Orozco et al. 1998).

5. CONTROLS ON THE Δ^{34}S OF ORGANOSULFUR COMPOUNDS DURING CATAGENESIS

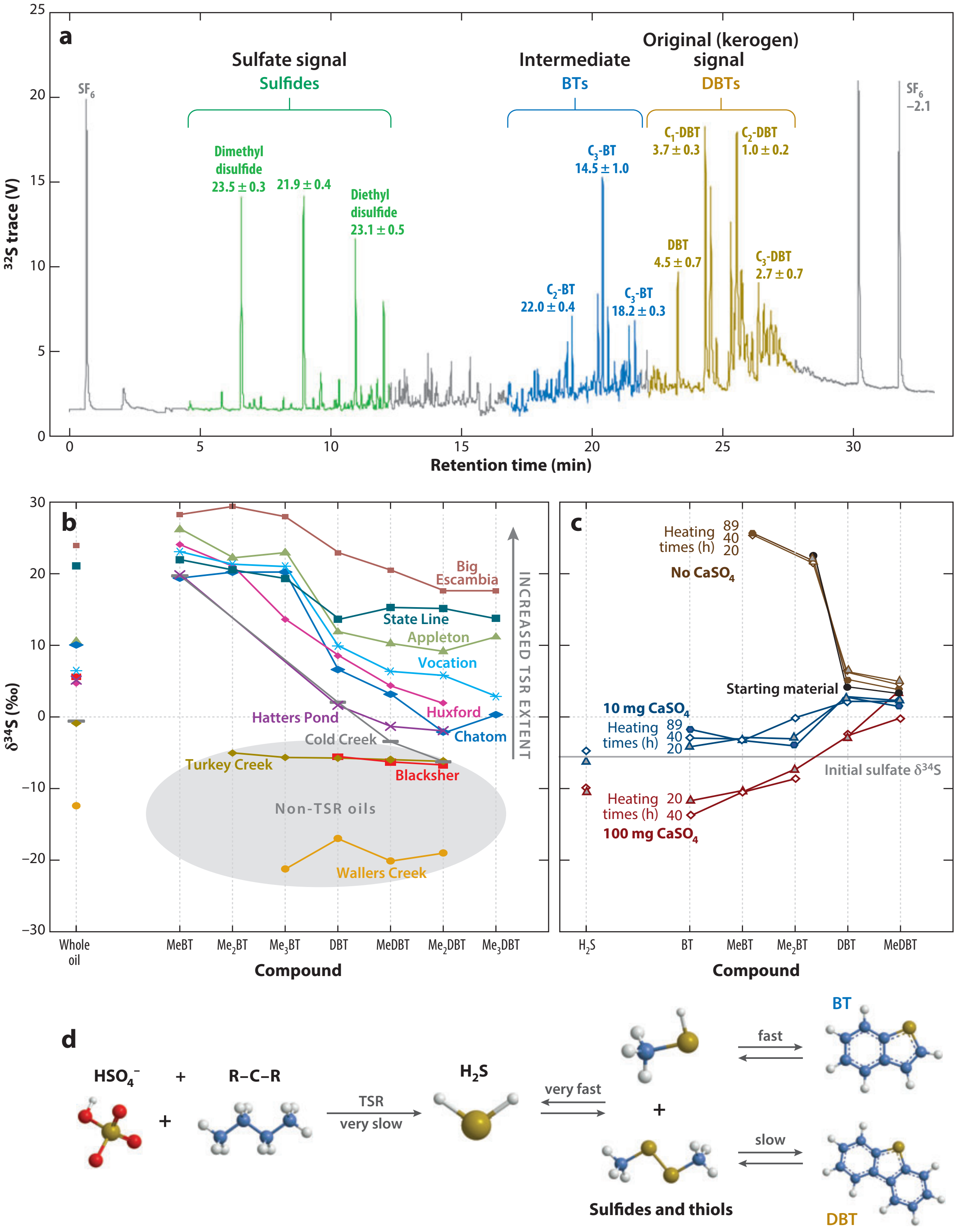
Closed-system pyrolysis experiments on isolated kerogen from the Monterey Formation showed that the S isotope fractionation associated with the formation of bitumen and petroleum from kerogen is relatively small (Idiz et al. 1990). Hydrous pyrolysis experiments (200°C to 360°C) of immature kerogen from the Ghareb Formation showed similar results, with less than 2‰ difference between kerogen, bitumen, oil, and H_2S of all thermal stages (**Figure 6*d***) (Amrani et al. 2005a). The oil samples were consistently ^{34}S enriched compared with their source kerogen (unheated), as has also been observed in natural maturation systems (Aizenshtat & Amrani 2004b, Orr 1986). Furthermore, compound-specific S isotope study of petroleum samples during artificial thermal maturation in closed system (360°C) showed that BTs and DBTs change only slightly (up to 3‰) (**Figure 7*c***) (Amrani et al. 2012a). These results suggest that thermally stable OSCs "lock" their S and preserve its isotopic signature.

Moreover, despite the notion that the δ^{34}S of oil is typically the collective product of different lateral and stratigraphic facies of a maturing source rock, there are numerous studies that report a relatively narrow range of δ^{34}S values for related oils in the same basin (oil-oil correlation). The standard deviation in many of these studies ranged between 1‰ and 3‰ (Gaffney et al. 1980, Manowitz et al. 1990, Thode 1981), which is in agreement with laboratory experiments (Amrani et al. 2005a). This further suggests that the δ^{34}S changes during thermal maturation are relatively small and supports the application of δ^{34}S for source rock–oil and oil-oil correlation studies (Orr 1986, Thode 1981).

However, these small observed fractionations are somewhat misleading, as there is a relatively large kinetic isotope effect in the cleavage of the C–S bond (Amrani et al. 2005b). This large fractionation can only be recorded in the initial stages during closed-system pyrolysis or in open pyrolysis systems where H_2S is instantaneously trapped after its formation (Amrani et al. 2005a). The pyrolysis of a synthesized S cross-linked polymer at 200°C resulted in fractionations of up to −9.5‰ from the earliest-trapped H_2S (**Figure 5**) (Amrani et al. 2005b). Larger fractionations of −20‰ were recorded between organic S (kerogen, bitumen, and oil) and H_2S in the initial stages of hydrous pyrolysis experiments using mass balance calculations based on the composition of secondary pyrite formed by the thermal degradation of OSCs (Amrani et al. 2005a).

Vredenburgh & Cheney (1971) suggested that preferential loss of isotopically light H_2S during maturation through migration from its source kerogen could yield ^{34}S-enriched oil. Metal scrubbing of thermally released H_2S (Worden et al. 2003) can also prevent it from back-reacting with organic matter. In a closed system where H_2S cannot escape, isotopic mixing gradually erases this kinetic isotope effect of the initial C–S bond rupture, and the differences between OSCs and H_2S will decrease to small values (Amrani et al. 2005b, 2006b). Heating experiments with polysulfide cross-linked polymer and HS^- with distinct δ^{34}S values showed rapid (i.e., hours) isotope mixing between the two (**Figure 6*c***) (Amrani et al. 2006b).

A clear order of isotope mixing rates, from fastest to slowest, was observed for Ghareb Formation samples, immature kerogen > immature asphalt > oil, which correlates inversely with the thermal stability of their OSCs (Amrani et al. 2006b). This suggests that the isotopic mixing rates are dependent on the OSC structure, which in turn is influenced by the thermal maturity level (**Figure 6**), implying that S isotopes in thermally mature organic matter are homogenized. Differences between the asphaltene, saturate, aromatic, and NSO petroleum fractions are indeed small (Méhay et al. 2009, Thode 1981). Petroleum samples that were not affected by thermochemical processes show very uniform δ^{34}S values among individual OSCs (**Figure 7*b***) (Amrani et al. 2012a).


a
Sulfate signal
Sulfides
Intermediate
BTs
Original (kerogen) signal
DBTs
SF$_6$
SF$_6$ −2.1
Dimethyl disulfide 23.5 ± 0.3
21.9 ± 0.4
Diethyl disulfide 23.1 ± 0.5
C$_2$-BT 22.0 ± 0.4
C$_3$-BT 14.5 ± 1.0
C$_3$-BT 18.2 ± 0.3
C$_1$-DBT 3.7 ± 0.3
C$_2$-DBT 1.0 ± 0.2
DBT 4.5 ± 0.7
C$_3$-DBT 2.7 ± 0.7
^{32}S trace (V)
Retention time (min)
0
5
10
15
20
25
30
b
δ^{34}S (‰)
Big Escambia
State Line
Appleton
Vocation
Hatters Pond
Huxford
Cold Creek
Chatom
Turkey Creek
Blacksher
Non-TSR oils
Wallers Creek
INCREASED TSR EXTENT
Whole oil
MeBT
Me$_2$BT
Me$_3$BT
DBT
MeDBT
Me$_2$DBT
Me$_3$DBT
Compound
30
20
10
0
−10
−20
−30
c
Heating times (h) 89 40 20
No CaSO$_4$
Starting material
10 mg CaSO$_4$
Heating times (h) 89 40 20
Initial sulfate δ^{34}S
Heating times (h) 20 40
100 mg CaSO$_4$
H$_2$S
BT
MeBT
Me$_2$BT
DBT
MeDBT
Compound
d
HSO$_4^-$
+
R–C–R
+
TSR
very slow
H$_2$S
very fast
fast
BT
+
slow
Sulfides and thiols
DBT

In summary, correlation between oil and its source rock using $\delta^{34}S$ measurements can serve as a reliable tool only when thermal maturation and petroleum generation are known to have taken place in a closed system (Amrani et al. 2005b).

5.1. Exogenous Sulfur Incorporation into Organic Matter

Biological degradation, water washing, and hydrothermal alteration can significantly affect the composition of organic matter in petroleum reservoirs and the S isotope distribution of its organic and inorganic S species (Thode 1981). Two processes are particularly important: TSR and MSR. These processes oxidize organic matter in two distinct temperature regimes:

$$\begin{aligned}\text{Hydrocarbons} + \text{CaSO}_4 \rightarrow \text{CO}_2 + \text{H}_2\text{S (and other reduced S forms)} + \text{altered hydrocarbons}\\ + \text{solid bitumen (or pyrobitumen).}\end{aligned} \tag{5}$$

Microbial alteration of petroleum may occur when the burial depth of a reservoir is shallow or when a deeper reservoir is uplifted to shallower depths with a sufficient supply of sulfate minerals at temperatures up to 80°C (Machel 2001). TSR involves the abiogenic oxidation of hydrocarbons coupled to the reduction of sulfate in hot (>110°C) petroleum reservoirs (commonly carbonate). It is a multistep, thermodynamically driven, and kinetically controlled reaction that requires high activation energy to cleave the very stable sulfate ion bonds (Goldstein & Aizenshtat 1994, Ma et al. 2008).

These two processes produce high concentrations of H_2S that can react with petroleum hydrocarbons and form secondary OSCs (Cai et al. 2003). At high temperature under a TSR regime, a pyrobitumen, composed of condensed aromatic and thiophenic molecules, is commonly formed

Figure 7

(*a*) GC-MC-ICP-MS (gas chromatography–multicollector inductively coupled plasma mass spectrometry) chromatogram (^{32}S trace) of a low-sulfur Caspian Sea crude oil showing the large variability (~20‰) in $\delta^{34}S$ of specific organosulfur compounds (OSCs). The thermally labile sulfides carry the ^{34}S-enriched value of H_2S derived from thermochemical sulfate reduction. The dibenzothiophenes (DBTs) preserve their original $\delta^{34}S$ (from kerogen), and the benzothiophenes (BTs) have intermediate $\delta^{34}S$ values. Values are the averages of three separate injections, shown with their error ($\pm 1\sigma$) in per mill (‰) units. SF_6 ($\delta^{34}S = -2.1‰$) was used as an internal standard for isotopic calibration. Adapted with permission from Amrani et al. (2009). Copyright 2009 American Chemical Society. (*b*) $\delta^{34}S$ values of individual OSCs and bulk $\delta^{34}S$ values of whole oils sourced in the Smackover Formation (United States). The difference between individual compounds exceeds 50‰ and represents increasing levels of thermochemical sulfate reduction (TSR). The non-TSR-affected oils have lower $\delta^{34}S$ values, and the difference between BTs and DBTs is small. In TSR-affected oils, BTs are always ^{34}S enriched compared with DBTs, and the difference between the two OSC groups decreases with increasing TSR extent. Whole oils were injected with no pretreatment into the GC-MC-ICP-MS. Specific isomers for which data are plotted are 2-MeBT; 2,6/2,5-Me_2BT; 2,3,5/2,3,6-Me_3BT; DBT; 4-MeDBT; 2,6/3,6-Me_2DBT; and 2,4,6-Me_3DBT. (*c*) $\delta^{34}S$ values of individual BTs and DBTs from TSR laboratory simulation experiments, showing the significant effect of TSR on the $\delta^{34}S$ values of individual BTs and DBTs in petroleum (Caspian oil). The experiments were conducted in gold tubes at 360°C for different periods (20, 40, and 89 h) in confined pressure. Parallel experiments were conducted with no $CaSO_4$ (negative control), with 10 mg $CaSO_4$ (low sulfate), and with 100 mg $CaSO_4$ (high sulfate). The gray line represents the initial $\delta^{34}S$ value of the $CaSO_4$ that was added to the pyrolysis experiments (−5.3‰). The $\delta^{34}S$ values of individual S compounds were measured by GC-MC-ICP-MS and H_2S samples analyzed by EA-IRMS as Ag_2S. Panels *b* and *c* adapted from Amrani et al. (2012a) with permission. The experiments show that the $\delta^{34}S$ values of BTs change rapidly, whereas those of DBTs change at a much slower rate. (*d*) General scheme for the effect of TSR on the $\delta^{34}S$ of sulfides and thiols, BTs, and DBTs. The first stage is the reduction of SO_4^{2-} (in its reactive form HSO_4^-) by hydrocarbons; this stage is very slow and requires catalysis. The H_2S that forms from the reduction of sulfate typically has $\delta^{34}S$ similar to that of its precursor. In the next stage, H_2S reacts very quickly with hydrocarbons to form labile OSCs such as thiols and sulfides. These labile OSCs form and degrade rapidly and maintain a steady state with H_2S; thus, their $\delta^{34}S$ values are similar. Some of these labile molecules cyclize to form aromatic S compounds such as BTs and DBTs. The original and isotopically distinct BTs and DBTs of the oil mix with the newly generated ones. Because BTs are more reactive than DBTs, they change their $\delta^{34}S$ much more quickly and approach the $\delta^{34}S$ of H_2S. DBTs preserve their original (kerogen) values for a longer time.

(Walters et al. 2011). The TSR process in petroleum reservoirs significantly reduces the quality of petroleum. The toxicity and corrosiveness associated with the large amounts of H_2S and CO_2 gases lead to greater production costs and environmental risk. Hence, it is important to improve our geochemical understanding of TSR for petroleum exploration and development.

The introduction of evaporite-sourced S can have a significant impact on the $\delta^{34}S$ of OSCs (Cai et al. 2005, Manzano et al. 1997, Orr 1974, Zhang et al. 2005). Moreover, TSR or MSR can alter the $\delta^{34}S$ record of both pyrite and sulfate minerals and can thus bias the interpretation of ancient redox changes in the oceans or the geochemical system where kerogen and petroleum are generated and accumulated. Most TSR case studies show little or no fractionation between H_2S and its $CaSO_4$ source (Cai et al. 2003, Krouse 1977, Worden & Smalley 1996). Theoretical models predict a substantial kinetic isotopic effect associated with initial cleavage of the S-O bond in sulfate (Goldstein & Aizenshtat 1994, Harrison & Thode 1957). Experiments have shown that the fractionation between the $\delta^{34}S$ of SO_4 and H_2S can be greater than −10‰ (Kiyosu 1980, Kiyosu & Krouse 1993). Recent studies demonstrated an even larger fractionation of up to −21‰ (Amrani et al. 2011, Watanabe et al. 2009). A possible reason for the apparent contradiction between laboratory and field observations may be that the TSR reaction in oil reservoirs is limited by the dissolution of solid sulfate minerals (Machel et al. 1995, Powell & Macqueen 1984). Therefore, TSR in oil reservoirs is thought to produce ^{34}S-enriched H_2S close to its parent gypsum or anhydrite $\delta^{34}S$ value (Machel 2001). In contrast, MSR fractionates S isotopes, and the resulting H_2S is ^{34}S depleted, as described above. Therefore, back-reaction of MSR S with petroleum may yield ^{34}S-depleted OSCs (Machel et al. 1995, Méhay et al. 2009, Orr 1977). However, recent study suggests that there are no significant changes in the $\delta^{34}S$ of petroleum even under severe biodegradation (Marcano et al. 2013).

5.2. The Sulfur Isotopic Signature of Dibenzothiophenes and Benzothiophenes as a Proxy for Thermochemical Sulfate Reduction

Compound-specific analyses of the $^{34}S/^{32}S$ isotope ratios of individual OSCs in oil from the Caspian Sea area (**Figure 7*a***) revealed large variations (up to ∼20‰) in $\delta^{34}S$ between alkyl sulfides, BTs, and DBTs (Amrani et al. 2009). DBTs were significantly depleted in ^{34}S compared with alkyl sulfides, whereas BTs had intermediate values. These differences in $\delta^{34}S$ may be explained by the different thermal stabilities of these compounds. Alkyl sulfides are the most labile and thermally unstable compounds; they form and degrade instantly during TSR in the presence of H_2S (Amrani et al. 2008b, Zhang et al. 2008). Therefore, these compounds reflect the $\delta^{34}S$ of the instantaneous H_2S in the reservoir. In contrast, DBTs are more thermally and chemically stable; they thus form and degrade at a much slower rate and preserve their original, non-TSR-altered $\delta^{34}S$ values longer. BTs have intermediate stability. Therefore, the $\delta^{34}S$ variations between individual compounds (i.e., sulfides, BTs and DBTs) represent the difference between TSR-affected compounds and the original sedimentary OSCs (Amrani et al. 2012a).

A detailed compound-specific S isotope study was conducted with oil and condensate samples from the Upper Jurassic in the Smackover Formation (United States) (Amrani et al. 2012a). Differences of up to ∼50‰ were measured between individual OSCs in TSR-altered oils and those in unaltered oils (**Figure 7*b***). Oils that did experience TSR exhibit significant ^{34}S enrichment of BTs compared with DBTs, whereas in unaltered oils these compounds have similar isotopic compositions (**Figure 7*b***). The $\delta^{34}S$ values of BTs are close to those of sulfates in evaporites of the Smackover Formation, whereas the $\delta^{34}S$ values of DBTs are spread over a wider range and gradually approach those of the BTs.

Gold-tube hydrous pyrolysis experiments using three representative oil samples have shown that isotopic alteration readily occurs under TSR conditions and can significantly affect the $\delta^{34}S$ values of individual compounds (**Figure 7*c***). These results indicate that BTs can be a sensitive tracer for TSR, as they form readily under TSR conditions, with large ^{34}S enrichments relative to bulk oil. In contrast, DBTs exhibit relatively small changes in $\delta^{34}S$, preserving their original $\delta^{34}S$ values longer than do BTs because of their greater thermal stability and slow rate of formation (**Figure 7*d***). Therefore, the $\delta^{34}S$ values of BTs and DBTs can be used in conjunction to detect TSR alteration of oils from very early to highly altered oil (Amrani et al. 2012a).

5.3. Sulfurized Diamondoids as a Molecular Proxy for Thermochemical Sulfate Reduction

Diamondoids found in petroleum are believed to form by carbonium ion rearrangements of the appropriate organic precursors on clay mineral in the source rock during oil generation (Wei et al. 2006). Diamondoids have unusually high thermal stability relative to that of other crude-oil compounds. They therefore concentrate during petroleum maturation and oil cracking to gas and are used as a thermal maturation proxy (Dahl et al. 1999). At higher thermal and redox stress, even these extremely stable compounds may react with S species (Wei et al. 2007). Diamondoid sulfides (e.g., thiadiamondoids) and diamondoidthiols are the main sulfurized diamondoid compounds that are formed (Wei et al. 2011). **Figure 8*a*** presents some thiadiamondoids with differing numbers of cages.

Hanin et al. (2002) found that alkylated 2-thiaadamantanes are present only in TSR-altered oils and that their $\delta^{34}S$ value is similar to the parent anhydrite in the Smackover Formation reservoirs. The authors further proposed these compounds as molecular markers to indicate the occurrence of TSR in petroleum reservoirs. The relatively high abundance of polythiadiamondoids—including dithiaadamantanes, trithiaadamantanes, dithiadiamantanes, and trithiadiamantanes—in TSR-altered oils is indicative of cage cleavage occurring in the presence of reduced S species (Wei et al. 2011). Sulfurized diamondoids are suggested to originate exclusively from TSR alteration (Hanin et al. 2002, Wei et al. 2012) and have been found in numerous TSR-altered oil reservoirs, including the Tarim Basin, China (Cai et al. 2009b). Their high thermal stability allows them to preferentially survive TSR alteration if not exposed to extremely high reservoir temperatures. The thermal stability of thiadiamondoids is between that of DBTs and diamondoid hydrocarbons and increases with increasing cage number. There is a strong correlation between the concentrations of thiadiamondoids, DBTs, and H_2S in TSR-altered oils. Moreover, there is a positive correlation between the thiadiamondoid concentration and the $\delta^{34}S$ of oils (**Figure 8*b***). The increase in the $\delta^{34}S$ of the oils is expected because of the back-reaction of H_2S derived from ^{34}S-enriched $CaSO_4$ (Manzano et al. 1997, Orr 1974). It is therefore suggested that the abundance of these species reflects both the occurrence and the extent of TSR (Wei et al. 2012).

In general, sulfurized diamondoid data determined for samples of the Smackover Formation agree with the BT/DBT compound-specific S isotope approach, except for two cases (**Figure 7*c***). In these two cases, the sulfurized diamondoid data suggest that the oils did not experience TSR, whereas the BT/DBT data suggest that they are in very early stages of TSR (Amrani et al. 2012a). These data may indicate that the BT/DBT approach is more sensitive in the earliest stages of TSR and then loses sensitivity as TSR proceeds, because it reaches S isotope steady state between H_2S and OSCs (Amrani et al. 2012a). In contrast, sulfurized diamondoids seem to be more sensitive to high levels of TSR (Wei et al. 2011, 2012). The advantage of both of these molecular approaches is that all the information needed to assess TSR is embedded within the oil itself, and there is

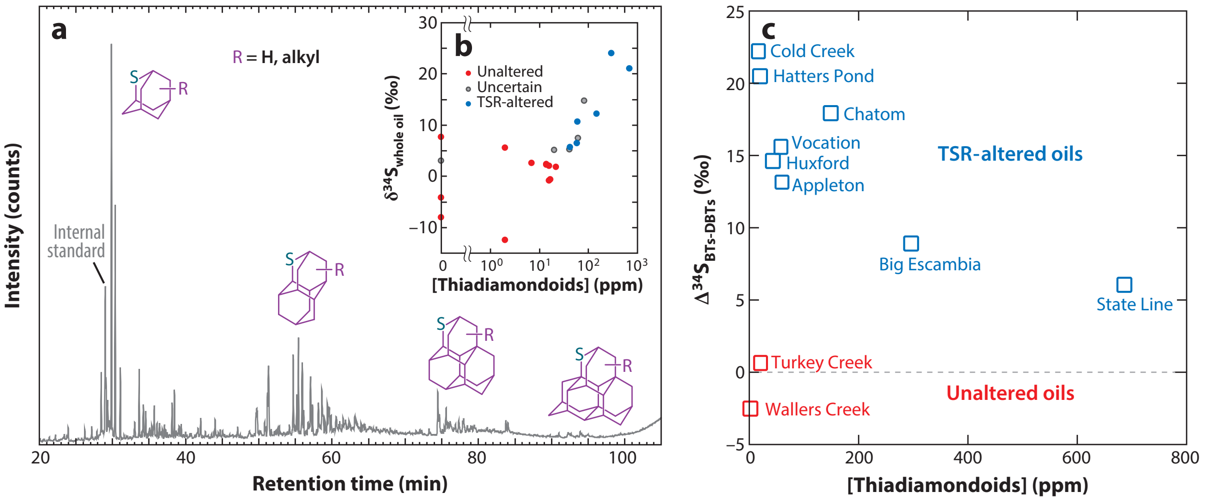


Figure 8

(*a*) Total ion chromatogram of thiadiamondoids separated from the OSC fraction of South State Line (Smackover Formation, United States) oil. This is a highly TSR-altered oil, and the thiadiamondoid fraction includes thiaadamantanes, thiadiamantanes, thiatriamantanes, and thiatetramantanes. The internal standard is D3-1-methyl- 2-thiaadamantane. Thiadiamondoids are found in high concentrations in TSR-altered oils. (*b*) Comparison of the abundance of thiadiamondoids (low volatility) with the δ^{34}S of whole oil known to reflect TSR alteration, showing a positive correlation. The high δ^{34}S values of whole oils are interpreted as indicating a TSR origin of their OSCs. These results show that thiadiamondoid concentration can be used as a tracer for TSR extent. Panels *a* and *b* adapted from Wei et al. (2012) with permission. (*c*) Sulfur isotope fractionation between benzothiophene (BT) and dibenzothiophene (DBT) isomers ($\Delta^{34}S_{BTs-DBTs}$) as a function of total thiadiamondoid concentration. Adapted from Amrani et al. (2012a) with permission. The fractionation between BTs and DBTs is negatively correlated with the extent of TSR as represented by increased thiadiamondoid concentration. Thiadiamondoids include trimethyl and tetramethyl thiaadamantanes; thia-, methyl, dimethyl, and trimethyl thiadiamantanes; and thia-, methyl, dimethyl, and trimethyl thiatriamantanes (Wei et al. 2011). The plotted δ^{34}S values for alkylated BTs and DBTs are the numerical averages of all measured isomers.

no need to collect gases or minerals from the reservoir. Application of the S isotope compound-specific approach on other compounds such as sulfurized diamondoids can create a multiparameter system, based on molecular and δ^{34}S values, that will be sensitive within a wide range of TSR and thermal maturation stages.

SUMMARY POINTS

1. Abiotic sulfurization of organic matter and the formation of OSCs are early diagenesis processes that occur rapidly in oxygen-depleted environments. The chemical structures and S isotopic compositions of OSCs are distinct from those of biosynthetic species and are dominated by reduced C–S and S–S bonds. The formation of S cross-linked macromolecules enhances the preservation of organic matter, as it decreases its availability for bacterial mineralization.
2. The ultimate source of reactive, inorganic reduced S species is MSR, which has an associated S isotope fractionation of up to −75‰. As a result, OSCs are ^{34}S depleted compared with their source sulfate and biosynthetic S.

3. Globally, bulk organic sulfur is ^{34}S enriched compared with co-occurring pyrite by an average of 10‰ and as much as 30‰. Compound-specific studies show larger S isotope variations relative to pyrite. This phenomenon can be explained by the timing and mechanisms of OSC formation during diagenesis. OSC isotopic signatures reflect variations in the magnitude of S isotope fractionation during the formation of OSCs, the specific S species incorporated, and the rate and extent of isotope mixing between OSCs and ^{34}S-enriched inorganic S species during burial.
4. Thermal maturation of OSCs has a significant effect on their chemical structure, gradually transforming them to aromatic OSCs and releasing large amounts of H_2S. There is a large kinetic isotope effect during the cleavage of C–S and S–S bonds that results in fractionations of up to −20‰ in the released H_2S. This can only be observed in the initial stages of thermal maturation or in an open system where H_2S can escape or be trapped (e.g., by metals). As a result, there is a general trend of ^{34}S enrichment with maturity. Rapid isotope mixing between OSCs and reduced inorganic S species causes a gradual isotope homogenization of both S pools in a closed system. This leads to small (1–3‰) overall fractionation between the source kerogen and its associated H_2S and oil.
5. Exogenous S incorporation to organic matter can significantly affect the S isotope composition of OSCs in petroleum reservoirs. Compound-specific S isotope studies show up to 50‰ variation between individual OSCs from the same source as a result of TSR. This S isotope effect is associated with the back-reaction of ^{34}S-enriched H_2S-sourced anhydrites with petroleum hydrocarbons. The δ^{34}S variations between individual compounds (i.e., sulfides, BTs, and DBTs) represent the difference between TSR-affected compounds and the original sedimentary OSCs. BTs can be a sensitive tracer for TSR because they form readily under TSR conditions, with large ^{34}S enrichments relative to bulk oil. In contrast, DBTs exhibit relatively small changes in δ^{34}S, preserving their original δ^{34}S values longer than do BTs because of their greater thermal stability and slow rate of formation. Therefore, the δ^{34}S values of BTs and DBTs can be used to detect TSR alteration of oils from the very early stages up to high degrees of alteration.
6. Compound-specific S isotope analysis of sedimentary organic matter can provide a valuable tool to determine past and ongoing processes. Combining detailed elucidation of structure and the associated S isotope values can help unravel the complex and dynamic organic-inorganic S cycle. Work is ongoing to develop more molecular and isotopic tools for a variety of geochemical problems in which S is an important player.

FUTURE ISSUES

1. The new analytical capabilities of S isotope measurements including compound-specific analysis, spatial solid-state analysis, and rare isotopes (^{33}S and ^{36}S) of OSCs provide us with a wealth of new information. However, this information remains difficult to interpret due to our limited understanding of the factors controlling S isotope distribution in OSCs throughout their formation and maturation.

2. Thus, one of the most important future challenges is the study of the magnitude and variation of S isotope fractionations during the different stages of OSC formation and maturation at the molecular level. This will require definitive structure identification, laboratory experiments, and field observations. The interaction and isotope mixing between organic and inorganic S species and their mutual effects on S isotope distribution should also be better understood in order to develop new or improved paleoenvironmental proxies (e.g., redox). The spatial distribution of S isotopes in both OSCs and S minerals (e.g., pyrite) in solid samples can also help in that regard.
3. Another important issue is the possible mass-independent fractionation record using ^{33}S and ^{36}S of ancient OSCs. OSCs may carry important signals that may not be seen in the bulk pyrite and sulfate that are conventionally measured.

DISCLOSURE STATEMENT

The author is not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

ACKNOWLEDGMENTS

I appreciate the helpful comments and suggestions on earlier versions of this article by Ron Hill, Baruch Spiro, Mike Lewan, Itay Reznik, Geoffrey Ellis, Sabine Méhay, and two anonymous reviewers. I thank Ward Said-Ahmad and Guy Dror for intensive assistance in formatting the figures and references.

Special thanks go to Zeev Aizenshtat, who introduced me to and guided me through the world of sulfur during my graduate studies at HUJI, and to Alex Sessions for the opportunity to develop and work on compound-specific S isotope analysis during my postdoctoral fellowship at Caltech.

This study was supported by the Israeli Science Foundation (ISF) grant number 0398654.

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