

## ***Organic sulfur biogeochemistry: Recent advances and future research directions***

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### **ABSTRACT**

**The biogeochemistry of sulfur is of widespread interest in the earth science community due to its impact on many different biogeochemical processes. Organic sulfur is of particular interest due to its impact on petroleum formation and refining and its relationship to microbial sedimentary processes, organic carbon accumulation, and the overall integrity of paleoenvironmental proxy records. This paper reviews many of the advances in organic sulfur biogeochemical research spanning the past ~15 years. These advances include (1) an improved mechanistic understanding of why sulfur-rich organic deposits form petroleum products earlier during diagenesis than sulfur-poor deposits, (2) constraints on the timing and pathways of organic sulfur formation as well as the forms of organic sulfur present in the environment, and (3) recognition of the impacts of organic matter sulfurization on organic carbon preservation at bulk and molecular scales and the implications of this enhanced preservation for paleoenvironmental studies.**

**Keywords:** Organic sulfur, sedimentary sulfur, sulfur isotopes, macromolecular sulfur, global sulfur cycle.

### **INTRODUCTION**

The sulfurization of organic matter is a globally significant biogeochemical process that has long been a topic of investigation. Among the reasons for this longstanding interest are the

relationships between organic sulfur and (1) petroleum formation and quality, (2) the coupled global biogeochemical cycles of carbon, sulfur, and oxygen, (3) sedimentary microbial activity, and (4) organic matter preservation and molecularly based paleoenvironmental reconstructions. Despite the importance of

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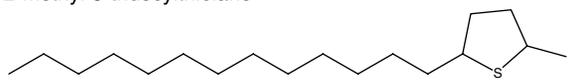
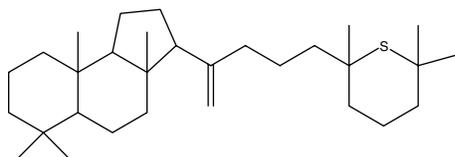
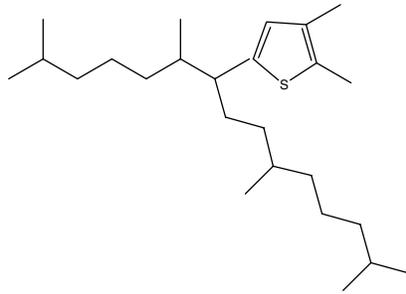
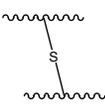
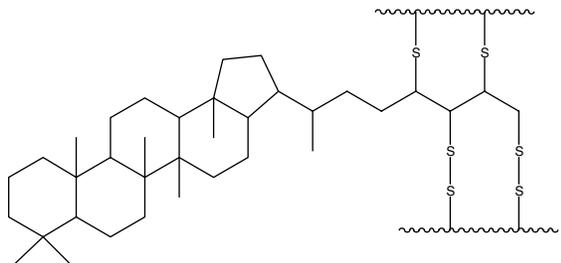
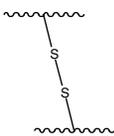
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organic sulfur, our understanding of the processes surrounding its formation remains incomplete. One reason that the sulfurization of organic matter is poorly constrained is the wide variety of organic sulfur compounds found in nature, which appear to form via a range of possible mechanisms. For example, sulfur can be incorporated intramolecularly into organic compounds, forming a cyclo-sulfur group such as a thiophene or thiane, or it can be incorporated intermolecularly, resulting in organic compounds linked via C-S<sub>x</sub>-C bonds into a macromolecular matrix. Table 1 illustrates some of the varieties of organic sulfur compounds identified in natural systems.

A second reason for gaps in our knowledge of organic sulfur formation is the complexity of biological and abiological sedi-

mentary sulfur cycling (Fig. 1). Pore-water sulfide, which can be incorporated into organic matter, can react with iron to form iron monosulfides and ultimately pyrite. Additional reactions include oxidation of sulfide to sulfate and partial oxidation of sulfide to "reactive intermediates" such as polysulfides, elemental sulfur, thiosulfate, polythionates, and sulfite (Table 2). Sulfide can be oxidized by many pathways involving, for example, oxygen diffusing down from the water column, nitrate, (iron) oxide or oxyhydroxide minerals, or microbes (e.g., *Beggiatoa* sp.). Reactive intermediates produced through partial oxidation can then undergo a number of reactions, including disproportionation to sulfate and sulfide, complete reduction, or complete oxidation. Finally, sulfide can also diffuse upward into the overlying water

TABLE 1. EXAMPLES OF TYPICALLY ENCOUNTERED ORGANIC SULFUR COMPOUNDS

OSC type	General structure	Example	Reference
<u>Intramolecular S incorporation</u>			
thiolane		2-methyl-5-tridecylthiolane 	Kohnen et al., 1991b
thiane		malabarica-thiane 	Werne et al., 2000
thiophene		highly-branched isoprenoid thiophene 	Respondek et al., 1997
<u>Intermolecular S incorporation</u>			
sulfide linked		intermolecularly bound bacteriohopanoid 	de Leeuw and Sinninghe Damsté, 1990
polysulfide linked			

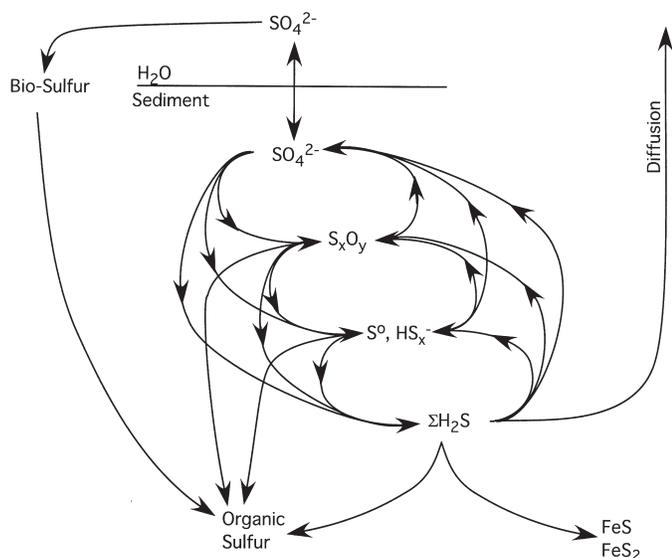


Figure 1. Schematic diagram illustrating the complex cycling of sulfur in sediments. The left side of the diagram shows reduction processes, including bacterial sulfate reduction and the reductive portion of disproportionation. The right side of the diagram shows oxidative processes, including microbial and/or abiotic (partial) sulfide oxidation as well as the oxidative portion of disproportionation. Arrows indicate directions of sulfur "flow" during sulfur cycling, whether chemical, as in the case of sulfate reduction or disproportionation reactions, or physical, as in diffusion of sulfide back into the overlying water column. Also included is the biological assimilation of sulfate into biomass and its deposition in sediments, and formation of iron sulfides. Possible immediate sources of organic sulfur include bio-sulfur, sulfides, and partially oxidized reactive intermediates such as elemental sulfur ( $S^0$ ), polysulfides ( $HS_x^-$ ), polythionates, thiosulfate, and sulfite (collectively represented as  $S_xO_y$  in the figure).

column. It is not known with certainty whether the sulfur that is incorporated into organic matter is pore-water sulfide, some other pool of reduced sulfur, such as polysulfides or elemental sulfur, or a mixture of different sources.

Dissimilatory bacterial reduction of dissolved sulfate is the primary means by which reduced sulfur (e.g.,  $H_2S$ ) is produced in the natural environment. There are many proposed chemical pathways to explain the incorporation of aqueous sulfides into organic matter, and in actuality, several are likely to be operating simultaneously. The dominant mechanisms would vary according to specific environmental conditions.

In order for organic sulfur formation to occur, certain depositional conditions must be met. First, there must be an adequate supply of reduced sulfur species, which implies the presence of anoxic conditions and sufficient sulfate reduction to produce the sulfide from which all other reduced sulfur species are derived. Second, there must be significant quantities of reactive organic matter present. This organic matter serves two purposes: it acts as a substrate supporting bacterial sulfate reduction, thus providing the reduced sulfur, and it reacts directly with the reactive reduced

TABLE 2. REACTIVE (R) AND NON-REACTIVE (NR) SULFUR SPECIES INVOLVED IN SEDIMENTARY CYCLE OF SULFUR AND THEIR OXIDATION STATES.

Compound	Formula	Oxidation state of sulfur	R/NR
sulfate	$SO_4^{2-}$	+6	R
sulfite	$SO_3^{2-}$	+4	R
tetrathionate	$S_4O_6^{2-}$	+2.5	R
thiosulfate	$S_2O_3^{2-}$	+2	R
elemental sulfur	$S_8 (S^0)$	0	R?
polysulfides	$HS_x^-, S_x^{2-}$	$\sim -0.5$	R
organic sulfur (disulfide)	R-S-S-R	-1	NR
pyrite	$FeS_2$	-1	NR
iron monosulfide	$FeS$	-2	R?
organic sulfur (thiol)	R-SH	-2	NR
bisulfide	$HS^-$	-2	R
hydrogen sulfide	$H_2S$	-2	R?

sulfur to form organic sulfur compounds. Organic matter content in sedimentary environments is typically enhanced by the presence of anoxic to euxinic conditions due to the exclusion of burrowing macrofauna. Finally, because pyrite formation is believed to be a kinetically favored process relative to organic matter sulfuration (Gransch and Posthuma, 1974), the environment must have a limited availability of reactive iron species (iron oxides and oxyhydroxides; Canfield, 1989; Canfield et al., 1992, 1996).

This final condition of the environment may not be absolutely required, as various studies have demonstrated the simultaneous formation of organic sulfur and iron sulfides (Brüchert and Pratt, 1996; Bates et al., 1995; Urban et al., 1999; Filley et al., 2002). Indeed, it may be that rapid input of iron oxides can actually promote both the sulfuration of organic matter and the formation of iron sulfides through the rapid production of polysulfides, as suggested by Filley et al. (2002). It has also been pointed out that frequent oscillations between oxidizing and reducing conditions may act as a catalyst for formation of both iron sulfides and organic sulfur through production of reactive intermediate sulfur species such as polysulfides, thiosulfate, and polythionates (Boulègue et al., 1982; Luther and Church, 1988; Ferdelman et al., 1991).

A full review of organic sulfur biogeochemistry is beyond the scope of this paper (for a thorough review of organic sulfur research up to 1990, see Sinninghe Damsté and de Leeuw [1990]). The focus of this paper is therefore on significant advances over the past 15 years.

## ORGANIC SULFUR AND PETROLEUM FORMATION

All fossil fuels contain sulfur, ranging from trace amounts to more than 14% by weight (Orr and Sinninghe Damsté, 1990). In fact, the largest petroleum systems in the world are carbonate-evaporite sequences, which are typically high in sulfur (Vairavamurthy et al., 1995). Few crude oils with more than 4% sulfur are produced industrially, however, because organic sulfur compounds react during the refining process to produce substances

such as sulfuric acid, which is corrosive and poisons catalysts, and sulfur dioxide, which contributes to numerous environmental problems such as acid rain (Orr, 1978; Tissot and Welte, 1984). In fact, the importance of organic sulfur in petroleum products has been recognized by a number of special sessions sponsored by the American Chemical Society Geochemistry Division, resulting in published proceedings volumes devoted to understanding the geochemistry of sulfur in fossil fuels (Orr and White, 1990) and the sedimentary environment (Vairavamurthy and Schoonen, 1995). Numerous research papers and reviews have been written about the geochemistry of sulfur in fossil fuels, including oils (Gransch and Posthuma, 1974; Orr and Sinninghe Damsté, 1990; Sinninghe Damsté et al., 1994), oil shales (Sinninghe Damsté et al., 1993; Barakat and Rüllkötter, 1995, 1999; de las Heras et al., 1997), and coals (Sinninghe Damsté and de Leeuw 1992; Sinninghe Damsté et al., 1999a; Sandison et al., 2002). Because of the large number of reviews on organic sulfur in petroleum systems in recent years, the focus here will be on a few studies that highlight the impact of organic sulfur on petroleum formation.

The quantity and forms of sulfur in petroleum systems are directly related to the properties of the source rocks from which their petroleum products were generated and therefore to the environment of deposition (Gransch and Posthuma, 1974). As mentioned previously, the organic sulfur content of a sedimentary deposit is controlled to a large extent by the availability of reduced sulfur species and by the availability of reactive iron (Canfield, 1989; Canfield et al., 1992, 1996). The formation of iron sulfides (e.g., pyrite,  $\text{FeS}_2$ ) in sedimentary systems is generally believed to be kinetically favored relative to the formation of organic sulfur in the presence of readily available reactive iron species (Gransch and Posthuma, 1974; Hartgers et al., 1997). Certain iron minerals, specifically the iron oxides and oxyhydroxides, are known to be highly reactive with respect to hydrogen sulfide (Canfield et al., 1992; Larson and Postma, 2001), and reactivities of different iron minerals have been shown to vary as a function of particle size distributions, among other factors (Larson and Postma, 2001). Thus, delivery of reactive iron minerals, which varies with climate and source area, could impact the availability of reactive iron in natural systems (G. Mora and L. Hinnov, 2003, personal commun.).

Sedimentary organic sulfur is often present as polysulfide linkages between compounds in the macromolecular matrix of organic-rich deposits (Aizenshtat et al., 1983; Kohnen et al., 1991a), though a number of different types of organic sulfur compounds have recently been identified in kerogens (see below). Sulfur-sulfur bonds are cleaved more easily than carbon-sulfur or carbon-carbon bonds (Aizenshtat et al., 1995). A number of recent studies have utilized artificial maturation of natural organic sulfur-rich kerogens and shales via hydrous pyrolysis (Lewan, 1993) to quantify the effect of these S-S bonds on petroleum formation (Krein and Aizenshtat, 1995; Nelson et al., 1995; Tomic et al., 1995; Koopmans et al., 1996; Putschew et al., 1998; Sinninghe Damsté et al., 1998a). All of these studies clearly demonstrated that sulfur-rich kerogens produced

petroleum under appreciably lower temperatures than their low sulfur counterparts, thus highlighting the impact of sulfur content on the kinetics of petroleum formation.

Of particular interest among the studies of hydrous pyrolysis is the investigation by Putschew et al. (1998), in which the remnant kerogens and pyrolysis products were also closely examined by molecular methods (stepwise selective chemical degradation) after artificial maturation. Although petroleum formation begins earlier due to the presence of organic sulfur, this study demonstrated that not all of the organic sulfur compounds were released. Indeed, much of the organic sulfur remained in the form of nonextractable, macromolecular organic matter (Putschew et al., 1998). Because this sulfur is no longer present in the kerogen, or in the petroleum products, it would be easily missed without molecular-level investigations.

These and many other studies implicate the relative weakness of S-S and C-S bonds compared to C-C bonds in petroleum formation. Alternatively, a recent study by Lewan (1998) suggested that it is not actually the relative weakness of S-S and C-S bonds that contributes to the early formation of high sulfur petroleum products. Instead, the presence of sulfur radicals may control petroleum formation rates. More specifically, the concentration of sulfur radicals generated during the initial stages of thermal maturation may be the critical factor, with greater concentration of sulfur radicals leading to more rapid petroleum generation (Lewan 1998). A second implication of the sulfur radical model is that once the petroleum products are generated and migrate away from the initial site of production, they will no longer be in contact with the sulfur radicals, which would slow the production of natural gas formed by continued cracking of C-C bonds. Lewan's (1998) study therefore provides an organic sulfur-dependent explanation for observed variation in petroleum formation rates (cf. Nelson et al., 1995; Tomic et al., 1995; Koopmans et al., 1996; Putschew et al., 1998; Sinninghe Damsté et al., 1998a) as well as the overall composition of the resulting petroleum.

## ORGANIC SULFUR AND GLOBAL BIOGEOCHEMICAL CYCLES

The global biogeochemical cycles of carbon, sulfur, and oxygen are linked through a complex system of oxidation-reduction reactions that occur at the surface of the Earth. These reactions moderate the balance between reduced and oxidized forms of C and S on time scales of millions of years. Modeling studies have demonstrated that the sequestration of reduced sulfur in sediments affects the biogeochemical cycles of sulfur, carbon, and oxygen and therefore the evolution of atmospheric  $\text{CO}_2$  and  $\text{O}_2$  concentrations over geologic time (Garrels and Lerman, 1981, 1984; Kump and Garrels, 1986; Berner, 1987; Petsch and Berner, 1998; Canfield et al., 2000). Pyrite is clearly the most quantitatively significant sink for reduced sulfur in the sedimentary environment (Garrels and Lerman, 1984; Berner and Raiswell, 1983), and global biogeochemical models have typically approximated

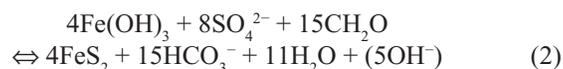
the total reduced sulfur pool as entirely pyrite sulfur. Recent studies, however, have shown that organic sulfur is also a significant pool of reduced sulfur (Anderson and Pratt, 1995; Vairavamurthy et al., 1995). Indeed, as much as 80% of the total reduced sulfur in some environments is present as organic sulfur (e.g., the Miocene Monterey Formation; see Fig. 2; Zaback and Pratt, 1992; Anderson and Pratt, 1995). A second potential source for error in model-based reconstructions of ancient atmospheric compositions is the fact that most models are dependent on assumptions made about the sulfur isotope offset between oxidized and reduced forms of sulfur (Garrels and Lerman, 1984; Kump and Garrels, 1986; Petsch and Berner, 1998). In general, a constant offset is assumed between the sulfur isotope composition of the total oxidized sulfur pool (estimated as sulfate in evaporite deposits) and the total reduced sulfur pool (estimated as pyrite). In a series of papers, however, Canfield and Teske (1996), Canfield (1998), Canfield and Raiswell (1999), Canfield et al. (2000), and Shen et al. (2001) argued that the offset between the sulfur isotope composition of sulfate and sulfides has changed significantly over geologic time. In addition, organic sulfur is generally enriched in  $^{34}\text{S}$  relative to pyrite (Fig. 2; Anderson and Pratt, 1995; Werne et al., 2003). Thus, because the percent of total reduced sulfur that is organic can vary with time, the actual isotopic offset between oxidized and reduced forms of sulfur in the natural environment is not constant. These factors suggest that organic sulfur formation and burial may have affected the evolution of the atmosphere over geologic time scales, and our ability

to model such changes is dependent on a better understanding of organic sulfur formation processes (Werne, 2000).

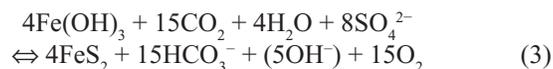
While the full suite of reactions involved in the coupled C, S, and O biogeochemical cycles is extremely complex, the reactions directly related to reduced sulfur burial and its relationship to atmospheric  $\text{O}_2$  and  $\text{CO}_2$  can be simplified. The first critical reaction is the production of organic matter via photosynthesis:



This reaction in reverse (noted by the bi-directional arrow) is aerobic respiration (organic oxidation). The second critical reaction is the formation and burial of reduced sulfur as pyrite.



Lumped into this overall reaction is both the production of hydrogen sulfide via bacterial sulfate reduction and concomitant organic matter oxidation and the reaction of the resulting  $\text{H}_2\text{S}$  with iron oxides and oxyhydroxides to form pyrite. By adding Equations (1) and (2), we see that the coupling of organic matter production with pyrite burial represents a net sink of  $\text{CO}_2$  and a net source of  $\text{O}_2$  to the atmosphere.



Alternatively, we can consider the formation and burial of organic sulfur. The relevant simplified equation for this process is a combination of production of hydrogen sulfide via bacterial sulfate reduction and organic matter oxidation and the reaction of sulfide with organic matter to produce organic sulfur.



Coupling this equation with organic matter production yields a net equation for organic matter production and organic sulfur burial.



This equation demonstrates that, as was the case for pyrite burial, organic sulfur burial is a net sink of  $\text{CO}_2$  and source for  $\text{O}_2$ .

There are two critical observations related to organic sulfur formation and burial that affect model-based reconstructions of atmospheric  $\text{O}_2$  and  $\text{CO}_2$ . The first is the change in molar stoichiometry from 15/8 ( $\text{O}_2$ /pyrite-S, Equation 3) to 15/5 ( $\text{O}_2$ /Org-S, Equation 5). This change in the molar ratio between  $\text{O}_2$  and S in itself implies a greater flux of  $\text{O}_2$  to the atmosphere per mole of sulfur buried. The second critical observation is related to the isotopic composition of reduced sulfur species. Models predicting atmospheric composition based on biogeochemical cycling of C and S typically assume an offset between oxidized sulfur

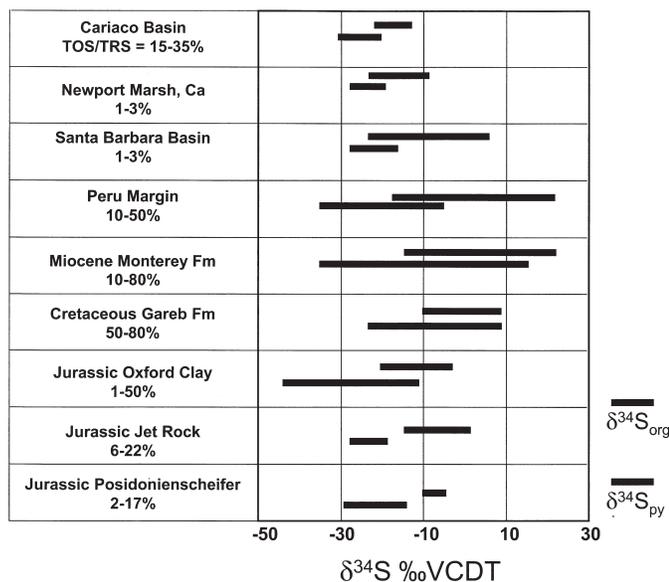


Figure 2. Summary diagram showing ranges of sulfur isotope compositions for pyrite sulfur ( $\delta^{34}\text{S}_{\text{py}}$ , black bars) and organic sulfur ( $\delta^{34}\text{S}_{\text{org}}$ , gray bars) in several environments. Beneath the name of each locality is the percent of the total reduced sulfur present as organic sulfur. Data are from Werne et al. (2003) and Anderson and Pratt (1995) and references therein. VCDT—Vienna Canyon Diablo Troilite.

(gypsum) and reduced sulfur (pyrite) of 35‰, based on the assumption that all reduced sulfur is present as pyrite. Organic sulfur is typically enriched in  $^{34}\text{S}$  by  $\sim 10\%$  relative to pyrite sulfur in coeval sediments (Anderson and Pratt, 1995), which would give an isotopic offset of 25‰ if all reduced sulfur were present as organic sulfur. Thus, by simple isotopic mass balance calculation it is clear that if all reduced sulfur is buried as organic sulfur, nearly 40% more sulfur must be buried in sediments in order to generate the sulfur isotope composition of seawater sulfate expressed in evaporite deposits over time (cf. Garrels and Lerman, 1981, 1984; Kump and Garrels, 1986; Berner, 1987; Petsch and Berner, 1998). This increased sulfur burial would have increased the flux of  $\text{CO}_2$  and  $\text{O}_2$  to the atmosphere during periods of organic sulfur burial.

While organic sulfur burial may be volumetrically significant in some environments such as the Miocene Monterey Formation, where up to 80% of the total reduced S is organic-bound (Fig. 2; Anderson and Pratt, 1995), the paucity of data available for organic sulfur abundance and  $\delta^{34}\text{S}$  through the Phanerozoic makes its impact difficult to assess. Because burial of organic sulfur is largely controlled by the relative availability of reduced inorganic sulfides and reactive iron species, it is likely that its influence would be most pronounced during times of widespread oceanic anoxia or euxinia, when sulfide is abundant and reactive Fe supplies are often limited. For example, mid-Cretaceous sediments from the proto-North Atlantic have very high organic sulfur contents of up to 80% of the total reduced sulfur (M.M. Kuypers, 2002, personal commun.).

## ORGANIC SULFUR AND MICROBIAL ACTIVITY

The sulfur isotope composition of organic sulfur is dependent on (1) the sulfur isotope composition of the source sulfur, specifically reactive inorganic sulfur species, and (2) any isotopic fractionations associated with organic matter sulfurization. Because isotope fractionations associated with incorporation of inorganic sulfur species into organic matter are generally believed to be small (Price and Shieh, 1979; Fry et al., 1984, 1986, 1988), we will focus our discussion on the factors controlling the sulfur isotope composition of the sulfur source (though this belief is being challenged; Amrani and Aizenshtat, 2003). All of the possible inorganic sulfur sources, including sulfate ( $\text{SO}_4^{2-}$ ), sulfide ( $\Sigma\text{H}_2\text{S}$ ), and reactive intermediates such as elemental sulfur ( $\text{S}^0$ ), polysulfides ( $\text{HS}_x$ ), and thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ) can be produced in the natural environment by microbial processes. Many can also be produced by abiotic processes, such as the formation of polysulfides via reactions between iron oxides and bisulfide or between dissolved sulfide and elemental sulfur (Pyzik and Sommer, 1981). Thus, the fundamental control on the biogeochemistry of sulfur isotopes, and specifically on the sulfur isotope composition of organic matter, is the microbial oxidative and reductive cycling of different forms of sulfur. Microbial fractionations of sulfur have recently been reviewed by Canfield (2001a) and are also discussed in several papers in this volume.

We will therefore present only a brief summary here as required for our discussion of organic sulfur isotopes below and refer the interested reader to these other papers for a more detailed treatment of the subject.

The distribution of sulfur isotopes in the natural environment is controlled primarily by the fractionation imparted by dissimilatory bacterial sulfate reduction, which results in sulfide that is depleted in  $^{34}\text{S}$  relative to the source sulfate (Chambers and Trudinger, 1979; Canfield, 2001a, 2001b, and references therein). This fractionation is highly variable but generally lies between 19‰ and 46‰, with values observed as low as 2‰ (Habicht and Canfield, 1997, 2001; Detmers et al., 2001; Brüchert et al., 2001). A second major control on the distribution of sulfur isotopes in sediments, which has only recently been identified, is the sedimentary cycle of microbial sulfide oxidation and subsequent disproportionation of intermediate phases of sulfur (e.g., elemental sulfur, thiosulfate) to sulfide and sulfate (Jørgensen, 1990; Canfield and Thamdrup, 1994; Canfield et al., 1998a; Habicht et al., 1998; Böttcher and Thamdrup, 2001; Böttcher et al., 2001). While the fractionations associated with sulfide oxidation are generally small (Fry et al., 1986), those associated with microbial disproportionation can be quite large. For example, the fractionations during elemental sulfur disproportionation have been shown to produce sulfide that is 6‰ depleted and sulfate that is 18‰ enriched in  $^{34}\text{S}$  relative to the precursor elemental sulfur (Canfield et al., 1998a). In addition, disproportionation of sulfite will produce sulfide that is up to 37‰ depleted and sulfate that is up to 12‰ enriched in  $^{34}\text{S}$  relative to the precursor sulfite (Habicht et al., 1998). Finally, disproportionation of thiosulfate in cultures has produced sulfide that is  $^{34}\text{S}$  depleted relative to the sulfane sulfur in the precursor thiosulfate, though by extremely variable amounts ranging from  $\sim 2\%$  to 20‰ (Habicht et al., 1998; Cypionka et al., 1998).

Discovery of the disproportionation pathway for sulfur cycling (Bak and Cypionka, 1987; Bak and Pfennig, 1987) and the substantial sulfur isotope fractionations associated with it (Canfield et al., 1998a; Habicht et al., 1998; Cypionka et al., 1998) ranks among the most significant discoveries in sulfur biogeochemistry in recent years. Among other implications, the disproportionation pathway provides an explanation for the discrepancy between fractionations observed in nature and those occurring experimentally during bacterial sulfate reduction. It has been proposed that the sedimentary cycling of sulfur, comprised of repeating cycles of sulfate reduction, sulfide oxidation, and disproportionation of elemental sulfur and other intermediates, is responsible for offsets between the sulfur isotope composition of sulfate and sulfide of up to and exceeding 65‰ (Canfield and Thamdrup, 1994), such as those observed in the modern Cariaco Basin (Werne et al., 2003). When compared to fractionations during one step sulfate reduction, which don't exceed  $\sim 46\%$ , it is clear that such a mechanism is required to produce the large values observed in nature. Furthermore, this refined understanding of microbial fractionations has spawned a proposal that the global ocean was insufficiently oxidizing to

support disproportionation reactions until the Neoproterozoic (Canfield and Teske, 1996; Canfield, 1998).

There are two basic pathways by which organic sulfur is formed. The first is assimilatory sulfate reduction, which is the active uptake of sulfate into the cell, followed by its reduction to produce amino acids and other sulfur-requiring cellular components. There is generally little sulfur isotope fractionation associated with assimilatory sulfate reduction (Kaplan and Rittenberg, 1964; Trust and Fry, 1992), so this primary biogenic sulfur typically has an isotope composition similar to the ambient dissolved sulfate, which is  $\sim +21\%$  for modern seawater (Rees et al., 1978; Böttcher et al., 2000). The second and more significant pathway is the incorporation of reduced sulfur into organic matter during diagenesis. The mechanisms of diagenetic sulfur incorporation into organic matter are still debated (see discussion below addressing pathways of organic matter sulfurization) but fundamentally require that the sulfur is derived from pore-water sulfide, either directly or via reactive intermediates. Thus, the sulfur isotope composition of diagenetic organic sulfur is typically  $^{34}\text{S}$  depleted relative to primary biogenic sulfur by 20%–60%. Mass balance modeling suggests that biogenic sulfur typically accounts for  $\sim 20\%$ –25% of the total sedimentary organic sulfur in most marine settings (Anderson and Pratt, 1995; Werne et al., 2003).

#### TIMING OF ORGANIC MATTER SULFURIZATION

One of the most perplexing issues plaguing organic sulfur research is the timing of diagenetic S incorporation by organic compounds. It has been generally accepted that inorganic sulfides are incorporated into organic matter during early diagenesis, based on the identification of organic sulfur compounds in apolar fractions of organic extracts from near-surface sediments (Brassell et al., 1986; Kohnen et al., 1990, 1991b). Timing estimates range from several thousand years to only a few decades following initial deposition of the organic matter (Wakeham et al., 1995). Formation of macromolecular organic sulfur has also been identified in near-surface sediments (Francois, 1987; Eglinton et al., 1994). The organic sulfur compounds identified were typically algal lipids such as highly branched isoprenoids (Kohnen et al., 1990; Wakeham et al., 1995; Hartgers et al., 1997), other isoprenoids such as phytol derivatives (Peakman et al., 1989; Kenig and Huc, 1990), and steroids (Sinninghe Damsté et al., 1999b; Schouten et al., 1995a; Adam et al., 2000; Kok et al., 2000a), as well as sulfurized bacterial hopanoids (de las Heras et al., 1997) and fatty acids (Russell et al., 2000). Many lipids, such as phytane, are released from the nonextractable macromolecular organic matter (kerogen) from near-surface sediments upon treatment with desulfurizing agents like Raney Nickel or nickel boride (Schouten et al., 1993a). These compounds have typically been interpreted to represent the incorporation of sulfur into organic matter during early diagenesis, primarily because the sulfur compounds have not been identified in extant organisms. Unfortunately, due to a lack of clearly identifiable precursor-product relationships, constraining the timing of organic matter

sulfurization any more precisely than “early diagenesis” was impossible in these studies.

A number of recent results, however, have more precisely bracketed the timing of early diagenetic sulfurization of organic matter. The first-ever precursor-product relationship for a diagenetic organic matter sulfurization reaction was identified in the sediments of the Cariaco Basin (Werne et al., 2000a). In this study, the near complete conversion of a tricyclic triterpenoid, (17E)-13 $\beta$ (H)-malabarica-14(27),17,21-triene, to a triterpenoid thiane was observed to span the upper  $\sim 3$  m of sediment (Werne et al., 2000a). This depth interval represents  $\sim 10,000$  yr, thus the timing of organic matter sulfurization, at least for this reaction, is constrained to be occurring over a 10 k.y. period. Other organic sulfur compounds, such as highly branched isoprenoid thiophenes and thiolanes, were identified in shallower sediments, suggesting that sulfurization of these compounds occurs more quickly than the 10 k.y. time period identified for the malabaricatriene to triterpenoid thiane conversion (Werne et al., 2000a). Similar results were obtained in a study of sediments from Ace Lake, Antarctica (Kok et al., 2000a). In their study, Kok et al. (2000a) found that steroids in Ace Lake sediments were sulfurized on a time scale of 1–3 k.y. Although they did not unambiguously identify a precursor-product relationship, they presented a convincing argument that their sulfurized steroids were formed through sulfurization of steroidal ketones deriving from biohydrogenation of  $\Delta^5$  sterols (sterols with a double bond at the 5 carbon position) by anaerobic bacteria (Kok et al., 2000a).

These two studies are consistent in that it appears that the order of magnitude of early diagenetic sulfurization of organic matter is  $10^3$  yr, but the specific rates of sulfurization of individual compounds may vary substantially. Studies in other settings with less well constrained timing have suggested a similar timeframe for sulfurization (e.g., Kohnen et al., 1990; Wakeham et al. 1995). Additional studies have attempted to investigate the timing and precursor-product relationships by using stable carbon isotope techniques. By comparing the carbon isotope composition of the organic sulfur compounds with suspected precursor compounds, these studies were able to reduce the number of potential precursors, which was adequate to support inferences about the timing of sulfurization (Filley et al., 1996, 2002). These studies also suggested a sulfurization time scale of 3–5 k.y. (Filley et al., 2002).

Much shorter time scales have also been suggested for the sulfurization. One study of lacustrine organic matter identified significant sulfurization in sediments that were all younger than  $\sim 60$  yr (Urban et al., 1999), indicating that time scales of  $10^3$  yr are not always required for organic matter sulfurization (unless this material was reworked). A study by Adam et al. (1998) suggests that organic matter could become sulfurized through photochemically induced reactions in the water column. These findings are based on a laboratory study in which many different organic compounds were shown to be readily sulfurized under high light conditions following the addition of elemental sulfur, producing compounds very similar to those observed in nature. Unfortunately, while photochemical sulfurization appears to be

likely in nature, particularly given the high concentrations of organic sulfur compounds present in some surface sediments (Wakeham et al., 1995), this rapid process has not yet been identified in a field study.

Support for a rapid sulfurization pathway can also be found in the results of Poinso et al. (1998), who found sulfurization of polprenoids occurring in <1000 yr. Studies in the sediments of Lake Cadagno, Switzerland, indicate significant sulfurization of phytol derivatives (phytane) in sediments (Putschew et al., 1996). All of the sediments analyzed by Putschew et al. (1995, 1996) were younger than 100 yr. The very high concentrations of sulfur-bound phytane in the upper 2 cm are particularly intriguing given the carbon isotope data from the phytane and phytol compounds in these sediments. Putschew et al. (1995, 1996) showed that the sulfur-bound phytane has a carbon isotope composition that most closely matches that of the phytane in the microbes living in the chemocline portion of the water column. In contrast, the phytol and free phytane in the sediments are an isotopic match with the algae and higher plants in and around the lake (Putschew et al., 1995, 1996). While Putschew et al. (1996) attributed the differences in the depth profiles of concentration and carbon isotope composition of these phytol compounds to differences in the stabilities of microbial versus algal organic matter, it is also possible that they result from a temporal change in the relative inputs of microbial versus algal phytol compounds. An increase in the inputs of microbial phytanes in recent years could be a consequence of intensification of chemocline activity coupled with photochemical sulfurization of microbial organic matter in the water column.

The different time scales discussed above are not necessarily mutually exclusive. It is quite possible that both photochemical and sedimentary diagenetic sulfurization reactions are occurring in some environments, making the total time scale of sulfurization span from days to  $10^3$  yr. Furthermore, it is also likely that sulfurization could be continuing after the currently identified upper limit of  $10^3$  yr, particularly given the high concentrations of organic sulfur identified in ancient sedimentary environments worldwide (Kenig et al., 1995; Schaeffer et al., 1995; Schouten et al., 2001).

## ORGANIC SULFUR AND ORGANIC MATTER PRESERVATION

In recent years, two new models have been proposed to explain enhanced preservation of organic matter in the sedimentary environment. The first implicates the selective preservation of biomacromolecules such as algaenans (de Leeuw and Largeau, 1993; Gelin et al., 1996a, 1996b, 1997, 1999; Blokker et al., 1998, 2000). The second model calls for the sulfurization of natural organic matter as a preservation mechanism (Valisollalao et al., 1984; Brassell et al., 1986; Sinninghe Damsté and de Leeuw, 1990). Reactions between sedimentary organic matter and reduced inorganic sulfur lead to a combination of low molecular weight organic sulfur compounds (through intramolecular

sulfur incorporation) and high molecular weight macromolecules (through intermolecular sulfur incorporation). The nature of the macromolecular organic sulfur compounds formed, for example, through sulfide cross-linking (Schouten et al., 1995b), prevents or at least significantly hinders microbial attack and degradation by binding individual functionalized compounds into a macromolecular matrix, thereby preserving the organic compounds on geologic time scales.

### Biomarker Sequestration

One of the most informative pathways of paleoenvironmental investigation is through the use of molecular biomarkers, which are organic compounds in the geologic records that can be linked unambiguously to a source organism and its associated ecological context (Eglinton and Hamilton, 1967). Furthermore, we can use changes in the relative distribution of different biomarkers to identify past variability in biological communities (Werne et al., 2000b).

Organic matter sulfurization has been shown to preserve the carbon skeletons of functionalized organic compounds in sediments (Brassell et al., 1986; Sinninghe Damsté and de Leeuw, 1990). The implications of this observation are twofold. First, organic matter sulfurization has the potential to preserve biomarkers that would otherwise be lost to degradation. For example, Sinninghe Damsté et al. (1990) used thiophenic biomarkers for paleoenvironmental assessment of the Jurf ed Darawish oil shale in Jordan. These compounds would likely not have been present without sulfurization. Other studies have investigated the compounds released from macromolecular organic matter via desulfurization, rather than investigating "free" organic sulfur compounds as in the study by Sinninghe Damsté et al. (1990). For example, Grice et al. (1998) found biomarkers for freshwater algae in the macromolecular organic matter of an ancient hypersaline euxinic ecosystem, which were released only upon cleavage of the sulfur bonds.

The second implication of biomarker preservation through sulfurization is that paleoenvironmental reconstructions can be significantly biased if selective sulfurization is not considered (Kohnen et al., 1991c, 1992). Specific compounds are not necessarily sulfurized to completion in the natural environment. Thus, because intramolecularly incorporated sulfur leads to organic sulfur compounds with a mass spectrum that is different from the original biomarker compound (cf. Werne et al., 2000a), the sulfurized portion of a particular biomarker compound could easily be overlooked in a molecularly based paleoenvironmental study. Furthermore, the biomarker compounds that are intermolecularly bound into the macromolecular matrix via sulfurization are generally not released by traditional organic extraction techniques, and many common organic geochemical techniques, such as pyrolysis, are destructive to the original (precursor) compound (Sinninghe Damsté and de Leeuw, 1990). These precursor compounds would therefore not be analyzed in a molecular paleoenvironmental study that did not consider the possibility of

biomarkers becoming sulfur bound and requiring release from the kerogen or macromolecular bitumen.

### Carbohydrate Preservation

One of the most interesting hypotheses to result from organic sulfur geochemical studies is that sulfurization of carbohydrates may substantially enhance organic carbon preservation in the geological environment. Carbohydrates are known to be labile compounds with high potential for rapid loss in sedimentary and aquatic environments. In a recent series of papers, however, Sinninghe Damsté and colleagues demonstrated that reaction with sulfur could sequester carbohydrates in sediments. Van Kaam-Peters et al. (1998) showed that intervals of high organic carbon content in the Jurassic Kimmeridge Clay Formation were characterized by high sulfur content and  $^{13}\text{C}$ -enriched carbon isotope values. Because carbohydrates are known to be enriched in  $^{13}\text{C}$  relative to total cell material (e.g., van Dongen et al., 2002), Van Kaam-Peters et al. (1998) hypothesized that these relationships reflected preservation of carbohydrate carbon through sulfurization during early diagenesis. Further support for this hypothesis was provided by experiments in which glucose and algae were sulfurized in the laboratory, resulting in sulfur-rich macromolecular organic matter (Sinninghe Damsté et al., 1998b; Kok et al., 2000b; van Dongen et al., 2003a). Upon pyrolysis, this macromolecular organic matter was found to have a molecular distribution very similar to that found in the Kimmeridge Clay (Sinninghe Damsté et al., 1998b; Kok et al., 2000b; van Dongen et al., 2003a).

The hypothesis that sulfurization leads to enhanced carbohydrate preservation was confirmed by detailed studies of the macromolecular organic matter in kerogen pyrolysates and through comparison with macromolecular organic matter produced from laboratory sulfurization of carbohydrates (van Dongen et al., 2003b; van Dongen 2003). These findings are critical because it was previously thought that carbohydrates are degraded much more readily than other classes of organic matter in the natural environment, and their preservation in sulfur-rich environments could potentially affect interpretations based on bulk organic carbon concentrations and isotope compositions alone (Sinninghe Damsté et al., 1998b).

### Macromolecular Organic Sulfur

The combination of intermolecular and intramolecular sulfurization of organic matter can lead to a complex set of organic sulfur compounds in macromolecular organic matter. Detailed understanding of this pool of organic sulfur is still lacking, but significant steps have been made in recent years. The classical method of investigating macromolecular organic matter is through pyrolysis gas chromatography–mass spectrometry (pyGC-MS; Sinninghe Damsté and de Leeuw, 1990). This method involves the flash combustion of kerogens, followed by gas chromatographic separation and mass spectrometric identification of the

pyrolysis products. pyGC-MS is useful for identifying the carbon skeletons bound to macromolecular organic matter by sulfur linkages (Eglinton et al., 1992; Sinninghe Damsté et al., 1998a; Luckge et al., 2002). For example, studies using pyGC-MS have identified molecular fossils of the alga *Gloeocapsomorpha prisca* in Ordovician kerogens (Douglas et al., 1991). However, because the technique is destructive, it does not yield information about the chemical form (e.g., polysulfide, sulfonate, etc.) of the organic sulfur itself. Researchers have therefore turned to other methods in addition to pyGC-MS to study the composition of macromolecular organic sulfur.

One method that has proven to be useful is the stepwise selective chemical degradation of the kerogen, which involves treating the kerogen with a sequence of different reagents and analyzing the released compounds. Early studies emphasized “total desulfurization” techniques, such as Raney-Nickel or nickel-boride (Perakis, 1986; Sinninghe Damsté et al., 1988; Schouten et al., 1993a). Studies of this type have confirmed that sulfurization can enhance the preservation of both macromolecular organic matter and specific biomarkers in sediments, and many types of organic matter vulnerable to sulfurization have been identified (Grice et al., 1998; Hefter et al., 1995; Putschew et al., 1996; Russell et al., 2000). Unfortunately, the sulfur is lost with these methods, eliminating our ability to identify the forms of sulfur present.

Other chemical degradation techniques have proven more fruitful (e.g., Schaeffer-Reiss et al., 1998). Specifically, cleavage of only S-S bonds using methyl lithium/methyl iodide (Kohnen et al., 1991a, 1993), superheated methyl iodide (Schouten et al., 1993b), and  $\text{LiAlH}_4$  (Adam et al., 1991, 1992, 1993; Schaeffer et al., 1995) proved the presence of polysulfide (or disulfide) linkages in organic sulfur-rich macromolecular organic matter. These findings support the polysulfide pathway of organic matter sulfurization (cf. Aizenshtat et al., 1983; LaLonde et al., 1987).

There are also several nondestructive spectroscopic methods for investigating the forms of sulfur present in macromolecular organic matter. One of the most informative in recent years has been X-ray absorption near-edge structure spectroscopy (XANES), which was first applied in studies of petroleum products (Spiro et al., 1984; George and Gorbaty, 1989; Huffman et al., 1991, 1995; Waldo et al., 1991). Due to its sensitivity to the electronic structure, oxidation state, and geometry of neighboring atoms, this spectroscopic method has the capability of providing specific information about the functional groups of sulfur present (Vairavamurthy et al., 1994; 1997). One very intriguing result from the XANES studies is that 20%–40% of the total organic sulfur is actually present as sulfonates, an oxidized form of organic sulfur that was previously not known to exist in sediments (Vairavamurthy et al., 1994). Other sulfur-bearing compound types identified by XANES include reduced forms such as thiols, thiophenes, and disulfides and polysulfides, moderate oxidation state forms such as sulfones, and oxidized forms such as organic sulfates and sulfonates (Vairavamurthy et al., 1995, 1997). Other recent studies using XANES to investigate sulfur in ancient systems found that reduced forms such as thiophenes dominate (Sarret et al., 1999,

2002). It remains unclear what factors may be controlling the relative distribution of different forms of oxidized and reduced sulfur in modern and ancient organic-rich sediments.

### PATHWAYS OF ORGANIC MATTER SULFURIZATION: CONSTRAINTS FROM LABORATORY SIMULATIONS AND SULFUR ISOTOPES

#### Laboratory Sulfurization Experiments

Despite intensive study, the geochemical pathways of organic matter sulfurization remain unclear. This uncertainty is compounded by the likely existence of multiple pathways in natural systems, which vary as a function of the specific conditions present. Most researchers currently favor the idea that the preferred pathway for the diagenetic formation of organic sulfur is the reaction of organic matter with inorganic polysulfides (Aizenshtat et al., 1983), but other mechanisms such as reaction directly with  $H_2S$ , elemental sulfur, or other intermediates such as thiosulfate cannot be eliminated. It is also not clear whether the sulfur reacts preferentially at sites of unsaturation (Sinninghe Damsté et al., 1989) or with functional groups such as ketones (Schneckenburger et al., 1998). Among the evidence in support of the polysulfide pathway, in addition to the presence of polysulfide linkages in sulfur-rich macromolecular organic matter (Kohnen et al., 1991a; Adam et al., 1993; Schaeffer et al., 1995), are the many laboratory experiments in which organic matter has been artificially sulfurized. All these studies were carried out under mild laboratory conditions (e.g., 50 °C) intended to be as similar to natural conditions as possible while still increasing the rate of sulfurization enough to enable laboratory study. These studies resulted in the sulfurization of phytol (de Graaf et al., 1992; Rowland et al., 1993), ketones and aldehydes (Schouten et al., 1994a, 1994b), olefins (de Graaf et al., 1995), algae (Gelin et al., 1998), and carbohydrates (Kok et al., 2000b; van Dongen et al., 2003a), yielding compounds similar to those identified in natural sedimentary systems.

Additional support for the polysulfide pathway of organic sulfur formation was provided in a study by Vairavamurthy et al. (1992) in which natural sediment samples were reacted with acrylic acid in a slurry to investigate the distribution and reactivity of polysulfides in sediments. This study determined that polysulfides, in addition to being dissolved in the aqueous phase, can be present in the solid fraction. As solid particles, polysulfides were bound to sediment grains and organic matter, which helped to bind the organic matter to the sediment particles (Vairavamurthy et al., 1992). This process may play an important role in the preservation of organic matter in sediments (Vairavamurthy et al., 1992).

#### Sulfur Speciation and Isotopic Studies

One of the most promising areas of organic sulfur research is detailed sulfur speciation coupled with sulfur isotope measure-

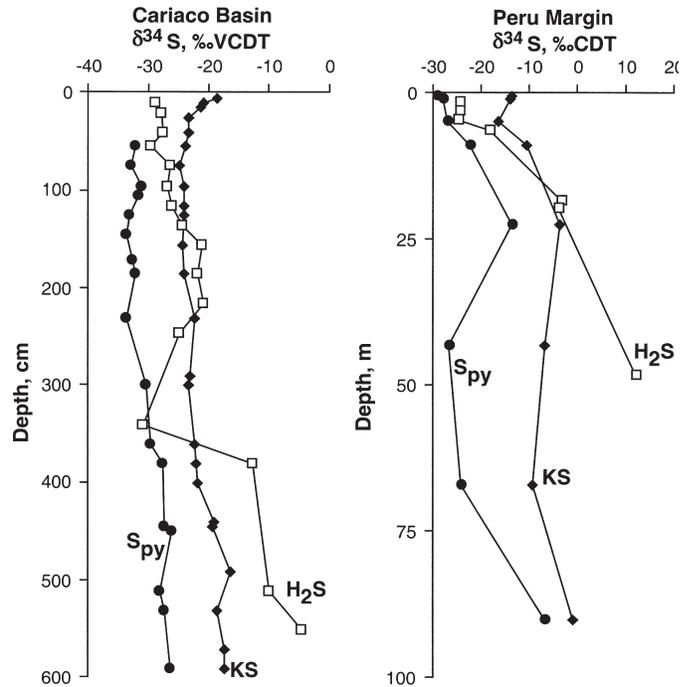


Figure 3. Depth trends of the sulfur isotope composition of the major reduced sulfur species in the Cariaco Basin and the Peru Margin (data from Werne et al. [2003] and Mossmann et al. [1991], respectively). Note the consistency among the trends, which are suggestive of restricted environments in which the consumption of the pore-water sulfur species, primarily sulfate via sulfate reduction to form sulfide, is faster than the supply through diffusion. VCDT—Vienna Canyon Diablo Troilite.

ments. The theory underlying these studies is that environments conducive to the formation of organic sulfur typically also favor the formation of inorganic sulfides such as pyrite (Mossmann et al., 1991; Brüchert and Pratt, 1996). Furthermore, because of the wide range of sulfur isotope fractionations observed in nature (Canfield, 2001; Bottrell and Raiswell, 2000), isotope measurements can be used in combination with concentration data to trace pathways of sulfur cycling in sedimentary environments (Mossmann et al., 1991; Zaback and Pratt, 1992; Anderson and Pratt 1995; Henneke et al., 1997; Passier et al., 1997; Bates et al., 1995, 1998; Canfield et al., 1998b; Werne et al., 2003). Figure 3 shows depth trends of the  $\delta^{34}S$  values of the major reduced sulfur species (pore-water sulfide, pyrite sulfur, and organic sulfur) in the Cariaco Basin (data from Werne et al., 2003) and the Peru Margin (data from Mossmann et al., 1991). Environments in which the supply of sulfate is restricted in deeper sediments lead ultimately to down core enrichment in  $^{34}S$  in all the sulfur species.

Speciation studies have shown clearly that organic sulfur represents a significant portion of the total reduced sulfur in the sediments of many different environments. For example, organic sulfur is up to 50% of the total sulfur in a Delaware salt marsh (Ferdelman et al., 1991), 50% in St. Andrew Bay, Florida (Brüchert and Pratt, 1996), 17%–43% in the hypersaline Tyro

and Bannock Basins in the Mediterranean (Henneke et al., 1997), 85%–90% in Mangrove Lake, Bermuda (Canfield et al., 1998b), 50%–75% in the Everglades (Bates et al., 1998), 40% in the Peru Margin (Mossmann et al., 1991; Suits and Arthur, 2000), and up to 30% in the Cariaco Basin, Venezuela (Werne et al., 2003). Anderson and Pratt (1995) summarized results from a number of other environments in which organic sulfur is found to be as much as 80% of the total reduced sulfur.

Brüchert (1998) investigated organic sulfur bound in humic and fulvic acids and found that a portion of the fulvic acid sulfur in the upper centimeters of the sediments of St. Andrew Bay, Florida, was evidently recycled back to pore-water sulfur species. An additional portion was transferred into humic acids and protokerogens (the macromolecular organic matter discussed above). Furthermore, because of the characteristic isotopic signature of assimilated primary biogenic sulfur compared to organic sulfur incorporated during diagenesis, a number of studies have been able to demonstrate that this biogenic sulfur makes up 20%–25% of the sedimentary organic sulfur in many environments (Anderson and Pratt, 1995; Brüchert and Pratt, 1996; Werne et al., 2003). The remaining organic sulfur appears to be derived from pore-water sulfide or associated reactive intermediate, such as polysulfides (Werne et al., 2003; Brüchert, 1998; Canfield et al., 1998b).

Some of the strongest recent support for the polysulfide pathway of organic sulfur formation in fact comes from sulfur isotope analyses. In a recent study, Werne et al. (2003) measured the sulfur isotope composition of bulk organic matter. Based on the identification of a sulfurization reaction in Cariaco Basin sediments (Werne et al., 2000a), they then used mass balance considerations to model the isotope composition of sulfur incorporated diagenetically into a specific organic compound (Werne et al., 2003). Assuming that sulfur was incorporated into organic matter directly from pore-water sulfide with no isotopic fractionation, and using the depth profile for the isotopic composition of pore-water sulfide, they estimated values for their model organic sulfur compound that were very similar to those measured for bulk organic sulfur. This result suggested that their assumptions were correct and gave support to the direct reaction of organic matter with  $\text{H}_2\text{S}$  (Werne et al., 2003). Due to recent technical advances, however, it is now possible to measure the sulfur isotope composition of specific organic compounds. In a follow-up study, Werne et al. (2001) measured the sulfur isotope composition of the actual compound they had modeled and found that its sulfur isotope composition was in fact 10‰ heavier ( $^{34}\text{S}$  enriched) relative to model values and bulk organic sulfur.

These results indicate one or both of two possibilities: either the assumptions about the lack of sulfur isotope fractionation accompanying organic matter sulfurization were incorrect, or the sulfur is not derived directly from  $\text{H}_2\text{S}$  but rather from some other inorganic sulfur species that is  $^{34}\text{S}$  enriched relative to  $\text{H}_2\text{S}$ , such as polysulfides. Studies of isotope fractionation associated with incorporation of S into organic matter are sparse and contradictory. Brüchert and Pratt (1996) proposed a kinetic

fractionation (based on carbon isotope work of Schouten et al., 1995c) that would result in organic sulfur that was  $^{34}\text{S}$  depleted relative to sulfide or polysulfides. More recently, Amrani and Aizenshtat (2003) hypothesized that organic matter sulfurization is an equilibrium process, with equilibrium S isotope fractionation leading to polysulfides that are  $^{34}\text{S}$  enriched relative to sulfide. This second hypothesis fits well with the observations that elemental sulfur is enriched relative to solid phase sulfides (e.g.,  $\text{FeS}_2$ ) in sediments (Anderson and Pratt, 1995; Werne et al., 2003). Furthermore,  $^{35}\text{S}$  radiolabel experiments have shown that there is rapid isotopic mixing between the various inorganic sulfur species (e.g.,  $\text{H}_2\text{S}$ ,  $\text{S}^0$ ,  $\text{S}_x^{2-}$ ,  $\text{FeS}$ ; Fossing et al., 1992). Fractionations associated with microbial sulfide oxidation are generally small (Kaplan and Rittenberg, 1964; Fry et al., 1984, 1986, 1988); however, those associated with disproportionation can be large, with the reduced sulfur resulting from disproportionation being much more depleted than the oxidized sulfur (Canfield and Thamdrup, 1994; Canfield et al., 1998a; Habicht et al., 1998; Böttcher and Thamdrup, 2001; Böttcher et al., 2001). Thus, successive cycles of partial oxidation and disproportionation *could* lead to intermediate forms of sulfur that are enriched in  $^{34}\text{S}$  relative to aqueous sulfide, though this has never been unequivocally observed.

Based on the above S isotope observations, elemental sulfur and polysulfides are the most likely candidates for direct incorporation in organic matter that could produce a  $^{34}\text{S}$  enriched organic sulfur product. Both polysulfides and elemental sulfur are strong nucleophiles, with longer chain length polysulfides being stronger nucleophiles than the shorter chains (LaLonde et al., 1987). Because the pH values of most marine sedimentary systems are slightly basic, they favor the incorporation of polysulfides (via nucleophilic additions) over incorporation of elemental sulfur (Giggenbach, 1972; LaLonde et al., 1987; Aizenshtat et al., 1995). Thus, Werne et al. (2001) proposed that their isotopic data are best explained by the incorporation of inorganic sulfur into organic matter as polysulfides.

## SUMMARY AND FUTURE RESEARCH DIRECTIONS

Our goal has been to review the most significant advances in organic sulfur biogeochemistry over the last decade. The highlights include:

1. the possibility that sulfur radical formation may play a central role in early petroleum formation from organic-rich sediments;
2. the potential of organic sulfur burial on the coupled global biogeochemical cycles of C, S, and O resulting in an underestimate in the reduced sulfur burial flux and thus on the fluxes of  $\text{CO}_2$  and  $\text{O}_2$  to the atmosphere on geological time scales;
3. the constraints placed on the timing of early diagenetic sulfurization of organic matter (e.g., 10s to 1000s of years);
4. the ability for sulfurization to enhance the preservation of organic matter, both specific biomarkers as well as classes of labile organic matter such as carbohydrates;

5. the identification of many different forms of organic sulfur in macromolecular organic matter, including partially oxidized forms such as sulfonates; and

6. the constraints placed on organic sulfur formation by studies combining sulfur speciation and parallel measurements of organic sulfur isotope compositions, particularly the recent advance of being able to measure the  $\delta^{34}\text{S}$  of organic S at the level of individual organic compounds.

Most important, these results advance our comparatively weak understanding of the overall roles played by organic sulfur in the global biogeochemical cycles for C and S.

To continue moving forward, we need to identify the many forms of organic sulfur present in sediments, both specific organic sulfur compounds and macromolecular organic sulfur. There are many methods by which such goals can be achieved. Integrated approaches—e.g., a combination of selective chemical degradations and mass spectrometric analyses with nondestructive spectroscopic methods such as XANES—are likely to yield the best results. It is also clear that we have not quantified the extent to which organic matter preservation can be enhanced via sulfurization, nor do we have a good understanding of the kinetics of OM sulfurization.

Recent advances in the field of sulfur isotope geochemistry are increasing the sensitivity of sulfur isotope measurements and thus resolution of analyses now performed at the level of individual organic compounds (Fry et al., 2002; Studley et al., 2002). Eventually, such advances will make compound-specific sulfur isotope analyses commonplace.

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## REFERENCES CITED

- Adam, P., Schmid, J.C., Albrecht, P., and Connan, J., 1991,  $2\alpha$  and  $3\beta$  steroid thiols from reductive cleavage of macromolecular petroleum fraction: *Tetrahedron Letters*, v. 32, p. 2955–2958, doi: 10.1016/0040-4039(91)80661-O.
- Adam, P., Mycke, B., Schmid, J.C., Connan, J., and Albrecht, P., 1992, Steroid moieties attached to macromolecular petroleum fraction via di- or polysulfide bridges: *Energy & Fuels*, v. 6, p. 553–559.
- Adam, P., Schmid, J.C., Mycke, B., Strazielle, C., Connan, J., Huc, A., Riva, A., and Albrecht, P., 1993, Structural investigation of nonpolar sulfur cross-linked macromolecules in petroleum: *Geochimica et Cosmochimica Acta*, v. 57, p. 3395–3419, doi: 10.1016/0016-7037(93)90547-A.
- Adam, P., Phillippe, E., and Albrecht, P., 1998, Photochemical sulfurization of sedimentary organic matter: A widespread process occurring at early diagenesis in natural environments?: *Geochimica et Cosmochimica Acta*, v. 62, p. 265–271, doi: 10.1016/S0016-7037(97)00332-3.
- Adam, P., Schneckeburger, P., Schaeffer, P., and Albrecht, P., 2000, Clues to early diagenetic sulfurization processes from mild chemical cleavage of labile sulfur-rich geomacromolecules: *Geochimica et Cosmochimica Acta*, v. 64, p. 3485–3503.
- Aizenshtat, Z., Stoler, A., Cohen, Y., and Nielsen, H., 1983, The geochemical sulphur enrichment of recent organic matter by polysulfides in the Solar-Lake, in Bjorøy, M., et al., eds., *Advances in Organic Geochemistry 1981*: New York, John Wiley & Sons Limited, p. 279–288.
- Aizenshtat, Z., Krein, E., Vairavamurthy, M., and Goldstein, T., 1995, Role of sulfur in the transformations of sedimentary organic matter: A mechanistic overview, in Vairavamurthy, M.A., and Schoonen, M.A.A., eds., *Geochemical transformations of sedimentary sulfur*: Washington, D.C., American Chemical Society Symposium Series 612, p. 378–396.
- Amrani, A., and Aizenshtat, Z., 2003, Mechanisms of sulfur introduction chemically controlled:  $\delta^{34}\text{S}$  imprint: Proceedings, 21st IMOG meeting, Krakow, Poland, p. 39–40.
- Anderson, T.F., and Pratt, L.M., 1995, Isotope evidence for the origin of organic sulfur and elemental sulfur in marine sediments, in Vairavamurthy, M.A., and Schoonen, M.A.A., eds., *Geochemical transformations of sedimentary sulfur*: Washington, D.C., American Chemical Society Symposium Series 612, p. 378–396.
- Bak, F., and Cypionka, H., 1987, A novel type of energy metabolism involving fermentation of inorganic sulphur compounds: *Nature*, v. 326, p. 891–892, doi: 10.1038/326891A0.
- Bak, F., and Pfennig, N., 1987, Chemolithotrophic growth of *Desulfovibrio sulfodismutans* sp. nov. by disproportionation of inorganic sulfur compounds: *Archives of Microbiology*, v. 147, p. 184–189.
- Barakat, A.O., and Rüllkötter, J., 1995, The distribution of free organic sulfur compounds in sediments from the Nördlinger Ries, Southern Germany, in Vairavamurthy, M.A., and Schoonen, M.A.A., eds., *Geochemical transformations of sedimentary sulfur*: Washington, D.C., American Chemical Society Symposium Series 612, p. 311–331.
- Barakat, A.O., and Rüllkötter, J., 1999, Origin of organic sulfur compounds in sediments from the Nördlinger Ries (Southern Germany): *Journal of Petroleum Science and Engineering*, v. 22, p. 103–119, doi: 10.1016/S0920-4105(98)00060-6.
- Bates, A., Spiker, E., Hatcher, P., Stout, S., and Weintraub, V., 1995, Sulfur geochemistry of organic-rich sediments from Mud Lake, Florida, USA: *Chemical Geology*, v. 121, p. 245–262, doi: 10.1016/0009-2541(94)00122-O.
- Bates, A., Spiker, E., and Holmes, C., 1998, Speciation and isotopic composition of sedimentary sulfur in the Everglades, Florida, USA: *Chemical Geology*, v. 146, p. 155–170, doi: 10.1016/S0009-2541(98)00008-4.
- Berner, R.A., 1987, Models for carbon and sulfur cycles and atmospheric oxygen: application to Paleozoic geologic history: *American Journal of Science*, v. 287, p. 177–196.
- Berner, R.A., and Raiswell, R., 1983, Burial of organic carbon and pyrite sulfur in sediments over Phanerozoic time: a new theory: *Geochimica et Cosmochimica Acta*, v. 47, p. 855–862, doi: 10.1016/0016-7037(83)90151-5.
- Blokker, P., Schouten, S., van den Ende, H., de Leeuw, J.W., Hatcher, P.G., and Sinninghe Damsté, J.S., 1998, Chemical structure of algaenans from the fresh water algae *Tetraedron minimum*, *Scenedesmus communis* and *Pediastrum boryanum*: *Organic Geochemistry*, v. 29, p. 1453–1468, doi: 10.1016/S0146-6380(98)00111-9.
- Blokker, P., Schouten, S., de Leeuw, J.W., Sinninghe Damsté, J.S., and van den Ende, H., 2000, A comparative study of fossil and extant algaenans using ruthenium tetroxide degradation: *Geochimica et Cosmochimica Acta*, v. 64, p. 2055–2065, doi: 10.1016/S0016-7037(00)00367-7.
- Böttcher, M.E., and Thamdrup, B., 2001, Anaerobic sulfide oxidation and stable isotope fractionation associated with bacterial sulfur disproportionation in the presence of  $\text{MnO}_2$ : *Geochimica et Cosmochimica Acta*, v. 65, p. 1573–1581, doi: 10.1016/S0016-7037(00)00622-0.
- Böttcher, M.E., Thamdrup, B., and Vennemann, T.W., 2001, Oxygen and sulfur isotope fractionation during anaerobic bacterial disproportionation of elemental sulfur: *Geochimica et Cosmochimica Acta*, v. 65, no. 10, p. 1601–1609, doi: 10.1016/S0016-7037(00)00628-1.
- Böttcher, M.E., Schale, H., Schnetger, B., Wallmann, K., and Brumsack, H.-J., 2000, Stable sulfur isotopes indicate net sulfate reduction in near-surface sediments of the deep Arabian Sea: *Deep-Sea Research II*, v. 47, p. 2769–2783.
- Bottrell, S.H., and Raiswell, R., 2000, Sulphur isotopes and microbial sulphur cycling, in Riding, R.E., and Awramik, S.M., eds., *Microbial sediments*: Berlin, Springer-Verlag, p. 96–104.
- Boulègue, J., Lord, C.J., III, and Church, T.M., 1982, Sulfur speciation and associated trace metals (Fe, Cu) in the pore waters of Great Marsh, Delaware: *Geochimica et Cosmochimica Acta*, v. 46, p. 453–464, doi: 10.1016/0016-7037(82)90236-8.

- Brassell, S.C., Lewis, C.A., de Leeuw, J.W., de Lange, F., and Sinninghe Damsté, J.S., 1986, Isoprenoid thiophenes: Novel diagenetic products in sediments?: *Nature*, v. 320, p. 160–162.
- Brüchert, V., 1998, Early diagenesis of sulfur in estuarine sediments: The role of sedimentary humic and fulvic acids: *Geochimica et Cosmochimica Acta*, v. 62, p. 1567–1586, doi: 10.1016/S0016-7037(98)00089-1.
- Brüchert, V., and Pratt, L.M., 1996, Contemporaneous early diagenetic formation of organic and inorganic sulfur in estuarine sediments from St. Andrew Bay, Florida, USA: *Geochimica et Cosmochimica Acta*, v. 60, no. 13, p. 2325–2332, doi: 10.1016/0016-7037(96)00087-7.
- Brüchert, V., Knoblauch, C., and Jørgensen, B.B., 2001, Controls on stable sulfur isotope fractionation during bacterial sulfate reduction in Arctic sediments: *Geochimica et Cosmochimica Acta*, v. 65, p. 763–776, doi: 10.1016/S0016-7037(00)00557-3.
- Canfield, D.E., 1989, Reactive iron in marine sediments: *Geochimica et Cosmochimica Acta*, v. 53, p. 619–632, doi: 10.1016/0016-7037(89)90005-7.
- Canfield, D.E., 1998, A new model for Proterozoic ocean chemistry: *Nature*, v. 396, p. 450–453, doi: 10.1038/24839.
- Canfield, D.E., 2001a, Biogeochemistry of sulfur isotopes, in Valley, J.W., and Cole, D.R., eds., *Stable isotope geochemistry*: Washington, D.C., The Mineralogical Society of America Reviews in Mineralogy and Geochemistry 43, p. 607–636.
- Canfield, D.E., 2001b, Isotope fractionation by natural populations of sulfate-reducing bacteria: *Geochimica et Cosmochimica Acta*, v. 65, no. 7, p. 1117–1124, doi: 10.1016/S0016-7037(00)00584-6.
- Canfield, D.E., and Raiswell, R., 1999, The evolution of the sulfur cycle: *American Journal of Science*, v. 299, p. 697–723.
- Canfield, D.E., and Teske, A., 1996, Late Proterozoic rise in atmospheric oxygen concentration inferred from phylogenetic and sulphur-isotope studies: *Nature*, v. 382, p. 127–132, doi: 10.1038/382127A0.
- Canfield, D.E., and Thamdrup, B., 1994, The production of  $^{34}\text{S}$ -depleted sulfide during bacterial disproportionation of elemental sulfur: *Science*, v. 266, p. 1973–1975.
- Canfield, D.E., Raiswell, R., and Bottrell, S., 1992, The reactivity of sedimentary iron minerals toward sulfide: *American Journal of Science*, v. 292, p. 818–834.
- Canfield, D.E., Lyons, T.W., and Raiswell, R., 1996, A model for iron deposition to euxinic Black Sea sediments: *American Journal of Science*, v. 296, p. 818–834.
- Canfield, D.E., Thamdrup, B., and Fleischer, S., 1998a, Isotope fractionation and sulfur metabolism by pure and enrichment cultures of elemental sulfur-disproportionating bacteria: *Limnology and Oceanography*, v. 43, p. 253–264.
- Canfield, D.E., Boudreau, B.P., Mucci, A., and Gundersen, J.K., 1998b, The early diagenetic formation of organic sulfur in the sediments of Mangrove Lake, Bermuda: *Geochimica et Cosmochimica Acta*, v. 62, p. 767–781, doi: 10.1016/S0016-7037(98)00032-5.
- Canfield, D.E., Habicht, K.S., and Thamdrup, B., 2000, The Archean sulfur cycle and the early history of atmospheric oxygen: *Science*, v. 288, p. 658–661.
- Chambers, L.A., and Trudinger, P.A., 1979, Microbiological fractionation of stable sulfur isotopes: a review and critique: *Geomicrobiology Journal*, v. 1, p. 249–293.
- Cypionka, H., Smock, A., and Böttcher, M., 1998, A combined pathway of sulfur compound disproportionation in *Desulfovibrio desulfuricans*: *FEMS Microbiology Letters*, v. 166, p. 181–186, doi: 10.1016/S0378-1097(98)00330-9.
- de Graaf, W., Sinninghe Damsté, J., and de Leeuw, J., 1992, Laboratory simulation of natural sulphurization: I. Formation of monomeric and oligomeric isoprenoid polysulphides by low-temperature reactions of inorganic polysulphides with phytol and phytadienes: *Geochimica et Cosmochimica Acta*, v. 56, p. 4321–4328, doi: 10.1016/0016-7037(92)90275-N.
- de Graaf, W., Sinninghe Damsté, J., and de Leeuw, J., 1995, Low-temperature addition of hydrogen polysulfides to olefins: Formation of 2,2'-dialkyl polysulfides from alk-1-enes and cyclic (poly)sulfides and polymeric organic sulfur compounds from  $\alpha,\omega$ -dienes: *Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry*, v. 1, p. 634–640.
- de las Heras, F.X.C., Grimalt, J.O., Lopez, J.F., Albaiges, J., Sinninghe Damsté, J.S., Schouten, S., and de Leeuw, J.W., 1997, Free and sulphurized hopanoids and highly branched isoprenoids in immature lacustrine oil shales: *Organic Geochemistry*, v. 27, p. 41–63.
- de Leeuw, J.W., and Largeau, C., 1993, A review of macromolecular organic compounds that comprise living organisms and their role in kerogen, coal and petroleum formation, in Engel, M.H., and Macko, S.A., eds., *Organic geochemistry, principles and applications—Topics in Geobiology: New York*, Plenum, v. 11, p. 23–72.
- de Leeuw, J.W., and Sinninghe Damsté, J.S., 1990, Organic sulphur compounds and other biomarkers as indicators of Palaeosalinity: A critical evaluation, in Orr, W.L., and White, C.M., *Geochemistry of sulfur in fossil fuels: Washington, D.C.*, American Chemical Society Symposium Series 249, p. 417–443.
- Detmers, J., Brüchert, V., Habicht, K.S., and Kuever, J., 2001, Diversity of sulfur isotope fractionations by sulfate-reducing prokaryotes: *Applied and Environmental Microbiology*, v. 67, p. 888–894, doi: 10.1128/AEM.67.2.888-894.2001.
- Douglas, A., Sinninghe Damsté, J., Fowler, M., Eglinton, T., and de Leeuw, J., 1991, Unique distributions of hydrocarbons and sulphur compounds released by flash pyrolysis from the fossilized alga *Gloecapsomorpha prisca*, a major constituent in one of four Ordovician kerogens: *Geochimica et Cosmochimica Acta*, v. 55, p. 275–291, doi: 10.1016/0016-7037(91)90417-4.
- Eglinton, G., and Hamilton, R.J., 1967, Leaf epicuticular waxes: *Science*, v. 156, p. 1322–1335.
- Eglinton, T.I., Irvine, J.E., Vairavamurthy, A., Zhou, W., and Manowitz, B., 1994, Formation and diagenesis of macromolecular organic sulfur in Peru margin sediments, in Telnæs, N., van Graas, G., and Øygard, K., eds., *Advances in Organic Geochemistry 1993: Organic Geochemistry*, v. 22, p. 781–799.
- Eglinton, T.I., Sinninghe Damsté, J.S., Pool, W., de Leeuw, J.W., Eijkel, G., and Boon, J.J., 1992, Organic sulphur in macromolecular sedimentary organic matter. II. Analysis of distributions of sulphur-containing pyrolysis products using multivariate techniques: *Geochimica et Cosmochimica Acta*, v. 56, p. 1545–1560, doi: 10.1016/0016-7037(92)90224-7.
- Ferdelman, T.G., Church, T.M., and Luther, G.W., III, 1991, Sulfur enrichment of humic substances in a Delaware salt marsh sediment core: *Geochimica et Cosmochimica Acta*, v. 55, p. 979–988, doi: 10.1016/0016-7037(91)90156-Y.
- Filley, T., Freeman, K., Wilkin, R., and Hatcher, P., 2002, Biogeochemical controls on reaction of sedimentary organic matter and aqueous sulfides in Holocene sediments of Mud Lake, Florida: *Geochimica et Cosmochimica Acta*, v. 66, p. 937–954, doi: 10.1016/S0016-7037(01)00829-8.
- Filley, T.R., Freeman, K.H., and Hatcher, P.G., 1996, Carbon isotope relationships between sulfide-bound steroids and proposed functionalized lipid precursors in sediments from the Santa Barbara Basin, California: *Organic Geochemistry*, v. 25, p. 367–377, doi: 10.1016/S0146-6380(96)00142-8.
- Fossing, H., Thode-Andersen, S., and Jørgensen, B.B., 1992, Sulfur isotope exchange between  $^{35}\text{S}$ -labeled inorganic sulfur compounds in anoxic marine sediments: *Marine Chemistry*, v. 38, p. 117–132, doi: 10.1016/0304-4203(92)90071-H.
- Francois, R., 1987, A study of sulphur enrichment in the humic fraction of marine sediments during early diagenesis: *Geochimica et Cosmochimica Acta*, v. 51, p. 17–27, doi: 10.1016/0016-7037(87)90003-2.
- Fry, B., Gest, H., and Hayes, J.M., 1984, Isotope effects associated with the anaerobic oxidation of sulfide by the purple photosynthetic bacterium, *Chromatium vinosum*: *FEMS Microbiology Letters*, v. 22, p. 283–287, doi: 10.1016/0378-1097(84)90025-9.
- Fry, B., Cox, J., Gest, H., and Hayes, J., 1986, Discrimination between  $^{34}\text{S}$  and  $^{32}\text{S}$  during bacterial metabolism of inorganic sulfur compounds: *Journal of Bacteriology*, v. 165, p. 328–330.
- Fry, B., Gest, H., and Hayes, J.M., 1988,  $^{34}\text{S}/^{32}\text{S}$  fractionation in sulfur cycles catalyzed by anaerobic bacteria: *Applied and Environmental Microbiology*, v. 54, no. 1, p. 250–256.
- Fry, B., Silva, S.R., Kendall, C., and Anderson, R.K., 2002, Oxygen isotope corrections for online  $\delta^{34}\text{S}$  analysis: *Rapid Communications in Mass Spectrometry*, v. 16, p. 854–858, doi: 10.1002/RCM.651.
- Garrels, R.M., and Lerman, A., 1981, Phanerozoic cycles of sedimentary carbon and sulfur: *Proceedings of the National Academy of Sciences of the United States of America*, v. 78, no. 8, p. 4652–4656.
- Garrels, R.M., and Lerman, A., 1984, Coupling of the sedimentary sulfur and carbon cycles—An improved model: *American Journal of Science*, v. 284, p. 989–1007.
- Gelin, F., Boogers, I., Noordeloos, A.A.M., Sinninghe Damsté, J.S., Hatcher, P.G., and de Leeuw, J.W., 1996a, Novel, resistant microalgal polyethers: an important sink of organic carbon in the marine environment?: *Geochimica et Cosmochimica Acta*, v. 60, p. 1275–1280, doi: 10.1016/0016-7037(96)00038-5.
- Gelin, F., Sinninghe Damsté, J.S., Harrison, W.N., Reiss, C., Maxwell, J.R., and de Leeuw, J.W., 1996b, Variations in origin and composition of

- kerogen constituents as revealed by analytical pyrolysis of immature kerogens before and after desulphurization: *Organic Geochemistry*, v. 24, p. 705–714, doi: 10.1016/0146-6380(96)00061-7.
- Gelin, F., Boogers, I., Noordeloos, A.A.M., Sinninghe Damsté, J.S., Riegman, R., and de Leeuw, J.W., 1997, Resistant biomacromolecules in five marine microalgae of the classes Eustigmatophyceae and Chlorophyceae: Geochemical implications: *Organic Geochemistry*, v. 26, p. 659–675, doi: 10.1016/S0146-6380(97)00035-1.
- Gelin, F., Kok, M., de Leeuw, J., and Sinninghe Damsté, J., 1998, Laboratory sulfuration of the marine microalga *Nannochloropsis salina*: *Organic Geochemistry*, v. 29, p. 1837–1848, doi: 10.1016/S0146-6380(98)00171-5.
- Gelin, F., Volkman, J.K., Largeau, C., Derenne, S., Sinninghe Damsté, J.S., and de Leeuw, J.W., 1999, Distribution of aliphatic, nonhydrolyzable biopolymers in marine microalgae: *Organic Geochemistry*, v. 30, p. 147–159, doi: 10.1016/S0146-6380(98)00206-X.
- George, G.N., and Gobaty, M.L., 1989, Sulfur K-edge x-ray absorption spectroscopy of petroleum asphaltens and model compounds: *Journal of the American Chemical Society*, v. 111, p. 3182–3186.
- Giggenbach, W., 1972, Optical spectra and equilibrium distribution of polysulfide ions in aqueous solution at 20 °C: *Inorganic Chemistry*, v. 11, p. 1201–1207.
- Gransch, J.A., and Posthuma, J., 1974, On the origin of sulphur in crudes, in Tissot, B., and Biener, F., *Advances in Organic Geochemistry 1973*: Paris, Editions Technip, p. 727–739.
- Grice, K., Schouten, S., Nissenbaum, A., Charrach, J., and Sinninghe Damsté, J., 1998, A remarkable paradox: Sulfurised freshwater algal (*Botryococcus braunii*) lipids in an ancient hypersaline euxinic ecosystem: *Organic Geochemistry*, v. 28, p. 195–216, doi: 10.1016/S0146-6380(97)00127-7.
- Habicht, K.S., and Canfield, D.E., 1997, Sulfur isotope fractionation during bacterial sulfate reduction in organic-rich sediments: *Geochimica et Cosmochimica Acta*, v. 61, p. 5351–5361.
- Habicht, K.S., and Canfield, D.E., 2001, Isotope fractionation by sulfate-reducing natural populations and the isotopic composition of sulfide in marine sediments: *Geology*, v. 29, p. 555–558, doi: 10.1130/0091-7613(2001)0292.0.CO;2.
- Habicht, K.S., Canfield, D.E., and Rethmeier, J., 1998, Sulfur isotope fractionation during bacterial reduction and disproportionation of thiosulfate and sulfite: *Geochimica et Cosmochimica Acta*, v. 62, p. 2585–2595, doi: 10.1016/S0016-7037(98)00167-7.
- Hartgers, W.A., Lopez, J.F., Sinninghe Damsté, J.S., Reiss, C., Maxwell, J.R., and Grimalt, J.O., 1997, Sulfur-binding in recent environments: II. Speciation of sulfur and iron and implications for the occurrence of organo-sulfur compounds: *Geochimica et Cosmochimica Acta*, v. 61, p. 4769–4788, doi: 10.1016/S0016-7037(97)00279-2.
- Heffer, J., Hauke, V., Richnow, H.H., and Michaelis, W., 1995, Alkanoic subunits in sulfur-rich geomacromolecules, in Vairavamurthy, M.A., and Schoonen, M.A.A., eds., *Geochemical transformations of sedimentary sulfur*: Washington, D.C., American Chemical Society Symposium Series 612, p. 91–109.
- Henneke, E., Luther, G., de Lange, G., and Hoefs, J., 1997, Sulphur speciation in anoxic hypersaline sediments from the eastern Mediterranean Sea: *Geochimica et Cosmochimica Acta*, v. 61, p. 307–321, doi: 10.1016/S0016-7037(96)00355-9.
- Huffman, G.P., Mitra, S., Huggins, F.E., Shah, N.S., Vaidya, N., and Lu, F., 1991, Quantitative analysis of all major forms of sulfur in coal by x-ray absorption fine structure spectroscopy: *Energy & Fuels*, v. 5, p. 574–581.
- Huffman, G.P., Shah, N., Huggins, F.E., Stock, L.M., Chatterjee, K., Kilbane, J.J., Chou, M., and Buchanan, D.H., 1995, Sulfur speciation of desulfurized coals by XANES spectroscopy: *Fuel*, v. 74, p. 549–555, doi: 10.1016/0016-2361(95)98358-L.
- Jørgensen, B.B., 1990, A thiosulfate shunt in the sulfur cycle of marine sediments: *Science*, v. 249, p. 152–154.
- Kaplan, I., and Rittenberg, S., 1964, Microbiological fractionation of sulphur isotopes: *Journal of General Microbiology*, v. 34, p. 195–212.
- Kenig, F., and Huc, A.Y., 1990, Incorporation of sulfur into recent organic matter in a carbonate environment (Abu Dhabi, United Arab Emirates), in Orr, W.L., and White, C.M., *Geochemistry of sulfur in fossil fuels*: Washington, D.C., American Chemical Society Symposium Series 249, p. 170–185.
- Kenig, F., Sinninghe Damsté, J.S., Frewin, N.L., Hayes, J.M., and de Leeuw, J.W., 1995, Molecular indicators for paleoenvironmental change in a Messinian evaporitic sequence (Vena del Gesso, Italy). II. High-resolution variations in abundances in  $\delta^{13}\text{C}$  contents of free and sulphur-bound carbon skeletons in a single marl bed: *Organic Geochemistry*, v. 23, p. 485–526, doi: 10.1016/0146-6380(95)00049-K.
- Kohnen, M.E.L., Sinninghe Damsté, J.S., Kock-van Dalen, A.C., ten Haven, H.L., Rüllkötter, J., and de Leeuw, J.W., 1990, Origin and diagenetic transformations of  $\text{C}_{25}$  and  $\text{C}_{30}$  highly branched isoprenoid sulphur compounds: Further evidence for the formation of organically bound sulphur during early diagenesis: *Geochimica et Cosmochimica Acta*, v. 54, p. 3053–3063, doi: 10.1016/0016-7037(90)90121-Z.
- Kohnen, M.E.L., Sinninghe Damsté, J.S., Kock-van Dalen, A.C., and de Leeuw, J.W., 1991a, Di- or polysulphide-bound biomarkers in sulphur-rich geomacromolecules as revealed by selective chemolysis: *Geochimica et Cosmochimica Acta*, v. 55, p. 1375–1394, doi: 10.1016/0016-7037(91)90315-V.
- Kohnen, M.E.L., Sinninghe Damsté, J.S., ten Haven, H.L., Kock-van Dalen, A.C., Schouten, S., and de Leeuw, J.W., 1991b, Identification and geochemical significance of cyclic di- and trisulphides with linear and acyclic isoprenoid skeletons in immature sediments: *Geochimica et Cosmochimica Acta*, v. 55, p. 3685–3695, doi: 10.1016/0016-7037(91)90067-F.
- Kohnen, M.E.L., Sinninghe Damsté, J.S., and de Leeuw, J.W., 1991c, Biases from natural sulphurization in palaeoenvironmental reconstruction based on hydrocarbon biomarker distributions: *Nature*, v. 349, p. 775–778, doi: 10.1038/349775A0.
- Kohnen, M., Schouten, S., Sinninghe Damsté, J., de Leeuw, J., Merrit, D., and Hayes, J., 1992, The combined application of organic sulphur and isotope geochemistry to assess multiple sources of palaeochemicals with identical carbon skeletons: *Organic Geochemistry*, v. 19, p. 403–419, doi: 10.1016/0146-6380(92)90008-L.
- Kohnen, M.E.L., Sinninghe Damsté, J.S., Baas, M., Kock-van Dalen, A.C., and de Leeuw, J.W., 1993, Sulphur-bound steroid and phytane carbon skeletons in geomacromolecules: Implications for the mechanism of incorporation of sulphur into organic matter: *Geochimica et Cosmochimica Acta*, v. 57, p. 2515–2528, doi: 10.1016/0016-7037(93)90414-R.
- Kok, M.D., Rijpstra, W.I.C., Robertson, L., Volkman, J., and Sinninghe Damsté, J.S., 2000a, Early steroid sulfuration in surface sediments of a permanently stratified lake (Ace Lake, Antarctica): *Geochimica et Cosmochimica Acta*, v. 64, p. 1425–1436, doi: 10.1016/S0016-7037(99)00430-5.
- Kok, M.D., Schouten, S., and Sinninghe Damsté, J.S., 2000b, Formation of insoluble, nonhydrolyzable, sulfur-rich macromolecules via incorporation of inorganic sulfur species into algal carbohydrates: *Geochimica et Cosmochimica Acta*, v. 64, p. 2689–2699, doi: 10.1016/S0016-7037(00)00382-3.
- Koopmans, M.P., de Leeuw, J.W., Lewan, M.D., and Sinninghe Damsté, J.S., 1996, Impact of dia- and catagenesis on sulphur and oxygen sequestration of biomarkers as revealed by artificial maturation of an immature sedimentary rock: *Organic Geochemistry*, v. 25, p. 391–426, doi: 10.1016/S0146-6380(96)00144-1.
- Krein, E.B., and Aizenshtat, Z., 1995, Proposed thermal pathways for sulfur transformations in organic macromolecules: laboratory simulation experiments, in Vairavamurthy, M.A., and Schoonen, M.A.A., eds., *Geochemical transformations of sedimentary sulfur*: Washington, D.C., American Chemical Society Symposium Series 612, p. 110–137.
- Kump, L.R., and Garrels, R.M., 1986, Modeling atmospheric  $\text{O}_2$  in the global sedimentary redox cycle: *American Journal of Science*, v. 286, p. 337–360.
- LaLonde, R., Ferrara, L., and Hayes, M., 1987, Low-temperature, polysulfide reactions of conjugated ene carbonyls: A reaction model for the geologic origin of S-heterocycles: *Organic Geochemistry*, v. 11, p. 563–571, doi: 10.1016/0146-6380(87)90010-6.
- Larsen, O., and Potsma, D., 2001, Kinetics of reductive bulk dissolution of lepidocrocite, ferrihydrite, and goethite: *Geochimica et Cosmochimica Acta*, v. 65, p. 1367–1379.
- Lewan, M., 1993, Laboratory simulation of petroleum formation: Hydrous Pyrolysis, in Engel M.H., and Macko, S.A., eds., *Organic geochemistry, principles and applications—Topics in geobiology*: New York, Plenum, v. 11, p. 419–444.
- Lewan, M.D., 1998, Sulphur-radical control on petroleum formation rates: *Nature*, v. 391, p. 164–166, doi: 10.1038/34391.
- Luckge, A., Horsfield, B., Littke, R., and Scheeder, G., 2002, Organic matter preservation and sulfur uptake in sediments from the continental margin off Pakistan: *Organic Geochemistry*, v. 33, p. 477–488, doi: 10.1016/S0146-6380(01)00171-1.
- Luther, George W. III, Church, Thomas M., 1988, Seasonal cycling of sulfur and iron in pore-waters of a Delaware salt marsh: *Marine Chemistry*, v. 23, p. 295–309.
- Mossmann, J.R., Aplin, A.C., Curtis, C.D., and Coleman, M.L., 1991, Geochemistry of inorganic and organic sulphur in organic-rich sediments

- from the Peru Margin: *Geochimica et Cosmochimica Acta*, v. 55, p. 3581–3595, doi: 10.1016/0016-7037(91)90057-C.
- Nelson, B.C., Eglinton, T.L., Seewald, J.S., Vairavamurthy, M.A., and Miknis, F.P., (1995) Transformations in organic sulfur speciation during maturation of Monterey Shale: constraints from laboratory experiments, in Vairavamurthy, M.A., and Schoonen, M.A.A., eds., *Geochemical transformations of sedimentary sulfur*: Washington, D.C., American Chemical Society Symposium Series 612, p. 138–166.
- Orr, W., 1978, Sulphur in heavy oils, oils sands and oil shales, in Strausz, O., and Lown, E., eds., *Oil sand and oil shale chemistry*: Berlin, Verlag Chemie Int., p. 223–243.
- Orr, W., and White, C., editors, 1990, *Geochemistry of sulfur in fossil fuels*: Washington, D.C., American Chemical Society Symposium Series 429, 708 p.
- Orr, W.L., and Sinninghe Damsté, J.S., 1990, Geochemistry of sulfur in petroleum systems, in Orr, W.L., and C.M. White, eds., *Geochemistry of sulfur in fossil fuels*: Washington, D.C., American Chemical Society Symposium Series 429, p. 2–29.
- Passier, H.F., Luther, G.W., III, and de Lange, G.J., 1997, Early diagenesis and sulphur speciation in sediments of the Oman Margin, northwestern Arabian Sea: *Deep-Sea Research II*, v. 44, p. 1361–1380, doi: 10.1016/S0967-0645(97)00014-3.
- Peakman, T.M., Sinninghe Damsté, J.S., and de Leeuw, J.W., 1989, The identification and geochemical significance of a second series of alkylthiophene comprising a linearly extended phytane skeleton in sediments and oils: *Geochimica et Cosmochimica Acta*, v. 53, p. 3317–3322, doi: 10.1016/0016-7037(89)90111-7.
- Perakis, N., 1986, Séparation et détection sélective de composés soufrés dans les fractions Lourdes de pétroles: Géochimie des benzo[b]thiophènes [Ph.D. Dissertation]: University of Strasbourg.
- Petsch, S.T., and Berner, R.A., 1998, Coupling the geochemical cycles of C, P, Fe, and S: The effects on atmospheric O<sub>2</sub> and the isotopic records of carbon and sulfur: *American Journal of Science*, v. 298, p. 246–262.
- Poinsot, J.P., Schneckeburger, P., Adam, P., Schaeffer, P., Trendel, J.M., Riva, A., and Albrecht, P., 1998, Novel polycyclic sulfides derived from regular polyprenoids in sediments: Characterization, distribution and geochemical significance: *Geochimica et Cosmochimica Acta*, v. 62, p. 805–814, doi: 10.1016/S0016-7037(98)00022-2.
- Price, F.T., and Shieh, Y.N., 1979, Fractionation of sulfur isotopes during laboratory synthesis of pyrite at low temperatures: *Chemical Geology*, v. 27, p. 245–253, doi: 10.1016/0009-2541(79)90042-1.
- Putschew, A., Scholz-Böttcher, B.M., and Rullkötter, J., 1995, Organic geochemistry of sulphur-rich surface sediments of meromictic Lake Cadagno, Swiss Alps, in Vairavamurthy, M.A., and Schoonen, M.A.A., eds., *Geochemical transformations of sedimentary sulfur*: Washington, D.C., American Chemical Society Symposium Series 612, p. 59–79.
- Putschew, A., Scholz-Böttcher, B.M., and Rullkötter, J., 1996, Early diagenesis of organic matter and related sulphur incorporation on surface sediments of meromictic Lake Cadagno in the Swiss Alps: *Organic Geochemistry*, v. 25, p. 379–390, doi: 10.1016/S0146-6380(96)00143-X.
- Putschew, A., Schaeffer-Reiss, C., Schaeffer, P., Koopmans, M.P., de Leeuw, J.W., Lewan, M.D., Sinninghe Damsté, J.S., and Maxwell, J.R., 1998, Release of sulfur- and oxygen-bound components from a sulfur-rich kerogen during simulated maturation by hydrous pyrolysis: *Organic Geochemistry*, v. 29, p. 1875–1890, doi: 10.1016/S0146-6380(98)00191-0.
- Pyzik, A.J., and Sommer, S.E., 1981, Sedimentary iron monosulfides: Kinetics and mechanism of formation: *Geochimica et Cosmochimica Acta*, v. 45, p. 687–698, doi: 10.1016/0016-7037(81)90042-9.
- Rees, C.E., Jenkins, W.J., and Monster, J., 1978, The sulfur isotopic composition of ocean water sulfate: *Geochimica et Cosmochimica Acta*, v. 42, p. 377–381, doi: 10.1016/0016-7037(78)90268-5.
- Rospondek, M.J., Köster, J., and Sinninghe Damsté, J.S., 1997, Novel C<sub>26</sub> highly branched isoprenoid thiophenes and alkane from the Menilite Formation, Outer Carpathians, SE Poland: *Organic Geochemistry*, v. 26, p. 295–304, doi: 10.1016/S0146-6380(97)00021-1.
- Rowland, S., Rockey, C., al-Lihaibi, S.S., and Wolff, G.A., 1993, Incorporation of sulphur into phytol derivatives during simulated early diagenesis: *Organic Geochemistry*, v. 20, p. 1–5, doi: 10.1016/0146-6380(93)90075-M.
- Russell, M., Hartgers, W., and Grimalt, J., 2000, Identification and geochemical significance of sulphurized fatty acids in sedimentary organic matter from the Lorca Basin, SE Spain: *Geochimica et Cosmochimica Acta*, v. 64, p. 3711–3723, doi: 10.1016/S0016-7037(00)00470-1.
- Sandison, C.M., Alexander, R., Kagi, R.I., and Boreham, C.J., 2002, Sulfurisation of lipids in a marine-influenced lignite: *Organic Geochemistry*, v. 33, p. 1053–1077, doi: 10.1016/S0146-6380(02)00083-9.
- Sarret, G., Connan, J., Kasrai, M., Bancroft, G.M., Charrié-Duhaut, A., Lemoine, S., Adam, P., Albrecht, P., and Eybert-Bérard, L., 1999, Chemical forms of sulfur in geological and archeological asphaltenes from Middle East, France, and Spain determined by sulfur K- and L-edge X-ray absorption near-edge structure spectroscopy: *Geochimica et Cosmochimica Acta*, v. 63, p. 3767–3779, doi: 10.1016/S0016-7037(99)00205-7.
- Sarret, G., Mongenet, T., Connan, J., Derenne, S., Kasrai, M., Bancroft, G., and Largeau, C., 2002, Sulfur speciation in kerogens of the Orbagnoux deposit (Upper Kimmeridgian, Jura) by XANES spectroscopy and pyrolysis: *Organic Geochemistry*, v. 33, p. 877–895, doi: 10.1016/S0146-6380(02)00066-9.
- Schaeffer, P., Reiss, C., and Albrecht, P., 1995, Geochemical study of macromolecular organic matter from sulfur-rich sediments of evaporitic origin (Messinian of Sicily) by chemical degradations: *Organic Geochemistry*, v. 23, p. 567–581, doi: 10.1016/0146-6380(95)00045-G.
- Schaeffer-Reiss, C., Schaeffer, P., Putschew, A., and Maxwell, J.R., 1998, Stepwise chemical degradation of immature S-rich kerogens from Vena del Gesso (Italy): *Organic Geochemistry*, v. 29, p. 1857–1873, doi: 10.1016/S0146-6380(98)00175-2.
- Schneckenburger, P., Adam, P., and Albrecht, P., 1998, Thioketones as key intermediates in the reduction of ketones to thiols by HS<sup>-</sup> in natural environments: *Tetrahedron Letters*, v. 39, p. 447–450, doi: 10.1016/S0040-4039(97)10572-X.
- Schouten, S., Pavlovic, D., Sinninghe Damsté, J., and de Leeuw, J., 1993a, Nickel boride: An improved desulphurizing agent for sulphur-rich geomacromolecules in polar and asphaltene fractions: *Organic Geochemistry*, v. 20, p. 901–909, doi: 10.1016/0146-6380(93)90101-G.
- Schouten, S., Pavlovic, D., Sinninghe Damsté, J.S., and de Leeuw, J.W., 1993b, Selective cleavage of acyclic sulphide moieties of sulphur-rich geomacromolecules by superheated methyl iodide: *Organic Geochemistry*, v. 20, p. 911–916, doi: 10.1016/0146-6380(93)90102-H.
- Schouten, S., de Graaf, W., Sinninghe Damsté, J.S., van Driel, G.B., and de Leeuw, J.W., 1994a, Laboratory simulation of natural sulphurization. II. Reaction of multifunctionalized lipids with inorganic polysulphides at low temperatures, in Telnæs, N., van Graas, G., and Øygaard, K., *Advances in organic geochemistry 1993*: *Organic Geochemistry*, v. 22, p. 825–834, doi: 10.1016/0146-6380(94)90142-2.
- Schouten, S., van Driel, G.B., Sinninghe Damsté, J.S., and de Leeuw, J.W., 1994b, Natural sulphurization of ketones and aldehydes: A key reaction in the formation of organic sulphur compounds: *Geochimica et Cosmochimica Acta*, v. 58, p. 5111–5116.
- Schouten, S., Sinninghe Damsté, J., Baas, M., Kock-van Dalen, A., Kohnen, M., and de Leeuw, J., 1995a, Quantitative assessment of mono- and polysulphide-linked carbon skeletons in sulphur-rich macromolecular aggregates present in bitumens and oils: *Organic Geochemistry*, v. 23, p. 765–775, doi: 10.1016/0146-6380(95)00055-J.
- Schouten, S., Eglinton, T.I., and Sinninghe Damsté, J.S., 1995b, Influence of sulphur cross-linking on the molecular-size distribution of sulphur-rich macromolecules in bitumen, in Vairavamurthy, M.A., and Schoonen, M.A.A., eds., *Geochemical transformations of sedimentary sulfur*: Washington, D.C., American Chemical Society Symposium Series 612, p. 80–92.
- Schouten, S., Sinninghe Damsté, J.S., Kohnen, M.E.L., and de Leeuw, J.W., 1995c, The effect of hydrosulphurization on stable carbon isotopic compositions of free and sulphur-bound lipids: *Geochimica et Cosmochimica Acta*, v. 59, p. 1605–1609, doi: 10.1016/0016-7037(95)00066-9.
- Schouten, S., de Loureiro, M.R.B., Sinninghe Damsté, J.S., and de Leeuw, J.W., 2001, Molecular biogeochemistry of Monterey sediments (Naples Beach, USA). I. distributions of hydrocarbons and organic sulphur compounds, in Isaacs, C.M., and Rullkötter, J., eds., *The Monterey Formation: From rocks to molecule*: Columbia University Press, p. 150–174.
- Shen, Y., Buick, R., and Canfield, D.E., 2001, Isotopic evidence for microbial sulphate reduction in the early Archean era: *Nature*, v. 410, p. 77–81, doi: 10.1038/35065071.
- Sinninghe Damsté, J.S., and de Leeuw, J.W., 1990, Analysis, structure and geochemical significance of organically-bound sulphur in the geosphere: State of the art and future research, in Durand B., and Behar, F., *Advances in organic geochemistry 1989*: *Organic Geochemistry*, v. 16, p. 1077–1101, doi: 10.1016/0146-6380(90)90145-P.
- Sinninghe Damsté, J.S., and de Leeuw, J.W., 1992, Organically bound sulphur in coal: A molecular approach: *Fuel Processing Technology*, v. 30, p. 109–178, doi: 10.1016/0378-3820(92)90045-R.

- Sinninghe Damsté, J.S., Rijpstra, W.I.C., de Leeuw, J.W., and Schenck, P.A., 1988, Origin of organic sulphur compounds and sulphur-containing high molecular weight substances in sediments and immature crude oils, *in* Matavelli, L., and Novelli, L., *Advances in organic geochemistry 1987: Organic Geochemistry*, v. 13, p. 593–606, doi: 10.1016/0146-6380(88)90079-4.
- Sinninghe Damsté, J.S., Rijpstra, W.I.C., Kock-van Dalen, A.C., de Leeuw, J.W., and Schenck, P.A., 1989, Quenching of labile functionalised lipids by inorganic sulphur species: Evidence for the formation of sedimentary organic sulphur compounds at the early stages of diagenesis: *Geochimica et Cosmochimica Acta*, v. 53, p. 1343–1355, doi: 10.1016/0016-7037(89)90067-7.
- Sinninghe Damsté, J.S., Kohnen, M.E.L., and de Leeuw, J.W., 1990, Thiophenic biomarkers for palaeoenvironmental assessment and molecular stratigraphy: *Nature*, v. 345, p. 609–611, doi: 10.1038/345609A0.
- Sinninghe Damsté, J.S., de las Heras, X.F.C., van Bergen, P.F., and de Leeuw, J.W., 1993, Characterization of Tertiary Catalan lacustrine oil shales: Discovery of extremely organic sulphur-rich Type I kerogens: *Geochimica et Cosmochimica Acta*, v. 57, p. 389–415.
- Sinninghe Damsté, J.S., Rijpstra, W.I.C., de Leeuw, J.W., and Lijmbach, G.W.M., 1994, Molecular characterization of organically-bound sulfur in crude oils: A feasibility study for the application of Raney Ni desulfurization as a new method to characterize crude oils: *Journal of High Resolution Chromatography*, v. 17, p. 489–500.
- Sinninghe Damsté, J.S., Kohnen, M.E.L., and Horsfield, B., 1998a, Origin of low-molecular-weight alkylthiophenes in pyrolysates of sulphur-rich kerogens as revealed by micro-scale sealed vessel pyrolysis: *Organic Geochemistry*, v. 29, p. 1891–1903, doi: 10.1016/S0146-6380(98)00166-1.
- Sinninghe Damsté, J., Kok, M., Köster, J., and Schouten, S., 1998b, Sulfurized carbohydrates: an important sedimentary sink for organic carbon?: *Earth and Planetary Science Letters*, v. 164, p. 7–13, doi: 10.1016/S0012-821X(98)00234-9.
- Sinninghe Damsté, J.S., White, C.M., Green, J.B., and de Leeuw, J.W., 1999a, Organosulfur compounds in sulfur-rich Rasa Coal: *Energy & Fuels*, v. 13, p. 728–738, doi: 10.1021/EF980236C.
- Sinninghe Damsté, J.S., Schouten, S., de Leeuw, J.W., van Duin, A.C.T., and Geenevasen, J.A.J., 1999b, Identification of novel sulfur-containing steroids in sediments and petroleum: Probably incorporation of sulfur into D5,7-sterols during early diagenesis: *Geochimica et Cosmochimica Acta*, v. 63, p. 31–38, doi: 10.1016/S0016-7037(98)00295-6.
- Spiro, C.L., Wong, J., Lytle, F.W., Gregor, R.B., Maylotte, D.H., and Lamson, S.H., 1984, X-ray absorption spectroscopic investigation of sulfur sites in coals: organic sulfur identification: *Science*, v. 226, p. 48–50.
- Studley, S.A., Ripley, E.M., Elswick, E.R., Dorais, M.J., Fong, J., Finkelstein, D., and Pratt, L.M., 2002, Analysis of sulfides in whole rock matrices by elemental analyzer–continuous flow isotope ratio mass spectrometry: *Chemical Geology*, v. 192, p. 141–148, doi: 10.1016/S0009-2541(02)00162-6.
- Suits, N., and Arthur, M., 2000, Sulfur diagenesis and partitioning in Holocene Peru shelf and upper slope sediments: *Chemical Geology*, v. 163, p. 219–234, doi: 10.1016/S0009-2541(99)00114-X.
- Tissot, B., and Welte, D., 1984, *Petroleum formation and occurrence*, 2nd edition: Heidelberg, Springer, 699 p.
- Tomic, J., Behar, F., Vandenbrouke, M., and Tang, Y., 1995, Artificial maturation of Monterey kerogen (Type II-S) in a closed system and comparison with Type II kerogen: implications on the fate of sulfur: *Organic Geochemistry*, v. 23, p. 647–660, doi: 10.1016/0146-6380(95)00043-E.
- Trust, B.A., and Fry, B., 1992, Sulphur isotopes in plants: a review: *Plant, Cell & Environment*, v. 15, p. 1105–1110.
- Urban, N., Ernst, K., and Bernasconi, S., 1999, Addition of sulfur to organic matter during early diagenesis of lake sediments: *Geochimica et Cosmochimica Acta*, v. 63, p. 837–853, doi: 10.1016/S0016-7037(98)00306-8.
- Vairavamurthy, M., and Schoonen, M., editors, 1995, *Geochemical transformations of sedimentary sulfur*: Washington, D.C., American Chemical Society Symposium Series 612, 467 p.
- Vairavamurthy, A., Mopper, K., and Taylor, B., 1992, Occurrence of particle-bound polysulfides and significance of their reaction with organic matters in marine sediments: *Geophysical Research Letters*, v. 19, p. 2043–2046.
- Vairavamurthy, A., Zhou, W., Eglinton, T., and Manowitz, B., 1994, Sulfonates: A novel class of organic sulfur compounds in marine sediments: *Geochimica et Cosmochimica Acta*, v. 58, p. 4681–4687, doi: 10.1016/0016-7037(94)90200-3.
- Vairavamurthy, M., Orr, W., and Manowitz, B., 1995, Geochemical transformations of sedimentary sulfur: An introduction, *in* Vairavamurthy, M.A., and Schoonen, M.A.A., eds., *Geochemical transformations of sedimentary sulfur*: Washington, D.C., American Chemical Society Symposium Series 612, p. 1–15.
- Vairavamurthy, M., Maletic, D., Want, S., Manowitz, B., Eglinton, T., and Lyons, T., 1997, Characterization of sulfur-containing functional groups in sedimentary humic substances by X-ray absorption near-edge structure spectroscopy: *Energy & Fuels*, v. 11, p. 546–553, doi: 10.1021/EF960212A.
- Valisolalao, J., Perakis, N., Chappe, B., and Albrecht, P., 1984, A novel sulfur containing C<sub>35</sub> hopanoid in sediments: *Tetrahedron Letters*, v. 25, p. 1183–1186, doi: 10.1016/S0040-4039(01)91555-2.
- van Dongen, B.E., 2003, *Natural sulfurization of carbohydrates in marine sediments: consequences for the chemical and carbon isotopic composition of sedimentary organic matter* [Ph.D. thesis]: University of Utrecht, 149 p.
- van Dongen, S., Schouten, S., and Sinninghe Damsté, J., 2002, Carbon isotope variability in monosaccharides and lipids of aquatic algae and terrestrial plants: *Marine Ecology Progress Series*, v. 232, p. 83–92.
- van Dongen, B.E., Schouten, S., Baas, M., Geenevasen, J.A.J., and Sinninghe Damsté, J.S., 2003a, An experimental study of the low-temperature sulfurization of carbohydrates: *Organic Geochemistry*, v. 34, p. 1129–1144, doi: 10.1016/S0146-6380(03)00060-3.
- van Dongen, B.E., Schouten, S., and Sinninghe Damsté, J.S., 2003b, Sulfurization of carbohydrates results in n S-rich, unresolved complex mixture in kerogen pyrolysates: *Energy & Fuels*, v. 17, p. 1109–1118, doi: 10.1021/EF0202283.
- Van Kaam-Peters, H.M.E., Schouten, S., Köster, J., and Sinninghe Damsté, J.S., 1998, Controls on the molecular and carbon isotopic composition of organic matter deposited in a Kimmeridgian euxinic shelf sea: Evidence for preservation of carbohydrates through sulfurisation: *Geochimica et Cosmochimica Acta*, v. 62, p. 3259–3283, doi: 10.1016/S0016-7037(98)00231-2.
- Wakeham, S.G., Sinninghe Damsté, J.S., Kohnen, M.E.L., and de Leeuw, J.W., 1995, Organic sulfur compounds formed during early diagenesis in Black Sea sediments: *Geochimica et Cosmochimica Acta*, v. 59, no. 3, p. 521–533, doi: 10.1016/0016-7037(94)00361-0.
- Waldo, G.S., Carlson, M.K., Moldowan, J.M., Peters, K.E., and Penner-Hahn, J.E., 1991, Sulfur speciation in heavy petroleum: Information from x-ray absorption near edge structure: *Geochimica et Cosmochimica Acta*, v. 55, p. 801–814, doi: 10.1016/0016-7037(91)90343-4.
- Werne, J., 2000, *A geochemical evaluation of depositional controls and paleoenvironmental reconstructions in organic rich sedimentary deposits: Evidence from the modern Cariaco Basin, Venezuela, and application to the Devonian Appalachian Basin* [Ph.D. dissertation]: Northwestern University, 310 p.
- Werne, J.P., Hollander, D.J., Behrens, A., Schaeffer, P., Albrecht, P., and Sinninghe Damsté, J.S.S., 2000a, Timing of early diagenetic sulfurization of organic matter: A precursor-product relationship in Holocene sediments of the anoxic Cariaco Basin, Venezuela: *Geochimica et Cosmochimica Acta*, v. 64, p. 1741–1751.
- Werne, J.P., Hollander, D.J., Lyons, T.W., and Peterson, L.C., 2000b, Climate-induced variations in productivity and planktonic ecosystem structure from the Younger Dryas to Holocene in the Cariaco Basin, Venezuela: *Paleoceanography*, v. 15, no. 1, p. 19–29.
- Werne, J.P., Hollander, D.J., Lyons, T.W., and Sinninghe Damsté, J.S., 2001, Compound-specific sulfur isotope constraints on the pathway(s) of diagenetic sulfurization of organic matter, *Geological Society of America Abstracts with Programs*, v. 33, no. 6, p. A-94.
- Werne, J.P., Lyons, T.W., Hollander, D.J., Formolo, M., and Sinninghe Damsté, J.S., 2003, Reduced sulfur in euxinic sediments of the Cariaco Basin: Sulfur isotope constraints on organic sulfur formation: *Chemical Geology*, v. 195, p. 159–179, doi: 10.1016/S0009-2541(02)00393-5.
- Zaback, D.A., and Pratt, L.M., 1992, Isotope composition and speciation of sulfur in the Miocene Monterey Formation: Reevaluation of sulfur reactions during early diagenesis in marine environments: *Geochimica et Cosmochimica Acta*, v. 56, p. 763–774, doi: 10.1016/0016-7037(92)90096-2.