

CHAPTER 10

Development and Initial Biogeochemical Applications of Compound-Specific Sulfur Isotope Analysis

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10.1 Introduction

Compound-specific isotope analysis (CSIA) has previously been applied to the stable isotopes of hydrogen, carbon, nitrogen, and oxygen, but has only recently been extended to sulfur. The $\delta^{34}\text{S}$ values of chromatographically resolved organic analytes can now be reliably measured by modern

commercial multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) instruments providing high mass resolution. The m/z 32 chromatogram and $\delta^{34}\text{S}$ values of resolved hydrocarbons from the gas chromatography (GC)-ICPMS analysis of a Caspian Sea oil is shown in Figure 10.1 and was similar to the data reported from the same oil in the first practical application of this technology to a natural sample.¹

Gas-source isotope ratio mass spectrometry (irMS), traditionally used for stable isotope measurements, is unable to support the analysis of sulfur isotopes in organic sulfur compounds (OSCs) isolated by GC. The main hurdle in this pursuit is the need for continuous oxidation of OSCs to sulfur dioxide and the separation of other combustion products (*e.g.* water, carbon dioxide). ICPMS overcomes this problem by atomising and ionising OSCs in the plasma source enabling the direct measurement of monoatomic sulfur ions (*i.e.* $^{32}\text{S}^+$ and $^{34}\text{S}^+$). A new problem arises in that the isotopologues of oxygen interfere with those of sulfur at both m/z 32 and 34. A theoretical mass-resolving power ($m/\Delta m$) of 1808 is required to distinguish $^{32}\text{S}^+$ (31.9721 Da) from $^{16}\text{O}_2^+$ (31.9898 Da), and of 1221 to distinguish $^{34}\text{S}^+$ (33.9678 Da) from $^{16}\text{O}^{18}\text{O}^+$ (33.9940 Da). In practice, mass resolution of several thousand is needed to achieve stable isotope ratios,²⁻⁴ but this is well within the capabilities of most modern MC-ICPMS instruments. The use of plasma ionisation to produce monoatomic ions yields several other benefits, including the lack of oxidative combustion reactors and catalysts that must be regenerated, and eliminating the need for oxygen isotope corrections in calculating $\delta^{34}\text{S}$. A substantial drawback, however, is the complexity and cost of MC-ICPMS instrumentation.

Early steps to use organic sulfur fractions included extraction methods to gain at least similar functional groups (*e.g.* humic acids).^{5,6} Just before the emergence of the GC-ICPMS procedure for continuous-flow sulfur-CSIA,

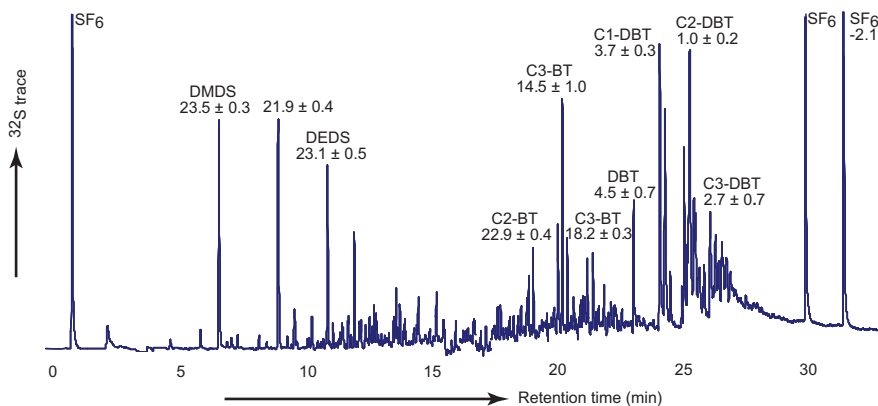


Figure 10.1 M/z 32 chromatogram from GC-ICPMS of a low-sulfur Caspian Sea crude oil. $\delta^{34}\text{S}$ values are shown atop peaks corresponding to major organic sulfur compounds.

(Figure modified from Amrani *et al.*¹)

measurement of the $\delta^{34}\text{S}$ values of individual OSC was performed by EA-irMS analysis following their isolation using preparative high-performance liquid chromatography (HPLC).⁷ These were very labour-intensive and time-consuming analyses, but they demonstrated the concept of sulfur-CSIA which represents a major step forward for sulfur biogeochemical studies. The prototype GC-ICPMS technology for sulfur-CSIA was developed in 2009¹ and two other similar facilities have since been established.^{8,9}

10.1.1 Sulfur Biogeochemistry and $\delta^{34}\text{S}$

Organic sulfur (OS) is the second major pool of reduced sulfur in sediments after pyrite, and has significant influence on the coupled global biogeochemical cycles of carbon, sulfur, and oxygen. Sulfurisation is thought to play a key role in the preservation of organic matter,¹⁰ including functionalised organic compounds which retain a structural link to their biological source (*i.e.* biomarkers). Whereas biomolecules with abundant functional groups (*e.g.* carbohydrates)^{11,12} are highly labile and subject to rapid microbial mineralisation,^{13–15} their reaction with reduced sulfur species during diagenesis leads to cross-linking of molecules and a highly polymerised, stable molecular structure that is more resistant to low-temperature degradation.^{16–19} Sulfurisation can thus sequester certain labile compounds otherwise vulnerable to diagenetic processes. Reduced sulfur can also participate in catalytic reduction of unsaturated compounds.²⁰

The sulfur incorporated into sedimentary organic matter may potentially derive from biotic as well as abiotic pathways. OS species (*e.g.* the amino acid cysteine) are synthesized through direct reduction and assimilation of dissolved sulfate. These OS compounds are quite labile, however, and seem unlikely to survive diagenesis and contribute significantly to sedimentary OS.^{13,21} Nevertheless, the contribution of biotic sulfur to sedimentary organic matter remains debated. Abiotic sulfur derives from the incorporation of reduced inorganic sulfur species, mainly HS^- and S_x^{2-} . Although the reduced sulfur species are themselves derived from biotic processes (*e.g.* microbial sulfate reduction), they are thought to be incorporated into OS by abiotic reactions during diagenesis.^{22,23}

The occurrences and stable isotopic relationships of reduced inorganic and OS species in sediments have helped us to understand the timing and pathways of OS formation in a variety of environments, including modern oceans,^{24,25} hypersaline basins,²⁶ freshwater environments,²⁷ and ancient systems such as the Miocene Monterey Formation.²⁸ The distribution of sulfur isotopes in the environment is controlled to first order by fractionations imparted during abiotic sulfate reduction. Many studies have shown this process strongly favours the lighter isotope, yielding under open system conditions sulfides that are significantly depleted in ^{34}S relative to the source sulfate,^{22,29–35} sometimes by more than 70%.^{34,35} In contrast, OS derived from biotic pathways typically has a $\delta^{34}\text{S}$ value similar to that of seawater sulfate (present-day value of 21.0‰).^{36,37} A second control on $\delta^{34}\text{S}$ is the

microbial cycle of sulfide oxidation and subsequent disproportionation of intermediate oxidation phases of sulfur, such as elemental sulfur, thio-sulfate, or polysulfides.^{31,32,38–40} These forms of sulfur are generally enriched in ^{34}S relative to co-occurring sulfide.⁴¹ While the fractionations associated with sulfide oxidation are generally small,²³ those associated with microbial disproportionation can be up to 37%.^{32,39} It has been assumed that repeated cycles of reduction, oxidation, and disproportionation may lead to a large offset between the $\delta^{34}\text{S}$ values of sulfate and sulfide,³¹ thereby also impacting the OS fractions.

Sedimentary OS often has $\delta^{34}\text{S}$ values between those of biotic and abiotic end members, suggesting possible contributions from both processes.^{42–45} However, without the ability to measure $\delta^{34}\text{S}$ in individual compounds, the occurrence of significant isotope effects accompanying the incorporation of reduced sulfur species has not yet been carefully evaluated. It remains possible that most OS is derived from pore water sulfide or polysulfide (*i.e. via* abiotic reactions) but with fractionations that lead to greater ^{34}S enrichments in OSCs.

10.2 GC-ICPMS Instrumentation and Analytical Performance

Continuous-flow compound-specific sulfur isotope analysis was achieved by interfacing GC with MC-ICPMS. The coupling of GC with MC-ICPMS for isotope ratio measurements was first applied to other elements^{46–49} and later adapted at Caltech for the study of sulfur isotopes in organic compounds.¹ Two similar instruments have recently been established at the Hebrew University, Israel⁸ and The University of Western Australia (UWA).⁹ The Caltech and UWA facilities both use an Agilent GC while the Hebrew University has a Perkin Elmer (Clarus 580) GC, but essentially any commercially available GC could be used with minor modifications. All three instruments employ a ThermoFisher Scientific Neptune MC-ICPMS which has the important characteristic of having a grounded interface. The high mass resolution ($m/\Delta m$) it can provide is required to clearly separate (by ~ 15 mDa) sulfur and oxygen isotopes, such as the minor isobaric interference of $^{16}\text{O}_2$ from the ^{32}S signal.

The UWA instrument is shown in Figure 10.2, along with a schematic layout of the instrument currently in use at Caltech.

It should be noted that GC peak resolution remains constrained by the complexity of the sample mixture. Coeluting peaks, noisy backgrounds, and unresolved complex mixtures all create difficulties and thus can reduce the accuracy and precision of $\delta^{34}\text{S}$ measurements. The same limitation impacts CSIA for other elements. In all of these cases, chromatographic complexity can sometimes be overcome with chemical, thermal, or other separation procedures to reduce organic extracts into less complex fractions more amenable to uncompromised GC resolution of individual compounds.^{1,7}

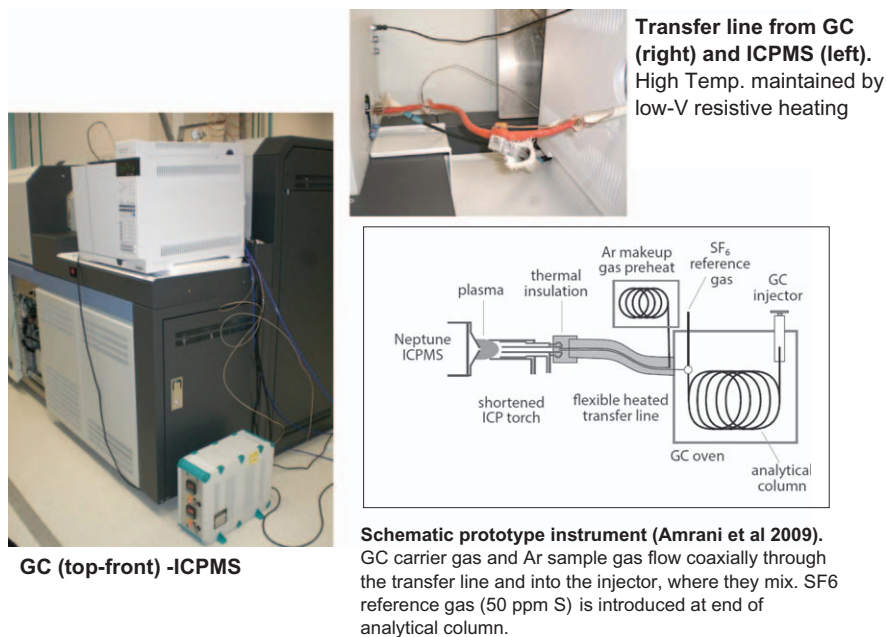


Figure 10.2 GC-ICPMS facility at the University of Western Australia and schematic layout of first GC-IPMS instrument at Caltech.

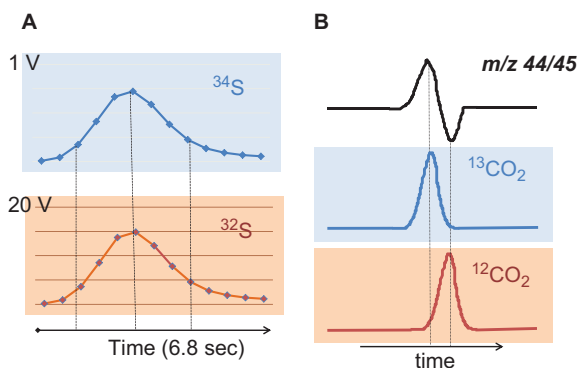


Figure 10.3 Comparison of the temporal profiles typical of (A) ^{32}S and ^{34}S signals from GC-ICPMS measurement of an organic sulfur compound; and (B) $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$ (and corresponding m/z 44/45) signals from GC-irMS analysis of an organic analyte.

Unlike for $\delta^{13}\text{C}$ and δD analysis, however, there seems to be little chromatographic separation of the sulfur isotopologues (*i.e.* molecules having a ^{34}S substitution). The temporal profiles of ^{32}S and ^{34}S measured from GC-ICPMS analysis of a representative OSC are shown in Figure 10.3, and are compared to the $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$ signals from the GC-irMS analysis of an organic

analyte. In the absence of an isotope chromatographic effect, partial integration of the sides of co-eluting peaks, or of the central most intense part of a peak, may still yield accurate $\delta^{34}\text{S}$ measurements. Amrani *et al.*¹ compared the integration of whole *versus* centre parts of sulfur hexafluoride and hexylthiophene peaks and found the latter partial peak strategy provided a slight improvement in precision (approaching the shot-noise limit) and only a slight difference ($\sim 0.2\%$) in accuracy.

A related, ongoing challenge of sulfur-CSIA is the identification of analytes. Because the ICPMS operates as an element-specific detector, lone organosulfur peaks eluting in the midst of many other (non-sulfur-bearing) hydrocarbons can still be accurately measured with only minor reduction in accuracy and precision.¹ However, the molecular mass spectra (*e.g.* obtained by a GC-MS) of these coeluting mixtures are sufficiently complex that analyte identification can be difficult or impossible. S-CSIA thus presents a challenge that is somewhat unique in the stable isotope world, namely that we can measure the $\delta^{34}\text{S}$ values of many peaks that we cannot identify.

There have been other analytical challenges more specific to the GC-ICPMS technology, perhaps most significantly the efficient transfer of GC-resolved analytes (particularly less volatile high molecular weight OSCs) to the ICP torch. Fortunately, this issue has been recently addressed by more effective heating of the transfer line and, particularly the connection to the ICP torch, such that analysis of the traditional GC range of organic analytes can now be supported.

Several key aspects of the analytical technology are separately described below.

10.2.1 GC-ICPMS Interface

Coupling of the GC to the ICPMS is achieved *via* a flexible, high-temperature ($>300\text{ }^\circ\text{C}$) transfer line between the GC and the ICP torch (Figure 10.2). Extension of the analytical column inside the GC oven to the GC torch can be achieved by passing a capillary through $1/8''$ (3.175 mm) stainless steel tubing maintained at high temperature by heating tape or low-voltage resistive heating. The main purpose of the transfer line is to maintain GC-resolved analytes in the gas phase during their transfer to the ICP torch. Flexibility of the transfer line is critical to preserve the ability of the ICPMS to 'tune' torch position relative to the cone/skimmer orifice.

Argon makeup gas is required at relatively high flow ($1\text{--}2\text{ L min}^{-1}$) to operate the inductively coupled plasma, and should be preheated to minimise the condensation of analytes as they elute from the transfer capillary into the torch. This was initially achieved by diverting the argon flow through the GC oven (so as to track with oven temperature) and then flowing coaxially with the GC carrier gas through the heated transfer line.¹ However, it was subsequently discovered that such a setup leads to variable gas flow rates and associated ICPMS tuning problems, probably due to an imperfect response of mass flow controllers to changing flow resistance in the GC

oven. Currently, the argon sample gas supply is heated by passage through a separate, heated box maintained at 300 °C.

10.2.2 Sulfur Hexafluoride Reference Gas

Sulfur hexafluoride, an inert, odourless, and inexpensive gas, has proved convenient for instrument tuning and isotopic calibration. A simple gas inlet system can be constructed to provide either continuous or pulsed introduction of sulfur hexafluoride diluted in helium to the mass spectrometer.¹ A continuous supply of sulfur hexafluoride is required for instrument tuning and this exercise also benefits from a capacity to control the sulfur hexafluoride concentration *via* the level of helium dilution. Microvolume capillary loops can introduce known volumes of sulfur hexafluoride–helium to the GC carrier gas stream as discrete peaks. This produces sulfur hexafluoride peaks during sample analysis, useful for $\delta^{34}\text{S}$ calibration. Calibration can alternatively be achieved by reference to coinjected internal standards, as is often done for $\delta^{13}\text{C}$ and δD CSIA, although the requirement for a tuning gas still remains.

10.2.3 Data Processing and Calibration

As for other CSIA methods, an MS scan cycle of sufficiently short duration (<200 ms) is required to provide adequate temporal resolution of chromatographic peaks. Current Neptune software does not support the data processing of transient (time-varying) signals, so data must be exported and processed separately. Current solutions include Microsoft Excel, MatLAB, or Isodat (Thermo IRMS software). Analyte isotope ratios ($^{34}\text{S}/^{32}\text{S}$) are measured from background-subtracted peak areas. Various algorithms could be implemented to speed the processing of the exported data, especially for complex chromatograms. However, manual peak and baseline interval identification in Isodat generally produces more accurate data than simple peak detection algorithms.

The results are expressed in conventional $\delta^{34}\text{S}$ notation as a ‰ deviation from the international standard Vienna Canyon Diablo Troilite (V-CDT) according to the following equation:

$$\delta^{34}\text{S}(\text{‰}) = (R_a/R_s) - 1$$

where R_a is the $^{34}\text{S}/^{32}\text{S}$ ratio of analyte and R_s is the $^{34}\text{S}/^{32}\text{S}$ ratio of V-CDT standard ($\equiv 0.044151$).⁵⁰

The ICPMS data can then be converted into $\delta^{34}\text{S}$ values through reference to a normalisation curve constructed using the $\delta^{34}\text{S}$ values of known standards (*e.g.* measured in isolation by EA-irMS or ICPMS) covering a broad range of $\delta^{34}\text{S}$ values, as demonstrated in Figure 10.4. The ICPMS-determined $\delta^{34}\text{S}_{\text{analyte}}$ values are further calibrated against $\delta^{34}\text{S}_{\text{SF}_6}$ values of the same chromatogram.

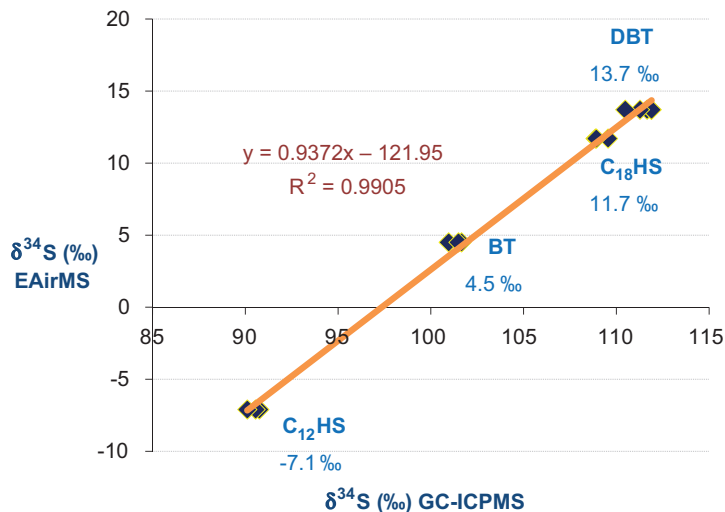


Figure 10.4 Normalisation curve from EA-irMS versus GC-ICPMS measured $\delta^{34}\text{S}$ values of several commercial standards.

10.2.4 Sensitivity and Precision

The typically low relative concentrations of many OSCs in natural samples such as oils or sedimentary organic matter can be a challenge to the precision of $\delta^{34}\text{S}$ analysis. GC-ICPMS measurements of commercial standards have demonstrated impressive precision ($<0.2\text{‰}$) and accuracy ($<0.3\text{‰}$) for peaks containing <100 pmol sulfur per compound, yielding ^{34}S peak areas of 0.5–2 V s in the medium resolution (~ 4000 , $m/\Delta m$, 5–95%) mode of the MC-ICPMS system.¹ Based solely on counting statistics, *i.e.* assuming no other sources of error, roughly 5 billion sulfur ions (0.2 billion ^{34}S ions; ~ 8 fmol of sulfur) must be counted to achieve a standard deviation for $\delta^{34}\text{S}$ of 0.1‰. Assuming a useful ion yield in the ICPMS of 10 ppm (which is typical at medium resolution), this corresponds to a requirement for injecting ~ 800 pmol of sulfur. A 10-fold reduction in the demand for precision (*i.e.* to 1.0‰ standard deviation, still sufficient for many biogeochemical problems of interest) leads to a 100-fold reduction in sample requirement (to 8 pmol of sulfur). In real-world analyses, additional sources of error mean that results are typically a factor of 2 or 3 above this ‘shot-noise’ limit.¹ Nevertheless, sulfur-CSIA can exceed the sensitivity of carbon and hydrogen CSIA, primarily because of the relatively high abundance of the rare isotope ^{34}S (4.21%, versus 1.11% for ^{13}C and 0.015% for ^2H).

The recent analysis of seawater dimethylsulfide (DMS) and dimethylsulfoniopropionate (DMSP) on a separate GC-ICPMS facility with a purge and trap GC inlet and operating in high mass resolution mode (*n.b.*, sensitivity reduced by ~ 2 -fold relative to medium resolution) on just 23–179 pmol

synthetic DMS or DMSP was conducted with precision better than 0.3‰.⁸ A sub-ppb level of sensitivity is comparable to standard GC-MS.

10.3 $\delta^{34}\text{S}$ Model of a Sedimentary Sulfur Cycle

As an example of sedimentary sulfur cycling and associated $\delta^{34}\text{S}$ behaviour, a simple flowchart of predicted mechanism and $\delta^{34}\text{S}$ values associated with the Here's Your Chance (HYC) sediment-hosted metal sulfide deposit is shown in Figure 10.5. Sedimentary recycling processes are critical in the formation of reduced sulfur species crucial to the deposition of many mineral types (*e.g.* transportation and precipitation of metal species from hydrothermal fluids).

The HYC ore body, the largest Palaeoproterozoic Pb–Zn–Ag deposit of north-east Australia, is hosted in the $1640 \pm 3 \text{ Ma}$ ⁵¹ Barney Creek Formation (BCF) of the McArthur Group. The deposit contains eight separate ore bodies,^{52,53} and several different sulfide phases with distinctive $\delta^{34}\text{S}$ values reflecting multiple sulfur sources.⁵⁴ For instance, the ^{34}S enriched nature of one major pyrite phase ($\delta^{34}\text{S}$ up to +45‰) relative to an earlier diagenetic pyrite phase (–13 to +15‰) was attributed to closed-system reduction of sulfate limited within the sediment pile.⁵⁴

The unmineralised organic matter at HYC was only marginally mature with H/C >1.6 and Rock-Eval T_{max} values as low as 435 °C, reflecting exceptional preservation for its age.⁵⁵ Hydrocarbon biomarkers from several different microbial sources have been detected, including aliphatic biomarkers of sulfide-oxidising bacteria.⁵⁶ Dibenzothiophenes (DBTs) and

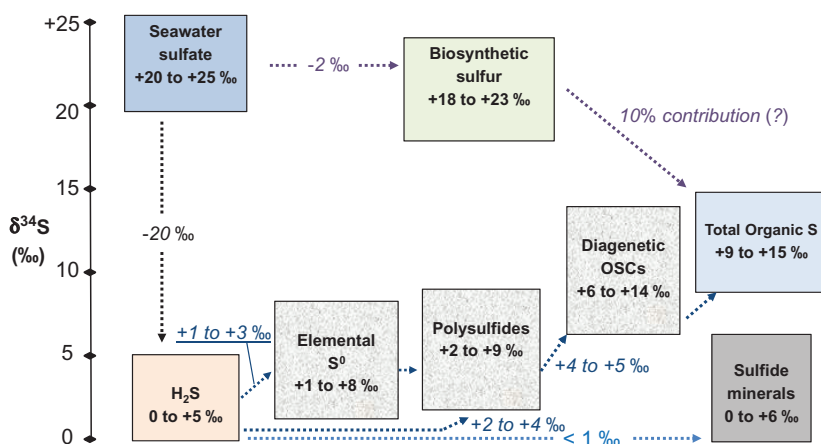


Figure 10.5 Proposed sulfur cycle model and associated $\delta^{34}\text{S}$ behaviour at the HYC mine (McArthur River Station, northern Australia), a sediment-hosted massive sulfide deposit. From Holman *et al.*⁶⁴ with $\delta^{34}\text{S}$ values and fractionations predicted from several previous studies.^{33,67,69}

other OSCs have also been detected in the HYC organic matter.⁵⁷ A number of studies have proposed that organic sulfur are sourced from polysulfides^{7,24,44} or elemental sulfur,⁵⁸ and DBTs can be produced by the reaction of reduced sulfur with unsaturated hydrocarbons^{59,60} or from thermochemical sulfate reduction (TSR).⁶¹ Other sedimentary studies have similarly shown that metal sulfide mineralisation and organic matter sulfuration can occur simultaneously.^{44,62} This is true even with pyrite formation, despite the kinetic preference for pyrite,⁶³ presumably reflecting a subset of organic compounds that are more highly reactive than the bulk organic matter.

The sulfur cycle and $\delta^{34}\text{S}$ model shown in Figure 10.5 represents an extension of a previous scheme³³ for sulfur isotopic fractionation in nature.⁶⁴ Briefly, bacterial reduction of seawater sulfate, estimated from measurement of evaporite deposits to have Paleoproterozoic $\delta^{34}\text{S}$ value of +20 to +25‰⁶⁵ produced ^{34}S -depleted hydrogen sulfide with a $\delta^{34}\text{S}$ value of $\sim +2\%$ ($\sim 20\%$ depletion)—based on $\delta^{34}\text{S}$ values of Wollogorang pyrite, underlying the BCF and through which mineralising fluid is believed to have flowed.⁶⁶ The $\delta^{34}\text{S}$ fractionation associated with biotic sulfate reduction will be comparatively negligible ($< -2\%$).³³ Sulfide minerals in the HYC (PbS, ZnS, AgS) have $\delta^{34}\text{S}$ values of 0 to +8‰,⁵⁴ consistent with very little fractionation ($< +1\%$) of dissolved hydrogen sulfide driven precipitation.³³ Elemental sulfur and polysulfides, if produced by phototrophic sulfur-oxidising bacteria would be expected to show a small (~ 1 to 3‰) enrichment in ^{34}S compared to hydrogen sulfide.⁶⁷ Laboratory experiments have shown that polysulfides in chemical equilibrium with elemental sulfur and dissolved sulfide are typically 2–4‰ enriched compared to sulfide, although as high as 6‰ enrichment is also possible.⁶⁸ The incorporation of polysulfide anions of intermediate oxidation state into sedimentary organic matter during diagenesis might be expected with enrichment of 4–5‰,⁶⁹ producing OSCs with a predicted $\delta^{34}\text{S}$ of +6 to +11‰.

Sedimentary OS, however, commonly exhibits bulk $\delta^{34}\text{S}$ values that lie between those of biotic and abiotic end members, a result that has been interpreted as reflecting contributions from both processes.^{42,44,45} Biosynthetic sulfur has been historically estimated to contribute 10–25% of OS in marine sediments,⁵⁸ although a lower proportion is likely in thermally mature sediments because of the rapid mineralisation of highly labile biosynthetic OSCs.⁴⁴ However, a biological contribution to sedimentary OS has not yet been unequivocally established, and in the following section on early diagenetic sulfuration in Cariaco Basin (Venezuela) sediments we note the data showed no OSCs with $\delta^{34}\text{S}$ values approaching seawater sulfate, thus no evidence for biotic-sourced OS. Despite these uncertainties, the total OS range of the present model is based on a 10% contribution of biologically sourced sulfur.

$\delta^{34}\text{S}$ values for elemental sulfur (+6 to +8‰), OS (+5 to +8‰) and early phase sulfide minerals (–5 to +6‰) recently measured in HYC sediments were in the ranges predicted by this model.⁶⁴ Furthermore, preliminary $\delta^{34}\text{S}$

values of several DBTs isolated from the OM of HYC sediments were +10 to +11‰ (within the +6 to +14‰ range predicted for diagenetic OSCs, Figure 10.5), although this sulfur-CSIA data is considered tentative because of the low concentrations and precision of analysis.

10.4 Early Applications of Sulfur-CSIA

Several contemporary research questions in sulfur biogeochemistry that have attracted initial attention include the mechanism and timeframes of diagenetic organic sulfurisation, the characterisation of ocean derived sulfur aerosols and both oil and mineral (as discussed above for the HYC model) exploration applications. Results and analytical insights from these initial sulfur-CSIA studies are summarised below.

10.4.1 Diagenetic Formation of Organosulfur Compounds

The concentrations and sulfur isotopic compositions of sedimentary sulfur species have been used to investigate organic matter sulfurisation in a variety of environments, including modern oceans,^{24,25} hypersaline basins,²⁶ freshwater environments,²⁷ and ancient systems such as the Miocene Monterey Formation.²⁸ Most sulfur is incorporated into kerogen on timescales of thousands of years or less, so kerogen $\delta^{34}\text{S}$ will reflect early diagenetic and sedimentary processes. The heterogeneity of sedimentary organic matter, however, necessitates a compound-specific approach to interpreting the ancient kerogen $\delta^{34}\text{S}$ record. Sulfur isotopic signals generated by the organic matter sulfurisation process may make it possible to use sulfur-CSIA to inform studies of the intertwined sulfur, carbon, and oxygen cycles in Earth's history. Additionally, sulfur-CSIA itself is a powerful tool for improving our understanding of organic sulfurisation mechanisms. Sulfur isotopic compositions of individual OSC can indicate the timescale and location of their formation because inorganic sulfur species exhibit strong isotopic gradients in many anoxic sediments.

Case Study: Early Diagenetic Sulfurisation in the Cariaco Basin

Werne and colleagues conducted the first compound-specific $\delta^{34}\text{S}$ analyses on OSC from the sediments of the Cariaco Basin.⁷ Individual sulfurised isoprenoids were isolated from large (200–250 g) samples by preparative chromatography (prep-HPLC) prior to EA-irMS analysis. The $\delta^{34}\text{S}$ values of these OSCs were typically around -15‰ , substantially ^{34}S -enriched relative to other coexisting sulfur pools, including both kerogen sulfur and dissolved sulfide. The sulfur isotopic enrichment of roughly 10‰ could be only partially explained by an equilibrium isotope effect during formation identified in previous laboratory experiments.⁶⁹

Sulfur-CSIA by GC-ICPMS requires much smaller sediment samples (~ 5 g) which eliminates the need for laborious manual separation. By this method,

the same OSCs from the same core (ODP Core 1002B) yielded different results⁷⁰ to the previous EA-irMS based measurements.⁷ The GC-ICPMS data on previously investigated isoprenoids and other OSCs were consistently ³⁴S-depleted relative to kerogen and dissolved sulfide. The $\delta^{34}\text{S}$ profiles of selected OSCs are shown in Figure 10.6, and reflect progressive ³⁴S enrichment with depth, consistent with continuous formation from inorganic sulfur species, which also become increasingly ³⁴S-enriched with depth. The $\delta^{34}\text{S}$ discrepancy of these studies^{7,70} is likely due to the presence of elemental sulfur in the fractions isolated by HPLC. Elemental sulfur in Cariaco Basin sediments is abundant in non-polar lipid extracts and was relatively ³⁴S-enriched, with preliminary $\delta^{34}\text{S}$ measurements, ranging from roughly -19% to $+5\%$,⁶⁶ that are capable of explaining the more enriched values previously reported.⁷ Sulfur-CSIA by GC-ICPMS avoids this problem caused by homogenisation of an isolated, imperfectly purified fraction.

The ³⁴S-depleted nature of volatile OSCs was similar to that of coexisting pyrite. Like pyrite, these OSCs appear to have a combination of syngenetic (water column) and diagenetic (sediment) sources, the relative importance of which varies for different individual compounds. For example, one of the isoprenoid compounds that was measured in the earlier study and also shown to accumulate in Cariaco Basin sediments may have an exclusively diagenetic source.⁷ Accumulation and isotopic patterns for the C₂₀ isoprenoid thiophene, another dominant OSC, indicate a substantial syngenetic source and do not conclusively establish diagenetic formation.⁷⁰

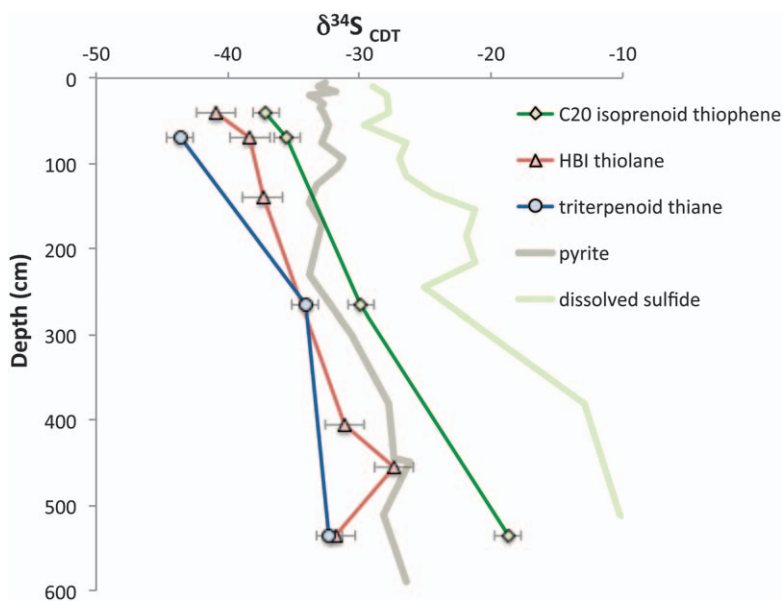


Figure 10.6 $\delta^{34}\text{S}$ profile of selected organic sulfur compounds detected in Cariaco Basin sediments and also for co-occurring pyrite and dissolved sulfide at different water column depths.

Syngenetic and diagenetic sulfurisation may also have different reaction mechanisms and isotope effects. The ^{34}S -depleted volatile OSC in Cariaco Basin sediments appear to record a kinetic isotope effect with respect to their sulfur source, which is likely dissolved bisulfide (HS^-). Syngenetic organic sulfurisation, in contrast, may have a more reversible reaction mechanism and record equilibrium isotope effects like those seen for OSC polymers in experimental studies.⁶⁹ Bulk kerogen $\delta^{34}\text{S}$ values would then reflect a complex mixture of OSCs, each potentially recording distinct information about the sedimentary sulfur cycle.

Thus far, no evidence of individual OSC with $\delta^{34}\text{S}$ values approaching that of seawater sulfate, and that might be candidates for the postulated addition of biosynthetic sulfur.

10.4.2 Oceanic Emissions of DMS

Sulfur-CSIA has also been extended to target gaseous-range OS analytes such as DMS. DMS is a degradation product of DMSP, a metabolite of marine phytoplankton, and represents the largest natural source of biogenic sulfur to the global atmosphere. DMS is emitted to the atmosphere and rapidly oxidises to sulfate, a significant constituent of submicrometre aerosols. These aerosols scatter incoming solar radiation and may act as cloud condensation nuclei (CCN) that change the albedo of clouds. There are multiple sources of sulfur to the atmosphere including biogenic, sea-spray, anthropogenics, volcanic emissions, dust, and biomass burning. Sulfur isotope ratios may offer a way to calculate the contribution of ocean-derived DMS to global sulfur cycling and aerosol budgets. However, the $\delta^{34}\text{S}$ of DMS emitted to the atmosphere from the ocean has been difficult to measure because of the low natural concentration of DMS in oceanic water (typically few nM) and a high volatility and reactivity that make such analysis very difficult. Recently, a multistep extraction procedure coupled with Raney nickel dehydrosulfurisation, and then fluorination (to sulfur hexafluoride) for sulfur isotope analysis by *irMS* was used to obtain $\delta^{34}\text{S}$ values for DMSP from intertidal macroalgae (+17.3 to +19.3‰) and an estuarine phytoplankton bloom (+19 to +20‰).⁷¹ These labour-intensive and time-consuming analyses of DMSP required processing of large quantities of algae and seawater (50 L) during blooms, where DMSP is at high concentrations, to obtain sufficient sulfur (>6 μmol) for isotope analysis.

The current coupling of GC and ICPMS technology offers the required sensitivity (pmol rather than μmol level) and a significantly simpler way for the sulfur isotope analysis of trace level compounds such as DMS, thereby enabling its measurement even at oligotrophic regions. Preliminary measurements using this technique on water samples from San Pedro, CA, Tasmania, and Pacific Costa Rica were the first $\delta^{34}\text{S}$ analysis of DMS in oceanic water and showed relatively uniform values of about +18 to +21‰.⁷² However, DMS recoveries were low (<50%) due to storage and transfer problems and uncertainties were thus relatively large. An improved purge

and trap method recently developed was able to concentrate the small amounts of DMS and DMSP with more than 98% recovery.⁸ A few millilitres of ocean water (> 23 pmol sulfur) were sufficient for precise and accurate ($< 0.3\text{‰}$) $\delta^{34}\text{S}$ analysis by GC-ICPMS. This purge and trap GC-ICPMS method was then used to measure the $\delta^{34}\text{S}$ of DMS and DMSP in a range of geographically distinct marine waters from around the globe.⁷³ These DMSP samples showed a remarkable $\delta^{34}\text{S}$ consistency of $+18.9$ to $+20.3\text{‰}$ in the surface ocean. Different seasons, ocean basins, phytoplankton blooms or non-blooms, did not seem to affect the $\delta^{34}\text{S}$ of DMSP at the ocean surface. Depth profiles (Figure 10.7) of DMS and DMSP in Eilat (Northern Red Sea, Israel) down to 140 m reveal less than 1‰ difference between DMS and its precursor DMSP.⁷³ Very little sulfur isotope fractionation ($< 0.5\text{‰}$) was observed during evaporation experiments of DMS from aqueous solution. This shows that the $\delta^{34}\text{S}$ of DMS emitted to the atmosphere is similar to that of DMS in the surface water which in turn is similar to that of DMSP. These data indicated that the $\delta^{34}\text{S}$ of oceanic DMSP is relatively homogenous, contributing to DMS with a quite distinctive $\delta^{34}\text{S}$ signature. Hence, $\delta^{34}\text{S}$ analysis might help measure the oceanic contribution of atmospheric DMS from anthropogenic sources of atmospheric sulfate, thereby enabling estimation of the DMS contribution to aerosols.

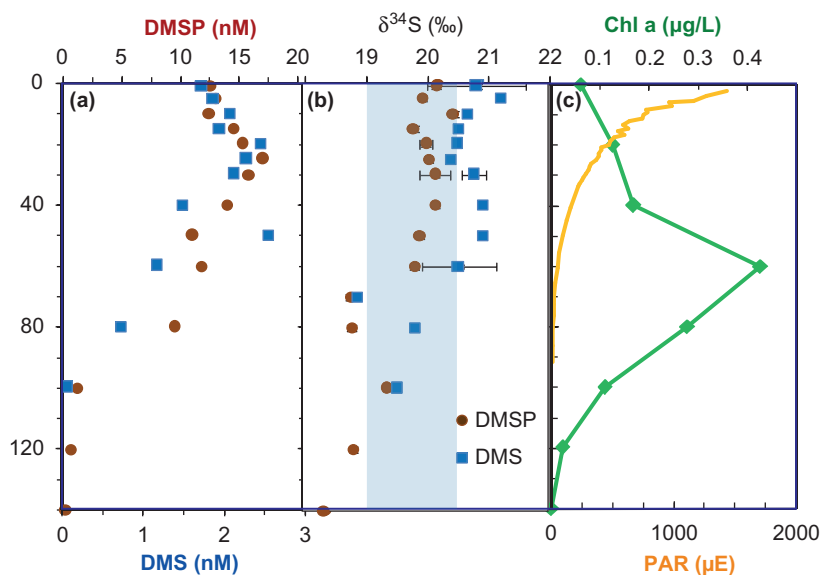


Figure 10.7 Depth distribution (0–140 m) in open water at Eilat, Red Sea of (A) DMSP and DMS concentrations; (B) $\delta^{34}\text{S}$ values of DMSP and DMS. The shaded area represents the range of $\delta^{34}\text{S}$ values of DMSP obtained for surface water (≤ 5 nm depth) from other locations around the globe; and (C) chlorophyll a concentration (green line) and photosynthetically active solar radiation (PAR, yellow line) between 400 and 700 nm (summer conditions of September 2012). Figure modified from Amrani *et al.*⁷³

10.4.3 Oil Analysis

The largest petroleum systems in the world are carbonate/evaporite sequences, which are typically high in sulfur.⁷⁴ However, crude oils with sulfur concentrations of 4% or more are often excluded from industrial processing because of the interference of OSCs during the refinery process^{41,75} and the effect relatively weak S–S bonds have on petroleum kinetics.

Unlike the large range of hydrocarbon biomarkers that have been detected in oils and source rocks, OSCs provide quite limited information about fossil fuel sources. Sulfur is usually incorporated into organic matter *via* secondary processes,⁷⁶ most significantly by TSR. Although TSR is a major control on the $\delta^{34}\text{S}$ of organic sulfur in oils, other factors such as depositional environment and thermal maturity may also influence the $\delta^{34}\text{S}$ of OSCs. Bulk $\delta^{34}\text{S}$ values of petroleum can vary over a wide range (–8 to 32‰)⁷⁷ and have proved quite useful for oil–oil correlations (see *e.g.* Gaffney *et al.*⁷⁸).

10.4.3.1 Thermochemical Sulfate Reduction and the $\delta^{34}\text{S}$ of Organic Sulfur

TSR is a high-temperature redox process in which sulfates such as gypsum or anhydrite are reduced and organic matter oxidised.^{79,80} It can have a drastically negative impact on oil quality since normal and branched alkanes, particularly in the gasoline range, are easily oxidised by TSR,^{81–83} and the high concentrations of hydrogen sulfide and carbon dioxide generated can result in sour gas reservoirs of low economic value.

Several studies of TSR-impacted organic matter have shown this process can lead to variances in the distribution and $\delta^{13}\text{C}$ of hydrocarbon products,^{84,85} from which certain trends were identified to reflect the extent of TSR.⁷⁶ For instance, loss of n-alkanes in preference to aromatics, and kinetic control over greater ^{12}C loss, leads to a saturate hydrocarbon fraction with a heavier $\delta^{13}\text{C}$ value. Likewise, the $\delta^{34}\text{S}$ of whole oils and their fractions can change with TSR.⁸⁰ The hydrogen sulfide produced has a value close to the source sulfate and its secondary reaction with hydrocarbons may lead to OS with similar $\delta^{34}\text{S}$ values.

The TSR process can lead to the formation of aromatic sulfur compounds such as benzothiophenes (BTs) and DBTs. The investigation of TSR and $\delta^{34}\text{S}$ was extended to the molecular level by separately measuring the $\delta^{34}\text{S}$ of parent and methyl BTs and DBTs in oils impacted by TSR.⁶¹ The sample set comprised a number of Upper Jurassic oils including from the Smackover Formation (southern USA) where they had been varyingly impacted by TSR. These geological samples were complimented by a set of gold tube pyrolysis experiments conducted with three calcium sulfate spiked oils to simulate subsurface TSR occurrences.

Significantly, the oil and pyrolysis sample sets both showed the BT and methylated analogues were quick to adopt the $\delta^{34}\text{S}$ of the sulfate source at relatively low levels of TSR. A variance in the ^{34}S fractionation of BT and the

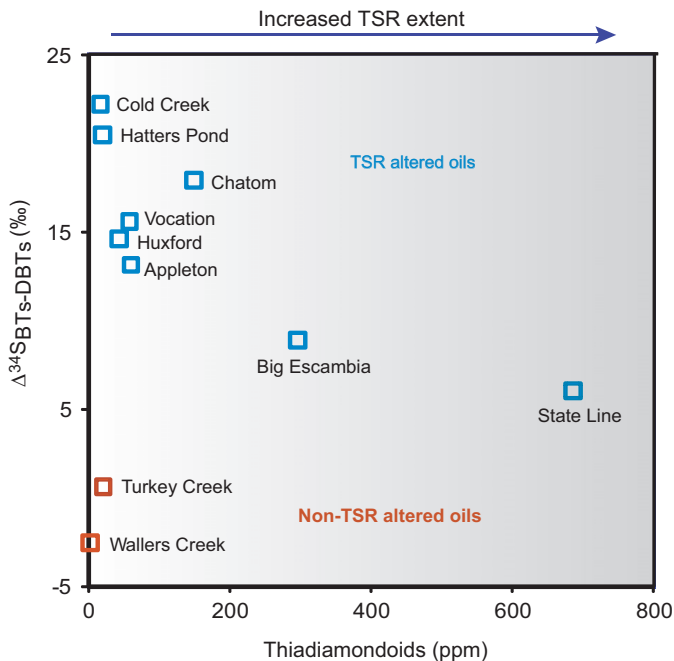


Figure 10.8 $\Delta\delta^{34}\text{S}_{\text{BT-DBT}}$ versus thiadiamondoid concentrations from a suite of Smackover Formation oils impacted to different degrees by thermochemical sulfate reduction (TSR). The concentrations of thiadiamondoids has previously been correlated against extent of TSR.⁹⁵ $\Delta\delta^{34}\text{S}_{\text{BT-DBT}}$ was measured using average $\delta^{34}\text{S}_{\text{BT}}$ and $\delta^{34}\text{S}_{\text{DBT}}$ values of all measured isomers. (Figure modified from Amrani *et al.*⁶¹)

higher molecular weight and more stable DBT, formed less rapidly by TSR, was shown to provide a good measure of the extent of TSR. As an example of the relationship between $\Delta\delta^{34}\text{S}_{\text{BT-DBT}}$ and TSR, GC-ICPMS measured values from several Smackover Formation oils impacted by TSR to different degrees are shown in Figure 10.8.⁶¹

$\Delta\delta^{34}\text{S}_{\text{BT-DBT}}$ was subsequently proposed as a sensitive indicator of the extent of early TSR and this new parameter should be of practical benefit in oil exploration studies. Further investigation of the $\delta^{34}\text{S}$ of, and $\Delta\delta^{34}\text{S}$ between, OSC products of TSR may also help illuminate the mechanistic complexities of this process which typically involves major alteration of the hydrocarbon composition of oils.⁶¹

10.4.3.2 Other Controls on the $\delta^{34}\text{S}$ of Petroleum OSCs

Thermal maturity. $\delta^{34}\text{S}$ values of particular OSCs may vary modestly with thermal maturity. Maturity has generally been observed to have only a small influence on the bulk $\delta^{34}\text{S}$ of oils and source rocks.^{76,86} Pyrolysis experiments of source rocks and kerogens support this observation, showing

relatively small sulfur isotope fractionation of $\sim 2\%$ between the kerogen, and the free hydrocarbons (*i.e.* oil/bitumen) and hydrogen sulfide thermally produced from it.^{87,88}

Laboratory-controlled maturation experiments of an immature source rock were conducted to further investigate the impact of thermal maturity on the $\delta^{34}\text{S}$ of individual OSCs in fossil fuels.⁸⁹ Semi-batch pyrolysis experiments were operated at low pressures (up to 50 psi), at a slow heating rate of $4\text{ }^\circ\text{C day}^{-1}$ (200–400 $^\circ\text{C}$). The source rock used in the study was a Ghareb Formation oil shale attained from core samples from the Shfela Basin (Aderet 1 drillhole, Israel) exhibiting both high TOC (17.3 wt%) and high OS content (10 wt% from the kerogen).

The unheated bitumen showed a large distribution of OSCs with $\delta^{34}\text{S}$ values which ranged by about 15%. The $\delta^{34}\text{S}$ value of pyrite in the source rock was -27% . The OSCs consisted mainly of alkyl thiophenes ($>\text{C}_{10}$), and to a lesser extent sulfides and alkybenzothiophenes. The bitumen released from the residual rock on heating to 400 $^\circ\text{C}$ consisted mainly of DBTs and other more condensed aromatic sulfur species. These OSCs exhibited a very narrow $\delta^{34}\text{S}$ range (-0.9 to $+0.9\%$), centred on the bulk kerogen $\delta^{34}\text{S}$ value of $+0.6\%$. The $\delta^{34}\text{S}$ value of a several OSCs identified as major products of the analytical pyrolysis as a function of temperature are shown in Figure 10.9.

Throughout these experiments the pyrolysates were condensed at 4 $^\circ\text{C}$ and collected in intervals of approximately 25 $^\circ\text{C}$. Preliminary results show that the OSCs (*i.e.* thiolanes, alkylated thiophenes, benzothiophenes, and dibenzothiophenes) have a unique thermally dependent sequential molecular distribution. The $\delta^{34}\text{S}$ values generally increased with temperature by up to 3–4‰ for alkylthiophenes and sulfides relative to the initial samples that were collected at 250 $^\circ\text{C}$ and the kerogen. Benzothiophenes and dibenzothiophenes were consistently ^{34}S depleted compared with alkylated

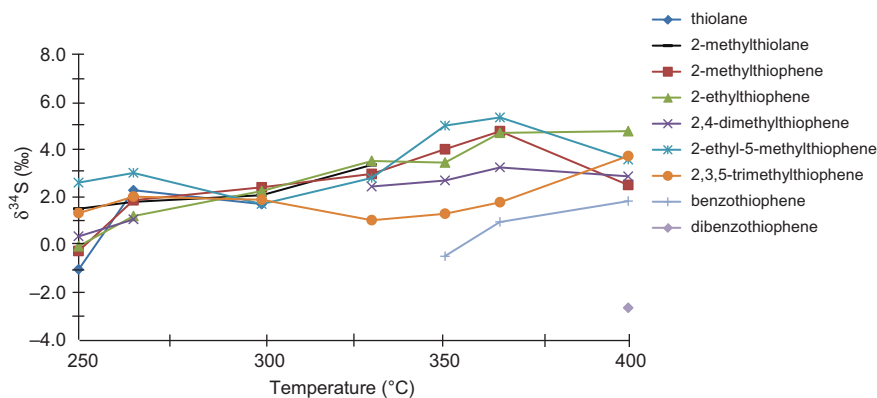


Figure 10.9 $\delta^{34}\text{S}$ profiles of selected organic sulfur compounds from oils that collected at different pyrolysis temperatures of Gahreb Formation source rock.

thiophenes and were closer to those in the raw kerogen. Differences in the $\delta^{34}\text{S}$ values for the different OSC families may be due to their formation from different types of sulfur bonding in the kerogen controlled by the thermal stability of the C–S bonds. Since BTs and DBTs form at relatively higher thermal maturities they probably form by cleavage of the more stable C–S bonds in the kerogen.

In general, the condensed oil fraction exhibits significantly less sulfur isotope variability than that of the unheated bitumen. This observation suggests that sulfur isotope mixing during thermal maturation may be responsible for the relative homogeneity of unaltered oils (*e.g.* by TSR or bacterial sulfate reduction (BSR)). Moreover, the 3–4‰ difference evident between some OSCs in the generated oils and the source rock further support the applicability of sulfur isotopes in oil–source rock correlations.

These preliminary results indicate that the molecular and $\delta^{34}\text{S}$ distribution of OSCs show a promising potential for indicating the thermal maturation stage of the source rock and its structural transformations.

Oil Source/Deposition Environment. Despite the fact that OSCs are not as diagnostic of organic matter inputs as hydrocarbon biomarkers, sulfur-CSIA may still extend the oil source correlations of bulk $\delta^{34}\text{S}$. Bulk $\delta^{34}\text{S}$ values of petroleum can vary over a wide range (–8 to +32‰)⁷⁷ and have proved quite useful for oil–oil correlations.⁷⁸

The $\delta^{34}\text{S}$ of BTs and DBTs from a small range of oils not impacted by TSR have now been measured across several GC-ICPMS studies. These include oils from the Smackover Formation (Gulf of Mexico; *n.b.* these are not TSR affected),⁶¹ Oman,⁶¹ Tarim Basin (north-west China),⁹ and Jinxian Sag (northern China)⁹ although the $\delta^{34}\text{S}$ values of the latter two oils were considered with some caution due to low analyte concentrations and the limited oil volumes available for analysis. Characteristic features of these oils are briefly given in Table 10.1.

The $\delta^{34}\text{S}$ values of parent and methyl BT and DBTs from the different oils are shown in Figure 10.10. The values for the methyl analogues are the average of all polymethyl ($\text{C}_1\text{--C}_3$) isomers analysed.

There are some clear differences in the $\delta^{34}\text{S}$ data of these oils. Most notably, the mBT, DBT, and mDBT values of the two Smackover Formation oils were more than 20‰ lighter than those of five Tarim Basin oils. Such isotopic differences are much larger than could be attributed to any maturity differences. Different palaeo-depositional environments might be a more plausible explanation for the large deviation in the $\delta^{34}\text{S}$ values of the OSCs in these oils.

The $\delta^{34}\text{S}_{\text{OSC}}$ data of the Smackover Formation oils were consistently less than 5‰, which was significantly lighter than the same products from a larger suite of TSR-affected oils from the Smackover Formation,⁶¹ and is likely more indicative of the $\delta^{34}\text{S}$ of the source kerogen.

The sulfur-CSIA data for the Jinxian Sag oil was between the relatively high $\delta^{34}\text{S}_{\text{OSC}}$ values of the Tarim Basin oils and low $\delta^{34}\text{S}_{\text{OSC}}$ values in the

Table 10.1 Oils for which sulfur-CSIA data has been measured.

Oil name	Brief description
Smackover Formation oils, Gulf of Mexico	Upper Jurassic age; many Smackover oils have been impacted by TSR, data is presented here for the Turkeys Creek and Wallers Creek oils which were not thought to be TSR affected ⁶¹
Oman oil	High-sulfur (3 wt%), relatively immature oil
Tarim Basin oils (NW China)	Numerous episodes of hydrocarbon generation, migration and accumulation. Multiple source rocks, but mainly of Cambrian or Ordovician age. Ordovician oils characterised by high DBT/phenanthrene ratio ⁹⁶ .
Jinxian Sag oil (China)	Tertiary age, Lacustrine; hydrocarbon reservoirs typically contain high sour gas and hydrogen sulfide concentrations, with much speculation about whether these are due to TSR or BSR ⁸⁶

BSR, bacterial sulfate reduction; DBT, dibenzothiophene; TSR, thermochemical sulfate reduction.

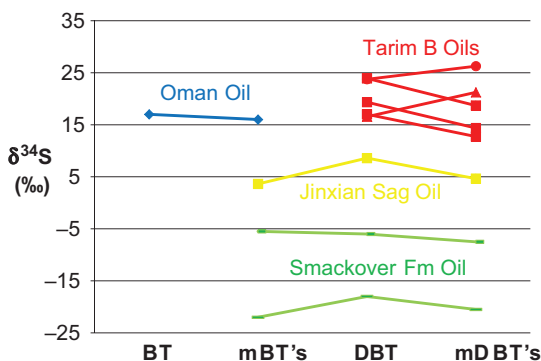


Figure 10.10 $\delta^{34}\text{S}$ data of benzothiophene (BT), dibenzothiophene (DBT), and $\text{C}_1\text{-C}_3$ polymethylated analogues (average of all measured isomers) from the GC-ICPMS analysis of several different oils unaffected by thermochemical sulfate reduction.^{9,61}

Smackover Formation oils. Significantly, the $\delta^{34}\text{S}$ of the mBTs are similar to that of co-occurring DBT and mDBTs which suggests they had not been exposed to TSR, and implies instead a BSR influence on this oil. There has been much conjecture about the control on the sour gas and hydrogen sulfide-rich nature of Jinxian Sag hydrocarbon reservoirs.⁹⁰

The concentrations of BTs and DBTs in the Oman oil were below detection limits, but the $\delta^{34}\text{S}$ of a range of BTs could be measured following their concentration by sealed gold tube pyrolysis. The data reported here corresponds to pyrolysis conditions of 360 °C applied for 40 or 89 h in the absence of calcium sulfate (n.b. added to other pyrolysis experiments to promote TSR). These $\delta^{34}\text{S}$ values were in the lower $\delta^{34}\text{S}$ range of the Tarim Basin oil analytes.

10.5 Conclusions and Future Application

Compound-specific $\delta^{34}\text{S}$ represents an entirely new analytical capability which could be applied to much of the OS system, with applications ranging from atmospheric and ocean chemistry to sediment diagenesis and ancient proxies. Already impressive precision and reproducibility with $\delta^{34}\text{S}$ of less than 0.5‰ has been demonstrated for the $\delta^{34}\text{S}$ analysis of volatile OSCs in seawater and associated aerosols, sediment extracts, crude oils and rock extracts. Following the development and subsequent commercial availability of continuous-flow CSIA technology for other light stable isotopes, particularly carbon and hydrogen, there was a rapid transition from measuring the isotopic compositions of bulk organic fractions to measuring individual molecular species. A similar trend might now be anticipated following the recent invention of sulfur-CSIA.

The $\delta^{34}\text{S}$ value of bulk sedimentary OS largely reflects that of the major sulfur source (*e.g.* porewater H_2S) and lacks the resolution to provide detail about the factors influencing $\delta^{34}\text{S}$ at the molecular level. The $\delta^{34}\text{S}$ values of specific OSCs can vary substantially and cover a wide range of values in different environments reflecting differences in (1) inorganic sulfur source; (2) pathway of OSC formation; (3) environmental conditions such as redox state; (4) timing of diagenetic sulfurisation of OM; and (5) diagenetic overprinting, including that from microbial sulfur cycling. Over two decades ago, the sedimentary occurrences of more than 1500 novel OSCs was reported,¹⁰ but their geochemical significance was limited by a lack of knowledge about their formations mechanism(s) and reactivity with sulfur in the natural environment. These remain critical areas of study and will be well served by a capacity to measure the $\delta^{34}\text{S}$ of individual OSCs in ancient sediments or extant precursors.

Measurement of the $\delta^{34}\text{S}$ values of OSCs by GC-ICPMS has enormous analytical potential extending from biogeochemical studies to characterisation of synthetic chemicals and environmental contaminants and possibly even source correlation of chemical warfare agents. Sulfur-CSIA may help address a wide variety of questions in biogeoscience, including reconstruction of biomarker taphonomy, microbial sulfur cycling, and frontier petroleum basins. However, careful evaluation of the controls on sulfurisation and connection of the major pathways of sulfur incorporation during sedimentary diagenesis to patterns of $\delta^{34}\text{S}$ in individual molecules will be required to fully exploit this unique capability. This will require the acquisition of a substantial amount of compound-specific $\delta^{34}\text{S}$ data in modern and palaeoenvironments, as well as supporting data on inorganic sulfur species, from different compounds, depths, and environments. Measurement of the $\delta^{34}\text{S}$ of OSCs produced by reaction of organic matter with reduced inorganic sulfur and preserved in the sedimentary record for long time periods at natural abundance levels will help to greatly improve our understanding of past organic sulfur systems.

An example of one geoscience sulfur-CSIA application worthy of further exploration relates to the behaviour of organic and inorganic sulfur species during mass extinctions and the recovery periods that followed. The $\delta^{34}\text{S}$ values of sedimentary OSCs could help reconstruct the sulfur cycles associated with these key evolutionary periods. Some of the most significant pulses of evolution throughout Earth's history have coincided with extinction events. Fossil and geochemical evidence tends to suggest the five major mass extinctions—end-Ordovician, Frasnian–Famennian (F/F), Permian–Triassic (P/Tr), Triassic–Jurassic (Tr/J) and Cretaceous–Tertiary (K/T)—were prolonged periods of biotic stress triggered by a combination of tectonically induced hydrothermal and volcanic processes, leading to eutrophic oceans, global warming, sea-level rise, and global anoxia.⁹¹ Perturbations in the marine sulfur cycle and thus the redox state of the ancient seas during mass extinctions have been reflected in the $\delta^{34}\text{S}$ of pyrite, showing a general positive shift when conditions are highly euxinic (rapid burial of pyrite) and a negative shift when hydrogen sulfide is rapidly oxidised.^{92,93} A number of carotenoid biomarkers (*e.g.* isorenieratane) specific to Chlorobi (biological proxies of photic zone euxinic conditions), strict anaerobes which can photosynthesise using hydrogen sulfide as an electron donor have been identified within P/Tr, Tr/J, and end-Devonian sections.^{91,94} GC-ICPMS measurement of these biomarkers and other OSCs in sediments spanning these boundaries should help reveal the extent and consequences of euxinic conditions during the mass extinctions periods and subsequent recovery phases.

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