



The sulfur-isotopic compositions of benzothiophenes and dibenzothiophenes as a proxy for thermochemical sulfate reduction

Alon Amrani^{a,*}, Andrei Deev^b, Alex L. Sessions^c, Yongchun Tang^b,
Jess F. Adkins^c, Ronald J. Hill^d, J. Michael Moldowan^e, Zhibin Wei^f

^a Institute of Earth Sciences, The Hebrew University, Jerusalem 91904, Israel

^b Power, Environmental, and Energy Research Institute, 738 Arrow grand Circle, Covina, California 91722, USA

^c Division of Geological and Planetary Sciences, California Institute of Technology, 1200 E. California Blvd, Pasadena, CA, USA

^d Marathon Oil Company, Houston, TX, USA

^e Department of Geological & Environmental Sciences, Stanford University, Stanford, CA 94325, USA

^f Exxon Mobil Exploration Company, 222 Benmar Drive, Houston, TX 77060, USA

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Abstract

Compound-specific analyses of the $^{34}\text{S}/^{32}\text{S}$ isotope ratios of individual organosulfur compounds in Upper Jurassic oil and condensate samples from the Smackover Fm. reveal differences of up to $\sim 50\%$ between compounds. There is a clear distinction between oils altered by thermochemical sulfate reduction (TSR) versus those that are not. Oils that did experience TSR exhibit significant ^{34}S enrichment of benzothiophenes (BTs) compared to dibenzothiophenes (DBTs), while in unaltered oils these compounds have similar isotopic compositions. The $\delta^{34}\text{S}$ values of BTs are close to those of sulfate-bearing evaporites of the Smackover Fm., whereas the $\delta^{34}\text{S}$ values of DBTs are spread over a wider range and gradually approach those of the BTs.

Gold-tube hydrous pyrolysis experiments using three representative oils show that isotopic alteration readily occurs under TSR conditions and can significantly affect the $\delta^{34}\text{S}$ values of individual compounds. Our results indicate that BTs can be a sensitive tracer for TSR as they form readily under TSR conditions, with large ^{34}S enrichments relative to the bulk oil. In contrast, DBTs exhibit relatively small changes in $\delta^{34}\text{S}$, preserving their original $\delta^{34}\text{S}$ values longer than do BTs because of their greater thermal stability and slow rate of formation. We propose that comparison of the $\delta^{34}\text{S}$ values of BT and DBT can be used to detect TSR alteration of oils from the very early stages up to highly altered oils. The approach should find numerous uses in petroleum exploration, as well as for understanding the basic reaction mechanisms and kinetics of thermochemical sulfate reduction and secondary sulfur incorporation into oils.

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1. INTRODUCTION

Thermochemical sulfate reduction (TSR) to sulfide coupled with oxidation of hydrocarbons occurs in hot carbonate petroleum reservoirs ($>110^\circ\text{C}$) and in hydrothermal environments (Machel et al., 1995; Worden and Smalley,

2001). The process is thermodynamically favored and kinetically controlled yielding CO_2 , H_2S , and highly refractory sulfur-rich solid bitumen (“pyrobitumen”) (Goldstein and Aizenshtat, 1994). TSR is one of the most important organic–inorganic interactions and it is well documented in many geologic environments from around the world (Orr, 1974, 1977; Worden and Smalley, 1996; Nöth, 1997; Machel, 2001; Cai et al., 2003; Seewald, 2003). TSR is detrimental to oil quality and produces high concentrations of H_2S and CO_2 in petroleum reservoirs. The toxicity and

* Corresponding author.

E-mail address: alon.amrani@mail.huji.ac.il (A. Amrani).

corrosiveness of these gases lead to greater production costs and risk to human health and the environment. Predicting and measuring the extent of TSR is an important element in risk assessment for hydrocarbon quality and H₂S concentration in petroleum reservoirs. Moreover, studies of TSR isotopic imprints and mechanisms may shed light on important events in the early history of Earth. A recent study suggests that TSR may have played an important role in the diagenesis of sulfur in the Precambrian world based on mass-independent fractionation of S isotopes (Watanabe et al., 2009).

The thermochemical reduction of sulfate in oil reservoirs produces ³⁴S-enriched H₂S close to its parent gypsum or anhydrite $\delta^{34}\text{S}$ value (Machel, 2001). Back-reactions of petroleum with TSR-derived H₂S have been proposed to produce organic sulfur compounds (OSC) with ³⁴S-enriched values, distinct from the original $\delta^{34}\text{S}$ values of sedimentary organic sulfur (Orr, 1974; Powell and Macqueen, 1984; Hanin et al., 2002; Cai et al., 2003, 2009). This makes sulfur isotopes in petroleum useful tracers for the occurrence and extent of TSR (Machel, 2001).

Until recently, there has been no method for measuring $\delta^{34}\text{S}$ in individual organic compounds, thus the isotopic imprint of TSR at the molecular level remained unknown. We have recently developed instrumentation and methods capable of measuring accurate $\delta^{34}\text{S}$ values in individual compounds at the sub-nanogram level (Amrani et al., 2009). The system employs chromatographic separation by gas chromatography (GC) and subsequent ³⁴S/³²S ratio measurements by multi-collector inductively-coupled plasma mass spectrometry (MC-ICP-MS). We previously employed this new technique to study oil from the Caspian Sea area and observed large (up to ~20‰) variations in $\delta^{34}\text{S}$ between alkylsulfides, benzothiophenes (BTs), and dibenzothiophenes (DBTs) (Amrani et al., 2009). DBTs were significantly depleted in ³⁴S compared to alkylsulfides whereas the BTs had intermediate values. These $\delta^{34}\text{S}$ variations may represent the difference between TSR-affected compounds versus the original sedimentary organic sulfur represented by more thermally stable DBTs.

In the present study, we attempt to understand the factors controlling these isotopic changes. We measured a suite of Upper Jurassic oil and condensate samples generated from the Smackover Formation source rock in the Gulf of Mexico. These oils exhibit different degrees of TSR alteration and provide for a systematic study of $\delta^{34}\text{S}$ changes in individual compounds during TSR. In addition, we conducted a series of gold-tube hydrous pyrolysis experiments with three representative oils and isotopically distinct CaSO₄ to simulate TSR in a controlled environment.

2. EXPERIMENTAL

2.1. Model compounds and crude oils

2.1.1. Reagents and standard compounds

All chemicals were purchased from Sigma–Aldrich (St. Louis, MO) and are analytical grade (>97% purity) with no further purification. Reference gas SF₆ was purchased from Scott Specialty Gases (PA) as a 2% mixture in He.

The sulfur isotope reference materials NBS-127 (BaSO₄; $\delta^{34}\text{S} = 21.3\text{‰}$) and IAEA-S-1 (Ag₂S; -0.3‰) were used in our EA-IRMS analysis (Hebrew University, Jerusalem) of H₂S (as Ag₂S) and were purchased from NIST (Coplen and Krouse, 1998; Qi and Coplen, 2003).

2.1.2. Crude oils

A series of oils and condensates were taken from various oil fields in the Gulf of Mexico. These samples included both TSR-altered and non-altered oils and condensates covering a broad range of thermal maturities. All were produced from the Upper Jurassic Smackover Formation at different depths, and experienced different thermal histories as suggested by their associated reservoir temperatures ranging from 87 °C to 160 °C (Table 1). A detailed description of the oils and their geological setting is provided by (Claypool and Mancini, 1989).

In addition, two other oils (from the Caspian Sea area and from Oman) were used for laboratory TSR experiments. Their geochemical characteristics are described elsewhere (Zhang et al., 2007). Briefly, the Caspian oil is a low-sulfur oil (0.5 wt.% S) produced from a Carboniferous-aged carbonate reservoir in an onshore field near the Caspian Sea in Kazakhstan. The oil has an approximate API gravity of 45, (SG = 0.80 g/mL) and contains no asphaltene fraction and 4% resins. The Oman oil is a high-sulfur (3.0 wt.%) oil produced from an onshore field in Oman, has an API gravity of 31.0, (0.88 g/mL), and contains 15.3% asphaltenes and 7.5% resins.

The petroleum samples were injected with no pretreatment or polarity separation, i.e. as ‘whole oils’, into the GC-MC-ICPMS for $\delta^{34}\text{S}$ analysis of individual compounds.

2.2. Pyrolysis and TSR simulation experiments

All experiments were conducted in sealed gold tubes with an internal diameter of 3.5 mm and wall thickness of 0.45 mm. Each tube was between 60–70 mm long, giving a total reactor volume of approximately 0.5 mL. Prior to loading the samples, the open-ended tubes were heated to 600 °C to remove any residual organic material. One end of each tube was then crimped and sealed using an argon arc welder. Solid anhydrite (CaSO₄), silica (SiO₂), and talc (3MgO·4SiO₂·H₂O) powders were weighed and transferred to the tubes by a funnel. Liquid organic reactants (oils and model compounds) and aqueous solutions were loaded into the tubes with an auto-pipette. The quantities of reagents used were: 5 mg oil; 0, 10, or 100 mg CaSO₄; 30 mg talc; 30 mg silica; and 450 mg water containing 5.6 wt.% MgCl₂, 0.56 wt.% CaSO₄, and 10 wt.% NaCl.

The solubility of CaSO₄ in water is positively correlated with salinity of the aqueous solution (Blount and Dickson, 1969). Therefore, we prepared a solution with relatively high ionic strength (3.91 M) by adjusting the NaCl concentration. We used the Mg²⁺-talc-silica system as a mineral buffer at elevated temperatures to keep the *in-situ* pH in a narrow range (pH ~3). The approach used to regulate *in-situ* chemical conditions for our study relies on chemical reactions that are known to proceed rapidly at the temperature and pressure conditions of the experiments (Saccocia

Table 1
Bulk geochemical data for oil and condensate samples used in this study (after Wei et al., 2012).

Field ^a	Depth m	Temp °C	ρ° (API ^o) g/mL	H ₂ S Mole %	S wt.%	$\delta^{34}\text{S}_{(\text{oil})}$ ‰	$\delta^{13}\text{C}_{(\text{oil})}$ ‰	DBTs ^c ppm	Thiadiam ^d ppm
<i>TSR unaltered^b</i>									
Turkey Creek	4056–4062	93	0.757 (55.5)	0.0	0.8	−0.9	−23.93	431	21
Walters Creek	4758–4762	126	0.835 (38)	0.0	0.1	−12.5	−23.94	192	2
Blacksher	5142–5146	138	0.828 (39.4)	0.0	0.1	5.6	−23.90	270	2
<i>Slightly TSR altered</i>									
Hatters Pond	6005–6011	160	0.756 (55.6)	0.6	0.1	5.1	−23.0	81	20
Cold Creek	6049–6058	160	0.757 (55.5)	0.0	0.1	−0.6	−23.70	118	17
<i>TSR altered</i>									
Appleton	4230–4242	137	0.781 (49.7)	2.0	0.35	10.7	−24.30	691	60
Vocation	4588–4591	127	0.775 (51.1)	5.7	0.3	6.4	−22.50	803	58
Huxford	4835–4841	132	0.774 (51.2)	6.1	0.2	5.7	−22.80	983	43
Chatom	5303–5340	138	0.787 (48.3)	16.7	1	12.2	−21.70	1564	149
Big Escambia Creek	5043–5067	143	0.828 (39.4)	20.0	1.4	24	−20.85	2345	296
South State Line	5683–5719	151	0.863 (32.4)	31.4	0.8	21	−20.13	6313	685

^a The oil samples are from the Smackover Fm. from different fields in the Gulf of Mexico (after Wei et al., 2012).

^b The degree of TSR alteration is based on the present S isotope compound specific study.

^c DBTs refer to dibenzothiophene and its alkylated groups including methyl-, dimethyl- and trimethyl-dibenzothiophenes.

^d Thiadiam stands for thiadiamondoids including thiaadamantanes (trimethyl- and tetramethyl-thiaadamantanes), thiadiamantanes (thiadiamantane, methyl-, dimethyl- and trimethyl-thiadiamantanes) and thiatriamantanes (thiatriamantane, methyl-, dimethyl- and trimethyl-thiatriamantanes).

and Seyfried, 1990; Seewald et al., 2000). More details regarding the mineral buffer approach are given by Zhang et al. (2008).

After loading the chemicals into gold tubes, the tubes were flushed with Ar for 3 min to remove air. The open end of the tube was crimped and welded, while the closed end remained submerged in liquid nitrogen (−196 °C) to trap volatiles created during the welding process. Individual sealed gold tubes were subsequently placed in separate stainless-steel autoclaves and inserted into a pyrolysis oven. Pyrolysis experiments were conducted under isothermal conditions at a temperature of 360 °C for 10–180 h. Temperature was controlled to within 1 °C of the set value, and was monitored using a pair of thermocouples secured to the outer wall of each autoclave. Constant hydrostatic confining pressure was maintained at approximately 24.1 MPa (3500 psi) by a water pump to prevent rupturing of the gold tubes at elevated temperatures and to eliminate possible variations as a function of pressure. When the desired reaction time was reached, the stainless steel autoclave was withdrawn from the oven and rapidly cooled to room temperature by quenching in water. Once the autoclaves were depressurized, the gold tubes could be recovered for detailed analysis of their contents.

The gold tubes were pierced in a glass tube that was filled with 4–5 mL of 4:1 hexane/dichloromethane to above the piercing point such that all escaping gas (mainly H₂S) bubbled through the solvent. The liquid and gold tube were then transferred into a glass vial. The gold tube was cut open from both ends and in the middle and inserted back into the vial to allow the solvent to contact the inside of the gold tube. The vial was then closed and shaken by hand for a minute and soaked for several minutes before the solvent was collected and concentrated under a gentle stream

of N₂. The concentrated sample was then injected into the GCMS and GC-MC-ICPMS without further purification.

2.3. Instrumentation

Details of the instrument set-up including schemes are presented in (Amrani et al., 2009). The GC-ICP-MS system employed here consists of an Agilent 6890 GC equipped with a split/splitless injector that is coupled to a Thermo Scientific Neptune multicollector ICP-MS via a heated transfer line. Faraday detectors were positioned to simultaneously collect ³²S⁺, ³³S⁺, and ³⁴S⁺, and the mass spectrometer was operated in medium resolution. It was tuned to maximize the ³²S signal while minimizing ¹⁶O₂ isobaric interference. The system was operated in a ‘dry’ plasma condition, i.e. with no aqueous vapor added to the gas streams. Relevant GC and ICP-MS parameters are listed in Table 2.

2.3.1. Calibration and data processing

Results of isotopic analyses are expressed in conventional $\delta^{34}\text{S}$ notation as per mil (‰) deviations from the VCDT standard:

$$\delta^{34}\text{S} = \left(\frac{{}^{34}R_{\text{sample}}}{{}^{34}R_{\text{std}}} \right) - 1$$

where ³⁴R is the integrated ³⁴S/³²S ion-current ratio of the sample and standard peaks.

Calibrated isotope ratios were obtained by comparison of analytes to SF₆ reference gas peaks in the same chromatogram. Precision of $\delta^{34}\text{S}$ values for SF₆ peaks in the present study was better than 0.3‰, which agrees well with the expected precision of their peak sizes (1–1.2 V s) according to our previous study (Fig. 5, Amrani et al., 2009). Accuracy was assessed each day of analysis by measuring

Table 2
Operating parameters for the GC/MCICPMS system employed in this study.

Gas Chromatograph	Agilent 6890
Capillary column	HP DB-5, 30 m × 0.25 mm × 0.25 μm
Injector	S/SL, 300 °C
Carrier gas	He, 1.4 mL/min
Oven temperature program	60 °C (5 min), 10 °C/min, 300 °C (10 min)
Transfer line temperature	330 °C
Reference/make-up gas flow	He, 7.7 mL/min
Mass Spectrometer	Thermo, Neptune
Coolant flow (Ar)	15 L/min
Auxiliary flow (Ar)	1 L/min
Sample gas flow (Ar)	1.55–1.65 L/min
Extraction voltage	2000 V
Resolution	Medium resolution, 5000 resolving power (m/Δm, 5%, 95%)
RF power	1200 W
Sample cone	Nickel 1.1 mm aperture
Skimmer cone	Nickel 0.8 mm aperture
Ion lenses	Optimized for sensitivity and peak shape
Detection system	Faraday cups
Integration time	0.189 s

organosulfur standards (DBT, C₁₈-SH, C₁₂-SH, and 4,6-diethyl-DBT) with known δ³⁴S values. We used relatively low concentrations (10–30 pmol, producing 0.5–1.5 V s³⁴S peak areas for each injection) of the standard compounds to match the size of typical peaks in petroleum samples. Average results for these external standards, using DBT as the reference compound (IRMS value: 3.3 ± 0.2‰), were: C₁₂-SH, −5.9 ± 0.5‰, n = 15 (IRMS value: −6.8 ± 0.4‰); C₁₈-SH, 30.0 ± 0.8‰, n = 9 (IRMS value: 30.6 ± 0.6‰); 4,6-diethyl-DBT, −3.2 ± 0.5‰, n = 5 (IRMS value: −3.5 ± 0.2‰). The calibrated δ³⁴S value of the SF₆ reference gas measured against the DBT reference compound was −1.9‰ (±0.5‰, 1σ standard deviation) and we used this value to calibrate analytes in the same chromatogram.

Data processing employed algorithms that are implemented in VisualBasic code within Microsoft Excel (Ricci et al., 1994; Sessions et al., 2001). Ion currents were integrated by the Neptune software (v. 3.1.0.27) in 189-ms increments and exported to Excel in ASCII format. Chromatographic peaks were defined using the m/z 32 data stream with a starting slope of 0.2 mV s^{−1} and ending slope of 0.4 mV s^{−1}, and this peak definition was transferred to all three data channels (i.e. m/z 32, 33, and 34) without adjusting for time shifts caused by isotope chromatography, which are negligible. Background signals were estimated independently for each data channel by averaging 20–30 points preceding each peak, depending on the complexity of the chromatogram. Peak areas (i.e. integrated ion currents) were then calculated with background subtraction, raw ion-current ratios (³⁴S/³²S) were calculated from peak areas, and calibrated δ³⁴S values were obtained

by comparison to the ion-current ratios for SF₆ reference gas peaks in the same chromatogram.

2.3.2. Estimation of measurement uncertainties

Analyses of external standards yielded precision for δ³⁴S values of better than 0.3‰ and external accuracy of better than 0.9‰. Nevertheless, crude petroleum samples present additional analytical difficulties that make the estimation of accuracy for these samples more difficult than for cleanly-separated standards. The dense and noisy chromatograms, wide dynamic range of peak sizes, coelution of peaks, and the matrix effect that is created by non-sulfur hydrocarbons (HC) all complicate the situation and degrade precision and accuracy. We have previously shown that precision is significantly reduced by coelution of non-S-bearing hydrocarbons when the ratio of hydrocarbons to OSC is more than 10:1. Even so, accuracy was only slightly affected by the HC matrix even at a ratio of 200:1 (Amrani et al., 2009).

For the current samples, we estimated precision by running duplicate (or in some cases triplicate) injections and this data is presented as a [Supplementary Table S1](#). In general, BTs have worse precision than do DBTs, mainly because of their relatively low abundance. Nevertheless, the mean standard deviation of δ³⁴S values for all compounds was typically better than 1‰ (1σ). In a few cases with moderate coelutions, it exceeded 2‰ (1σ). For cases with severe coelutions, or very low compound abundance, we integrated groups of related peaks (such as all methyl-BT isomers) together to yield a single composite δ³⁴S value. Experience from other compound specific isotope analyses suggests that more reliable results are obtained by this approach (Sessions, 2006), and indeed precision was typically better than 1‰ for these grouped peaks.

The accuracy of compound-specific isotopic measurements in a crowded chromatogram is very difficult to constrain quantitatively, because it depends heavily on isotopic contrasts between coeluting peaks. Given that we have not observed large differences in δ³⁴S for adjacent peaks, and based on results for external standard compounds, we conservatively estimate the accuracy of our analyses of petroleum samples to be better than 2‰. This uncertainty is more than an order of magnitude smaller than the variations that we observe between samples.

2.3.3. Identification of peaks and standard compounds

There are multiple isomers of each DBT, BT, thiophene, and labile sulfur compound (LSC) structure. It is difficult to positively identify each of these isomers since reference materials are not commercially available for many of them, especially the alkylated BTs. Where possible, we identified specific compounds by comparison of retention times to authentic standards. In other cases we identified compounds by comparison of the elution order and peak height to published data (Depauw and Froment, 1997; Garcia et al., 2002). In some cases where the abundance of OSC is very high – such as the case for DBTs in the Big Escambia Creek and state Line oils – it was possible to identify compounds by GCMS (Agilent 6890 N/5975B equipped with

Agilent DB5 (30 m × 0.25 mm × 0.25 μm) using the same GC oven conditions.

3. RESULTS

3.1. Bulk oil composition

Bulk parameters of the Smackover oils derived from published data (Claypool and Mancini, 1989; Wei et al., 2012) are presented in Table 1, and include reservoir temperature, carbon and sulfur isotope composition, sulfur content, density, and thiadiazole concentrations. This dataset is used to distinguish the degree of TSR alteration of the oils. Fig. 1 plots the bulk $\delta^{34}\text{S}$ values of Smackover oils as a function of coexisting H_2S concentrations in the wells. There is a good correlation between the two, which is usually indicative of increasing TSR alteration. This suggests that TSR-derived H_2S produced from ^{34}S -enriched sulfate reacted with organic compounds in the oils and gradually changed their bulk $\delta^{34}\text{S}$ values (Claypool et al., 1980; Claypool and Mancini, 1989).

The $\delta^{34}\text{S}$ values of condensates from Chatom, Big Escambia Creek, and South State Line fields are ^{34}S enriched compared with samples from other fields, and are similar to those of Jurassic anhydrite (Table 1). These samples are moderately or strongly altered by TSR as indicated by high H_2S and sulfur contents, high abundance of DBTs, sulfurized adamantanes, and high $\delta^{34}\text{S}$ values between 12.2‰ and 24‰. They are located in petroleum reservoirs close to Smackover depocenters at depths ranging from 5.1 to 5.8 km and at temperatures of 138–151 °C (Claypool and Mancini, 1989). The $\delta^{34}\text{S}$ values of oil and condensate samples from the Appleton, Vocation, and Huxford fields range from +4.7 to +10.7‰ and have intermediate H_2S content, indicating slight to moderate TSR alteration. Hatters Pond, Cold Creek, Turkey Creek, Blacksher, and Wallers Creek oils do not show evidences of TSR, and have

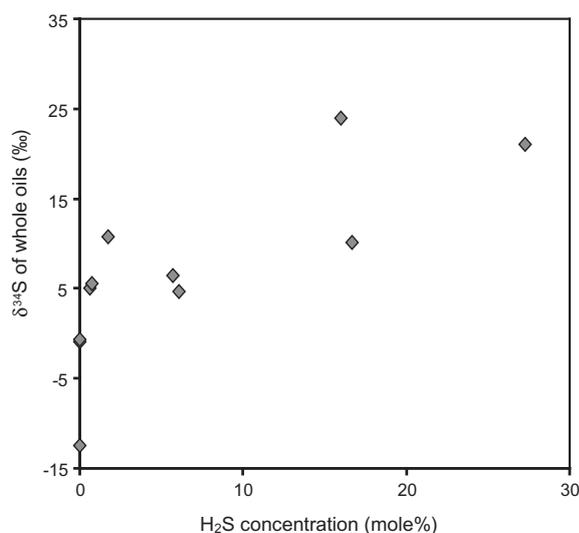


Fig. 1. Bulk $\delta^{34}\text{S}$ values of Smackover oils plotted against abundance of H_2S coexisting in the well.

relatively low $\delta^{34}\text{S}$ values (−12.5‰ to +5.6‰) with no H_2S detected.

3.2. Individual OSCs from crude oils

GC-MC-ICPMS analyses revealed a wide distribution of $\delta^{34}\text{S}$ values for individual OSC compounds in the oils, ranging from −20‰ to +28‰ (Fig. 2). The maximum difference between individual compounds within the same oil reaches up to 25‰. The oils can be divided into two groups based on this data: those that have more negative $\delta^{34}\text{S}$ values and little variation between individual compounds, and those that have more positive $\delta^{34}\text{S}$ values and large differences between individual compounds.

The first group of oils includes Turkey Creek, Blacksher, and Wallers Creek oils with $\delta^{34}\text{S}$ values that are probably close to those of their source kerogen. The differences in $\delta^{34}\text{S}$ between BTs and DBTs are relatively small, typically <3‰. In contrast, in the second group of oils $\delta^{34}\text{S}$ values of BTs are significantly higher than those of DBTs, between 5‰ and 25‰. As the extent of TSR increases (Table 1), the isotopic contrast between BTs and DBTs is reduced and all compounds become ^{34}S enriched (Fig. 2). Big Escambia Creek oil is the most ^{34}S enriched with $\delta^{34}\text{S}$ values of 28–29.3‰ for BTs and 17.5–22.8‰ for DBTs. There are smaller differences within families of similar compounds, i.e. DBTs and BTs. DBT is consistently enriched in ^{34}S relative to its methylated homologs, with differences between them reaching up to ~9‰ in the case of the Chatom oil.

Hatters Pond and Cold Creek oils have high $\delta^{34}\text{S}$ values (~20‰) for BT while DBTs are significantly ^{34}S depleted (down to −5.9‰). The abundance of BT peaks is relatively low, which can considerably degrade precision and accuracy. We therefore integrated all of the methyl-benzothio- phene (MeBT) isomers together as a single peak to achieve a larger peak area (~0.5 V s).

In general, bulk $\delta^{34}\text{S}$ values of the oils are similar to those of the individual compounds (Fig. 2). There are, however, three oils (Turkey Creek, Wallers Creek, Blacksher) for which compound-specific $\delta^{34}\text{S}$ values deviate significantly from the bulk values. Interestingly, none of them are thought to be TSR altered, yet all show ^{34}S enrichment in the bulk $\delta^{34}\text{S}$ value. The reason for this is not clear yet. A possible explanation is that GC-amenable compounds are quantitatively smaller than other organic sulfur fractions in oil such as asphaltene and polar (NSO) fractions. If these fractions are ^{34}S enriched then the bulk $\delta^{34}\text{S}$ value could be determined mostly by them.

3.3. Pyrolysis experiments

Three types of pyrolysis experiments were conducted at 360 °C for three periods of time (20, 40 and 89 h) using a mineral buffer mixture of silica/talc (Zhang et al., 2008). The first used a limited amount of solid CaSO_4 (10 mg), in which more than 60% of the initial CaSO_4 was consumed after 89 h. In the second type of experiment we used a large excess of CaSO_4 (100 mg), where only few percent of CaSO_4 was consumed by the end of the longest reaction time. We refer to these experimental conditions as ‘low’ and ‘high’

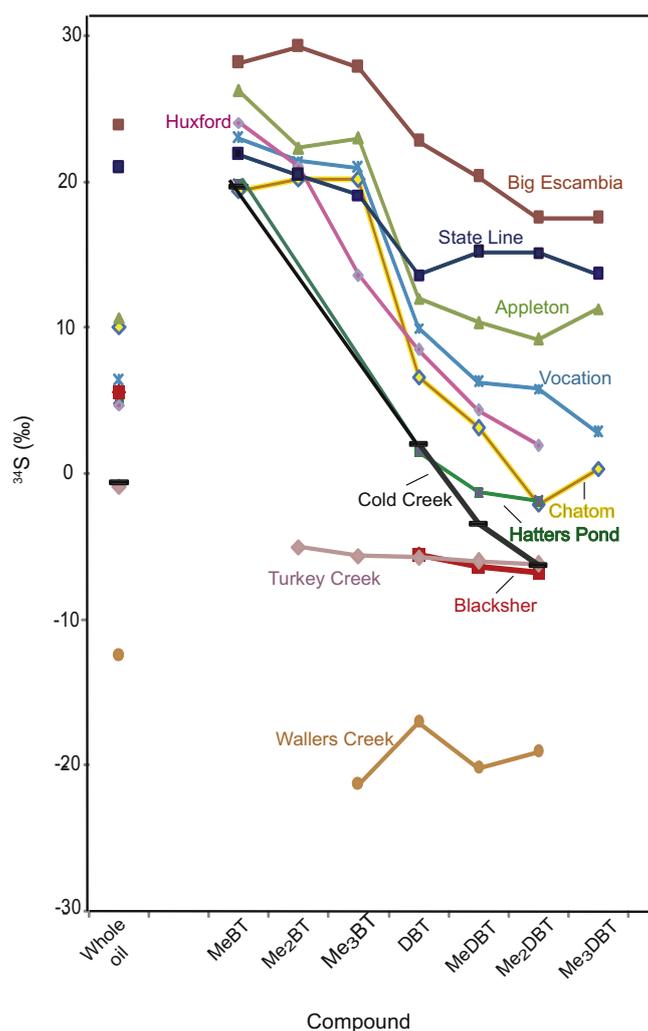


Fig. 2. $\delta^{34}\text{S}$ values of individual organosulfur compounds from whole oils sourced in the Smackover Fm., Gulf of Mexico. Whole oils were injected with no pretreatment to the GC-MC-ICPMS. Specific isomers for which data are plotted are: 2-MeBT, 2,6/2,5-Me₂BT, 2,3,5/2,3,6-Me₃BT, DBT, 4-MeDBT, 2,6/3,6-Me₂DBT, 2,4,6-Me₃DBT. BT = Benzothiophene, DBT = Dibenzothiophene, Me = methyl, Et = ethyl.

sulfate, respectively. The third type of experiment was a negative control, and comprised heating without CaSO_4 for comparison.

For our experiments, we synthesized CaSO_4 that has a $\delta^{34}\text{S}$ value (-5.3‰) that is distinct compared to those of the oils (up to 24‰), in order to demonstrate large $\delta^{34}\text{S}$ changes. In nature, the difference between the $\delta^{34}\text{S}$ of oils and CaSO_4 can be even larger, but is typically reversed, i.e. with the oil depleted in ^{34}S relative to sulfate. Three oils were chosen for these experiments with different geochemical characteristics and degrees of TSR alteration to study different aspects of the TSR process.

3.3.1. Caspian oil

The Caspian oil is a low-sulfur crude oil from the Caspian Sea area. It is a light crude oil that contains 0.5 wt.% sulfur with no asphaltene fraction and very low amounts of resins (4%), as described by Zhang et al. (2007). We analyzed this oil previously and suggested that

it is in the earliest stages of TSR alteration based on S-isotopic differences between BTs and DBTs of about 30‰ , and on the fact that the $\delta^{34}\text{S}$ values of LSC approached those of sulfate from evaporites in the reservoir (Amrani et al., 2009).

In negative control samples (no CaSO_4 added), the $\delta^{34}\text{S}$ values of the refractory S compounds (BTs and DBTs) did not change significantly ($<3\text{‰}$) compared to the unheated oil (Fig. 3a). Pyrolysis with CaSO_4 (i.e. TSR simulation) has a dramatic effect on the isotopic compositions of the organosulfur compounds, with S-isotopic differences reaching up to 28‰ compared with the unheated oil (Fig. 3a). These isotopic changes mainly affected the BTs, with $\delta^{34}\text{S}$ values that are approaching and eventually exceeding that of the CaSO_4 (-5.3‰ , broken line in Fig. 3a). There are relatively small $\delta^{34}\text{S}$ changes for DBTs, up to $2\text{--}4\text{‰}$ in the low-sulfate experiments and up to $7\text{--}9\text{‰}$ in the high-sulfate ones, though they did change toward the $\delta^{34}\text{S}$ values of CaSO_4 as expected.

In the high-sulfate experiments, BTs are more depleted in ^{34}S than CaSO_4 , suggesting isotopic fractionation in the process. There are two possible steps at which fractionation may occur: (i) during H_2S generation from sulfate during TSR, and (ii) during the reaction of H_2S with organic compounds. Both effects could exist simultaneously. To further study this issue, we trapped H_2S that was generated in the gold tubes during TSR and analyzed it as Ag_2S by EA-IRMS. The results of these measurements are plotted in Fig. 3a, showing no fractionation for the low- SO_4 experiments and a $\sim 4.5\text{‰}$ depletion of ^{34}S in H_2S from the high- SO_4 experiments. This $\text{SO}_4^{2-}/\text{H}_2\text{S}$ fractionation is in the range of previous TSR studies at similar temperatures (Kiyosu and Krouse, 1993).

The $\delta^{34}\text{S}$ values of H_2S are close to those of BTs in the same samples. However, in the case of low CaSO_4 experiments, H_2S is depleted in ^{34}S by $\sim 2\text{‰}$ relative to BTs, and enriched in ^{34}S by about 3‰ relative to BTs in the high CaSO_4 experiments. In both cases the reaction time did not significantly alter the isotopic composition of H_2S . These results show that most of the isotopic fractionation that is imprinted in OSC resulted from the reduction of sulfate to H_2S and subsequent reaction with organic compounds. Any fractionation in the formation of OSC by H_2S or elemental S is relatively small ($1\text{--}3\text{‰}$) in agreement with previous laboratory studies (Amrani et al., 2006, 2011).

3.3.2. Oman oil

The Oman oil is sulfur-rich (3 wt.%), relatively immature, and has not been significantly affected by TSR. It contains high concentrations of LSC and low concentrations of BTs and DBTs, below our detection limit. The bulk $\delta^{34}\text{S}$ value of the oil is $15.7 \pm 0.7\text{‰}$. The $\delta^{34}\text{S}$ values of the individual OSC compounds range between $\sim 10\text{‰}$ and 20‰ . Heating this oil with no CaSO_4 produced BTs with a narrow range of $\delta^{34}\text{S}$ values between 16‰ and 18.5‰ and only trace amounts of DBTs were formed, below our detection limit (Fig. 3b). Low- CaSO_4 experiments shifted the $\delta^{34}\text{S}$ values toward that of the CaSO_4 , up to about 15‰ from the original values with positive correlation with pyrolysis time. Unlike the Caspian oil, there is only a small difference in $\delta^{34}\text{S}$ values between the individual compounds after TSR. High- CaSO_4 experiments exhibit a different behavior, where BTs reached more negative $\delta^{34}\text{S}$ values than CaSO_4 , similar to the experiments with the Caspian oil. In these experiments, the $\delta^{34}\text{S}$ value of DBT is significantly higher than those of BTs. The experiments with longer pyrolysis time were not measurable due to a sulfur-containing unresolved complex mixture (UCM).

3.3.3. Big Escambia Creek oil

The Big Escambia Creek oil is in advanced stages of TSR alteration with a bulk $\delta^{34}\text{S}$ value of 24‰ (Table 1) and relatively small S-isotopic differences between individual compounds (Fig. 3c). Unlike the Caspian oil, all of the OSC compounds in this oil – including DBTs – already reflect a ^{34}S enriched composition due to TSR inputs. Big Escambia Creek oil contains an intermediate amount of sulfur (1.4 wt.%), between that of the Caspian and Oman oils.

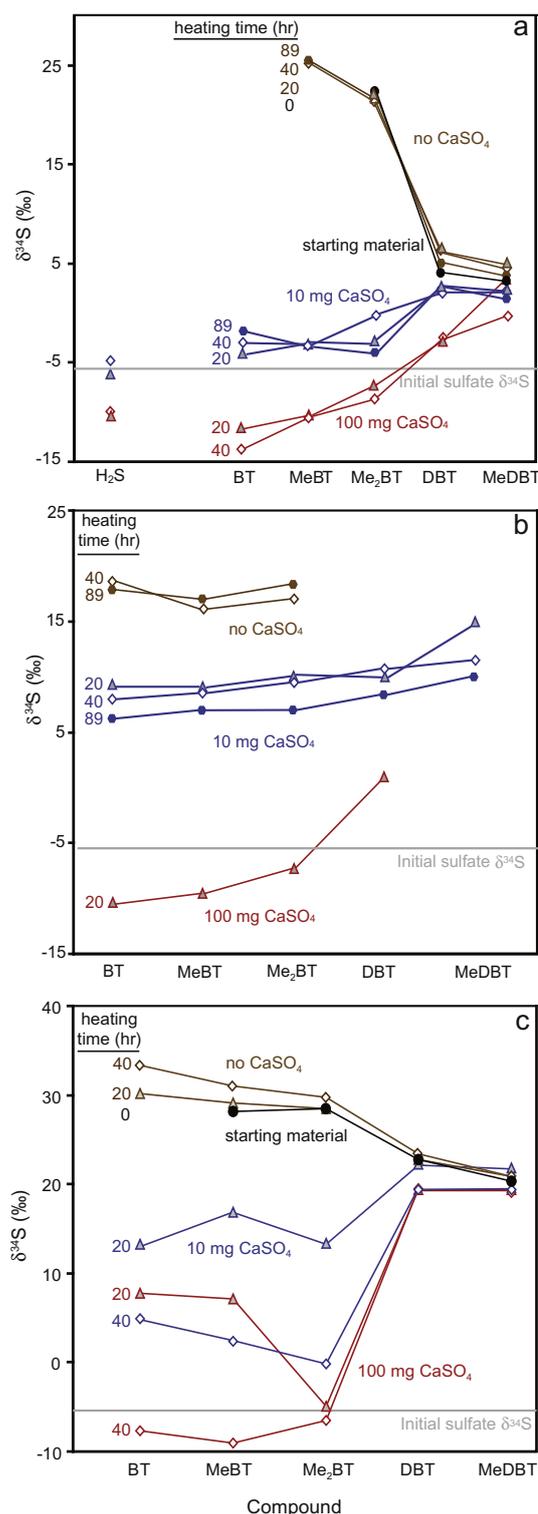


Fig. 3. $\delta^{34}\text{S}$ values of individual BTs and DBTs from pyrolysis experiments of (a) Caspian oil, (b) Oman oil, and (c) Big Escambia Creek oil. Parallel experiments were conducted for each oil with no CaSO_4 (negative control), with 10 mg CaSO_4 ('low sulfate'), and with 100 mg CaSO_4 ('high sulfate'). Broken line represents the $\delta^{34}\text{S}$ value of CaSO_4 that was added to the pyrolysis experiments. The $\delta^{34}\text{S}$ values of H_2S were analyzed by EA-IRMS as Ag_2S .

As in the case of the Caspian oil, heating experiments did not significantly change the $\delta^{34}\text{S}$ values of the refractory compounds.

When heated in the presence of low amounts of CaSO_4 for 20 h, $\delta^{34}\text{S}$ values of BTs changed by about 15‰ whereas DBTs did not. After 40 h, BTs changed by 25–30‰ while DBTs changed by only 2–3‰. As expected, high- CaSO_4 experiments increased the isotopic changes in BTs and after 40 h shifted the $\delta^{34}\text{S}$ values to below those of CaSO_4 , with a total change of up to 35–40‰. DBTs changed as well

toward the CaSO_4 value but to a much smaller degree, <4‰. The magnitude of these changes is between those of the Caspian and Oman oils, in accordance with the original sulfur content of the oils.

During heating experiments of all three oils, thermally labile sulfur compounds such as sulfides and thiols disappeared, and the chromatograms became dominated by more stable molecules – BTs and DBTs, as demonstrated by the Big Escambia Creek oil (Fig. 4a and b). In contrast, experiments in the presence of CaSO_4 showed increased

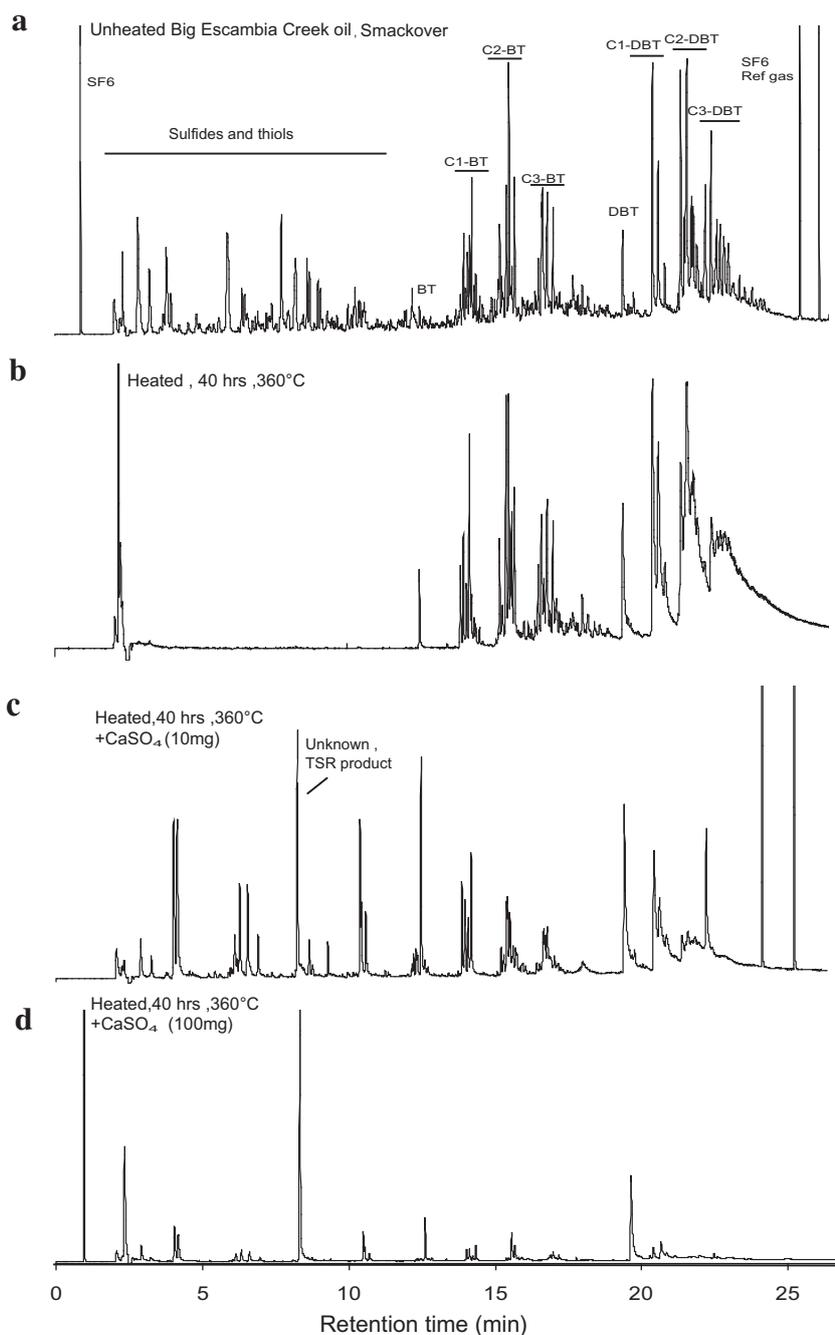


Fig. 4. Gas chromatograms of Big Escambia Creek oil obtained by GC-MC-ICPMS (^{32}S trace) before and after hydrous pyrolysis experiments at 360 °C for 40 h. (a) Unheated oil, (b) Heated with no sulfate, (c) heated with low sulfate (10 mg), (d) heated with high sulfate (100 mg).

amounts of LSC (Fig. 4c and d). Under these conditions, BTs became much more abundant. This especially affected the lower molecular weight isomers such as MeBT and BT that were at low concentration in the unheated oil. At the early end of the chromatogram, there are also unidentified sulfur compounds, most of them probably LSC as evidenced by their disappearance upon heating (Fig. 4b).

The most abundant compound at a retention time of 8.4 min (“unknown TSR product”) is clearly formed during TSR and becomes the dominant species as TSR continues (Fig. 4d). We could not identify its structure by GCMS because there are significant non-sulfur hydrocarbon interferences in the TIC chromatogram around this retention time. None of our organic sulfur standards, including methylated

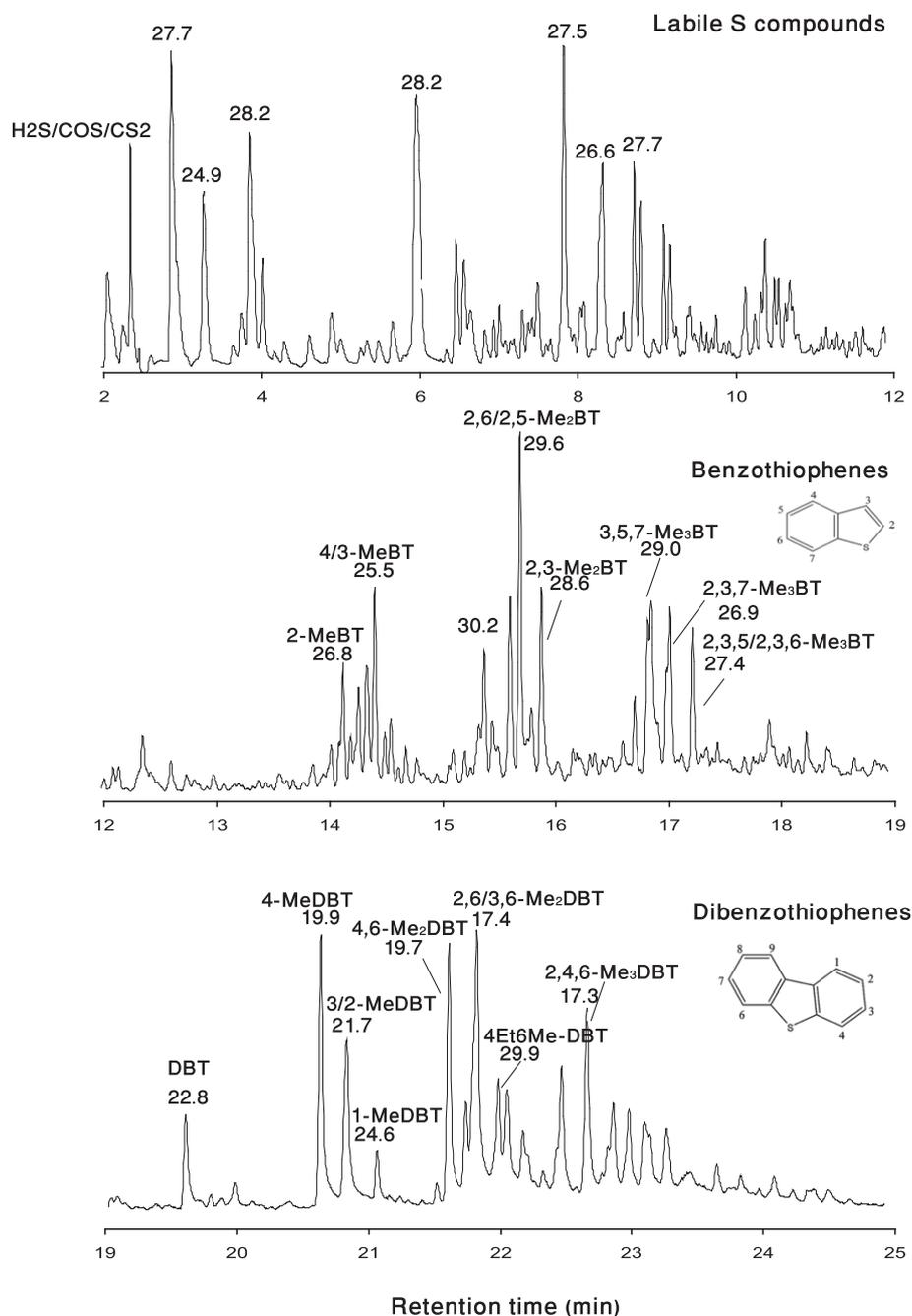


Fig. 5. Partial gas chromatograms (by GC-MC-ICPMS, ³²S trace) of unheated Big Escambia Creek oil (see Fig. 4a for the complete chromatogram, bulk $\delta^{34}\text{S}$ of the oil is 24‰) showing three groups of OSC with identification of specific compounds and their $\delta^{34}\text{S}$ values (‰): (a) Labile S compounds (LSC), mainly alkyl sulfides and thiols, (b) benzothiophene (BT) isomers, (c) dibenzothiophene (DBT) isomers. Me = methyl, Et = ethyl. Numbers represent the specific molecular positions of alkyl (Me or Et) groups on the aromatic rings.

thiophenes, matched its retention time. Attempts to isolate this compound by off-line liquid chromatography failed due to the low amount of OSC present in the gold tube and the high volatility of this compound. We speculate that this compound is likely thiaadamantane, as this is a well-known TSR product and has a single isomer with shorter retention time than BT (Wei et al., 2012). Further experiments with higher amounts of reactants are needed for a firm identification of this unknown compound. The $\delta^{34}\text{S}$ value of the putative thiaadamantane is similar to the other LSC. In the unheated Big Escambia Creek oil the $\delta^{34}\text{S}$ values of LSC were around 27–28‰, similar to BTs (Fig. 5a and b). This observation is valid for all TSR affected oils that were measured in the present study.

Multiple isomers of each parent structure (DBTs, BTs, thiophenes, and LSC) exist in these oils, as can be seen in Fig. 5. There are relatively small isotopic differences between related groups of isomers, typically 2–4‰. This could be the result of different mechanisms or timing of formation of the isomers. However, some of the minor differences within the same groups could also be caused by analytical error due to the low abundance and incomplete resolution of many of these peaks, especially in the case of BTs in low TSR altered oils. While the $\delta^{34}\text{S}$ values of LSC and BTs are quite uniform, DBTs exhibit relatively large variations between ethylated DBT (4 ethyl, 6 methyl DBT) and the methylated DBTs (Fig. 5c), probably because of differences in their thermal stabilities.

4. DISCUSSION

4.1. Mechanisms controlling $\delta^{34}\text{S}$ in individual organosulfur compounds

4.1.1. Mixed sources for H_2S during TSR

Hydrogen sulfide in petroleum reservoirs comes from two main sources: (i) thermal degradation of LSC (including asphaltenes and NSO compounds), which results in an isotopic composition that is close to its parent oil (Orr, 1986; Idiz et al., 1990; Amrani et al., 2005), and (ii) reduction of sulfate minerals in evaporate deposits, resulting in an isotopic composition close to that of seawater sulfate (Machel et al., 1995). The mixing ratio between these two H_2S sources will then determine the $\delta^{34}\text{S}$ value of H_2S in the reservoir. If this H_2S mixture reacts with hydrocarbons, it will produce OSC compounds with intermediate $\delta^{34}\text{S}$ values (Orr, 1974; Powell and Macqueen, 1984; Cai et al., 2001, 2003; Amrani et al., 2006). Laboratory and field data show that there is a positive correlation between OSC and H_2S concentrations in petroleum reservoirs (Ho et al., 1974; Cai et al., 2003; Zhang et al., 2008; Wei et al., 2012).

The two sources of S are apparent in our experimental results (Fig. 3a and b). The low-sulfur (0.5 wt.%) Caspian oil responds immediately to addition of exogenous sulfur from TSR, resulting in a shift in $\delta^{34}\text{S}$ of BTs sharply toward that of CaSO_4 (Fig. 3a). In contrast, the ~6-fold higher sulfur content of the Oman oil significantly increases the amount of H_2S released from the oil during heating (Zhang et al., 2007; Amrani et al., 2008). This H_2S is strongly enriched in ^{34}S (~16‰) relative to that from CaSO_4 reduction

(−5.3‰). As a result, the $\delta^{34}\text{S}$ values of BTs in the TSR experiments using Oman oil are shifted towards CaSO_4 to a lesser degree than are those from the Caspian oil. In the Oman oil experiments with high- CaSO_4 , the $\delta^{34}\text{S}$ values of BTs approached the CaSO_4 value (Fig. 3b). The extent of TSR is much higher and TSR-derived H_2S is becoming increasingly important, thus the $\delta^{34}\text{S}$ values of BTs are gradually approaching that of CaSO_4 in the reservoir. Big Escambia Creek oil has intermediate S content relative to the Oman and Caspian oils (Table 1) and its isotopic response to TSR is intermediate as well (Fig. 3c).

4.1.2. Formation and degradation of OSC during TSR

The large S-isotopic variations between BTs and DBTs in petroleum samples that are observed in this study represent different responses to thermal stress and redox conditions. The main factor determining the isotopic composition of individual OSC is the mixing ratio between sulfur contained in OSC within the original oil and that from reaction with sulfate-derived H_2S in the reservoir. This ratio in turn is controlled by the relative rates of formation and destruction of each OSC.

Loss of OSC is evident in our heating experiments of oils (with no CaSO_4) that show a complete disappearance of LSC from all the oils (Fig. 4b). However, during TSR, the dynamic formation and degradation of LSC maintains a steady-state concentration that can be detected even after thermal treatment that is far beyond their chemical stability (Fig. 4c and d). Experiments with high partial pressures of H_2S without TSR show similar formation of LSC, though under TSR their rate of formation is even higher (Amrani et al., 2008; Zhang et al., 2008). The $\delta^{34}\text{S}$ values of LSC thus reflect the near-instantaneous composition of H_2S in the reservoir, which in turn is controlled by the relative amounts of H_2S derived from TSR and the parent oil.

BTs and DBTs remain largely intact under our hydrocarbon pyrolysis conditions without CaSO_4 present (Fig. 3a–c) because of their high thermal stability (Katritzky et al., 2001; Dartiguelongue et al., 2006). However, under the severe oxidative stress accompanying TSR, even these stable compounds can gradually degrade (Katritzky et al., 2001). At the same time, the rate of formation of BTs and DBTs increases significantly under TSR conditions, as demonstrated by the high concentration of DBT in Smackover oils that experienced TSR compared with the non-TSR oils (Table 1). This suggests that substantial amounts of TSR-derived sulfur are added to the oils during TSR, and that this gradually masks the original $\delta^{34}\text{S}$ of the oil (Fig. 2). However, Fig. 4 demonstrates that the ratio of BT/DBT is actually decreasing throughout this process. We infer that a large portion of the original BTs decomposed under our pyrolysis conditions. Thus the rapid formation and degradation of BTs, and corresponding short residence time in the oil, can explain the rapid changes in the $\delta^{34}\text{S}$ values of BTs in response to TSR in our experiments (Fig. 3) and in petroleum reservoirs (Fig. 2).

In contrast, the $\delta^{34}\text{S}$ values of DBTs change at a much slower rate (Figs. 2 and 3). Their thermal stability is greater, and they are not expected to degrade under normal petroleum reservoir conditions (Dartiguelongue et al., 2006).

This is due to the added aromatic character resulting from the extra fused ring on the DBT molecule (Smith and March, 2001). They are also slower to form as can be seen in the heating experiments (no CaSO_4) with Oman oil where DBTs were not detected while BTs were abundant (Fig. 3b). Nevertheless, there are some DBT compounds that behave differently, namely ethylated DBTs (and longer alkyl substituents). These compounds have lower thermal stability because they preferentially cleave at the β position to yield the methylated aromatic ring (Silverstein and Bassler, 1962). Therefore, they are expected to degrade rapidly and be replaced by TSR-derived compounds. This can be seen clearly in Fig. 5c, where 4-ethyl, 6-methyl DBT has more positive $\delta^{34}\text{S}$ values than other DBTs, and similar to BTs.

4.2. Implications for TSR assessment

Numerous parameters are used to assess TSR, including petrographic appearance, fluid and fluid inclusion composition, oil chemistry, and stable isotopes of carbon and sulfur (Machel et al., 1995). A highly aromatic and sulfur-rich solid bitumen is also diagnostic for TSR, but is applicable mostly where severe TSR has occurred (Kelemen et al., 2008, 2010). A promising approach to assess TSR has been developed in the last decade using sulfurized thiaadamantanes as molecular indicators (Hanin et al., 2002; Wei et al., 2007, 2012). However, reliable determination of the occurrence and extent of TSR still requires integration of most of these parameters, especially when TSR extent is low to moderate (Machel et al., 1995; Machel, 2001).

The present study suggests a new and highly sensitive way to diagnose TSR effects by measuring the S-isotopic composition of individual BTs and DBTs. This analysis can be done with whole oils with little pretreatment and without any off-line separation. Moreover, all the data needed to assess TSR is embedded within the oil itself, and there is no need to collect gases or minerals from the reservoir. Our data show that the S isotopic differences between BTs and DBTs, the most abundant organosulfur compounds in oils (Krein, 1993), are themselves diagnostic. At the onset of TSR, differences in $\delta^{34}\text{S}$ between BTs and DBTs are the largest. BTs rapidly adopt the $\delta^{34}\text{S}$ value of sulfate participating in TSR, whereas DBTs change more slowly. As TSR advances and more H_2S is generated, DBTs gradually change their $\delta^{34}\text{S}$ values toward sulfate as well, thus the fractionation between the two compounds decreases. Thiadiamondoid concentrations reflect the extent of secondary addition of S into oils, which is positively correlated with the extent of TSR (Wei et al., 2012). Fig. 6 plots thiadiamondoid concentrations versus fractionations between the average $\delta^{34}\text{S}$ values of all measured isomers of BTs and DBTs ($\Delta^{34}\text{S}_{\text{BTs-DBTs}}$). The specific isomers and their $\delta^{34}\text{S}$ values that were used for this calculation are present in Table S2 in the Supplementary data. In oils affected by TSR, there is a clear decrease in fractionation between BTs and DBTs with increasing thiadiamondoid concentration. For the later stages of TSR alteration that are represented by Big Escambia Creek and State Line oils, $\Delta^{34}\text{S}_{\text{BTs-DBTs}}$ values are only slightly changed ($\sim 9\%$ to

6%) despite the large increase in thiadiamondoids. This is probably because OSC reached a steady state with H_2S in the reservoir. However, the Chatom oil seems to be anomalous as the thiadiamondoid concentration indicates that this oil is significantly TSR-altered while the $\Delta^{34}\text{S}_{\text{BTs-DBTs}}$ values suggest only slight TSR-alteration. Previous studies indicated that Chatom oil is significantly TSR-altered (Claypool and Mancini, 1989; Rooney et al., 1995; Wei et al., 2012). At this stage we cannot explain this anomaly from the general trend of $\Delta^{34}\text{S}_{\text{BTs-DBTs}}$ /thiadiamondoids, it clearly needs additional study.

Thiadiamondoid and H_2S concentrations in Hatters Pond and Cold Creek oils are similar to those of the non-TSR altered Turkey Creek, Wallers Creek, and Blacksher oils (Table 1 and Fig. 6). Indeed previous studies had considered Hatters Pond and Cold Creek oils to be unaffected by TSR based on these and other geochemical data (Claypool and Mancini, 1989; Rooney et al., 1995; Wei et al., 2012 see also Table 1). However, our results (Figs. 2 and 6) reveal substantial ^{34}S fractionations ($\sim 20\text{--}23\%$) between BTs and DBTs in these oils, similar to those observed in other TSR-altered oils but markedly different from those unaffected by TSR. Both Hatters Pond and Cold Creek reservoirs are at high temperature ($160\text{ }^\circ\text{C}$), which is consistent with this suggestion. The fact that H_2S concentration is low (Hatters Pond) or absent (Cold Creek) cannot discount the possibility of early TSR alteration. Such low intensities of TSR are expected to produce very low H_2S concentrations that can react rapidly with metals and petroleum hydrocarbons at reservoir temperature of $160\text{ }^\circ\text{C}$. Laboratory experiments have shown that even when H_2S cannot be detected, TSR already affects hydrocarbons and produce BTs and DBTs (Amrani et al., 2008, 2011). We therefore suggest that BTs in both oils are recording the very early onset of TSR

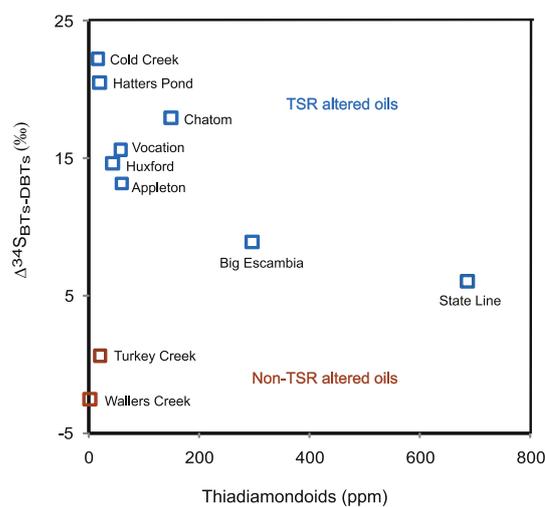


Fig. 6. ^{34}S fractionation between BTs and DBTs isomers ($\Delta^{34}\text{S}_{\text{BTs-DBTs}}$) as a function of total thiadiamondoid concentration (Wei et al., 2012), which includes thiaadamantanes (trimethyl- and tetramethyl-thiaadamantanes), thiadiamantanes (thiadiamantane, methyl-, dimethyl- and trimethyl-thiadiamantanes) and thiatriamantanes (thiatriamantane, methyl-, dimethyl- and trimethyl-thiatriamantanes). The plotted $\delta^{34}\text{S}$ values for alkylated BTs and DBTs are the numerical averages of all measured isomers.

alteration. If correct, the implication is that compound-specific S isotope measurements are more sensitive indicators of early TSR inputs than are other existing geochemical proxies, including thiadimondoids concentration. However, we cannot yet discount the possibility that some other, unidentified process in certain oils leads to a pattern of ^{34}S enrichment in BTs that is similar to the pattern produced by TSR.

5. CONCLUSIONS

Large S-isotopic fractionations between benzothiophenes (BTs) and dibenzothiophenes (DBTs) of up to 25‰ in the same oil have been observed in Smackover oils that were affected by addition of H_2S derived from TSR. BTs are ^{34}S enriched, close to the $\delta^{34}\text{S}$ values of sulfate from evaporites in the Smackover Fm. The $\delta^{34}\text{S}$ values of DBTs span a wider range, are more negative than the BTs, and change more gradually toward the sulfate isotopic composition. These fractionations between BTs and DBTs reflect differing degrees of TSR alteration of these oils.

Laboratory TSR experiments show that isotopic alteration of more than 30‰ readily occurs under TSR conditions. BTs are sensitive tracers for TSR as they form readily under TSR conditions, and have $\delta^{34}\text{S}$ values that are similar to that of H_2S derived from CaSO_4 . In contrast, DBTs show relatively small $\delta^{34}\text{S}$ changes, preserving their original $\delta^{34}\text{S}$ values longer because of their greater thermal stability and slow rate of formation. DBTs can therefore preserve the original (non TSR altered) $\delta^{34}\text{S}$ signals of the oils through low to moderate TSR alteration. The $\delta^{34}\text{S}$ of specific organosulfur compounds is controlled by the rates of addition of sulfate-derived H_2S and the destruction of the original OSC.

The isotopic compositions of individual BTs and DBTs allow us to detect TSR alteration of oils at the very earliest stages, and can also reveal the sulfur-isotopic composition of source bitumen even through more substantial TSR overprinting. The approach should find numerous uses in exploration, as well as for understanding the basic reaction mechanisms and kinetics of thermal sulfate reduction and the secondary sulfur incorporation into oils.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.gca.2012.01.023](https://doi.org/10.1016/j.gca.2012.01.023).

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