Note

δ^{34}S character of organosulfur compounds in kerogen and bitumen fractions of sedimentary rocks

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ABSTRACT

Hydropyrolysis (HyPy) of S-containing oil mature rock samples from two geologic settings each produced much higher concentrations of organosulfur compounds (OSCs) compared to their free occurrence in the bitumen. The δ^{34}S values of the most abundant OSCs from the kerogen and in the bitumen, were measured by gas chromatography inductively coupled plasma mass spectrometry (GC-ICP-MS). DBT and mDBTs from the HyPy processed kerogen fractions showed a distinct ^{34}S depletion, with δ^{34}S values up to 12‰ lighter than their bitumen occurrence. The different δ^{34}S values of OSCs from the kerogen and bitumen fractions is likely reflective of differences in timing of production, reduced sulfur sources or organic sulfurisation mechanism.

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1. Introduction

The emerging capability of compound specific S isotope analysis (CS-S-IA; Amrani et al., 2009; Greenwood et al., 2014) presents an opportunity to gain a much better understanding of the organic S-cycle and the nature of different S-pools in the Earth's system and may help distinguish different pathways of organic sulfurisation. The distributions and δ^{34}S character of different sedimentary S-pools has helped identify pathways of organic sulfurisation (e.g. Sinninghe Damste and de Leeuw, 1990; Raven et al., 2015). Compound specific δ^{34}S data is also attractive for being free of any inorganic S contribution, which can be problematic for bulk δ^{34}S analysis of sedimentary rocks or fractions due to difficulties in exhaustively removing all pyrite (Cai et al., 2009). Paleoenvironmental reconstructions using compound specific δ^{34}S of OSCs in sedimentary rocks requires knowledge about timing of organic matter (OM) deposition and its sulfurisation, the identity and δ^{34}S values of primary S-sources and the molecular and δ^{34}S fractionation of OSCs during diagenesis and thermal maturation. We measured the δ^{34}S values of OSCs generated from kerogens by hydropyrolysis (HyPy) treatment and compared them to free OSCs in the corresponding bitumen fractions for several different aged sediments from two geological settings. HyPy has been shown to release indigenous covalently bound hydrocarbons from the kerogen matrix of rock samples (e.g. Love et al., 1995).

2. Material and methods

Four Permian or Triassic shales recovered from the Hovea-3 well (Perth Basin, Western Australia; e.g., Thomas et al., 2004; Dawson et al., 2005) and calcareous shale samples from three separate wells of the Lower Cretaceous Toolebuc Formation (Queensland, Australia; Boreham and Powell, 1987; Woltering et al., 2016) were selected for this study. The Toolebuc rocks were much richer in organic matter and generally had slightly higher total sulfur (TS) content (Table 1). All samples had thermal maturities within the oil window (Table 1; R_c = 0.7 – 0.8%, calculated from MPI-1 index after Radke and Welte (1983); and C_{31} 22S/(22S + 22R) homohopane ratio approaching equilibrium, Peters et al. (2005)).

Using established procedures (Robert et al., 2016) powdered rocks were Soxhlet-extracted (9:1 DCM: MeOH; 72 h) to separate the solvent-soluble bitumen and solvent-insoluble kerogen fraction; elemental S (found to be negligible) was removed from the bitumen fraction with activated (HCl) copper (Robert et al., 2016). Column chromatography of the bitumen fraction on silica gel yielded aliphatic, aromatic and polar fractions. To further con-

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Table 1
Sample information and key compositional parameters of native sediment samples from the Hovea-3 core (Perth Basin, Western Australia) and the Toolebuc Formation (Queensland, Australia).

Sample number	Sample name	Age	TOC [wt.%]	TS [μmolS/g Rock]	C_{31} 22 S/(22 S + 22R) homohopane[a]	MPI-1[a,b]	R_c[c]
H1	Hovea-3 1975.6m	Triassic	2.1	218.8	0.59	0.64	0.83
H2	Hovea-3 1980.05m	Triassic	0.9	n.a	0.56	0.56	0.79
H3	Hovea-3 1980.94m	Permian/Triassic	4.6	1062.5	0.57	0.55	0.78
H4	Hovea-3 1990.2m	Permian	2.1	312.5	0.58	0.58	0.80
T1	Boulia-10B 43.35m	Cretaceous	28.8	1125	0.40	0.55	0.73
T2	Jericho-11 60.78m	Cretaceous	15.6	531.3	0.38	0.50	0.70
T3	Crydon-1 101m	Cretaceous	46.2	1156.3	0.44	0.66	0.80

[a] Determined in bitumen extract.
[b] Methyl phenanthrene index after Cassani et al. (1988); calculated from base ion abundances (phenanthrene *m/z* 178; methyl phenanthrene *m/z* 192).
[c] Calculated vitrinite reflectance (R_c); calculated from MPI-1 index after Radke and Welte (1983).

centrate OSCs, aromatic fractions were fractionated over aluminium oxide (Type 507C neutral; Fluka); using solutions of *n*-hexane:DCM (99:01 v/v), *n*-hexane:DCM (90:10 v/v) and DCM in a refined procedure outlined by Jiang et al. (2013) – the OSCs exclusively eluted in the third sub-fraction. Remnant carbonates were removed from the kerogen fraction by treatment with concentrated HCl at ~60 °C (24 h).

The kerogen (~1 g) and a DBT standard (Aldrich, 50 μL of 100 ppm solution on 0.5 g silica gel) were individually pyrolysed using a STRATA Technology Ltd Hydropyrolyser with standard operating conditions (e.g. Grotheer et al., 2015; Robert et al., 2016) and the exclusion of a sulfide catalyst to avoid cross-reactions between sample and catalyst S. The total HyPy products (from the kerogen) were separated into polarity based fractions by column chromatography and activated copper was again used to remove any elemental S as described above.

All fractions were analysed on a HP 6890 gas chromatograph (GC) coupled to an Agilent 5975 mass selective detector (MSD). Separation was achieved on a DB-5MS capillary column (60 m × 0.25 mm i.d. ×0.25 μm) with He carrier gas (ultra-high purity, constant flow: 1.3 mL/min) and the following temperature program: 40 °C (2 min), then ramped to 325 °C at 3 °C/min and held for 30 min. Full scan (*m/z* 30–530) spectra were acquired with 70 eV at a scan rate of ~4 scans per second. OSC identification was based on mass spectral and GC elution position correlated to published data (e.g. Asif et al., 2009). Quantification was measured from base ion abundances (dibenzothiophene (DBT) *m/z* 184; methyl dibenzothiophenes (mDBTs) *m/z* 198) relative to an external calibration curve established with pure DBT standards.

OSC $\delta^{34}S$ values were measured with a Thermo Neptune Plus multi-collector ICP-MS coupled to an Agilent 6890 GC inlet system (GC-ICP-MS; Greenwood et al., 2014) and are reported in permil (‰) relative to Vienna Canyon Diablo Troilite (VCDT). Analytical precision was assessed by daily analyses of a mixture of OSCs with a standard deviation better than 1.6‰. $\delta^{34}S_{OSC}$ values reported for Hovea-3 and Toolebuc rocks represent the average of at least duplicate analyses.

The total S content and bulk $\delta^{34}S$ of the untreated rock and the subsequently isolated kerogen fraction (following inorganic sulfur removal *via* Cr(II) distillation; Fossing and Jørgensen, 1989; Passier et al., 1999) were measured *via* combustion-isotope ratio monitoring mass spectrometry (C-irmMS) in a Thermo Flash 2000 connected to a Thermo Finnigan MAT 253 *via* a Thermo Conflow III interface (C-irmMS; Böttcher and Schnetger, 2004; Böttcher et al., 2006). $\delta^{34}S$ was calibrated to the VCDT scale following Mann et al. (2009).

3. Results

DBT Standard: HyPy fully consumed the DBT with a 77 ± 8 wt.% recovery in the pyrolysate, where losses are likely due to conden-

sation within the HyPy reactor or transfer line (Grotheer et al., 2015). No other reaction products were detected. The $\delta^{34}S$ of the pure DBT standard was +5.5‰ (± 1.1‰). Following HyPy treatment the DBT pyrolysate had a $\delta^{34}S$ of +6.6‰ (± 0.3‰), representing a minor enrichment (Table 2).

Hovea-3 and Toolebuc rocks: The Hovea-3 sedimentary rocks bitumen extracts contained very low concentration of OSCs, which principally consisted of DBT and C_1-C_3 alkyl DBTs. The bitumen concentrations of S bound to DBT and mDBT (sum of four isomers) ranged from 0.44–0.98 nmolS/gRock and 1.81–8.19 nmolS/gRock, respectively with DBT/mDBTs ratios between 0.3 and 1.3. Much higher concentrations of OSCs (4– 12× bitumen levels; Table 2; Fig. 1) with DBT/mDBT ratios of 0.3–0.6 were generally detected following HyPy treatment of the kerogen fraction. The Toolebuc rocks had a relatively high S content, but the bitumen extracted from these rocks contained very low DBT and mDBT S concentrations (0.01–0.24 nmolS/gRock and 0.04–0.87 nmolS/gRock). HyPy treatment of the Toolebuc kerogens generated significantly higher concentrations of OSCs, as much as 3 orders of magnitude above bitumen levels (Table 2).

$\delta^{34}S$ values of DBT and mDBT were measured from all bitumen and kerogen fractions (Table 2; Fig. 2), but lower concentration of C_2- and C_3- DBTs prevented their $\delta^{34}S$ analysis. $\delta^{34}S$ values of DBT in the Hovea-3 bitumens ranged from −16.8 to −10.7‰. The $\delta^{34}S$ values of kerogen OSCs produced by HyPy were consistently lower, with DBT up to 12.2‰ and mDBTs up to 9.4‰ lighter than their bitumen values (Table 2). $\delta^{34}S$ of mDBTs (average of 4 isomers) were usually depleted (by up to 4‰) relatively to co-occurring DBT, which seems a common feature of the $\delta^{34}S$ profile of methylated DBTs from oils (Greenwood et al., 2014).

$\delta^{34}S$ data from the Toolebuc sediments (Table 2) showed similar trends with DBT and mDBT from the kerogen being significantly lighter than in the bitumens (by up to 8.8‰) and mDBT values being slightly lighter (up to 3.3‰) than co-occurring DBT.

4. Discussion

HyPy treatment of kerogens produced much higher concentrations of OSCs than were present in the corresponding bitumen fractions. Enhanced hydrocarbon yields are typical of the HyPy treatment of carbonaceous materials (e.g. Love et al., 1998).

DBT and mDBTs from the kerogen were significantly depleted in ^{34}S, with $\delta^{34}S$ values up to 12‰ lower than their occurrence in the bitumen fraction of the rocks. This differential was much greater than the small ~1‰ $\delta^{34}S$ enrichment observed with the HyPy treatment of the DBT standard, which implied the HyPy procedure contributed minimal ^{34}S fractionation.

The lower kerogen $\delta^{34}S$ values is opposite to the common $\delta^{13}C$ trend of heavier values from the kerogen hydrocarbon compounds compared to bitumen hydrocarbons of sedimentary rocks. The kerogen enrichment in ^{13}C arises from preferential cleavage of

Table 2
Quantification, $\delta^{34}S$ values and relative abundances (DBT/mDBTs) of Soxhlet extractable (Bitumen) and HyPy released (Kerogen) OSCs.

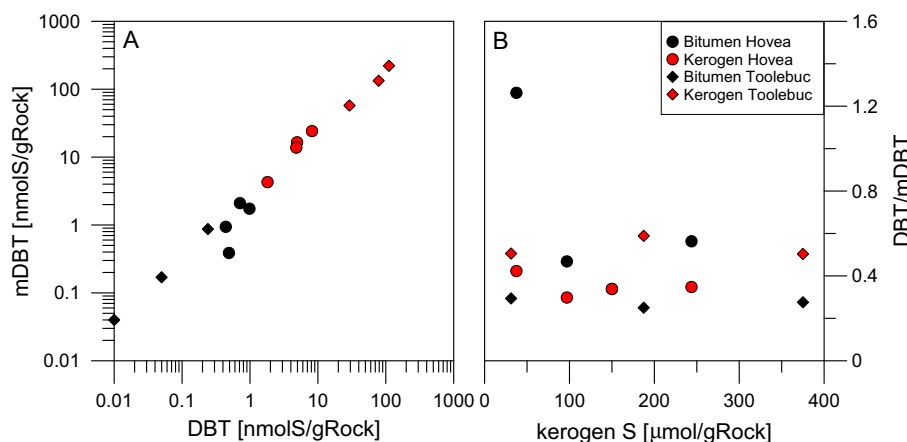| Sample number		Kerogen S [μmolS/g Rock]	C DBT [nmolS/g Rock]	C mDBTs [nmolS/g Rock]	DBT/mDBT	$\delta^{34}S$ Kerogen [‰ VCDT]	$\delta^{34}S$ DBT [‰ VCDT]	SV ±	$\delta^{34}S$ mDBT [‰ VCDT]	SV ±	$\Delta\delta^{34}S$ DBT (Ker-Bit)	$\Delta\delta^{34}S$ mDBT (Ker-Bit)
DBT	Native						5.5	1.1				
	HyPy						6.6	0.3				
H1	Bitumen		0.71	2.1	0.34		−15.5	0.1	−18.0	1.0		
	Kerogen	150	8.19	24.17	0.34	−28.0	−19.6	0.3	−19.8	1.1	−4.1	−1.8
H2	Bitumen		0.44	0.94	0.47		−16.8	0.3	−18.9	1.1		
	Kerogen	96.9	4.93	16.54	0.30	−33.7	−26.1	0.0	−24.6	0.0	−9.3	−5.7
H3	Bitumen		0.98	1.74	0.56		−15.6	0.8	−18.7	0.1		
	Kerogen	243.8	4.8	13.81	0.35	−34.7	−27.8	0.3	−26.7	0.8	−12.2	−8.0
H4	Bitumen		0.49	0.39	1.26		−10.7	0.4	−7.8	1.1		
	Kerogen	37.5	1.81	4.28	0.42	−38.1	−15.8	1.4	−17.2	0.8	−5.1	−9.4
T1	Bitumen		0.01	0.04	0.25		−12.1	0.3	−15.4	0.5		
	Kerogen	187.5	78.63	133.54	0.59	−30.3	−20.9	0.1	−20.3	1.0	−8.8	−4.9
T2	Bitumen		0.05	0.17	0.29		−28.4	1.6	−30.9	1.1		
	Kerogen	31.3	29.13	57.63	0.51	−28.2	−31.8	2.0	−32.5	1.2	−3.4	−1.6
T3	Bitumen		0.24	0.87	0.28		−22.5	0.1	−23.2	0.3		
	Kerogen	375	111.54	221.45	0.50	−34.5	−27.9		−29.5		−5.4	−6.3

Fig. 1. Concentration cross-plots of (A) of bitumen (black) and kerogen (red) DBT over mDBT showing a close abundance correlation; and (B) DBT/mDBT ratio over kerogen S showed no obvious relationship between the distribution of OSCs and kerogen S concentration. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
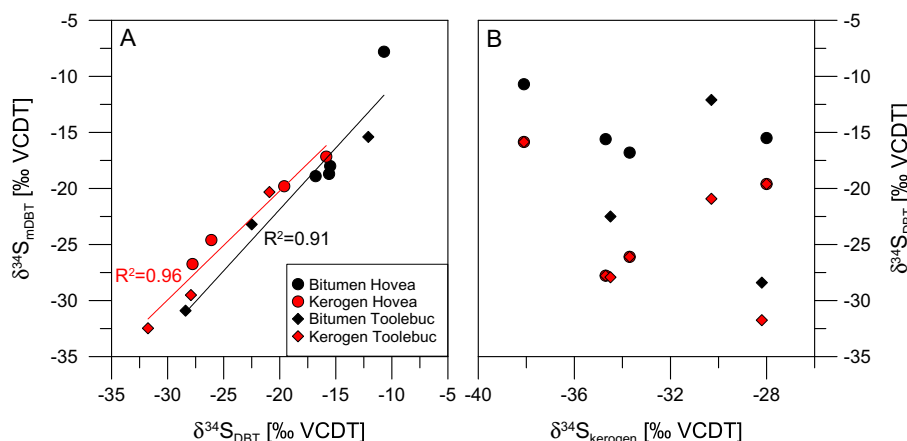

Fig. 2. $\delta^{34}S$ cross-plot (A) of bitumen (black) and kerogen (red) of DBT over mDBT which showed a close isotopic correlation and implied a generic link of OSCs in each fraction, as well that kerogen bound OSCs were generally ^{34}S depleted relative to bitumen OSCs; and (B) $\delta^{34}S_{DBT}$ over bulk $\delta^{34}S_{kerogen}$ showed no apparent isotopic relationship. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

^{12}C bonds during diagenesis and thermal cracking (e.g. Tang et al., 2000), although the respective $\delta^{13}C$ values can also be influenced by the varied bitumen and kerogen contribution of different sources (Love et al., 1998). The $\delta^{34}S$ differences observed in the

kerogen and bitumen fractions may similarly be due to a different representation of S-sources or sulfurisation pathways.

The OSCs in immature sediments from the Cariaco Basin formed during early diagenesis were proposed to form *via* multiple sulfurisation pathways characterised by distinct $\delta^{34}S$ values, with two

main organic sulfurisation mechanisms supported (Raven et al., 2015):

(i) Reaction of dissolved HS⁻ with OM resulting in the intramolecular addition of S. This kinetically favours incorporation of ^{32}S ($\delta^{34}S$ light organic S), and difficulties in releasing intramolecularly bound S make this a relatively irreversible reaction.

(ii) Intermolecular addition of polysulfides (S_x^{2-}) between different organic units. A reverse of this process could subsequently release the S_x-bridges from the organic moiety, and the equilibrium status of these reactions determines the $\delta^{34}S$ of this organic S.

Raven et al. (2015) considered pathway ii most likely responsible for the relative ^{34}S enrichment traditionally attributed to the organic incorporation of reduced S sources during diagenesis and measured in previous laboratory experiments (e.g., Amrani and Aizenshtat, 2004).

Catagenetic (i.e., temperature and pressure driven) cleavage reactions of the kerogens within the oil window maturity Hovea and Toolebuc rocks most likely contributed to their bitumen OSCs. The S of these compounds may derive from diagenetically incorporated intra- (C-S-C) or inter-molecularly (C-S_x-C) bound kerogen S. S-aromatic forming reactions during diagenesis or upon maturation would favour ring-closure with the smaller ^{32}S atom resulting in OSCs more depleted in ^{34}S than the initial S-source. On this basis, the bitumen OSCs might be expected to be more depleted than the S-structures remaining in the kerogen fraction. Further fractionation, however, may be encountered with subsequent geologic processes such as the secondary cracking of the bitumen OSCs to form H_2S. This process would also kinetically favour the release of ^{32}S enriched H_2S, such that the residual liquid phase OSCs become heavier in $\delta^{34}S$.

Alternatively, the bitumen fraction may subsequently incorporate or isotopically exchange with a relatively heavy S source. Raven et al. (2015) cautioned the possibility of $\delta^{34}S$ equilibration between different (organic and inorganic) S-pools within the immature Cariaco Bay basin sediments. A previous $\delta^{34}S$ comparison of the whole bitumen and kerogen fractions of Monterey Formation sediments also showed a trend of kerogen fractions being depleted in ^{34}S relative to corresponding bitumen (Idiz et al., 1990). These authors suggested that isotopically heavy, non-reacted pore water H_2S, may have been preferentially incorporated into the asphaltene fraction of kerogen released bitumens, reflecting a varied timing and mode of organic sulfurisation and different pathways of bitumen formation. The kerogen moiety of the rock might also have continued to develop after bitumen expulsion contributing to a change in the relative abundance or $\delta^{34}S$ nature of the main bound organic-S structures. S_x^{2-}-bridges can link organic functionalities to promote geo-polymerisation. The abundance of these S-linkages may have increased with kerogen development over geologic time and their later formation may have been from a relatively ^{34}S depleted source of S or involved reactions favoring the lighter isotope. The kerogen S of these rocks may thus have evolved into a more ^{34}S depleted form than from which the bitumen was earlier released. The bulk $\delta^{34}S$ of the kerogen fraction (Table 2; Fig. 2) were generally even more depleted than the $\delta^{34}S_{OSC}$ values measured, reflecting the presence of other isotopically lighter S-species within the kerogen matrix.

5. Conclusions

HyPy treatment of the kerogen fractions released significantly higher concentrations of OSCs as detected in the solvent extracta-ble bitumen fractions. The $\delta^{34}S$ composition of DBT and mDBTs in the HyPy produced kerogen fractions were significantly lighter (by up to 12‰) compared to their structurally free bitumen occurrence, indicating that the kerogen and bitumen of sedimentary rocks contain isotopically distinct pools of organic S. There are several possible causes of this isotopic differences including different processes, sources or timing of generation. Further $\delta^{34}S$ evaluation of the OSCs in sedimentary OM may help to resolve the relative importance of different organic sulfurisation pathways and their contribution to hydrocarbon biomarker preservation.

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