



TSR origin of sulfur in Permian and Triassic reservoir bitumen, East Sichuan Basin, China

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ABSTRACT

Solid bitumen, H₂S, pyrite and anhydrite samples from the Lower Triassic Feixianguan Formation and Upper Permian Changxing Formation, and source rock kerogen samples from the Cambrian, Ordovician, Silurian and Permian in the East Sichuan Basin were analyzed for their sulfur content and $\delta^{34}\text{S}$ values, to determine if the measurements were consistent with a thermochemical sulfate reduction (TSR) origin of the produced H₂S and solid bitumen. The results show that the solid bitumen samples have sulfur contents from 2.6 to 12.5 wt.% and $\delta^{34}\text{S}$ values from +13.4‰ to +22.1‰. The $\delta^{34}\text{S}$ values are significantly heavier than those of potential Upper Permian source rock kerogens that average +1.3‰ ($n = 3$), suggesting that most of the sulfur in the solid bitumen is derived from isotopically heavy H₂S of TSR origin (from +12.0‰ to +13.7‰). Interestingly, two gases produced from gas to water transition zones during drill stem testing (DST) show significantly lighter $\delta^{34}\text{S}$ values (+3.3‰ and +4.1‰) than the H₂S from gas-producing intervals. The isotopically light H₂S may be genetically linked to fracture-filling isotopically heavy anhydrite with $\delta^{34}\text{S}$ values from +38.5‰ to +39.6‰, which are significantly heavier than those of coeval seawater sulfate (+11.8‰ to +21.7‰) as measured for bedded anhydrite. The link may have resulted from reduction of part of the dissolved sulfate by hydrocarbons under sulfate-limited conditions. Source rock kerogens show a secular change in $\delta^{34}\text{S}$ values relative to source rock age. A dramatic decrease and then increase in $\delta^{34}\text{S}_{\text{kerogen}}$ was found toward the Permian/Triassic boundary for the first time in the East Sichuan Basin.

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1. Introduction

Solid bitumen is formed by various processes from kerogen, crude oil and/or condensate: bacterial sulfate reduction (BSR), TSR, anaerobic/aerobic biodegradation, thermal chemical alteration (TCA) with accompanying polymerization, gas deasphalting, water washing and/or inspissation (Curiale, 1986; George et al., 1994; Machel et al., 1995). Solid reservoir bitumen originating from TSR may petrographically resemble highly mature TCA bitumen and appear to be associated with, or incorporate, sulfur (Sassen, 1988; Stasiuk, 1997). Thus, TSR-altered solid bitumen has been proposed to have significantly higher sulfur content or S/N ratio than TCA bitumen (Powell and MacQueen, 1984; Stasiuk, 1997; Kelemen et al., 2008).

Considering that dissimilar organic compounds may be most susceptible to sulfurization under changing thermal or biochemical

conditions, the possibility exists for genetically discriminating between different solid bitumens by means of sulfur isotope ratios. TSR-altered bitumens have been shown to have $\delta^{34}\text{S}$ values heavier than non-TSR-altered bitumens and close to parent sulfates (Powell and MacQueen, 1984). It was proposed by Machel et al. (1995) that there are differences in $\delta^{34}\text{S}$ values of genetically related kerogen, crude oil and solid bitumen. However, few studies show $\delta^{34}\text{S}$ values for both bitumens and their parent kerogens (Powell and MacQueen, 1984; Cai et al., 2009a).

Solid bitumens in the Feixianguan (T₁f) and Changxing (P₃ch) formations in East Sichuan Basin gas fields (Fig. 1) are believed to be genetically related to Upper Permian source rocks on the basis of biomarker parameters and $\delta^{13}\text{C}$ values (Li et al., 2005; Ma, 2008; Zou et al., 2008). The bitumen is associated with large amounts of H₂S of TSR origin (Cai et al., 2004) and shows a significantly higher S/C ratio than Upper Triassic bitumen that is not altered by way of TSR (Zhu et al., 2008). However, the difference may not indicate that the sulfur in the bitumen derived from the incorporation of TSR–H₂S because the bitumen derived from different

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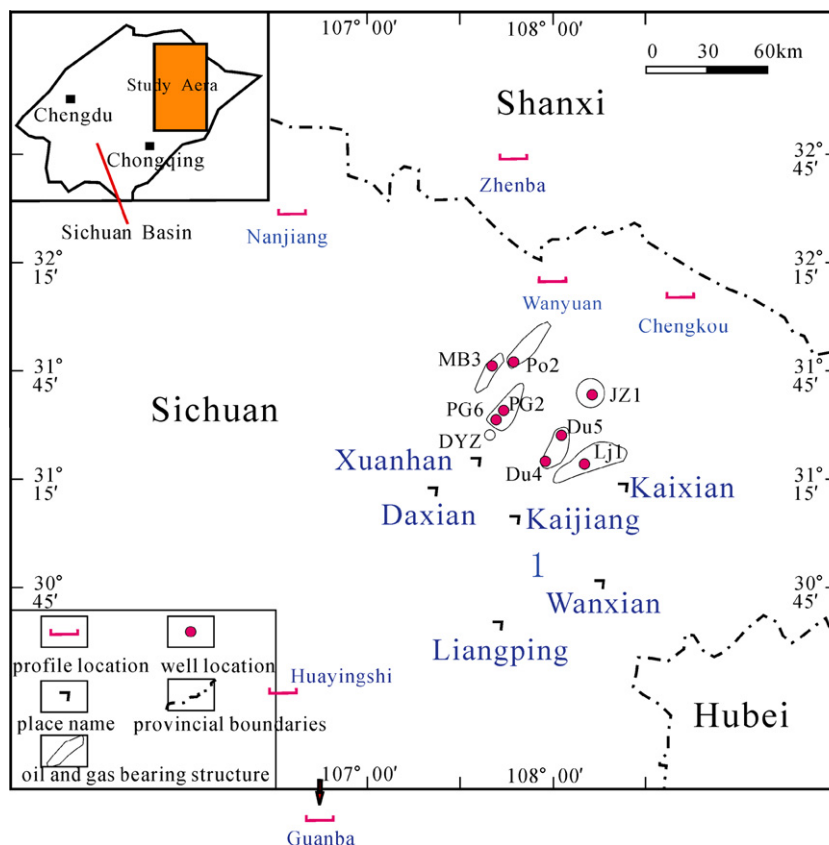


Fig. 1. Map of Eastern Sichuan Basin showing locations of sampling wells and outcrops.

source rocks: Upper Triassic bitumen derives from Upper Triassic non-marine source rocks, whereas T_{1f} – P_{3ch} bitumen derives from Upper Permian source rocks (Dai et al., 2009; Li et al., 2005).

In this paper, we present $\delta^{34}S$ values for different sulfur species, including solid bitumen and associated pyrite and elemental sulfur, organically-bound sulfur and pyrite sulfur of potential source rocks, and bedded and fracture-filling anhydrite. We sought to confirm that sulfur in solid bitumens in the East Sichuan Basin sour gas fields derived from H_2S of TSR origin. We also sought to address the question as to whether TSR can generate significantly ^{32}S -rich H_2S relative to its parent sulfate in nature, as was demonstrated in TSR experiments using acidic Na_2SO_4 solution as reactive sulfate (Harrison and Thode, 1957; Kiyosu and Krouse, 1990).

2. Geological setting

Puguang (PG), Maba (MB), Luojiashai (LJ), Dukouhe (Du), Tieshanpo (Po) and Jinzhu (JZ) sour gas fields occur in the northeastern Sichuan Basin, west China (Fig. 1). The geological setting of the basin was described by Cai et al. (2003, 2004), Li et al. (2005), Ma et al. (2007) and Hao et al. (2008). Briefly, it is a late Mesozoic–Cenozoic foreland basin overlying a Sinian–middle Mesozoic passive margin and experienced several orogenies, including regional extension during the Caledonian–Hercynian orogenies (Ordovician to Permian), a structural transitional phase during the Indosinian–early Yanshanian orogenies (T_3 – J_1) and extensive contractions during the late Yanshanian–Himalayan orogenies (K_1 – N).

In the East Sichuan Basin, the structures (Fig. 1) were formed and peak oil was generated from Upper Permian source rocks during the late Indosinian and early Yanshanian orogenies (T_3 – J_1 ; Li et al., 2005; Tang et al., 2008). Subsequently, the oils were thought

to be cracked to gas and bitumen during the middle Jurassic, on the basis of burial and thermal history, gas chemistry and carbon isotopic composition (Li et al., 2005; Zhu et al., 2008; Hao et al., 2008), followed by TSR by hydrocarbon gas dominated by methane (Cai et al., 2004, 2009c; Zhu et al., 2005 and references therein). From the middle of the late Yanshanian orogeny (about 110 ± 10 Ma) to the Himalayan orogeny (about 15 ± 5 Ma), thrusting in the southwest of the Puguang–Dongyuezhai (PG–DYZ) structure and in the west of the Luojiashai (LJ) structure was significantly greater than in the northeast and east, respectively, as the result of different structural stress, which was followed by extensive folding, resulting in the formation of complex lithological–structural traps and, thereby, the redistribution of gas and water (Li et al., 2005; Tang et al., 2008).

Potential source rocks for gas and solid bitumen in the gas fields include Upper Permian Longtan Formation (Fm; P_{3l}) mudstone and marls, Changxing Fm (P_{3ch}) micrites, Dalong Fm mudstone, and Lower Silurian Longmaqi Fm (S_{1lm}) mudstone and shale. In South China, the Changxing Fm and Dalong Fm are isochronous, with the former referring to a dominantly shallow marine limestone facies, whereas the latter comprise marls and shale from a much deeper basinal facies. We consider both as belonging to the Changxing Fm. These suites of source rocks show significant differences in organic facies, TOC, $\delta^{13}C_{kerogen}$ values and vitrinite reflectance (R_o ; Table 1; Wang et al., 2000; Yang et al., 2002; Zhu et al., 2008). Upper Permian Longtan Fm (P_{3l}) limy mudstone and marls are considered to be the source of T_{1f} – P_{3ch} gas and solid bitumen (Li et al., 2005; Zhu et al., 2008; Zou et al., 2008).

Reservoirs for the gas include the Feixianguan Fm (T_{1f}) platform margin shoal facies oolitic dolomites and the Changxing Fm (P_{3ch}) reef facies crystallized dolomites. Although buried to 4000–6000 m, the reservoirs have relatively high porosity and perme-

Table 1
Characteristics of organic matter from the Lower Silurian to Lower Triassic.^a

	Formation	Organic facies	Lithology	TOC (wt.%) ^b	Thickness (m)	$\delta^{13}\text{C}$ (‰)	R_o (%)
Lower Triassic	Feixianguan Fm (T ₁ f)	Basin	Dark micrite, marl and shale	0.1–0.7 ^b ; 2.0 ^c		–29.4 to –27.0 ^b	1.14–1.50 ^b
Upper Permian	Changxing Fm (P ₃ ch)	Basin and low-angled slope	Micrite	0.2–1.2 ^b ; 0.6–6.0 ^c ;	0–380 ^d	–29.6 to –26.6; –30 to –28 ^d	1.77–2.23 ^b ;
	Longtan Fm (P ₃ l)	Alternating marine and terrestrial	Carbonaceous mudstones (CM), and limey mudstones and marls (LMM)	0.9–7.5/2.9 ^b ; 0.5–12.6/2.9 ^d	10–150/49 ^d	–23.5 to –24.0 for CM ^b –29.0 to –28.1/–28.6 for LMM ^e	1.88–2.12/2.0 ^e 1.89–2.63 ^b ; 1.81–2.72/2.17 ^e
Lower Silurian	Longmaqi Fm (S ₁ lm)		Mudstone and shale	0.4–3.9 ^d	500–900 ^d	–30.2 to –28.8/–30.2 ^e	2.18–2.83 ^e

^a Data are expressed as range/average.

^b From Yang et al. (2002).

^c From Tenger et al. (2008).

^d From Zhu et al. (2008).

^e From Wang et al. (2000).

ability, with measured core porosity mainly from 6% to 20% and a maximum value of 28.2% (Li et al., 2005; Ma et al., 2007). Anhydrite occurs as nodules, with small amounts as cement and fracture-filling in the members one to three of the T₁f reservoirs, and as bedded anhydrite in the overlying member four (Cai et al., 2004). However, no anhydrite was found in the P₃ch reservoirs.

3. Experimental

3.1. Samples

Eight solid reservoir bitumen samples were analyzed for sulfur isotopes. Five of the eight were obtained from the Lower Triassic Feixianguan Fm (T₁f) and the other three from the Upper Permian Changxing Fm (P₃ch) in the MB, PG, LJ, Du and Po gas-fields, East Sichuan Basin (Fig. 1). Two bedded anhydrite and two fracture-filling anhydrite samples were collected from the Feixianguan Fm.

Twelve potential source rock samples, including 11 outcrops and a cuttings sample, were collected from the Lower Cambrian, Upper Ordovician, Lower Silurian, Middle and Upper Permian, and the bottom of the Lower Triassic in the eastern Sichuan Basin.

Three gas samples were collected from wells PG6, PG3 and MB3 and measured for H₂S $\delta^{34}\text{S}$ values. PG6 gas was produced from a gas interval with a producing rate of several hundred thousand cubic meters (m³) gas daily during DST, whereas PG3 and MB3 gas was sampled from gas to water transition zones with a producing rate of several hundred m³ gas daily and a gas saturation of about 35%.

3.2. Analytical methods

The method for analysis of sulfur isotopes of kerogen was reported by Cai et al. (2009a). A similar method was utilized for the analysis of solid bitumen samples, which were hand picked from dolomite, finely ground and extracted with dichloromethane (DCM) to remove soluble bitumen and elemental sulfur. The samples were then treated with hot 6N HCl to dissolve carbonate. The residue was analyzed using X-ray diffraction (XRD) and were shown to contain pyrite and quartz within the solid bitumen. Thus, a mixture of 6N HCl and 40% HF, and then 6N HCl was added to the solid bitumen after the initial HCl treatment. After dilution with distilled water and centrifugation, the remaining solid bitumen was separated from the residue (precipitate) using heavy liquids (KBr + ZnBr) with density 1.8–1.9 g/cm³. Subsequently, pyrite was removed using a method similar to that used for treating kerogen as reported by Cai et al. (2009a); a mixture of hot 6N HCl and CrCl₂ were added to the sample under N₂ with a gas flow carrying the H₂S to a trap where it was recovered as Ag₂S. Excess acid and acid

soluble salts were removed from the residue via water washing. After ca. 2 h, the residue was collected and reground to expose new pyrite surfaces, before the whole procedure was repeated.

After this treatment, a known amount (between 350 and 900 mg) of kerogen or solid bitumen, was combusted in a Parr bomb at ca. 25 atm O₂ to oxidize organically-bound sulfide to sulfate. Dissolved sulfate was precipitated as BaSO₄ and weighed to give total residual kerogen/bitumen sulfur. Dissolved iron was measured at pH < 2, using an atomic absorption spectrometer, to determine the maximal residual pyrite content in the kerogen and solid bitumen after chromium reduction (assuming that all Fe occurred as pyrite in the kerogen). Organic sulfur was subsequently calculated by subtracting the pyrite sulfur from the total residual kerogen/solid bitumen sulfur.

Elemental sulfur was hand picked from rocks and carefully separated under the microscope. SO₂ was collected after decomposing BaSO₄ by heating to 900 °C with NaPO₃, and by mixing elemental sulfur with V₂O₅ and heating to 1050 °C in a quartz tube, respectively, for isotopic analysis using the method of Halas et al. (1982). Isotope ratio measurements were carried out with a Thermo Finnigan Delta S mass spectrometer, calibrated with a series of IAEA standards. Results are presented as $\delta^{34}\text{S}$ values relative to the Vienna Canyon Diablo Troilite (VCDT) standard. The reproducibility for measurement was $\pm 0.3\%$.

4. Results

4.1. $\delta^{34}\text{S}$ values of reservoir bitumen and associated sulfur species

The solid bitumens have sulfur contents ranging from 2.6 to 12.5 wt.% and $\delta^{34}\text{S}$ values from +13.4‰ to +22.1‰ ($n = 8$; Table 2). No correlation exists between sulfur content and $\delta^{34}\text{S}$ value for all eight samples, but there is a positive correlation for the T₁f solid bitumens except for the well Po2 bitumen (not shown). The $\delta^{34}\text{S}$ values of the solid bitumen samples are slightly heavier than those of the associated H₂S, which range mostly from +11.5‰ to +13.7‰ ($n = 7$; Fig. 2) except for two abnormally light values of +4.11‰ and 3.33‰. The $\delta^{34}\text{S}$ values of the solid bitumens are nearer to those of bedded anhydrite, which ranges mainly from +21.0‰ to 21.7‰ in this study (Table 2) and from +11.8‰ to +21.7‰ ($n = 15$) in previous studies (Cai et al., 2004; Zhu et al., 2005). The associated elemental sulfur from the Changxing Fm has $\delta^{34}\text{S}$ values of +9.8‰ to +10.1‰ in this study, within the range +2.0‰ to 13.9‰ ($n = 7$) for T₁f elemental sulfur analyzed previously (Cai et al., 2004). The associated pyrite separated chemically from the solid bitumen has $\delta^{34}\text{S}$ values ranging from –4.6‰ to +0.9‰ ($n = 3$), significantly lighter than reported values (+18.7‰ and 20.1‰, $n = 2$), for pyrite hand picked from the rock samples. Interestingly, fracture-filling

Table 2
 $\delta^{34}\text{S}$ values of solid bitumen and associated pyrite, elemental sulfur and H_2S from dolomite reservoirs.

Well	Formation	Depth (m)	Bitumen				Associated H_2S		
			Pyrite $\delta^{34}\text{S}$ (‰)	Ele. sul. $\delta^{34}\text{S}$ (‰)	Bitumen $\delta^{34}\text{S}$ (‰)	Bitu. S (wt.%)	Content (vol.%)	$\delta^{34}\text{S}$ (‰)	Depth (m)
Du4	T ₁ f	4215	-3.62	- ^a	22.05	7.83	9.8	13.7/Du2 ^b	4191–4220
Po2	T ₁ f	4074	0.90	- ^a	13.42	8.37	10.6	12.0/Po1 ^b	4022–4162
LJ2	T ₁ f	3223	-4.55	- ^a	15.12	2.64	8.8	- ^a	3211–3286
PG2	T ₁ f	4916	- ^a	- ^a	16.71	2.89	15.58	- ^a	4911
PG6	T ₁ f	5146	- ^a	- ^a	18.15	5.32	14.05	12.4	5030–5158
PG3	T ₁ f	- ^a	- ^a	- ^a	- ^a	- ^a	9.27	3.33	5296–5349
PG6	P ₃ ch	5339	- ^a	9.76	16.18	6.62	14.74	- ^a	5338–5357
MB3	P ₃ ch	4358	- ^a	- ^a	15.02	11.35	11.89	- ^a	4340–4380
MB3	P ₃ ch	4379	- ^a	10.13	14.82	12.53	12.67	- ^a	4340–4420
MB3	P ₃ ch						35.8	4.11	4609–4630

^a No measurement or data available.

^b From neighbouring wells Du2 and Po1, respectively.

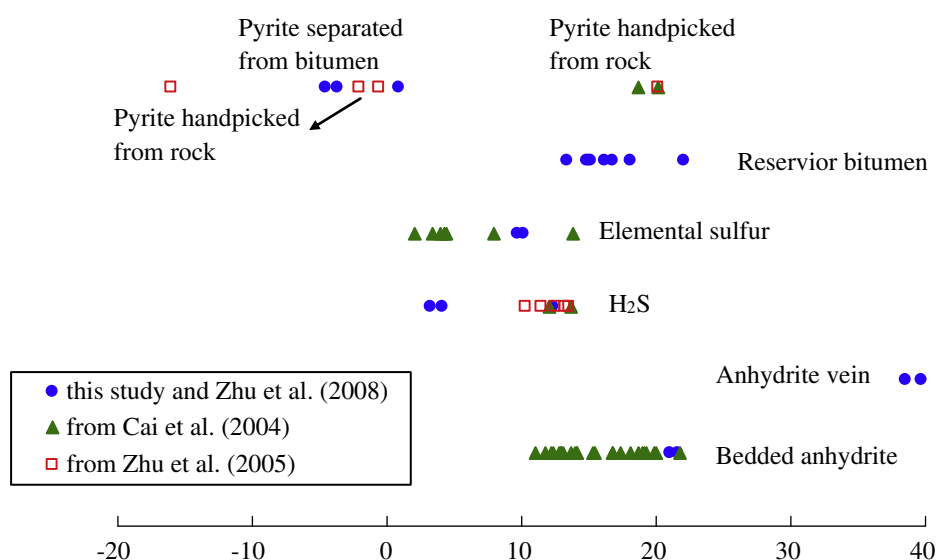


Fig. 2. Comparison of $\delta^{34}\text{S}$ values of different sulfur species from the Feixianguan Formation (T₁f) and an H_2S sample from the Upper Permian (P₃ch), East Sichuan Basin.

anhydrite from T₁f dolomite in the MB gas field has $\delta^{34}\text{S}$ values of +39.6‰ and +38.5‰ ($n = 2$; Table 3), significantly heavier than those of Phanerozoic seawater and the T₁f bedded anhydrite (Fig. 2). One gas sample from the Changxing Fm from the same well as the anhydrite samples shows an H_2S content of 35.8% by volume and an abnormally light $\delta^{34}\text{S}$ value (+4.1‰) vs. the other H_2S samples (Fig. 2).

4.2. $\delta^{34}\text{S}$ values of potential source rocks and associated pyrite

All 12 kerogen samples obtained after acidic CrCl_2 treatment were analyzed for pyrite sulfur and organic sulfur contents. The results show that the kerogens contain 0.10–0.61 wt.% pyrite and 0.02–0.32 wt.% pyrite sulfur. Total residual kerogen sulfur is 92–98% organically bound (Table 4).

Table 3
 $\delta^{34}\text{S}$ values of fracture filling and bedded anhydrite from Feixianguan Fm.

Well	Depth	Occurrence	$\delta^{34}\text{S}$ (‰)
JZh1	3011.85	Bedded	+20.99
Du5	4739.92	Bedded	+21.69
MB3	3873	Fracture filling	+39.64
MB3	3878	Fracture filling	+38.54

Among the 12 kerogens, the Lower Cambrian sample shows the highest total residual kerogen sulfur content of 6.4 wt.%, the heaviest $\delta^{34}\text{S}$ value of +14.5‰ and the heaviest associated pyrite sulfur of +13.5‰. The kerogen $\delta^{34}\text{S}$ values show a decreasing trend to +7.5‰ in the Upper Ordovician, +7.2‰ in the Lower Silurian (excluding two kerogens that still had high residual pyrite S after CrCl_2 treatment), +0.1‰ in the middle and lower Upper Permian (except for an abnormal value of +8.6‰), to the lightest value of -1.7‰ in the upper Changxing Formation (P₃ch) and finally a dramatic increase to +5.5‰ near the biota extinction event horizon (about 252.4 ± 0.3 Ma; Mundil et al., 2001) at the Triassic/Permian boundary (Fig. 3).

All four pyrite samples separated from the kerogen have $\delta^{34}\text{S}$ values lighter than or close to those of the coexisting kerogen (Table 4). Excluding an abnormal $\delta^{34}\text{S}$ value of -21.39‰ for pyrite from the P/T boundary, the other three pyrite samples show a gradual decrease in $\delta^{34}\text{S}$ value from the Lower Cambrian to the Upper Permian (Fig. 3), similar to the changing trend in $\delta^{34}\text{S}$ values of kerogen in this study and seawater sulfate with age.

5. Discussion

Based on biomarkers and carbon isotopes data, the solid bitumens in the T₁f and P₃ch reservoirs have hydrocarbons derived

Table 4TOC, total sulfur, pyrite sulfur contents and $\delta^{34}\text{S}$ values of kerogens and pyrite from main source rocks in East Sichuan Basin.

Location/well	Code	Stratum	Lithology	TOC (%)	Kerogen after the CrCl_2 treatment					
					S_{TR}^{a} (%)	$\delta^{34}\text{S}_{\text{TR}}$ (‰)	Py_{res} (%)	$\text{Py}_{\text{res}} \text{ S}$ (%)	$\delta^{34}\text{S}_{\text{Py}}$ (‰)	Org. S/TS (%)
Wanyuan	ZB18-5	T ₁ f	Dark gray marl	– ^b	0.2	–9.46	0.12	0.06	– ^b	92.4
Wanyuan	ZB-17-03	P ₃ ch	Back shale	3.59	1.1	+5.47	0.14	0.08	–21.39	93.3
Wanyuan	ZB-14-01	P ₃ ch	Back silicate	7.20	1.6	–1.65	0.10	0.05	–21.31	96.6
Zhenba	ZB-09-01	P ₃ l	Dark limestone	1.21	4.2	+0.05	0.44	0.24	– ^b	94.4
Huayinshi	HYS-38	P ₂ m ^a	Dark limestone	2.64	3.6	+0.13	0.57	0.31	–15.56	91.5
Zhenba	ZB6-1	P ₂ q ^a	Back shale	0.80	1.4	+8.56	0.23	0.12	– ^b	97.6
Guanba	GB-1	S ₁ lm ^a	Carbonaceous shale	0.69	0.5	+7.21	0.03	0.02	– ^b	96.7
Chengkou	ZB-21	S ₁ lm ^a	Back shale	6.00	0.3	–4.39	0.13	0.07	– ^b	87.6 ^d
Nanjiang	NJ-1-49.7 ^c	S ₁ lm ^a	Dark mudstone	1.30	1.5	+0.39	0.36	0.19	– ^b	87.4 ^d
Huayinshi	HYS-3	O ₃ w ^a	Back siliceous shale	– ^b	0.4	+7.49	0.03	0.019	– ^b	95.8
Tongjiang	TJ-7-6	Cam ₁ ^a	Back shale	– ^b	0.2	+7.74	0.61	0.32	– ^b	91.1 ^d
Chengkou	ZB-19	Cam ₁ ^a	Carbonaceous shale	5.26	6.4	+14.54	0.25	0.13	+13.47	97.9

^a S_{TR} : total residual sulfur, including residual pyrite sulfur and organic sulfur in kerogen after the CrCl_2 treatment; Org. S is organic sulfur; Py_{res} is residual pyrite after the CrCl_2 treatment; P₂m and P₂q: Middle Permian Maokou Fm and Qixia Fm, respectively; S₁lm: Lower Silurian Longmaqi Fm; O₃w: Upper Ordovician Wufeng Fm; Cam₁: Lower Cambrian.

^b No measurement or data available.

^c At depth of 49.7 m.

^d Residual pyrite sulfur too high.

from the Upper Permian source rocks (Li et al., 2005; Hao et al., 2008; Ma, 2008; Zou et al., 2008). In the following sections, we discuss the source of sulfur in the bitumen samples by comparison with source rock sulfur content and $\delta^{34}\text{S}$ values of coexisting anhydrite, pyrite and potential source rock kerogen.

5.1. Origin of ^{34}S -depleted H_2S and ^{34}S -rich fracture-filling anhydrite

In the vast majority of petroleum-related sour gas settings, H_2S of TSR origin is shown to have $\delta^{34}\text{S}$ values close to its parent sulfate (Orr, 1974; Krouse, 1977; Worden et al., 2000; Cai et al., 2003, 2004), which is supported by most of the H_2S in the T₁f reservoirs having $\delta^{34}\text{S}$ values within the range for bedded anhydrite. Although no H_2S from the P₃ch reservoirs was measured for $\delta^{34}\text{S}$ values, H_2S of TSR origin was shown to have $\delta^{34}\text{S}$ values close to elemental sulfur, a byproduct of TSR (Worden et al., 1997; Cai et al., 2004), so the H_2S from the P₃ch reservoirs is very likely to have $\delta^{34}\text{S}$ values similar to those from the T₁f reservoirs. Only very limited case studies show light H_2S in petroleum reservoirs (Machel et al., 1995; Cai et al., 2008, 2009a) although such H_2S was generated in TSR experiments using acidic Na_2SO_4 solution as reactive sulfate (Harrison and Thode, 1957; Kiyosu and Krouse, 1990).

In contrast, it is generally considered that BSR preferentially removes ^{32}S from the dissolved sulfate and leads to residual brines with SO_4^{2-} (and thus sulfate minerals) enriched in ^{34}S in a sulfate-limited environment (Holser and Kaplan, 1966; Taberner et al., 2002 and references therein).

In the case of the East Sichuan Basin, H_2S (3.3–4.1‰) is unlikely to have a BSR origin because of the high reservoir temperature and high H_2S content (up to 35.8%; Cai et al., 2004; Zhu et al., 2005; Hao et al., 2008), which are characteristics of TSR (Machel et al., 1995). Thus, it is very likely that the H_2S is derived from incomplete reactions, i.e. only part of the dissolved sulfate (30–70‰) is reduced by excess amounts of hydrocarbons to produce H_2S under sulfate-limited conditions. Thus, a significant sulfur isotope fractionation occurs, with residual sulfate being ^{34}S -enriched, whereas produced H_2S is ^{34}S -depleted relative to the parent sulfate (Cai et al., 2008, 2009b; Wynn et al., 2010). This mechanism is different from most of the TSR cases where sulfate is the limiting reactant. It is also different from the TSR experiments in which the produced H_2S /dissolved sulfate ratio was very low (e.g. <5–10‰). Heavy $\delta^{34}\text{S}$ values of residual sulfate after TSR reactions compared to initial sulfate were measured in some recent case studies in the Deardorff mine, Illinois basin (Richardson et al., 1988), Tarim Basin,

China (Cai et al., 2008, 2009b) and the thermo-mineral springs of the Cerna Valley, Romania (Wynn et al., 2010).

Unfortunately, no formation water was available for measurement of the $\delta^{34}\text{S}$ value of sulfate. However, fracture-filling anhydrite from one of the wells producing light H_2S gas shows heavy $\delta^{34}\text{S}$ values (+38.5‰ to +39.6‰). Although there is no direct evidence to state that the two sulfur species are genetically linked, it is very likely for isotopically heavy sulfate not to be restricted to the anhydrite samples. Thus, it is reasonable to assume that TSR produced two types of H_2S : one with heavy $\delta^{34}\text{S}$ values (11.5–13.7‰) and the other one with light $\delta^{34}\text{S}$ values (3.3–4.1‰) likely to be accompanied by isotopically heavy sulfate. Interestingly, gas samples with isotopically light H_2S and/or high H_2S content (>20% by volume) in the East Sichuan Basin are limited to gas–water transition with very low rate of gas recovery or low gas saturation. Two conclusions may be derived from this observation:

- (i) Low gas saturation and thus high amounts of dissolved sulfate may have resulted in TSR proceeding to greater extent and thus higher relative H_2S content in the gas. The TSR reaction may be incomplete with part of the sulfate remaining unreacted. In contrast, under high gas saturation conditions, the amount of dissolved sulfate is limited, and complete reduction of all available dissolved gypsum or anhydrite produced H_2S with a $\delta^{34}\text{S}$ value close to the bulk value of its parent sulfate (Machel et al., 1995; Worden et al., 2000). This explanation supports the proposal that TSR may have occurred both in gas intervals and gas–water transition zones (Worden et al., 2000; Cai et al., 2004) and is corroborated by the observation for the Nisku sour gas pools with a 10–18‰ difference between Fe sulfides and H_2S on the one hand and the source sulfate on the other at a temperature of 125–145 °C, where TSR is considered to be limited to gas–water transition zones (Machel et al., 1995). Thus, $\delta^{34}\text{S}$ values of TSR– H_2S can be utilized as a tool to determine where TSR occurs, in a gas interval or in a transition zone.
- (ii) High H_2S contents (>20%) measured from gas to water transition zones with low gas saturation in the East Sichuan Basin may not represent the real gas composition. Because H_2S and CO_2 have much greater solubility than hydrocarbon gas, much more H_2S and CO_2 are expected to exsolve from the water phase as a result of a decrease in temperature and pressure during gas recovery.

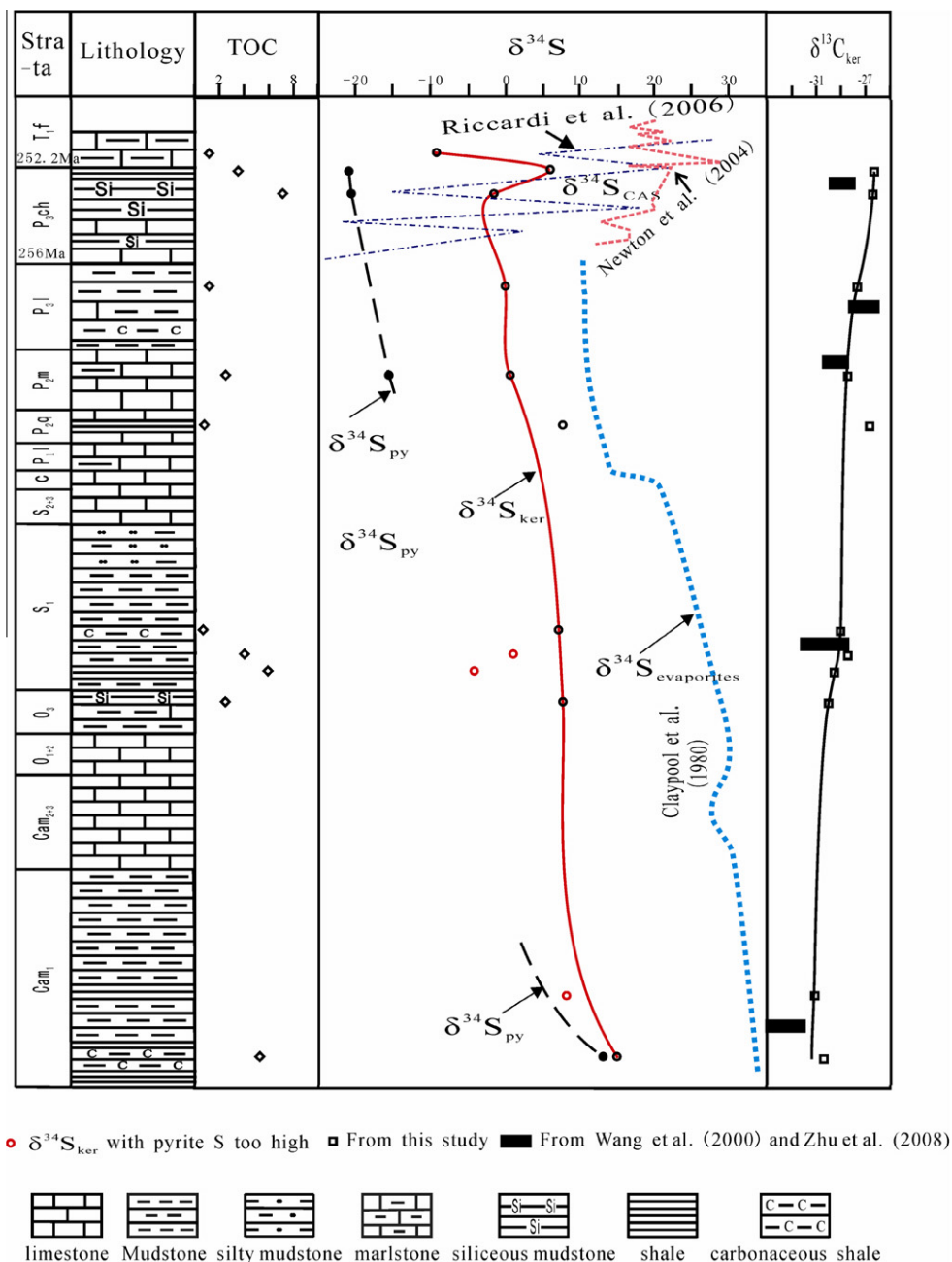


Fig. 3. Variations in TOC, sulfur and carbon isotopic composition of source rock kerogens and associated pyrite from the Lower Cambrian to the Permian/Triassic boundary, compared with seawater sulfate ^{34}S values inferred from evaporates of early Cambrian to late Permian age (Claypool et al., 1980), from carbonate-associated sulfate (CAS) at the Permian/Triassic boundary of the Shangsi section, NW Sichuan basin (Riccardi et al., 2006) and at Siusi in northern Italy (Newton et al., 2004), and with kerogen ^{13}C values from Wang et al. (2000) and Zhu et al. (2008).

As mentioned above, no sulfate minerals were found in the Changxing Fm, where up to 35.8% H_2S was detected. No stratigraphic juxtapositions caused by faulting have been found in the area, suggesting that H_2S is unlikely to have migrated downward from the T_{1f} reservoirs. Thus, reactive sulfate needed for TSR to proceed in the Changxing Fm may have come from: (a) formation water in situ, (b) carbonate-associated sulfate (CAS) released by dissolution of the carbonate or/and (c) dissolution of anhydrite and gypsum from the Carboniferous or overlying Feixianguan Fm. CAS was considered as TSR-reactive sulfate in thermo-mineral springs of the Cerna Valley, Romania (Wynn et al., 2010). Unfortunately, no CAS concentration was measured in this study. However, Changxing Fm age-equivalent formations have CAS concentrations

from 150 to 580 ppm in Siusi, northern Italy (Newton et al., 2004), from 32 to 2304 ppm in the Meishan section, and from 410 to 8947 ppm in the Shansi section, South China (Riccardi et al., 2006). Thus, CAS may have contributed a significant amount of reactive sulfate for TSR.

5.2. Secular differences of marine kerogen $\delta^{34}\text{S}$ values

Dramatic secular differences in marine sulfate and pyrite $\delta^{34}\text{S}$ values occur at the Permian/Triassic (P/T) boundary (Strauss, 1997; Worden et al., 1997; Newton et al., 2004; Riccardi et al., 2006). Sulfur organically bound to kerogen, shows a secular trend in $\delta^{34}\text{S}$ values relative to coeval seawater sulfate from the

Cambrian to the late Ordovician in the Tarim Basin (Cai et al., 2009a). However, it is not yet known if there are similar differences in kerogen sulfur in marine source rocks of other basins across the P/T boundary.

Kerogens analyzed here show a decrease in $\delta^{34}\text{S}$ value from Cambrian source rocks to the Ordovician, Silurian, and Middle and lower Upper Permian, with the lowest value occurring in the upper Changxing Fm, followed by a dramatic increase towards the P/T boundary (Fig. 2). This evolutionary trend is consistent with that of seawater $\delta^{34}\text{S}$ values measured in evaporites from this period (Claypool et al., 1980) and carbonate-associated sulfate from the P/T boundary at Siusi in northern Italy (Newton et al., 2004), as well as in the Shangsì and Meishan sections, NW Sichuan Basin, Zhejiang Province (Riccardi et al., 2006). The $\delta^{34}\text{S}$ difference between the kerogen samples and the coeval seawater sulfate (Claypool et al., 1980) is about 12–18‰. The pattern also resembles that of the kerogen samples from the Tarim Basin.

The secular differences in the $\delta^{34}\text{S}$ values of the mature to over-mature kerogens ($R_o > 1.14\%$, Table 1) suggest that the organically-bound sulfur was controlled by the seawater sulfate isotope composition and that organic matter (OM) maturity may have had a negligible effect on the $\delta^{34}\text{S}$ value of the mature kerogens, as also demonstrated in closed-system experiments (Amrani et al., 2005). Immature kerogen is expected to produce a small quantity of isotopically light H_2S , which may conceivably be removed from relatively little compacted sediments in a relatively open system. Mature residual kerogen is therefore expected to have a somewhat higher $\delta^{34}\text{S}$ value. With increasing burial and OM maturity, the system becomes more closed, especially in a rapidly buried basin, and no significant sulfur isotope fractionation is expected in the course of further OM maturation (Cai et al., 2009a).

The depositional environment being open or closed with respect to sulfate supply has a significant effect on $\delta^{34}\text{S}$ values of source rock OM (Cai et al., 2009a and references therein). We tentatively propose that the dramatic change in $\delta^{34}\text{S}$ values at the P/T boundary and abnormally heavy $\delta^{34}\text{S}$ and $\delta^{13}\text{C}$ values of the P_2Q kerogen, deviating from the secular trend of $\delta^{34}\text{S}_{\text{kerogen}}$ in the East Sichuan Basin, result from differences in depositional environment. Further studies of this aspect is in progress.

5.3. Origin of solid bitumen sulfur

Previous studies showed that TSR-derived H_2S may be incorporated into or exchanged with petroleum and bituminous tar to generate thiols, thiaadamantanes and thiolanes, resulting in oil and bitumen having $\delta^{34}\text{S}$ values close to the parent sulfate (Orr, 1974; Powell and MacQueen, 1984; Cai et al., 2003, 2009b). Thus, sulfur in solid bitumen with associated TSR- H_2S may have two sources, its parent oil as derived from its source rock and H_2S generated via TSR. It is possible to differentiate the two sources on the basis of the large difference in sulfur isotopic composition of the sources.

The solid bitumens have $\delta^{34}\text{S}$ values from +13.4‰ to +22.1‰, significantly heavier than those of the potential source rock kerogen samples (−1.7‰ to 5.5‰, $n = 4$), suggesting that it is unlikely for the solid bitumens to have sulfur significantly derived from the kerogens for the following reasons:

(i) If the thermal transformation of kerogen to oil and oil to bitumen occurs under closed system conditions, only a small difference in $\delta^{34}\text{S}$ values would be observed between residual kerogen, evolved H_2S and oil (up to only 2.0‰) in hydrous and anhydrous pyrolysis experiments and field data. This is due to sulfur isotope homogenization under such conditions.

(ii) If the oil was generated from kerogen in an open system, the instantaneously generated H_2S would escape and a strong isotope fractionation would occur. The residual kerogen would become isotopically heavier.

(iii) If oil was cracked to bitumen in an open system, the bitumen would become isotopically heavier. This is unlikely to have occurred, as indicated by a weak positive relationship of bitumen content with gas reserves and porosity (Li et al., 2005). It is hard to rule out the possibility that small amounts of H_2S and alkanes may have escaped; however, no significant isotope fractionation would be expected in this case.

The kerogen-derived oil and oil-derived solid bitumen are unlikely to have $\delta^{34}\text{S}$ values significantly heavier than the parent kerogen and oil, respectively. The solid bitumen with high sulfur content and heavy $\delta^{34}\text{S}$ values must have incorporated TSR-derived sulfide with isotopically heavy sulfur. As a result, the solid bitumens in the East Sichuan Basin have $\delta^{34}\text{S}$ values close to TSR- H_2S and bedded anhydrite (Powell and MacQueen, 1984; Cai et al., 2009b).

Assuming that the processes of reservoir bitumen generation (oil and kerogen cracking) took place in a semi-closed to closed system, the bitumen is expected to have $\delta^{34}\text{S}$ values up to +2‰ heavier than the parent kerogen (+1.3‰, an average for all three Permian kerogens), i.e. the $\delta^{34}\text{S}$ values would be about +3.3‰. H_2S derived from oil cracking prior to TSR may have been precipitated as pyrite with $\delta^{34}\text{S}$ values of −4.6 to +0.9‰, which is associated with the solid bitumen. Alternatively, the isotopically light pyrite may have an origin in BSR that may have occurred during early oil emplacement into the reservoirs. This is supported by isotopically light pyrite (from −16.0 to −0.6‰, $n = 3$), which was sampled from the T_1f reservoirs but not associated with solid bitumen (Zhu et al., 2005). Subsequently, TSR-derived H_2S may have been incorporated into the solid bitumen, resulting in the solid bitumen having a significantly positive shift in $\delta^{34}\text{S}$ values. The $\delta^{34}\text{S}$ values of the solid bitumen after the incorporation of the TSR- H_2S depend on residual organic sulfur/incorporated sulfur ratio, initial organic sulfur $\delta^{34}\text{S}$ value, and incorporated sulfur $\delta^{34}\text{S}$ value.

That sulfur was added to the solid bitumen during post-generation processes is supported by the significantly higher sulfur contents (ranging mainly from 5.3% to 12.5%) compared to potential Permian source rocks (1.1% to 4.2%, $n = 3$). A portion of the initial sulfur in the kerogen was lost in the transformation of kerogen to oil and from oil to bitumen. Post-generation processes can increase the sulfur content of oil and bitumen via biodegradation and incorporation of TSR- or BSR-derived sulfide (Orr, 1974; Powell and MacQueen, 1984; Cai et al., 2009b). There is no evidence of biodegradation of oil and bitumen in the study area (Zhu et al., 2008). Maturation does not increase the sulfur content of solid bitumen (Kelemen et al., 2008). Hence, we conclude that the high sulfur content of the solid bitumens must arise from the incorporation of inorganic sulfur that, in this case, must originate from TSR. Consequently, TSR-altered bitumens have significantly higher sulfur contents than their parent oils and the primary kerogens in the study area.

A positive correlation between sulfur content and $\delta^{34}\text{S}$ value for the T_1f solid bitumens is consistent with the concept that TSR- H_2S has reacted with bitumen, resulting in an increase in sulfur content of the solid bitumen and a progressive adoption of the anhydrite sulfur isotopic ratio. An exception is the solid bitumens from the Permian in well Po2 for reasons that are unclear. It is possible that the sulfur content was not measured correctly as a result of sample loss during the chemical treatment (Cai et al., 2009a).

6. Conclusions

The $\delta^{34}\text{S}$ values of different sulfur species in TSR-active gas fields show complex sulfur sources in the solid bitumen, including inheritance from kerogen and incorporation of TSR sulfide with a $\delta^{34}\text{S}$ value close to that of its parent sulfate. The solid bitumen has sulfur predominantly derived from TSR- H_2S , resulting in large differences in $\delta^{34}\text{S}$ values between the solid bitumen and the parent source rock kerogen. The incorporation of TSR- H_2S into the solid bitumen may have led to an increase in sulfur content and heavy sulfur isotopic values. However, significantly depleted H_2S relative to its parent sulfate was observed in the gas–water transition and is explained as reduction of part of the dissolved sulfate in a limited sulfate pool, resulting in residual sulfate with $\delta^{34}\text{S}$ values significantly heavier than coeval seawater. Thus, it is possible to utilize $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ values to determine where TSR occurred. Organically-bound sulfur in marine mature to over mature kerogen from the Cambrian to the P/T boundary shows a trend in $\delta^{34}\text{S}$ value as a function of source rock age and seawater sulfate evolution. A dramatic change in kerogen $\delta^{34}\text{S}$ value in the Permian/Triassic (P/T) boundary in the East Sichuan Basin is reported for the first time.

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