Methane-dominated thermochemical sulphate reduction in the Triassic Feixianguan Formation East Sichuan Basin, China: towards prediction of fatal H$_2$S concentrations

Chunfang Cai[a], Zengye Xie[b], Richard H. Worden[c,*], Guoyi Hu[b], Lansheng Wang[d], Hong He[e]

[a]*Institute of Geology and Geophysics, CAS, P.O. Box 9825, Qijiahuozi, Beijing, 100029, People's Republic of China*
[b]*Lanfang Branch of Petroleum Exploration and Development Institute, PetroChina, Lanfang, Hebei Province, People's Republic of China*
[c]*Jane Herdman Laboratories, Department of Earth and Ocean Sciences, University of Liverpool, 4 Brownlow Street, Liverpool, L69 3GP, UK*
[d]*Research Institute of Exploration and Development, Southwest Oil and Gasfield Company, PetroChina, Chengdu,*
Sichuan Province, People's Republic of China
[e]*Exploration and Production Research Institute, SINOPEC, Beijing 100083, People's Republic of China*

Abstract

New sour pools have recently found in the Lower Triassic Feixianguan Fm carbonate reservoirs in the East Sichuan Basin in China with H$_2$S up to 17.4% by volume. A recent blowout from a well drilled into this formation killed hundreds of people as a result of the percentage concentrations of H$_2$S. In order to assess the origin of fatal H$_2$S as well as the cause of petroleum alteration, H$_2$S concentrations and the isotopes, δ^{34}S and δ^{13}C have been collected and measured in gas samples from reservoirs. Anhydrite, pyrite and elemental sulphur δ^{34}S values have been measured for comparison. The high concentrations of H$_2$S gas are found to occur at depths > 3000 m (temperature now at ~ 100 °C) in evaporated platform facies oolitic dolomite or limestone that contains anhydrite nodule occurrence within the reservoirs. Where H$_2$S concentrations are greater than 10% its δ^{34}S values lie between +12.0 and +13.2‰ CDT. This is within the range of anhydrite δ^{34}S values found within the Feixianguan Fm (+11.0 to +21.7‰; average 15.5±3.5‰ CDT). Thus H$_2$S must have been generated by thermochemical sulphate reduction (TSR) locally within the reservoirs. Burial history analysis and fluid inclusion data reveal that the temperature at which TSR occurred was greater than about 130–140 °C, suggesting that the present depth-temperature minimum is an artifact of post-TSR uplift. Both methane and ethane were actively involved in TSR since the petroleum became almost totally dry (no alkanes except methane) and methane δ^{13}C values become significantly heavier as TSR proceeded. Methane δ^{13}C difference thus reflects the extent of TSR. While it is tempting to use a present-day depth control (> 3000 m) to predict the distribution of H$_2$S in the Feixianguan Fm, this is an invalid approach since TSR occurred when the formation was buried some 1000–2000 m deeper than it is at present. The likelihood of differential uplift across the basin means that it is important to develop a basinal understanding of the thermal history of the Feixianguan Fm so that it is possible to determine which parts of the basin have been hotter than 130–140 °C.
© 2004 Elsevier Ltd. All rights reserved.

Keywords: Northeast Sichuan; Thermochemical sulphate reduction; Anhydrite

1. Introduction

The Sichuan Basin is one of China's largest natural gas provinces with gas discovered in the Sinian and Carboniferous through to the Jurassic parts of the stratigraphy. Recently, gas pools have been found in the Lower Triassic Feixianguan Fm carbonate reservoirs in Northeast Sichuan (Chen, 2001) with a proven gas reserve of 850×10^8 m^3 and an estimated recoverable reserve of 327×10^8 m^3 in the Tieshanpo area (Chen, 2001; Xie, 2003; Yang & Wen, 2002). The reservoirs for the sour pools are oolitic grainstones and dolomitic carbonate (Wang, 1996) covering an area of about 4000 km^2. They have an average porosity of about 8% and an average thickness of 33.7 m (Yang & Wen, 2002). The gas contains

up to 17.4% H_2S by volume (Jiang, Xu, & Huang, 2002; Wang, Dou, Wen, Zhang, & Jiu, 2002; Yang et al., 2002).

A major blowout from a sour (H_2S-rich) gas well being drilled in the Feixianguan Fm occurred when a well (well LJ16H) was drilled in the Luojiazhai gas field in the East Sichuan to the depth of 4049.68 m on December 23, 2003 and led to the death of 243 persons (Gang, 2004). Deaths were mostly caused directly by the accidentally emitted H_2S and 'turned 10 square miles into a death zone' (Goodman, 2003). The well had a formation pressure of about 40 MPa and was approximately 23% overpressured. H_2S gas is not only corrosive and an economic problem for asset managers and petroleum processing facilities, it is environmentally damaging and, as the recent tragedy demonstrates, extremely dangerous to human beings. Understanding the origin, spatial distribution and relationship of the H_2S with hydrocarbon gases are of importance to petroleum exploration and development and are a paramount consideration for human health.

It has been suggested, but not proven, that H_2S in the Feixianguan Fm may have been derived by thermochemical sulphate reduction (TSR) within the reservoirs (Jiang et al., 2002; Wang Y. G. et al., 2002; Yang et al., 2002). Thermochemical sulphate reduction (TSR) occurs when sulphate, from whatever source, is chemically reduced by petroleum fluids at elevated temperature. The minimum temperature for TSR has been the subject of lively debate (Baric & Jungwirth, 1997; Machel, 1998; Worden, Smalley, & Oxtoby, 1995, 1997b, 1998) although it is conventionally assumed to be approximately 120 °C. The products of TSR include reduced forms of sulphur (H_2S, elemental sulphur) and oxidized forms of carbon (calcite, CO_2), as well as water and a variety of organo-sulphur compounds.

It is still not clear whether TSR occurs between light hydrocarbon and sulphate compounds or whether TSR affects light hydrocarbon gas carbon isotopes. It has been suggested that methane, reputedly the least reactive petroleum compound, does not undergo TSR, that being the preserve of liquid phase petroleum compounds (Machel, 2001). The location for the optimum rate of TSR in petroleum reservoirs has also been questioned. TSR has been shown to occur both at a gas–water transition zone (Machel, Krouse, & Sassen, 1995) and in a gas zone (Worden, Smalley, & Cross, 2000).

In this paper, we present gas chemistry, $\delta^{13}C$ and $\delta^{34}S$, anhydrite, pyrite and elemental sulphur $\delta^{34}S$ along with fluid inclusion data. We seek to confirm that TSR was responsible for the fatal occurrence of H_2S in the Feixianguan Fm. We also seek to address the questions of where TSR occurred in the petroleum system (gas zone or gas-water transition zone) and whether methane was involved in TSR in the Feixianguan Fm. Anhydrite is present in the low permeability caprock to the Feixianguan Fm reservoirs as well as being disseminated within the Feixianguan reservoirs. We will address whether one or both of these types of anhydrite are involved in TSR.

We will also assess what will be required to build a model capable of predicting the distribution of H_2S in the Feixianguan Fm in the Sichuan Basin.

2. Geological setting

The East Sichuan Basin (Fig. 1) is located to the east of the Huaying Mountains and the Zhongliang Mountains and to the west of the Qiyao Mountains and covers an area of approximately 50,000 km^2. This part of the basin is the main area for Carboniferous, Permian and Lower Triassic gas accumulations in the greater Sichuan Basin.

The basement of the East Sichuan Basin is presently buried to between 7000 m and approximately 10,000 m (Tong, 1992). Sitting above the basement are Sinian (Upper Proterozoic) through to Middle Silurian marine carbonates and Upper Silurian marine fine detrital rocks. As a result of the late Silurian Caledonian orogeny, the Lower Carboniferous section is absent although Middle Carboniferous sedimentation occurred. Marine transgression occurred during the earliest Permian. The Lower Permian section is composed of platform carbonates. The Upper Permian Longtan Fm is composed of alternating marine and terrestrial marl, mudstone and coal-bearing building. The overlying Upper Permian Changxing Fm is composed of platform carbonates with intercalated dark micrite developed in times of marine transgression and increased water depth (Wang, X.Z. et al., 2002; Wang, Y.G. et al., 2002).

The Lower Triassic Feixianguan Fm was deposited in a range of environments from basinal through a narrow slope to open platform and evaporated platform environments (Fig. 1). The Feixianguan Fm can be divided into four members in stratigraphic order: T_1f^1, T_1f^2, T_1f^3 and T_1f^4. The four divisions are clearly differentiated using core and wireline log analysis in the south of the East Sichuan Basin. Towards the north of the East Sichuan Basin, the divisions are less well-developed and only a two-fold division can be recognized (T_1f^4 and T_1f^{1-3}) (Fig. 2). In the south of the East Sichuan Basin, T_1f^1 is composed mainly of micrite, silt-crystalline limestone and oolitic limestone with negligible matrix porosity although enlarged fractures occur as open and connected porosity. T_1f^2 is laterally continuous marl intercalated with mudstone. T_1f^3 is composed of silt-crystalline limestone intercalated with oolitic limestone with low-porosity reservoirs discovered in the Xinshi and Mainan areas. In the north, the combined T_1f^{2-3} stratigraphic units are composed mainly of oolitic dolomite near the Dukouhe, Luojiazhai gas fields. Further north still, in the Jinzhuping and Laoyingyan areas, the lithofacies of the T_1f^{2-3} stratigraphic units is different since it contains idiomorphic dolomite, anhydritic dolomite and anhydrite. T_1f^4 is composed of purplish red mudstone and marl, locally intercalated with anhydrite beds with a thickness of about 40 m.
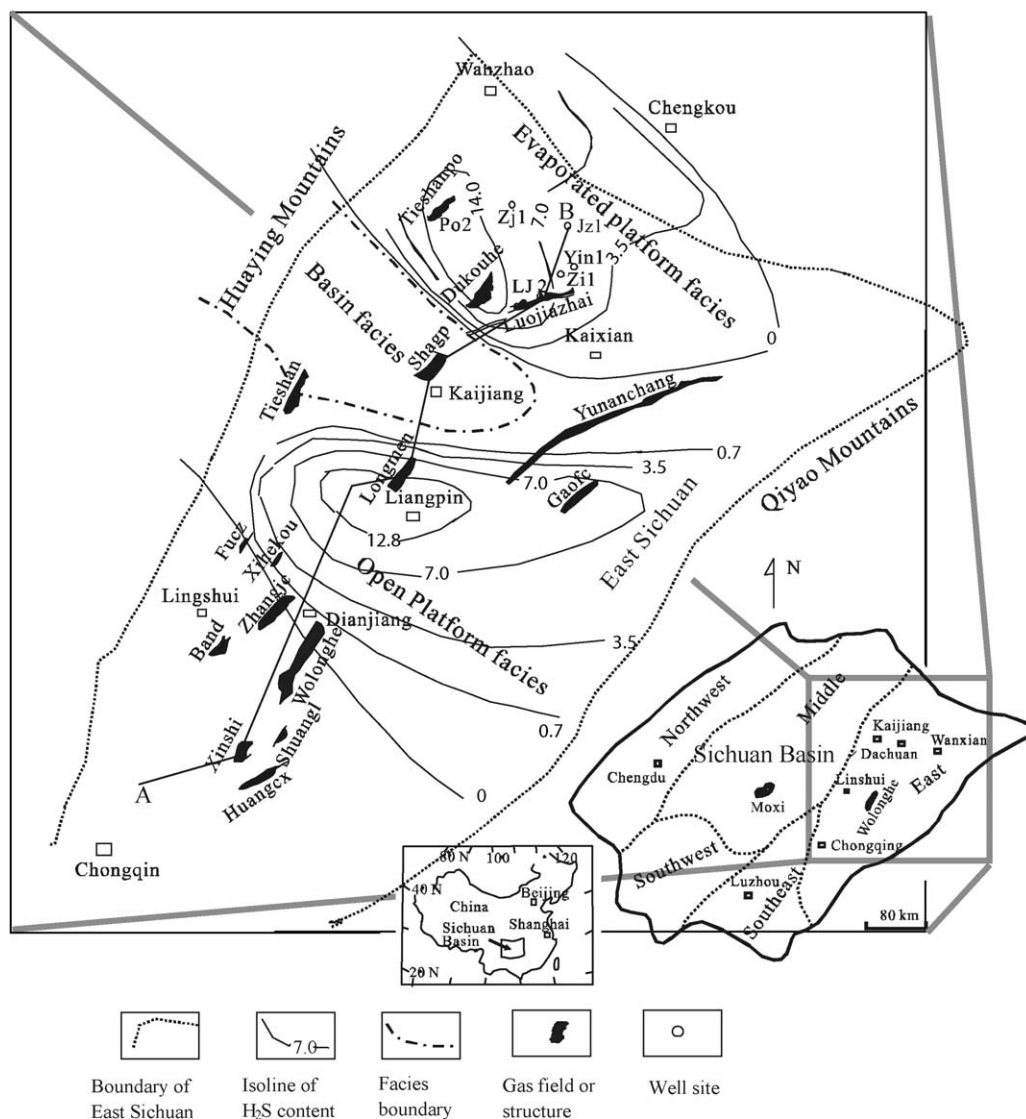
Fig. 1. Map showing distribution of gas fields or structures with Feixianguan Fm sedimentary facies and H$_2$S contents superimposed on it (adapted from Jiang et al. (2002)). The H$_2$S concentrations are shown to be related to facies thus planar distribution of anhydrite beds and nodules.

Potential petroleum source rocks for the Feixianguan Fm gas (Fig. 3 and Table 1) include Upper Permian Longtan Fm and Changxing Fm and even indigenous Lower Triassic Feixianguan Fm sources. The burial and geothermal history of the Well Po2 (Fig. 4) shows that rapid sedimentation took place during the early and late Triassic, Jurassic and the Cretaceous. Significant uplift occurred at the end of the middle Triassic, the late Jurassic and from the Cretaceous through to Quaternary. The stratigraphic section experienced maximum burial and maximum temperatures during the middle and later parts of the Jurassic. The maturation of sedimentary organic matter in the East Sichuan was influenced by various events. The Upper Permian source rock first became mature as the result of subsidence immediately before deposition of the Middle Triassic. Oil generation reached a peak from the late Triassic to the early Jurassic (Fig. 4, Xie, 2003). Oil accumulated in the

Lower Triassic Feixianguan Fm T$_1$f$^{1-3}$ oolitic grainstones below the sealing T$_1$f^4 anhydrite beds and mudstone. Middle Jurassic sedimentation resulted in natural gas generation from the Lower Permian source rocks through to the end of Cretaceous (Wang, Y.G. et al., 2002; Wang, Zhang, & Xie, 2003). The cracking of liquid hydrocarbon within the T$_1$f$^{1-3}$ reservoirs to natural gas has been proposed to take place during the Middle Jurassic as supported by coexistence of abundant bitumen and natural gas (Wang, Y.G. et al., 2002; Wang et al., 2003; Xie, 2003).

3. Sampling and analytical methods

Gas samples were obtained during drill stem testing (DST). Gas chemistry data have been collated from reports from the Southwest Oil and Gasfield Company,
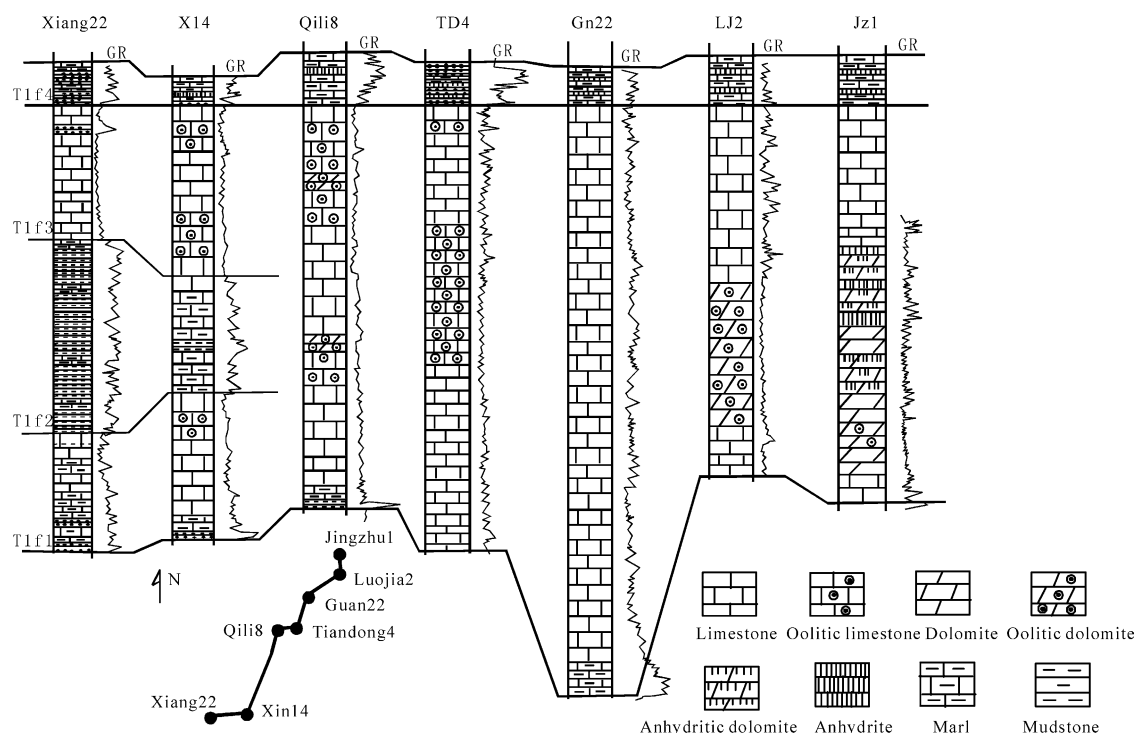
Fig. 2. Variation of sedimentary facies of Feixianguan Fm among the wells from the south to the north (AB) showing thicker anhydrite occurrence in the north (see Fig. 1 for the location of AB).

PetroChina with H_2S present in percentage terms volume (Table 2) or in g/m^3 measured under condition of 101.32 KPa and 20 °C. Light hydrocarbon gas $\delta^{13}C$ were measured on MAT251 and MAT 252 mass spectrometers employing industry standard techniques. The methods that were employed for sulphur isotope analysis of H_2S, elemental sulphur and anhydrite can be found in Cai, Hu, and Worden (2001).

Fig. 3. Stratigraphic systems from Carboniferous to Triassic for the East Sichuan Basin showing potential gas source rock and reservoirs and anhydrite distribution.

Table 1
Carboniferous to Lower Triassic source rock R_o, TOC and $\delta^{13}C$, and maximum H_2S percentages, $\delta^{34}S$, $^3He/^4He$ in natural gases and interpreted source rock for the gases in East Sichuan

Strata	Source rock			Gases in reservoirs and their interpreted source rock			
	R_o (%)	TOC[a] (%)	$\delta^{13}C^a$ (‰)	H_2S maxi (%)	$^3He/^4He^b \times 10^{-8}$	H_2S $\delta^{34}S$ (‰)	Source rock[c]
T_1j	1.2–1.5	0.05–0.27	–[d]	32.0	1.89–3.62 (n=2)	+22.2 to +31.0/+26.3 (n=6)	P_{2l} and T_1j
T_1f	1.14–1.50	0.06–0.73	−29.43 to −26.98	17.4	–	+12.7 to +13.2 (n=2) for $H_2S>$ 10 vol% −6.0 to +4.8 (n=2) for $H_2S<$ 0.2 vol%	P_{2l} and T_1f
P_{2ch}	1.77–2.23	0.19–1.17	−29.55 to −26.63	5.89 for P	1.83–2.20 (n=2) for P	+5.7 to +12.8/ +9.3 (n=2) for P	P_{2ch}
P_{2l}	1.61–2.63	0.86–7.47/2.91 for P_{2l} mudstone and coal; 0.17–3.06 for marl	−23.98 to −23.49 –				P_{2l}
P_1							P_1
C	2.6			1.46	2.09–2.72/2.50 (n=6)	−9.6 to +8.5/+ 2.2 (n=7)	S_1

Data present in the form of range/average (number of samples).
^a From Wang et al. (2003) and Yang et al. (2002).
^b From Xu et al. (1998).
^c from Huang et al. (1995; 1997), Wang et al. (2003) and Yang et al. (2002).
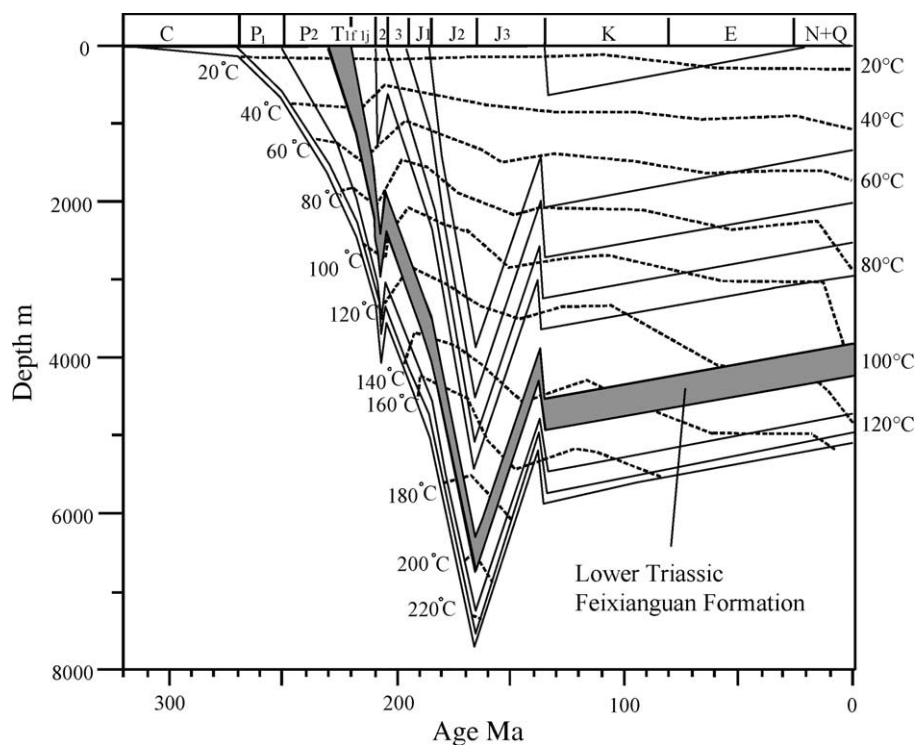^d No data available.

Fig. 4. Diagram showing a typical burial and palaeo-temperature history constructed from Well Po2 in the East Sichuan Basin. Isotherms are constrained by vitrinite reflectance and fluid inclusion measurements (modified from Xie (2003)).

Table 2
Chemistry and $\delta^{13}C$ and $\delta^{34}S$ values of natural gases from East Sichuan Basin

Gas fields/structures	Well	Age	Depth (m)	CH$_4$ (%)	C$_2$H$_6$ (%)	C$_3$H$_8$ (%)	H$_2$S (%)	CO$_2$ (%)	$\delta^{13}C_1$ (‰)	$\delta^{13}C_2$ (‰)	δ^{34}S-H$_2$S (‰)
Doukouhe	Du5	J$_2$s	1558–1569	90.08	3.37	0.79	0.02	0.11			
Shuangl	Sh16	T$_1$j	3121–3138	99.09	0.35	0.03	0.02	0.14			
Doukouhe	Du1	T$_1$f$^{3-1}$	4306–4354	82.7	0.04	0.04	16.21	0.46			
Doukouhe	Du2	T$_1$f$^{3-1}$	4362–4385	78.74	0.04	0.01	16.24	3.29			
Doukouhe	Du3	T$_1$f$^{3-1}$	4272–4342	73.71	0.06	0.05	17.06	8.27			+13.7
Doukouhe	Du4	T$_1$f$^{3-1}$	4191–4220	83.73	0.06	DT[a]	9.81	5.03	−29.83	−32.39	
Tieshanpo	Po1	T$_1$f$^{3-1}$	3400–3460	78.38	0.05	0.02	14.19	6.36	−30.12		+12.0
Tieshanpo	Po2	T$_1$f$^{3-1}$	4022–4162	80.79	0.03	0.02	10.59	7.22	−29.52		
Tieshanpo	Po4	T$_1$f$^{3-1}$	3365–3395	76.9	0.04	DT	14.2	7.62			
Luojiazhai	LJ1	T$_1$f	3457–3519	75.29	0.11	0.06	10.49	10.41			
Luojiazhai	LJ2	T$_1$f$^{3-1}$	3211–3286	84.68	0.08	0.03	8.77	5.44			
Luojiazhai	LJ6	T$_1$f^3	3911–3990	84.95	0.09	DT	8.28	6.21	−30.43		
Luojiazhai	LJ5	T$_1$f$^{3-1}$	2932–2997	76.66	0.05	DT	13.74	8.93			
Luojiazhai	LJ7	T$_1$f$^{3-1}$	3856–3956	81.37	0.07	DT	10.41	6.74	−30.33		
Gaofc	Feng4	T$_1$f^3	3810–3912	90.87	0.09	0.002	7.07	1.31			
Shagp	Gn22	T$_1$f^3	–[b]	97.75	0.28	0.01	DT	0.87			
Shagp	Gn6	T$_1$f$^{3-1}$	3051–3082	98.65	0.35	0.02	DT	0.18			
Shagp	Gn9	T$_1$f$^{3-1}$	3195–3220	99.05	0.33	0.02	DT	0.01			
Xihekou	LD2	T$_1$f$^{3-1}$	3398–3465	90.21	0.14	0.01	8.74	1.38			
Fucz	Ch22	T$_1$f$^{3-1}$	3024–3040	98.63	0.24	0.01	0.11	0.08	−32.03		
Xinshi	X9	T$_1$f$^{3-1}$	3112–3224	97.46	0.37	0.05	0.02	0.13			
Band	BD5	T$_1$f$^{3-1}$	2846–2860	97.99	0.46	0.1	0.012	0.19			
Tieshan	TS5	T$_1$f^2	2844–2921	98.6	0.23	0.01	0.02	0.6			
Tieshan	TS11	T$_1$f^3	2824–2970	97.99	0.23	0.1	0.12	0.73	−32.05	−33.8	+4.81
Tieshan	TS21	T$_1$f^2	2867–2918	97.64	0.2	0.02	0.59	0.57	−31.63		
Longmen	TD5	T$_1$f^3	–	90.82	0.22	0.02	6.35	2.28			
Longmen	TD56	T$_1$f^3	–	88.39	0.16	0.01	8.52	2.57			
Xinshi	X12	T$_1$f^3	3102–3188	98.55	0.35	0.05	DT^1	0.1			
Xinshi	X9	T$_1$f^3	3151–3233	97.46	0.37	0.05	0.02	0.81			
Fucz	Ch16	T$_1$f^3	2563–2669	98.75	0.37	0.02	0.114	0.001	−32.35		−6.0
Tieshan	TS14	P$_{2ch}$	3094–3261	97.9	0.29	DT	0.08	0.77			
Tieshan	TS21	P$_{2ch}$	3019–3261	98.04	0.25	0.01	0.08	0.67			
Tieshan	TS5	P$_{2ch}$	3053–3326	98.16	0.23	DT	0.08	0.65			
Wolonghe	Wo118	P$_{2ch}$	3795–3887	97.85	0.41	0.06	DT	0.94			
Longmen	TD10	P$_{2ch}$	–	95.99	0.26	0.04	0.19	2.79			
Zhangjc	Zh23	P$_{2ch}$	3376–3426	97.1	0.31	DT	0.13	1.9			
Huangcx	C16	P$_{2ch}$	2000–2008	98.48	0.31	0.02	0.09	0.17			
Band	BD4	P$_{2ch}$	3433–3552	97.61	0.54	0.16	DT	0.97			
Tieshan	TS4	P$_{2ch}$	3098–3102	98.32	0.23	0.01	0.26	0.41			
Shibaozhai	Bao1	P$_{2ch}$	3980–4051	90.73	0.14	0.01	3.66	4.94			
Huangcx	Cao6	P$_1$	2526–2614	98.36	0.49	0.05	0.17	0.04			
Tieshan	TS2	C$_{2hl}$	4077–4118	97.02	0.21	0.01	0.93	0.89			
Yunanchang	Yun6	C$_{2hl}$	4592–4642	97.3	0.41	0.02	0.08	0.59			
Dukouhe	Du4	C$_{2hl}$	5214–5227	97.83	0.2	0.01	0.1	1.0			

[a] DT represents detection limit.
[b] No data available.

4. Results

4.1. Source rock geochemistry

The Upper Permian Longtan Fm (Fig 3) contains alternating marine and terrestrial mudstone and coal and has TOC values from 0.86 to 7.47% (average of 2.91%) and $\delta^{13}C$ values of the kerogen from -23.5 to $-24.0‰$ PDB (Yang et al., 2002). Marine marl from the Longtan Fm has TOC values between 0.17% and 3.06% (Wang et al., 2003). The vitrinite reflectance (R_o) values of the Longtan Fm organic matter have been reported to fall between 1.89 and 2.63% (Wang et al., 2003; Yang et al., 2002), implying that the kerogen has reached the post-mature stage.

Stratigraphically above the Longtan Fm lies the Permian Changxing Fm. This is largely micritic carbonate formed in a basinal and low-angled slope environment and has TOC values between 0.19 and 1.17%. The organic matter extracted from Changxing Fm micrite has $\delta^{13}C$ values between -29.55 and $-26.63‰$ PDB, and shows a post-mature vitrinite reflectance characteristics (R_o from 1.77 to 2.23%, Wang et al., 2003; Yang et al., 2002).

The Lower Triassic Feixianguan Fm, which is 50–200 m in thickness contains basinal facies (dark micrite and shale) units as well as the shelfal carbonates that host the sour gas that are the subject of this study. The shale-rich part of the Feixianguan Fm has TOC values between 0.06% and 0.73%, and kerogen $\delta^{13}C$ between -29.43 and $-26.98‰$ PDB (Wang et al., 2003; Yang et al., 2002). The vitrinite reflectance values of the Feixianguan Fm range from 1.14 to 1.50% and suggest that the mature to post-mature petroleum generation stage has been achieved during burial. The Feixianguan Fm has similar kerogen type and $\delta^{13}C$ values to the Changxing Fm but has relatively low maturity and TOC values.

Biomarker correlations between bitumen extracted from the Upper Permian Longtan Fm source rocks and the Lower Triassic Feixianguan reservoir bitumen have the same general pattern. The petroleum gas in the Feixianguan Fm is likely to have been derived principally from Longtan Fm source rock (Wang, Y.G. et al., 2002; Wang et al., 2003; Yang et al., 2002). However there is a residual possibility of limited petroleum contributions from topmost Permian Changxing and Lower Triassic Feixianguan Fm source rocks (Yang et al., 2002).

4.2. H2S geochemistry

Natural gas samples in the Feixianguan Fm from the East Sichuan Basin contain variable quantities of H_2S from less than detection limit (fractions of a percent) to 17.4%, or 244.5 g/m³. Concentrations of $H_2S > 6.4\%$ have been found in Dukouhe, Tieshanpo, and Luojiazhai gas pools or structures in the north and in the Gaofc, Longmen and Xikouhe gas pools or structures in the south (Fig. 1 and Table 2). In the north, H_2S concentrations range from 8.9 to 10.7% in Luojiazhai area, from 14.4 to 14.7% in Tieshanpo and from 9.9 to 17.4% in Dukouhe.

The T_1f^4 caprock, dominated by anhydrite beds and mudstone, is common to the Feixianguan Fm. It occurs in regions that have both high and low H_2S concentrations. This suggests that the presence of anhydrite in the caprock is irrelevant to TSR. Moreover, it suggests that the caprock anhydrite is not involved in TSR.

High concentrations of H_2S tend to have been found in dolomitic rocks in the centre and north of the basin and evaporated platform sediment that contain anhydrite beds and/or anhydrite nodule beds in the north of the basin (Figs. 1 and 2). The dolomitic sediments in the centre and north of the basin likely also contain disseminated anhydrite although a full study of facies, sedimentology, diagenesis and mineralogy has yet to be made. Negligible H_2S is found in reservoirs formed in pure calcitic rocks found in the open platform and basin facies sediments (devoid of anhydrite; e.g. in the Kaijiang–Liangping area; Figs. 1 and 2). This strongly suggests that primary sedimentology exerts a major influence on the occurrence of H_2S; specifically the distribution of anhydrite is likely to be critical. However, the highest H_2S concentration (17.4%) is found in well Du3 which has a thinner anhydrite-bearing zone than the less sour well JZ1 (Wang et al., 2003; Xie, 2003), indicating that the extent of sulphate reduction is not solely controlled by the absolute quantity of anhydrite. In contrast, the highest H_2S concentrations tend to occur in the Dukouhe, Tieshanpo and Luojiazhai areas that contain a great number of anhydrite nodules. This indicates that the presence of finely-crystalline anhydrite within nodules may be more important than the presence of coarsely crystalline anhydrite that caps reservoirs, similar to the observation of Worden et al. (2000). Elemental sulphur, a common by-product of TSR (e.g. Worden, Smalley, & Fallick, 1997), is only found in wells that contain H_2S gas suggesting that there is a genetic link between the two. However pyrite, another non-gaseous reduced sulphur form, is found in both H_2S-rich and H_2S-free wells suggesting that pyrite is not exclusive to areas that have experienced TSR; pyrite may have more than one origin.

The H_2S concentration has been shown to increase with reservoir burial depth (temperature) (Fig. 5a). The H_2S concentrations are mainly less than 0.6% by volume in reservoirs buried to present-day depths of less than about 3000 m (Fig. 5a). Similarly an index of gas souring by TSR ($H_2S/(H_2S + C_nH_{2n+2})$; Worden et al., 1995) is only elevated at depths greater than about 3000 m (Fig. 5b). Concentrations of H_2S and CO_2, another possible byproduct of TSR, are loosely correlated (Fig. 5c) and a CO_2-based index of TSR ($CO_2/(CO_2 + C_nH_{2n+2})$; Krouse, Viau, Eliuk, Ueda, & Halas, 1988) largely mimics the H_2S-based measure of TSR (Fig. 5b). There is a large degree of scatter in both absolute H_2S concentration and the TSR-progress indices (Fig. 5a and b); this is likely to be a result of geographically-controlled primary facies variations that
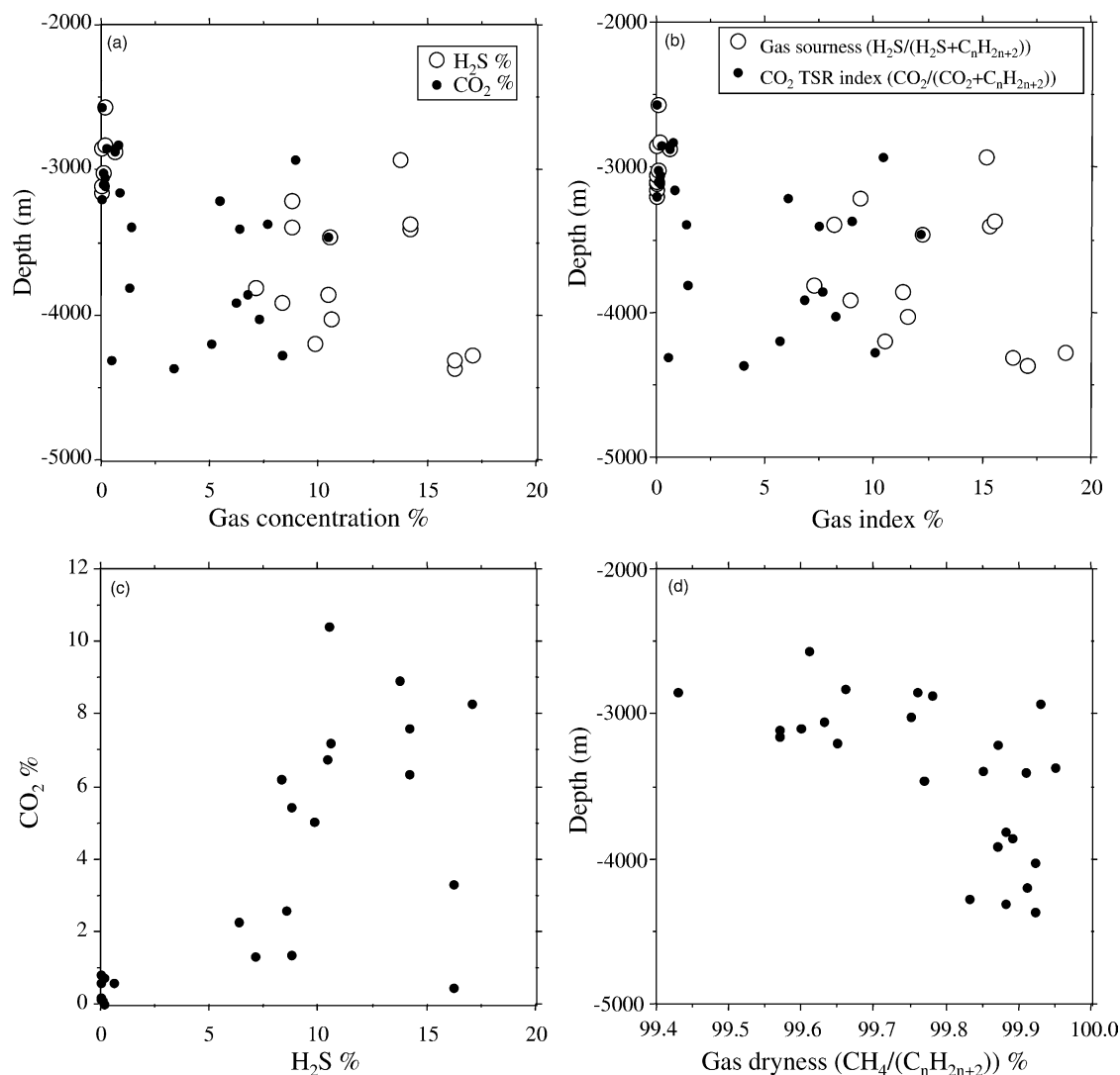
Fig. 5. Gas concentration data. (a) Non-hydrocarbon gases versus depth, (b) Two indices of gas sourness versus depth (H_2S after Worden et al. (1995); CO_2 after Krouse et al. (1988)), (c) Non-hydrocarbon gases plotted against each other, (d) Gas dryness versus depth.

limit the quantity of nodular anhydrite available for TSR as well as uncertainty in the thermal history of the basin (see later). It seems as if present-day depth has an influence on the degree of TSR although this possibility will be explored and discounted later.

4.3. Gas chemistry and $\delta^{13}C$–H_2S relationship

Hydrocarbon gas geochemistry data (Fig. 5d) reveal that the gases have very high dryness coefficient values ($CH_4/\sum C_nH_{2n+2}$) greater than 99.2%. There are no significant alkanes with carbon number > 3 (i.e. no detectable butane) and methane is much more abundant than ethane or propane. Gas dryness tends to become more extreme with increasing depth of burial although there is considerable scatter in the data (Fig. 5d). The gases from the Feixianguan Fm are significantly more methane-dominated (higher molar $CH_4/\sum C_nH_{2n+2}$ values) than gas from the overlying Jialingjiang

Fm or the underlying Permian reservoirs (Cai, Worden, Bottrell, Wang, & Yang, 2003).

Gas samples with $H_2S > 6\%$ have ethane concentrations mainly between 0.02 and 0.11% while gas samples with $H_2S < 0.6\%$ have ethane concentrations between 0.2 and 0.5%. There is a distinct relationship between gas dryness and gas sourness (Fig. 6). The gases only become sour (TSR index > 1%) when they have dryness coefficients > 99.75%. Thus, the gas seems to have become substantially drier (even more methane-dominated) as sulphate reduction proceeded in Feixianguan reservoirs. Such a pattern has also been reported from the TSR-affected Khuff Fm, Abu Dhabi (Worden & Smalley, 2004).

Methane in Feixianguan Fm gas samples has $\delta^{13}C$ values ranging from -29.83 to $-32.05\%o$ PDB and two ethane samples unusually have more negative $\delta^{13}C$ values than the coeval methane (Fig. 7; Table 2). There is an inverse correlation between $\delta^{13}C$-methane and the absolute
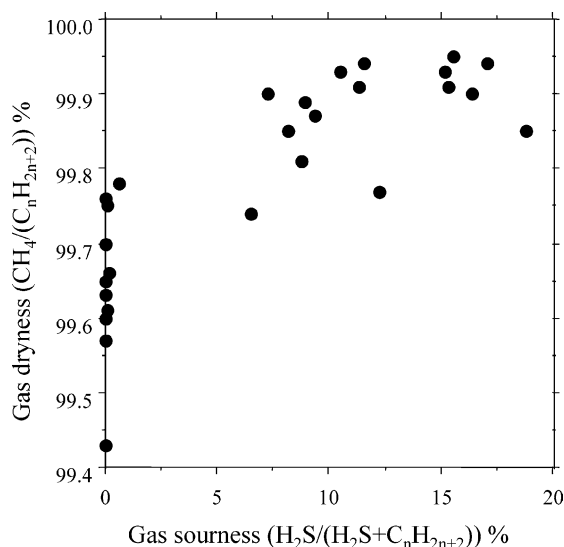
Fig. 6. Variation of gas dryness with gas sourness showing a positive relationship between the two implying that ethane and propane are effectively removed by the process of H_2S generation (TSR).

concentration of methane (Fig. 7a) that shows that while methane was replaced by other gases (mainly H_2S and CO_2), the remaining methane became isotopically heavier. There is a well-defined positive correlation between gas dryness and $\delta^{13}C$ values of methane (Fig. 7b). It seems that the process that led to the extreme dryness also led to more isotopically enriched methane. There is a fairly well developed correlation between gas sourness and $\delta^{13}C$–methane suggesting that TSR has directly induced an alteration of the carbon isotopes of the remaining methane (Fig. 7c). The positive relationship between methane $\delta^{13}C$ values and gas sourness leads to the inference that as sulphate reduction of methane proceeded, ^{12}C in methane was more rapidly depleted by TSR than ^{13}C as a result of kinetic isotope fractionation, with the residual methane thus becoming more enriched in ^{13}C.

In many petroleum accumulations, co-existing alkane gases tend to have progressively higher $\delta^{13}C$ values as the alkane chain length increases (e.g. Cai et al., 2002). This is not found to be the case in the Feixianguan Fm where two
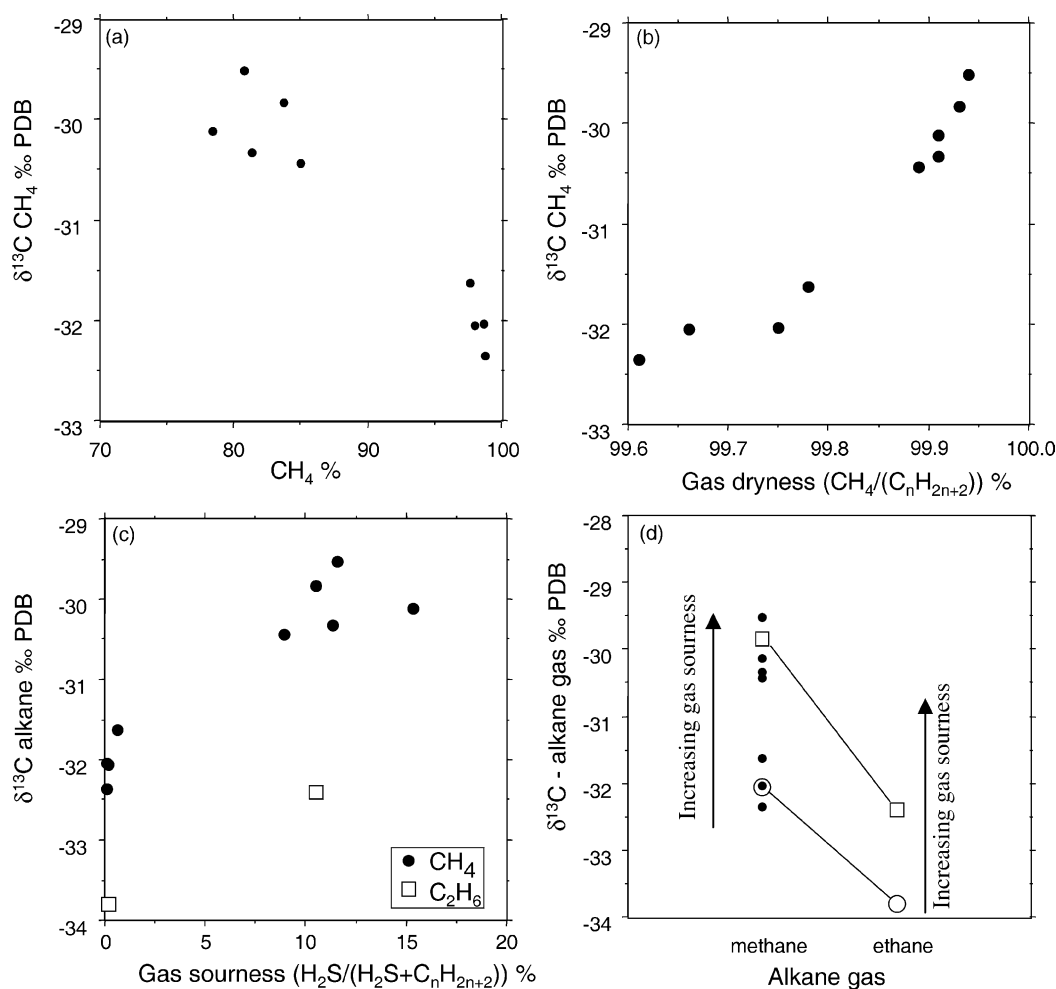

Fig. 7. Relationships between methane $\delta^{13}C$ and other parameters: (a) methane concentration, (b) gas dryness, (c) gas sourness. Plot (d) shows the relationship between methane and ethane $\delta^{13}C$ values. The two tie lines link co-existing ethane and methane and illustrate the anomalous relationship between the carbon isotopes of these gases in this formation. Methane must have been extensively involved in TSR since its carbon isotopes have been so altered.
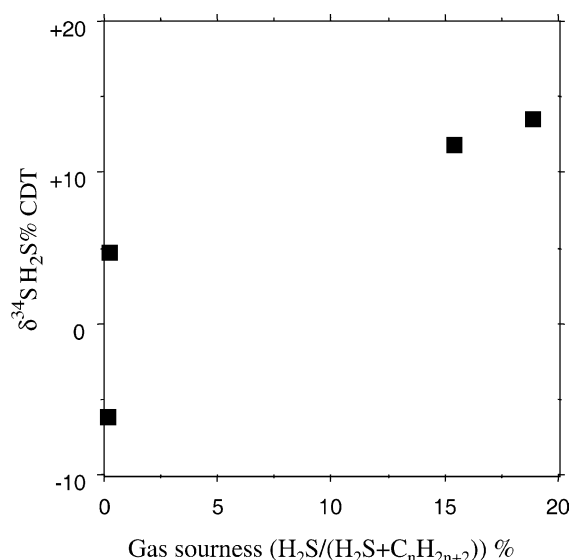
Fig. 8. Plot of H$_2$S content and δ^{34}S values of natural gases from Feixianguan Fm showing distinct δ^{34}S values for the formations and most likely organically derived sulphur with a negative value.

gas samples were analyzed for ethane as well as methane δ^{13}C. Ethane is almost 2‰ lighter than methane in both cases (Fig. 7d).

4.4. δ^{34}S data of H$_2$S, elemental sulphur, anhydrite and pyrite

Four H$_2$S samples have been measured for their δ^{34}S values. Interestingly, the resulting values have a wide range from -6 to $+13.2$‰ CDT (Table 2, Fig. 8). The two samples with H$_2$S contents >10% by volume have very similar relatively high δ^{34}S values of $+12.7$ and $+13.2$‰ (Figs. 8 and 9). One sample with a very low H$_2$S concentration (<0.2%) has a distinctly negative isotope value of -6.0‰ CDT. Such a value is similar to a sample from the basal Middle Triassic Leikoupo Formation (T$_2$l^1)
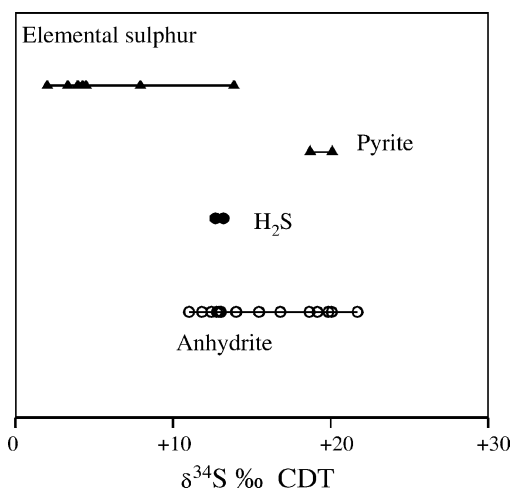

Fig. 9. Distribution of δ^{34}S of anhydrite, pyrite and elemental sulphur from the Feixianguan Fm.

in the Naxi gas field (Cai et al., 2003), which was concluded to have had an organic source rock origin.

Fifteen anhydrite samples from well ZJ1 have δ^{34}S values from $+11.0$ to $+21.7$‰ CDT with an average of $+15.5 \pm 3.5$‰ ($n = 15$) (Fig. 9), the values are close to those of anhydrite and elemental sulphur in the Khuff Formation, Abu Dhabi, near Permian–Triassic boundary (Worden, Smalley, & Fallick, 1997) and the interpreted primary seawater sulphate sulphur isotope (Chen & Chu, 1988; Claypool, Holser, Kaplan, Sakai, & Zak, 1980).

Elemental sulphur is a common, transient byproduct of TSR (Worden & Smalley, 1996). In the East Sichuan Basin, abundant elemental sulphur has been observed predominantly in areas with large gas reserves (Luojiazhai and Dukouhe areas; Jiang et al., 2002). Little elemental sulphur has been reported in small gas accumulations and those with low gas saturation (wells Du5 and Zi1). Seven elemental sulphur samples from the East Sichuan Basin have been analyzed for their δ^{34}S values. This elemental sulphur has δ^{34}S values from $+2.0$ to $+13.9$‰ CDT with an average of $+5.7 \pm 4.0$‰ ($n = 7$) while up to $+19.1$‰ was reported by Wang, Y. G. et al. (2002)

Two pyrite samples from Well Du4 and Po1 oolitic grainstones have been measured and have δ^{34}S values of $+18.7$ to $+20.1$‰ CDT respectively (Wang, Y.G. et al. 2002).

4.5. Replacement of anhydrite by calcite and calcite δ^{13}C

Thin-section analysis revealed that calcite is present as either a partial or total replacement product (pseudomorph) of microcrystalline anhydrite nodules. Calcite has grown from the outer edges of anhydrite nodules progressively towards the core of the nodule. The entire edge of anhydrite nodules typically have been replaced by calcite (Fig. 10a). Thus the replacement of anhydrite by calcite during TSR occurred in a strictly defined manner from the outside of a nodule towards its core. Within partially-replaced nodules, replacive calcite crystals coexist with elemental sulphur (Fig. 10b) and have sizes ranging from 350 μm to several millimeters, far greater than the component anhydrite crystals. Calcite from an anhydrite nodule in Well P1 has been measured to have a δ^{13}C value of -7.26‰, which is much lighter than the δ^{13}C range of contemporaneous micrite from the same basin ($+0.75$ to $+1.37$‰; Wang, Y.G. et al., 2002). This suggests that at least some of the carbonate in the calcite has been derived from organic matter (e.g. methane). It has been shown previously that TSR-derived calcite can have a wide range of δ^{13}C values ($+2$ to -30‰ PDB; Worden & Smalley, 1996) but a value of -7.26‰ is certainly within the realm of TSR calcite.

4.6. Fluid inclusion temperatures from calcite cement

Fluid inclusion analysis has been performed on calcite cement in Feixianguan Fm oolitic grainstones in
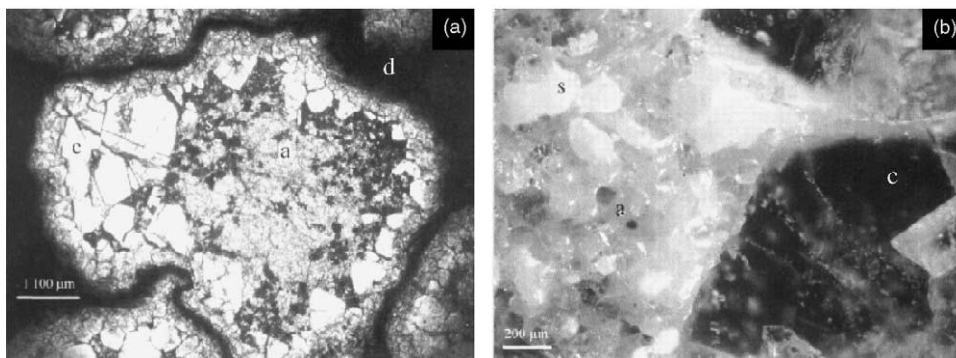
Fig. 10. Photomicrographs showing equant calcite, elemental sulphur and anhydrite occurrence in nodule. Well Po1 3464.8 m (taken from Wang, Y.G. et al., 2002). (a) planar polarized light; (b) cross-polarized light and reflected light. Note that in the photos, 'a' represents anhydrite, 'c' calcite, 's' sulphur and 'd' dolomite.

the Dukuohe and Luojiazhai gas fields. All of the inclusions are primary inclusions and have a variety of sizes from 5 to 25 μm with gas/liquid ratios mainly from 5 to 20. Goldstein (1986) and Prezbindowski and Larese (1987) found that fluid inclusions in carbonate cement, in some circumstances, undergo re-equilibration due to stresses imposed on the host mineral. The result is typically an increase in inclusion volume and an artificial increase in homogenization temperature. The inclusions in calcite cements from the Feixianguan Fm show no correlation between homogenization temperature and inclusion size, so that resetting of fluid inclusions is considered to have been negligible in this case (e.g. Worden et al., 1995).

Fluid inclusion temperatures range from 80 to 200 °C (Wang, Y.G. et al., 2002). The lower temperature values are probably from burial diagenetic calcite cementation that is

nothing to do with TSR since replacive calcite (after anhydrite) was reported to have fluid inclusion homogenization temperatures greater than 109 °C (Wang, Y.G. et al., 2002). More than 75% of the inclusions have homogenization temperatures 130–140 °C (Fig. 11). The fluid inclusion data tantalizingly seem to suggest that there might have been two episodes of TSR reaching their peaks at 150 °C and 190 °C although further work is required on these samples to ascertain this possibility. The first TSR peak at 150 °C accords with TSR studies of other dry gas-TSR provinces (e.g. Abu Dhabi; Worden et al., 1995). It is likely that TSR in the Feixianguan Fm occurred only when the rocks reached temperatures greater than about 130–140 °C.

The spread of fluid inclusion temperatures from calcite plotted against present day temperature (Fig. 11b) reveals that either: (1) the fluid inclusions represent growth during
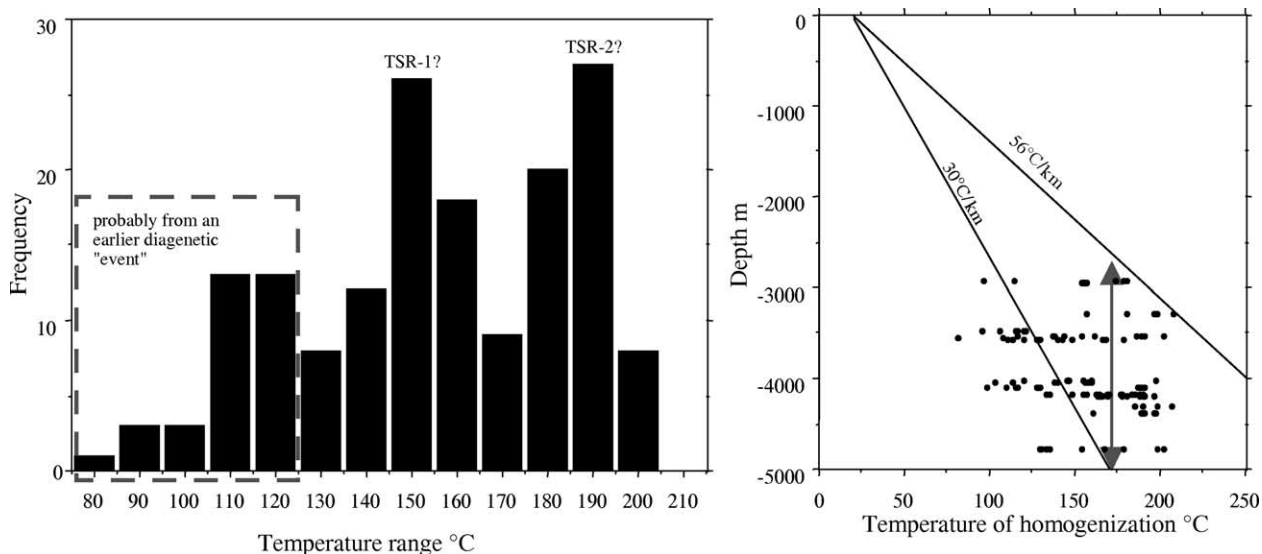
Fig. 11. Fluid inclusion data. (a) Histogram of homogenization temperatures in fluid inclusions in the calcite cements showing >75% inclusions have temperatures >140 °C. The lower temperature data came from calcite formed by processes other than TSR. The data intriguingly suggest that there may have been two pulses of TSR in the Feixianguan Fm. (b) Depth–homogenization temperature cross plot. The homogenization temperatures are high for the present depth of burial suggesting that there has either been uplift (by the extent indicated by the arrow), or the geothermal gradient was formerly much higher than it is at the present day.

a time of very high geothermal gradient (e.g. 56 °C/km versus the present day 30 °C/km), or (2) there has been uplift of approximately 2000 m for an approximately constant geothermal gradient of 30 °C/km. Examination of the burial and thermal history (Fig. 4) shows that there has been uplift and some cooling so that the actual explanation may lie in between these two extremes. Whatever the cause though, it is clear that the TSR occurred when the Feixianguan Fm was more deeply buried and hotter than it is at the present day.

5. Discussion

5.1. A local source of H_2S?

Trace quantities of the noble gas helium can be used, through the ratio of ^3He to ^4He, to reveal whether there has been a significant mantle component added to the fluids in the basin. No helium gas $^3He/^4He$ ratios were measured from the Lower Triassic Feixianguan Fm. However helium gas $^3He/^4He$ ratios were measured the overlying Lower Triassic Jialingjiang Fm and the underlying Permian reservoirs. Isotope ratios from these formations range from 1.9×10^{-8} to 3.6×10^{-8} for the Upper Triassic and from 1.8×10^{-8} to 2.2×10^{-8} for the Permian in the East Sichuan (Table 1; Cai et al., 2003). These ratios give no evidence of a mantle helium contribution. By interpolation, it is also unlikely that there was a mantle contribution of gas to the Feixianguan Fm. It is thus unlikely that H_2S in the Feixianguan Fm had a mantle origin.

One accumulation in the Feixianguan Fm that has a low H_2S concentration (0.1%) has $\delta^{34}S$ values of $-6.0‰$ (Fig. 8; Table 2; Sheng, Xu, Wang, & Wang, 1997). This value is commensurate with an organic source (e.g. Orr, 1977). In general then there may thus have been a very limited H_2S contribution from degradation of sulphur-bearing source rocks or even petroleum-based organo-sulphur compounds.

Gas accumulations in the Permian part of the section have H_2S concentrations mainly less than 1% by volume but locally reach 5.89% (Table 2; Wang et al., 2003). The H_2S content in the Permian part of the section is much less than the gas in the sour part of the Feixianguan Fm. Permian H_2S has elevated $\delta^{34}S$ values ($+20.4$ to $+29.7‰$ CDT; Cai et al., 2003) that are distinct from those in the sour part of the Feixianguan Fm ($+12.0$ to $+13.7‰$ CDT). Since H_2S is a very reactive molecule, during migration H_2S might be expected to react with common minerals that contain transition and base metals (e.g. Fe, Zn and Pb) in the carrier bed or fault zone. Thus it is unlikely that H_2S in the Feixianguan Fm had a Permian source (but note that a Permian source for hydrocarbons has been inferred, see earlier) since the Permian generally has little H_2S, it is isotopically distinct, and Permian H_2S would be unlikely to survive migration into the Lower Triassic Feixianguan Fm.

Although petroleum in the Lower Triassic Jialingjiang Fm has very high H_2S contents (up to 32%; Cai et al., 2003), this gas has much lower dryness coefficients and significantly higher H_2S $\delta^{34}S$ values ($+22.2‰$ to $+31.0‰$ CDT; Cai et al., 2003) than gas in the Feixianguan Fm, indicating that the sour gas in the Jialingjiang Fm cannot have migrated into the Lower Triassic Feixianguan Fm.

It is thus most likely that the H_2S in the Feixianguan Fm was not derived from neighbouring formations and so, by default, had a local source. The relatively high H_2S $\delta^{34}S$ values from the sour part of the Feixianguan Fm (Fig. 8) preclude an origin from source rock organic matter for the H_2S since such H_2S would be expected to have low $\delta^{34}S$ values of approximately $-5‰$ CDT (e.g. Orr, 1977). Anhydrite within the Feixianguan Fm has $\delta^{34}S$ values from approximately $+10$ to $+22‰$ CDT with a mean value of $+15.5‰$.

Experimental TSR studies (e.g. Cross, Manning, Bottrell, & Worden, 2004) have shown that the derived H_2S is about 20‰ lighter than the original sulphate. Conversely, studies of natural TSR systems have shown that TSR-H_2S typically has about the same $\delta^{34}S$ value as the original sulphate (e.g. Machel et al., 1995; Worden & Smalley, 1996). This apparent paradox arises because in natural TSR systems there is complete reaction (reduction) of each batch of anhydrite that dissolves so preventing any sort of isotope fractionation. In the experimental systems, the sulphate is already in solution thus avoiding the essential anhydrite dissolution step that characterizes the kinetics of natural TSR systems (e.g. Worden et al., 2000). The presence of calcite rims around anhydrite nodules (Fig. 10) is evidence of not only the importance of anhydrite dissolution but also the Feixianguan Formation being typical of other natural TSR occurrences. The measured H_2S $\delta^{34}S$ values of $+12.0$ to $+13.7‰$ are thus entirely typical of TSR in natural system, although the exact H_2S $\delta^{34}S$ value depends on the $\delta^{34}S$ value of the initial anhydrite.

The two H_2S $\delta^{34}S$ values from the sour part of the basin lie in the middle of the anhydrite range and the local anhydrite may plausibly have been a source, via TSR, for the H_2S. The replacement of nodular anhydrite by calcite (Fig. 10) provides petrographic evidence of the occurrence of TSR. The gas geochemistry, gas and rock isotope and petrographic data thus provide concrete scientific support for the initial speculation that TSR in the Feixianguan Fm reservoir was the cause of the elevated H_2S (Wang, Y. G. et al., 2002; Yang et al., 2002).

5.2. Was methane involved in TSR?

Both liquid and gaseous hydrocarbons can be involved in TSR (e.g. Cai et al., 2001, 2003; Connan & Lacrampe-Couloume, 1993; Machel et al., 1995; Orr, 1974, 1977; Sassen, 1988; Worden et al., 1995). Despite evidence from sour gas provinces (Worden & Smalley, 1996, 2004), it has been asserted that methane cannot be an important reducing

agent in TSR (Machel, 2001) since it is said to be the least reactive of all hydrocarbons (due to a relatively low Gibbs free energy of reaction for methane).

In the East Sichuan Basin, high concentrations of H_2S coexist with solid bitumen in the reservoirs. Solid bitumen inclusions were observed in calcite replacement of anhydrite (Wang, Y.G. et al., 2002), thus it is not impossible for H_2S to have been generated by the reaction of liquid hydrocarbons and anhydrite. However, several lines of evidence suggest that this is not the case for the Feixianguan gas.

Solid bitumen occurs in both sour and sweet reservoirs (i.e. both high and negligible concentrations of H_2S; Xie, 2003) and in parts of the basin where the Feixianguan Fm has no anhydrite nodules and no dolomitic rocks. *If* the solid bitumen were a product of thermochemical reaction between liquid hydrocarbons and sulphates, significant bitumen would only be expected in the TSR-affected (sour) parts of the basin.

As methane has been diluted by H_2S, the reduced methane concentration has become isotopically enriched with respect to ^{13}C (Fig. 7a). There is a positive relationship between methane-$\delta^{13}C$ values and gas sourness $H_2S/(H_2S + C_nH_{2n+2})$ (Fig. 7c). There is also a positive relationship between methane-$\delta^{13}C$ values and gas dryness ($CH_4/\Sigma C_{n-}H_{2n+2}$) (Fig. 7b). These patterns can be explained by kinetic isotope fractionation of carbon in methane during TSR, a phenomenon reported previously for dry gas TSR provinces (Worden & Smalley, 1996, 2004). The patterns suggest that at the earliest stages of TSR, ethane and propane were involved in chemically reducing sulphate to sulphide leading to increased gas dryness values. This implies that the overall reactivity of ethane and propane were slightly greater than methane (a conclusion reached previously by e.g. Connan & Lacrampe-Couloume, 1993; Krouse et al., 1988). Once most of the ethane and propane were exhausted by TSR, methane became heavily involved and underwent significant degrees of isotope fractionation. Ethane-$\delta^{13}C$ values also increase with gas souring index (Fig. 7c) proving that ethane was involved in TSR but seemingly there was a smaller kinetic isotope effect, explaining the unusual anomaly of the ethane $\delta^{13}C$ values being lower than methane $\delta^{13}C$ values (Fig. 7d). It is possible to conclude that gaseous hydrocarbons, dominated by methane, were involved in TSR in the Feixianguan Fm. An early TSR event, induced by an initial liquid petroleum charge, cannot be unequivocally ruled out, but it is certain that the later (present) dry gas charge was the dominant reducing agent involved in TSR.

The solid bitumen inclusion in calcite cement may indicate that (a) there was very limited reaction between liquid hydrocarbons and anhydrite to produce pyrobitumen, (b) liquid hydrocarbons cracked during reservoir heating to generate solid bitumen, (c) bitumen formed in the initially liquid petroleum as the gas-oil ratio (GOR) increased leading to de-asphalting (Cai et al., 1997, 2001). To be

valid, options (b) and (c) must have occurred prior to TSR to allow solid bitumen inclusions to form in TSR calcite. Solid bitumen was found within the intergranular porosity in pure oolitic grainstones, and may have precipitated during late-stage diagenesis (but pre-TSR) due to an influx of gas from the Permian during the middle Jurassic to Cretaceous, increasing the gas/oil ratio and leading to asphaltene exsolution from heavy oils. The evolved high GOR charge then underwent TSR. The widespread distribution of bitumen (in both sweet and sour parts of the basin) suggests that bitumen in the Feixianguan Fm is not due to TSR. Whether option (b) or (c) is valid requires further work that is beyond the scope of the present study.

Thus TSR occurred in the Feixianguan Fm due to reaction of methane-dominated alkane gases with anhydrite. These data prove that methane is an important reducing agent during TSR.

5.3. Temperature of TSR in the Feixianguan Fm

The present depth-distribution of sour gas in the Feixianguan Fm in the East Sichuan Basin (gas sour only at depths > 3000 m) seemingly represents a TSR temperature of greater than approximately 100 °C (Figs. 4, 5a and b). It is tempting to use this depth and temperature as a way of constraining the conditions under which TSR occurred. Moreover, it is also tempting to use this depth as a way of predicting the distribution of H_2S before drilling a well. However, the fluid inclusion data seem to suggest that TSR predominantly occurred at temperatures of greater than 130–140 °C. Burial and thermal history analysis (Fig. 4) show that the Feixianguan Fm has undergone considerable uplift and cooling since the Cretaceous. The present day temperature in the Feixianguan Fm does not represent the conditions under which TSR occurred since the formation has been uplifted and has reduced geothermal gradients in comparison to the heat flow during the Mesozoic. The present depth distribution is a direct function of the degree of uplift. If there has been locally variable uplift and cooling (typical of post-rift sedimentary basins) then it is totally inappropriate to use the present day depth to predict H_2S. In order to predict the parts of the basin that contain abundant H_2S as a result of TSR it will be necessary to produce a novel regional understanding of the burial and thermal history of the Feixianguan Fm.

5.4. Role of facies on the occurrence of TSR in the Feixianguan Fm

Elevated H_2S is only found where the Feixianguan Fm is locally dolomitic or contains abundant anhydrite nodules These facies mainly occur in the T_1f^{1-3} part of the stratigraphy in the center and north of the East Sichuan Basin (Figs. 1 and 2). Where the Feixianguan Fm is not dolomitic and is free of anhydrite, there is negligible H_2S. This strongly supports the paramount role of primary

sedimentary facies on TSR and H$_2$S generation. Any scheme to predict H$_2$S distribution should include some sort of appraisal of the range and geographic variability of sedimentary environments. The ubiquitous caprock anhydrite seems to play no significant role in TSR since there is no correlation between amount of H$_2$S and presence of anhydrite in the caprock.

5.5. TSR in a gas, gas–water transition, or water zone?

TSR has been shown to occur in both a gas–water transition zone (Machel et al., 1995) and in a gas zone (Worden et al., 2000). However, it is unclear which zone is more favourable for TSR.

Wells Du1, Du2, Du3 and Du4 in the Dukouhe gas field, and wells LJ1, LJ2 and LJ5 in the Luojiazhai gas field produce natural gas from reservoirs with very high gas saturation throughout the whole reservoirs. The gas from the wells has subtly variable gas concentrations and isotopic composition (Table 2), indicating that discrete compartments exist between wells in the same field within the Feixianguan Fm. In each compartment, H$_2$S was most likely generated locally by TSR within gas zones since no water legs or gas-water transition zone found. This observation supports the conclusion of Worden et al. (2000) that TSR can reach advanced stages far above aquifers. However, TSR is considered to take place between dissolved alkane gas and aqueous sulphate (Machel et al., 1995; Worden et al., 2000). Thus, in a gas zone, it is important to determine whether enough water exists to dissolve anhydrite and alkane gas to keep TSR proceeding. In gas fields, small quantities of residual water (left behind after gas charging) are always present in the gas zone and so thin films of water will coat the surfaces of anhydrite nodules. Anhydrite is considered to have a greater affinity (wettability) for water than hydrocarbon gases (Worden & Heasley, 2000). Thus, it is possible for TSR reactions to take place on the surface of anhydrite nodules. Worden et al. (2000) observed that in the Khuff Formation anhydrite is equally altered to calcite throughout the present gas zone, and so concluded that even the low water saturation found in a gas zone is sufficient to allow TSR reactions to proceed. This may be similar to the case in Dukouke and Luojiazhai gas fields.

Thus, it is possible to conclude that TSR occurred within the gas zone in the Feixianguan Fm. The presence of a gas-water transition zone is not a prerequisite for the occurrence of TSR in this basin. There must have been sufficient residual water in the gas zones of Feixianguan Fm to allow diagenetic TSR to occur.

6. Conclusions

(1) Petroleum gas in the Lower Triassic Feixianguan Fm, East Sichuan Basin, was sourced from post-mature Upper Permian Longtan Fm alternating marine and terrestrial mudstone, coal and marl.

(2) Stable sulphur isotope, petrographic and lithological data demonstrate that up to ~17% H$_2$S in the Feixianguan Fm is the result of thermochemical sulphate reduction (reaction between petroleum fluids and sulphate) that occurred within the reservoir.

(3) Thermochemical sulphate reduction occurred by reaction of alkane gases, dominated by methane, with anhydrite. Liquid phase petroleum was not the main cause of TSR.

(4) In contrast to recent assertions about the reactivity of methane to sulphate, methane was the main reducing agent in the Feixianguan Fm as illustrated by gas compositional patterns and carbon stable isotopes.

(5) H$_2$S is only found at concentrations greater than 6% where the Feixianguan Fm occurs as dolomitic limestones or evaporite-bearing platform facies. Anhydrite in the caprock was not discernibly involved in TSR. Prediction of H$_2$S in the subsurface will require a detailed sedimentological facies distribution model and, ideally, a detailed understanding of the distribution of disseminated anhydrite in the Feixianguan Fm.

(6) H$_2$S is only found at high concentrations in reservoirs deeper than ~3000 m.

(7) Thermochemical sulphate reduction occurred at temperatures greater than ~130–140 °C although locally variable uplift means that present day depths of burial (see item above) must not be employed in a scheme to predict the abundance of H$_2$S in the subsurface. A basin-scale understanding of the burial and thermal history of the Feixianguan Fm is required to predict where high concentrations of H$_2$S are most likely.

(8) TSR occurred throughout the gas zones and was not limited to the gas–water transition zone as has been found in other sour gas provinces.

References

Baric, G., & Jungwirth, M. (1997). Gas souring by thermochemical sulfate reduction at 140 °C: discussion. *American Association of Petroleum Geologists Bulletin, 81*, 814–815.

Cai, C. F., Hu, W. S., & Worden, R. H. (2001). Thermochemical sulphate reduction in Cambro-Ordovician carbonates in Central Tarim. *Marine and Petroleum Geology, 18*, 729–741.

Cai, C. F., Mei, B. W., Ma, T., Chen, C. P., Li, W., & Liu, C. Q. (1997). *Approach to Fluid-Rock Interaction in Tarim Basin*. Beijing: Geological Publishing House. 155pp. (in Chinese).

Cai, C. F., Worden, R. H., Bottrell, S. H., Wang, L. S., & Yang, C. C. (2003). Thermochemical sulphate reduction and the generation of hydrogen sulphide and thiols (mercaptans) in Triassic carbonate reservoirs from the Sichuan Basin, China. *Chemical Geology*, *202*, 39–57.

Cai, C. F., Worden, R. H., Wang, Q. H., Xiang, T. S., Zhu, J. Q., & Chu, X. L. (2002). Chemical and isotopic evidence for secondary alteration of natural gases in the Hetianhe Field, Bachu Uplift of the Tarim Basin. *Organic Geochemistry*, *43*, 1415–1427.

Chen, J. S., & Chu, X. L. (1988). Sulfur isotope composition of Triassic marine sulfates of South China. *Chemical Geology*, *72*, 155–161.

Chen, M. (2001). New gas pools in the Sichuan Basin-Feixianguan oolitic shoal. *Natural Gas Industry*, *21*(2), 103 (in Chinese).

Claypool, G. E., Holser, W. T., Kaplan, I. R., Sakai, K., & Zak, I. (1980). The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. *Chemical Geology*, *28*, 199–260.

Connan, J., & Lacrampe-Couloume, G. (1993). The origin of the Lacq Supérieur heavy oil accumulation and the giant Lacq Intérieur gas field (Aquitaine Basin, SW France). In M. L. Bordenave (Ed.), *Applied Petroleum Geochemistry* (pp. 465–488). Paris: Tchnip.

Cross, M. M., Manning, D. A. C., Bottrell, S., & Worden, R. H. (2004). Thermochemical sulphate reduction (TSR): experimental determination of reaction kinetics and implications of the observed reaction rates for petroleum reservoirs. *Organic Geochemistry*, *35*, 393–404.

Gang, W. (2004). Three arrested in gas disaster. http://www1.chinadaily.com.cn/en/doc2004-01/12content_298001.htm.

Goldstein, R. H. (1986). Re-equilibration of fluid inclusions in low temperature calcium carbonate cement. *Geology*, *14*, 792–795.

Goodman, P.S. (2003). China seals well as toll rises in blast. http://www.mercurynews.com/mld/mercurynews/2003/12/27/news/world/7579962.htm.

Huang, J. Z., Chen, S. J., Song, J. R., Wang, L. S., Wang, T. D., Gou, X. M., & Dai, H. M. (1995). *Study on main source rock distribution and organic matter evolution in the carbonates in the Sichuan Basin—Key national project of China (9-102)*. Sichuan Petroleum Bureau and Xinan Petroleum Institute (in Chinese).

Huang, J. Z., Chen, S. J., Song, J. R., Wang, L. S., Gou, X. M., Wang, T. D., & Dai, H. M. (1997). Hydrocarbon source systems and formation of gas fields in Sichuan Basin. *Science in China Series D—Earth Sciences*, *40*, 32–42.

Jiang, X. F., Xu, R. F., & Huang, J. Z. (2002). Characteristics of hydrogen sulfide distribution in Feixianguan Formation gas reservoirs in East Sichuan. *Natural Gas Industry*, *22*(2), 24–27 (in Chinese).

Krouse, H. R., Viau, C. A., Eliuk, L. S., Ueda, A., & Halas, S. (1988). Chemical and isotopic evidence of thermochemical sulfate reduction by light hydrocarbon gases in deep carbonate reservoirs. *Nature*, *333*, 415–419.

Machel, H. G., Krouse, H. R., & Sassen, R. (1995). Products and distinguishing criteria of bacterial and thermochemical sulfate reduction. *Applied Geochemistry*, *8*, 373–389.

Machel, H. G. (1998). Gas souring by thermochemical sulfate reduction at 140 °C: discussion. *American Association of Petroleum Geologists Bulletin*, *82*, 1870–1873.

Machel, H. G. (2001). Bacterial and thermochemical sulfate reduction in diagenetic settings-old and new insights. *Sedimentary Geology*, *140*, 143–175.

Orr, W. L. (1974). Changes in sulfur content and isotopic ratios of sulfur during petroleum maturation-Study of Big Horn Basin Palaeozoic oils. *American Association of Petroleum Geologists Bulletin*, *50*, 2295–2318.

Orr, W. L. (1977). Geologic and geochemical controls on the distribution of hydrogen sulfide in natural gas. In R. Campos, & J. Goni (Eds.), *Advances in Organic Geochemistry 1975* (pp. 571–597). Oxford: Pergmon press.

Prezbindowski, D. R., & Larese, R. E. (1987). Experimental stretching of fluid inclusions in calcite-implications for diagenetic studies. *Geology*, *15*, 333–336.

Sassen, R. (1988). Geochemical and carbon isotopic studies of crude oil destruction, bitumen precipitation and sulfate reduction in the deep Smackover Formation. *Organic Geochemistry*, *12*, 351–361.

Sheng, P., Xu, Y., Wang, J., & Wang, L. (1997). Sulfur isotopic compositions of hydrogen sulphides in natural gases and the sedimentary geochemical facies. *Acta Sedimentologica Sinica*, *15*(2), 55–60 (in Chinese).

Tong, X. G. (1992). *Tectonic evolution and oil and gas accumulation in the Sichuan Basin*. Beijing: Geological Publishing Press. 128pp. (in Chinese).

Wang, J. X. (1996). Diagensis of ooid limestone and reservoir characteristic of the third member of Feixianguan Formation. *Natural Gas Industry*, *16*(2), 28–33 (in Chinese).

Wang, L. S., Zhang, J., & Xie, B. H. (2003). *A study on the generation mechanism and distribution of H2S and its relation to the formation of natural gas pools (internal report) Key laboratory on natural gas pool formation mechanism, Langfang, Heibei Province and Chengdu, Sichuan Province*. 95pp. (in Chinese).

Wang, X. Z., Zhang, F., Ma, Q., Yang, M. P., Wang, Y. G., Wen, Y. C., Yang, Y., & Zhang, J. (2002). The characteristics of reef and bank and the fluctuation of sea level in Feixianguan period of late Permian to early Triassic, East Sichuan Basin. *Acta Sedimentologica Sinica*, *20*(2), 349–352 (in Chinese).

Wang, Y. G., Dou, L. R., Wen, Y. C., Zhang, J., & Jiu, H. Y. (2002). Origin of Triassic Feixianguan Formation gas pools in Northeastern Sichuan Basin, China. *Geochimica*, *21*(6), 517–524 (in Chinese).

Worden, R. H., & Heasley, E. C. (2000). Effects of petroleum emplacement on cementation in carbonate reservoirs. *Bulletin de la Societe Geologique de France*, *171*, 607–620.

Worden, R. H., & Smalley, P. C. (1996). H2S-producing reactions in deep carbonate gas reservoirs: Kuff Formation, Abu Dhabi. *Chemical Geology*, *133*, 157–171.

Worden, R. H., & Smalley, P. C. (2004). Does methane react during thermochemical sulphate reduction? *Proof from the Khuff Formation, Abu Dhabi*. In R. Wanty, & R. R. Seal. *Water–Rock Interaction* 2004 (pp. 1049–1053). London: Taylor and Francis Group.

Worden, R. H., Smalley, P. C., & Cross, M. M. (2000). The influences of rock fabric and mineralogy upon thermochemical sulfate reduction: Khuff Formation, Abu Dhabi. *Journal of Sedimentary Research*, *70*, 1218–1229.

Worden, R. H., Smalley, P. C., & Fallick, A. E. (1997). Sulfur cycle in buried evaporites. *Geology*, *25*, 643–646.

Worden, R. H., Smalley, P. C., & Oxtoby, N. H. (1995). Gas souring by thermochemical sulfate reduction at 140 °C. *American Association of Petroleum Geologists Bulletin*, *79*, 854–863.

Worden, R. H., Smalley, P. C., & Oxtoby, N. H. (1997). Gas souring by thermochemical sulphate reduction at 140 °C: reply. *Association of American of Petroleum Geologists Bulletin*, *81*, 816–817.

Worden, R. H., Smalley, P. C., & Oxtoby, N. H. (1998). Gas souring by thermochemical sulphate reduction at 140 °C: reply (2). *Association of American of Petroleum Geologists Bulletin*, *82*, 1874–1875.

Xie, Z.Y. (2003). *Study on the mechanism and the pool-forming model of oolitic gas reservoir at Feixianguan Formation in northeast area of Sichuan basin*. PhD dissertation, Beijing: The Chinese University of Geology, 131pp. (in Chinese).

Xu, Y., Sheng, P., Liu, W., Tao, M., Sun, M., & Du, J. (1998). *Geochemistry of rare gas in natural gas*. Beijing: Science Press. 231pp. (in Chinese).

Yang, J. J., Wang, Y. G., Wang, L. S., Wen, Y. C., Liu, H. Y., & Zhou, G. Y. (2002). The origin of natural gases and geochemical characteristics of Changxing reef and Feixianguan oolitic beach gas reservoirs in East Sichuan Basin. *Acta Sedimentologica Sinica*, *20*(2), 249–252 (in Chinese).

Yang, Y., & Wen, Y. C. (2002). Control of Kajiang-Liangping trough growing on T_1f oolite distribution in Northeast Sichuan Basin. *Natural Gas Industry*, *22*(Suppl.), 30–32 (in Chinese).