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ORIGINAL PAPER

Impact of formation water on the generation of H_2S in condensate reservoirs: a case study from the deep Ordovician in the Tazhong Uplift of the Tarim Basin, NW China

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Abstract A number of condensate reservoirs with high concentrations of H_2S have been discovered in the deep dolomite reservoirs of the lower Ordovician Yingshan Formation (O_1y) in the Tazhong Uplift, where the formation water has a high pH value. In the O_1y reservoir, the concentrations of Mg^{2+} and SO_4^{2-} in the formation water are higher than those in the upper Ordovician formation. The concentration of H_2S in the condensate reservoirs and the concentration of Mg^{2+} in the formation water correlate well in the O_1y reservoirs of the Tazhong Uplift, which indicates a presumed thermochemical sulfate reduction (TSR) origin of H_2S according to the oxidation theory of contact ion-pairs (CIPs). Besides, the pH values of the formation water are positively correlated with the concentration of H_2S in the condensate reservoirs, which may indicate that high pH might be another factor to promote and maintain TSR. Oil–source correlation of biomarkers in the sulfuretted condensates indicates the Cambrian source rocks could be the origin of condensates. The formation water in the condensate reservoirs of O_1y is similar to that in the Cambrian; therefore, the TSR of sulfate-CIPs likely occurred in the Cambrian. High H_2S-bearing condensates are mainly located near the No. 1 Fault and NE-SW strike-slip faults, which are the major migration pathway of deep fluids in the Tazhong Uplift. The redox between sulfate-CIPs and hydrocarbons is the generation mechanism of H_2S in the deep dolomite condensate reservoirs of the Tazhong Uplift. This finding should be helpful to predict the fluid properties of deep dolomite reservoirs.

1 Introduction

Formation water has been conventionally taken as a kind of undesirable by-product in petroleum exploration and development, while it would be one of the most crucial factors in hydrocarbon generation, migration and accumulation as well as the interaction between organic and inorganic geo-fluids. Detailed analysis of the geochemical properties of formation water could indicate the hydrodynamic conditions for hydrocarbon accumulation and the geochemical alteration of reservoirs (Jiang and Zhang 1999; Cai et al. 2001; Zha et a1. 2003; Chen and Zha 2005, 2006a, b, 2008), which are of great geological significance for interpreting the reaction mechanisms between ions and hydrocarbons. And then, the origin of multi-phase reservoirs could be deduced from the secondary geochemical alteration (Land 1995; Davisson and Criss 1996; Varsanyi and Kovacs 1997; Su et al. 2011). Palmer (1984) published research on the hydrocarbon composition variation in carbonate reservoirs as a result of the formation water flowing across the reservoirs. In particular, dibenzothiophene would be mostly altered in its composition

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(Kuo 1994; Lafargue and Tluez 1996). In addition, high H$_2$S concentration from microbial activities around the oil–water contact would increase the acidity and density of crude oil, which negatively impacts on the commercial value of petroleum and as well as the safe exploitation and development of reservoirs.

With the extension of hydrocarbon exploration to deep dolomite rocks in recent decades in China, a large number of gas reservoirs with high H$_2$S have been discovered. In domestic and overseas investigations, high concentrations of H$_2$S have generally been attributed to the thermochemical sulfate reduction (TSR) between anhydrite and hydrocarbons (Worden et al. 2000; Jiang et al. 2015), during which liquid hydrocarbons are enriched with sulfur and the drying coefficient of gas reservoirs may exceed 99%. In actual geological conditions, the formation water could act as the reaction agent of TSR. In the Tazhong Uplift of the Tarim Basin, H$_2$S-bearing condensates have been discovered on a large scale in deep dolomite reservoirs, which differs greatly from the geochemical properties of normal condensate reservoirs around the world and also differs from gas reservoirs with high H$_2$S. Previous study of sulfur isotopes and concentration of individual sulfur compounds in the condensate reservoirs has shown that the condensate reservoirs with high H$_2$S may have experienced TSR (Jiang et al. 2008; Zhang et al. 2015). Various soluble sulfate species act as the initial oxidant of TSR, mainly including free sulfate ions (SO$_4^{2-}$) and bisulfate ions (HSO$_4^-$), solvent-shared ion-pairs (SIPs) and contact ion-pairs (CIPs) (Eigen and Tamm 1962; Atkinson and Petrucci 1966). Therefore, the salts of formation water may be critical to activate and affect TSR. Recently, a series of gold-tube hydrous pyrolysis experiments have been conducted to address the reaction mechanism and the factors affecting TSR, which include compositions of hydrocarbons, labile organosulfur compounds (LSC) and the early generated H$_2$S (Tang et al. 2005; Ellis et al. 2007; Amrani et al. 2008). Because the relative concentration of H$_2$S is not a reliable reaction parameter to access the reaction intensity of TSR (Ma et al. 2008; Jendu et al. 2015), a systematic study on the genetic relationship between water and mineral composition of the Ordovician formation and high sulfur condensates would avail to clarify the formation mechanism of high sulfur condensate in the actual geological conditions. These new insights could indicate the effect of ions in the formation water on the alteration of hydrocarbons in deep dolomite reservoirs, which would be useful to predict the fluid properties of deep stratum and promote the exploration of dolomite reservoirs.

2 Geological background

The Tarim Basin experienced three important stages of hydrocarbon accumulation, i.e., the later Eopaleozoic, the Neopaleozoic to the early Mesozoic, and the late Cenozoic (Zhang et al. 2011), each of which had great impacts on the accumulation and distribution of hydrocarbons in the marine reservoirs (Zhang and Huang 2005). The Tarim Basin has become a petroliferous basin which has undergone multistage secondary alterations (Sun and Püttmann 1996; Su et al. 2010; Sun et al. 2009a, b). The Tazhong Uplift, as an inherited paleo-uplift, is located in the central of the Tarim Basin and neighbors the Bachu Uplift in the west, the Tadong Low Uplift in the east, the Tangguzibasi depression in the south and the North depression in the north (Fig. 1). After the successful exploration in the reef and beach reservoirs of the upper Ordovician Lianglitage Formation (O$_3$l), a large-scale petroleum resource has been discovered in dolomite reservoirs of the Yingshan Formation (O$_1$y), in the lower Ordovician in the North Slope of the Tazhong Uplift. It has proved that the lower Ordovician dolomite reservoirs are mainly distributed and developed below an unconformity surface, about 120 m deep. The distribution of dolomite reservoirs is not controlled by structural highs/lows.

The dolomite reservoirs of the Yingshan Formation (O$_1$y) are characterized by various hydrocarbon and fluid phases, as well as large discrepancies in gas/oil ratio (GOR). Most high-yield wells produce large volumes of gas and condensate oil; in contrast, low-yield wells mainly produce crude oil with low GOR. Based on the PVT curve, the types of reservoirs in the Tazhong Uplift include unsaturated and saturated condensates, and unsaturated and saturated oil (Fig. 1), which are heterogeneously distributed across the Tazhong Uplift and are not controlled by structure and burial depth. The difference in reservoir phases indicates that the distribution of condensates in the whole Tazhong Uplift roughly correlates with the fluid properties and burial depth and the dolomite reservoirs are correlated with NE-SW faults.

3 Samples and methods

3.1 Collection of samples

In order to investigate the origin of H$_2$S, hydrocarbon samples of 13 wells in the Tazhong Uplift were collected (Table 1). The saturated and aromatic hydrocarbons were quantified by GC–MS, including steranes and hopanes, as well as thiophenes. Diamantanes were detected by
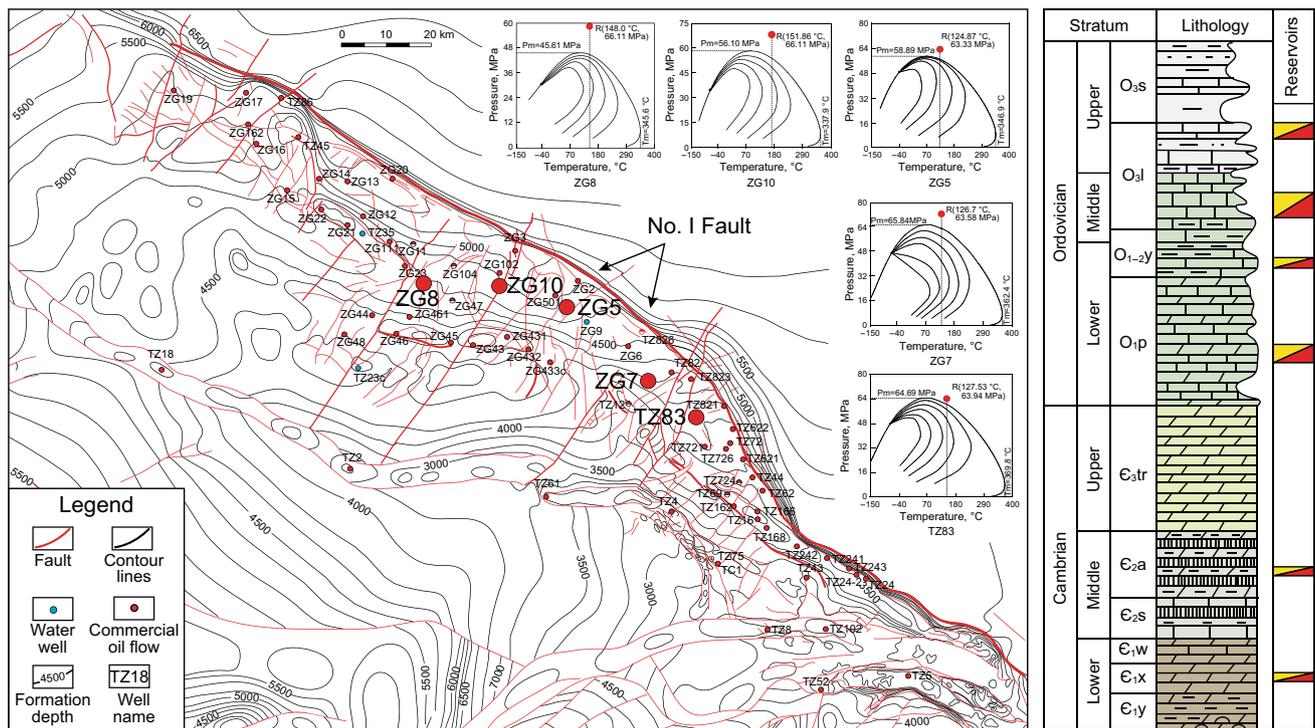
Fig. 1 Tectonic map of the Yingshan Formation and distribution of condensate reservoirs in the Tazhong Uplift

Table 1 Features of high sulfur condensate reservoir of Yingshan Formation in the Tazhong area

Well	Depth, m	H$_2$S content, mg/m^3	Bottom-hole		Critical condensate		Condensate oil content, g/m^3	Gas output, m^3/d
			Temperature, °C	Pressure, MPa	Pressure, MPa	Temperature, °C		
ZG14	6300	5103	141.80	72.51	62.40	361.1	305.6	130,921
ZG22	5736	2310	129.75	67.31	71.46	366.6	319.2	70,200
ZG12	6279	640	140.60	72.93	67.42	348.9	66.0	169,537
ZG11	6475	5300	141.39	73.88	60.73	332.6	376.1	95,540
ZG111	6250	3400	137.00	71.81	61.88	325.1	354.8	114,362
ZG8	6145	46,267	148.00	66.11	45.61	345.6	748.1	144,844
ZG441	5522	10,100	126.76	63.24	69.19	369.8	176.3	134,935
TZ201c	5779	20,700	126.68	63.58	65.84	362.4	195.0	74,270
ZG43	5334	36,537	124.87	63.33	50.89	346.9	451.6	83,679
ZG10	6309	36,540	151.86	68.11	56.10	337.9	386.9	218,703
ZG102	6287	77800	145.78	63.53	40.48	314.1	764.2	57,658
ZG103	6233	3867	140.30	71.58	50.29	327.0	378.5	74,366
ZG5	6460	49,480	150.60	75.09	51.02	297.3	312.2	130,518

H$_2$S content (mg/m^3) = the H$_2$S weight per m^3 condensate gas; condensate oil content (g/m^3) = the condensate oil weight per m^3 condensate gas

GC × GC to access the oil-cracking extent of hydrocarbons.

3.2 GC–MS analysis

GC–MS analysis was performed using a Trace GC Ultra gas chromatograph interfaced to a Thermo DSQII mass selective detector (MSD) for both saturated and aromatic hydrocarbon fractions. The HP-5 column is 30 m long × 0.25 mm ID × 0.25 µm thickness. Helium maintained at a constant flow rate of 1.0 cm^3/min was used as the carrier gas. The GC oven was programmed from 50 to 220 °C at 4 °C/min with an initial hold time of 5 min and then from 220 to 320 °C at 2 °C/min with a final hold time

of 25 min. Samples were injected in the splitless mode at a constant temperature of 300 °C. For quantitative determination of saturated and aromatic hydrocarbons, known concentrations of standard compounds (d4-cholestane and d10-anthracene) were added to the condensate and oil prior to the fractionation.

3.3 Diamondoid hydrocarbon analysis

For GC × GC-TOF–MS analysis, a whole condensate sample was dissolved in a solution of 5% dichloromethane (DCM) in *n*-hexane. Two Leco Pegasus 4D GC × GC systems were used in this study coupled with a TOF–MS and a FID, respectively. They were equipped with an Agilent 6890 N GC (TOF–MS) and an Agilent 7890A GC (FID system) and configured with a split/splitless auto-injector and a dual-stage cryogenic modulator. Two capillary GC columns were fitted in the GC. The first dimension chromatographic separation was performed by a nonpolar Petro-column (50 m × 0.2 mm I.D., 0.5 μm film thickness). The second column was connected to the TOF–MS instrument via a DB-17HT column (3 m × 0.1 mm I.D., 0.1 μm film thickness). Temperature was programmed for 35 °C (10 min) in the primary GC oven. Then, the temperature was increased to 60 °C at 0.5 °C/min and held for 0.2 min, from 60 to 220 °C at 2 °C/min and held for 0.2 min, followed by an increase at 4 °C/min to the final temperature of 300 °C and kept constant for 5.0 min. The secondary oven was programmed 20 °C above the primary GC oven gradient. The sample injection temperature was 300 °C with an injection volume of 0.5 μL. The carrier gas

was helium with flow rate of 1.8 mL/min. The modulation period was 10 s with a 3.0-s hot pulse duration. The TOF–MS instrument was operated in the electron impact mode (70 eV) with a range of 40–520 Da. The ion source temperature was 240 °C, the detector voltage was set at 1475 V, and the acquisition rate was 100 spectra/s.

Instrument control and data processing were done using ChromaToF (Leco) software and Microsoft Excel. The deconvoluted spectra were compared with the National Institute of Standards and Technology (NIST) software library for compound identification. The quantification of adamantanes was calculated by comparison with an internal standard of d16-adamantane, while the quantification of diamantanes required a linear correlation among the ratios of various diamantane standard concentrations to the constant d16-adamantane concentration.

3.4 Constituent analysis of formation water

We have reviewed more than 200 compositions of formation water in Tazhong Uplift, which were analyzed in the chemical laboratory of the Tarim Oilfield Company, in order to determine the origin of formation water in the condensate reservoirs. The analysis method for oil and gas field water is conducted to industry standard SY/T 5523-2000. As well, 14 formation water samples were collected to measure the concentration of ions at ambient temperature. Since the temperature of the reservoirs is mostly from 125 to 150 °C, the measured ionic concentrations had been converted to in situ conditions using thermodynamic modeling (Table 2).

Table 2 Concentrations of main ions in the condensate reservoirs converted to in situ geological condition by thermodynamic modeling

Wells	Formation	Depth, m	pH	Cl^-, mg/L	SO_4^{2-}, mg/L	Ca^{2+}, mg/L	Mg^{2+}, mg/L	Salinity, mg/L	H_2S, mg/m³
ZG9	O	6049.1	7.24	120,200	78	12,900	1420	197,700	616,000
ZG7	O	5865	7.81	102300	53	8890	532	168,100	47,500
ZG48	O_3	5498.1	6.85	88,030	400	7694	714	150,000	1000
ZG461	O	5479.64	6.24	56,990	891	19,800	810	6800	1300
ZG45	O_3	5637.2	7.33	42,100	894	4327	416	70,930	15,867
ZG44	O	5603.96	7.17	100,200	450	9635	770	169,500	10,600
ZG43	O	5380	8.21	6097	550	1576	1050	11,330	36,537
ZG26	O	6085.5	6.16	70,180	381	29,690	529	116,600	100
ZG164	O_3	6122.13	7.42	41,900	221	2014	399	72,020	7200
ZG163	O	6140	7.11	51,750	114	3364	461	85,210	6900
ZG162	O_1	6123	6.17	4624	1047	155	74	9607	21
ZG15-2	O_2	5918.5	7.11	63,510	209	4256	418	107,200	4900
ZG11	O_3	6165	6.83	64,570	97	3791	283	109,400	5300
ZG10	O_3	6198	6.91	107,000	31	11,900	772	179,200	36,540

4 Results and discussion

4.1 Geochemical features of high sulfur condensate reservoirs

For condensates in the O_1y reservoir of Tazhong Uplift, the burial depth is more than 5500 m. The reservoir temperature may rise beyond 130 °C with a gradient of 2.03 °C/100 m, and the pressure coefficient is 1.18. The reservoirs are weakly over-pressured (Table 1). The concentration of condensate oil in the reservoir is generally higher than 100 g/m^3 with a peak of 764.2 g/m^3 in well ZG102. According to the difference between formation pressure and dew point pressure, the condensates were classified as unsaturated (pressure difference > 0) and saturated reservoirs (pressure difference = 0). Most of the unsaturated condensates are distributed near strike-slip faults, while the saturated condensates are distributed far away from faults.

Another distinct feature of O_1y condensates is their high concentration of H_2S (Fig. 2), which is different from the condensate in the O_3l reservoirs around the Tazhong No. 1 structure. For the reservoirs around the Tazhong No. 1 fault, the concentration of H_2S correlates well with gas production. According to the previous literature (Zhang et al. 2015), the H_2S concentration in the condensate reservoirs of the Lianglitage Formation (O_3l) is presumed to originate from the charge of high-maturity gases in the late Himalayan (Zhao et al. 2009). In contrast, the H_2S in the condensates of the Yingshan Formation (O_1y) may have not dissolved and migrated in the gas phase. The production volume of formation water and the

concentration of H_2S in O_1y condensate reservoirs show that the high concentration of H_2S is correlated well with active formation water (Fig. 2). So, it is proposed that the origin of H_2S may be related to the geochemical properties of O_1y formation water. Therefore, a knowledge of the geochemical properties of formation water and the accumulation process of condensates will be essential to clarify the origin of H_2S in the condensates of deep dolomite reservoirs.

Previous studies confirmed that two sets of source rocks mainly developed in the Tarim Basin, which, respectively, developed in the Ordovician platform margin slope facies and Cambrian basin facies. The planktonic algae organic phase of Cambrian source rock is distributed in the eastern Manjia'er sag. A series of biomarkers (triaromatic dinosterane and 4-methyl-24-ethyl cholestane) indicating complex acritarchs, planktonic algae, such as diatoms and dinoflagellates, have been found in a large number of Cambrian source rocks. The mud mound organic facies of Ordovician source rock are mainly distributed in the platform edges and transition slopes. Some biomarkers of sponge and gloeocapsa, such as 24-norcholestane and 4-methyl-24-propyl cholestane have been detected in the lime-mud mounds (Zhang and Huang 2005). These molecular fossils have become an important marker of oil–source correlation in the Tarim Basin. Through the distribution of these special biomarkers in the condensates and normal oils in the Ordovician Yingshan Formation of Tazhong Uplift, the concentration of 4, 23, 24-trimethyl triaromatic dinosterane in the condensates was higher than that in the normal oils, while the concentration of
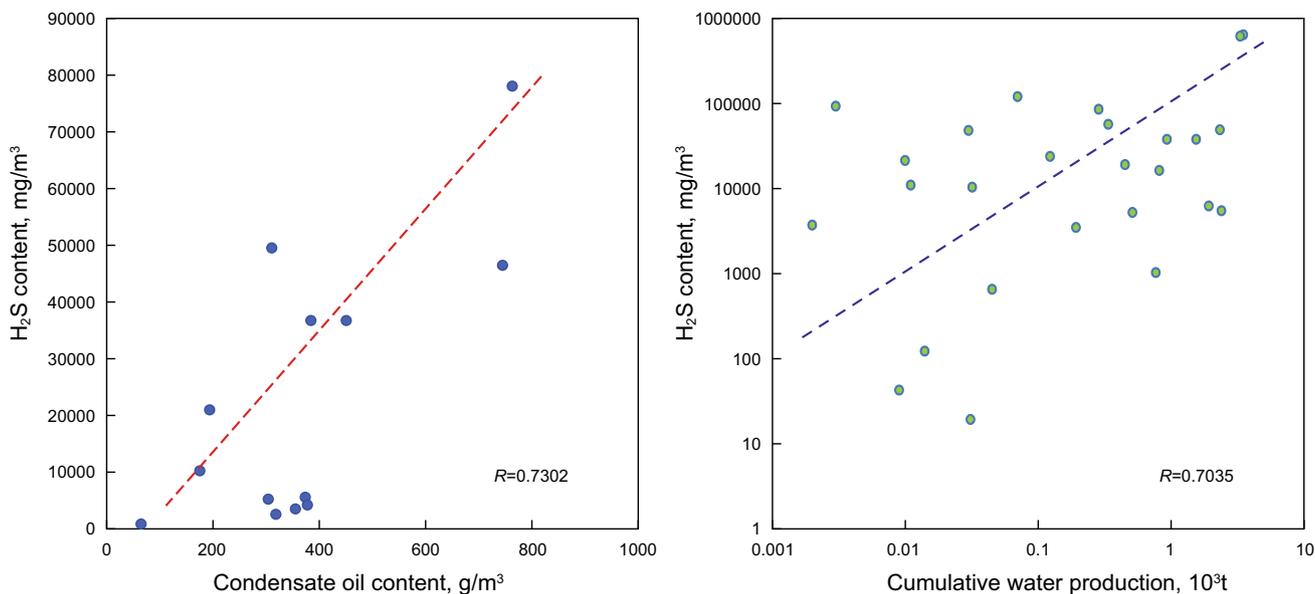

Fig. 2 Correlation between H_2S content and condensate oil content as well as cumulative water output of the Yingshan condensate gas reservoir in the Tazhong area

3-methyl-24-methyl triaromatic dinosterane in normal oils increases significantly (Fig. 3). This indicates that the condensates in the lower Ordovician Yingshan Formation (O_1y) of Tazhong Uplift mainly migrated from the deep Cambrian source rocks.

The exploration area around well ZG43 is one of the most hydrocarbon-rich tectonic zones in the Yingshan Formation (O_1y) and also one of the reservoirs with the highest H_2S concentration in the Tazhong Uplift. Well ZG43, for example, produced natural gas of 83,679 m^3 per day with a condensate concentration of 451.6 g/m^3 and an H_2S concentration of 36,537 mg/m^3. The condensate reservoirs distributed along strike-slip faults have high oil/gas yields and high GOR, while oil reservoirs located
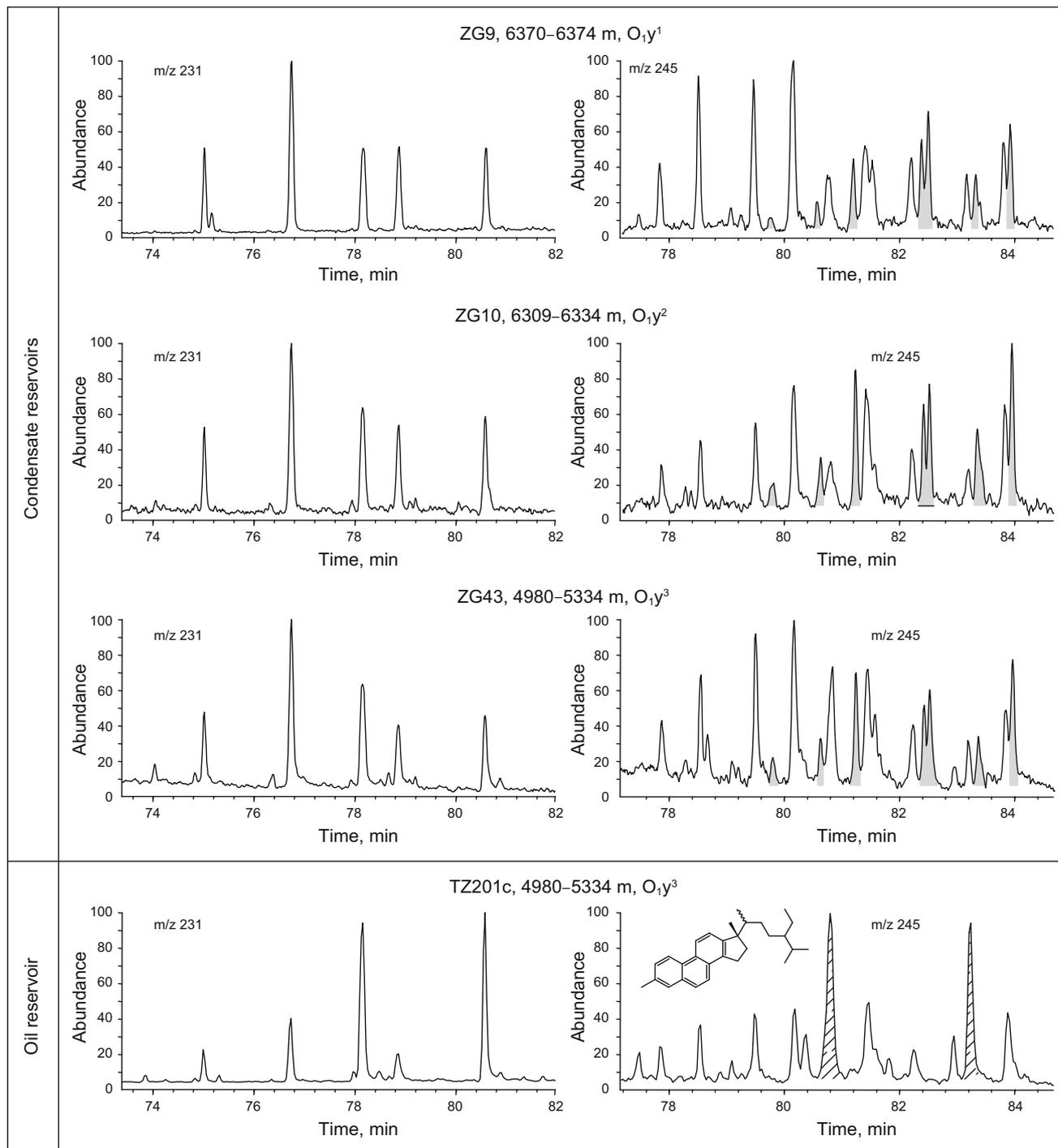

Fig. 3 Biomarker characteristics of multi-phase reservoirs in the lower Ordovician Yingshan Formation
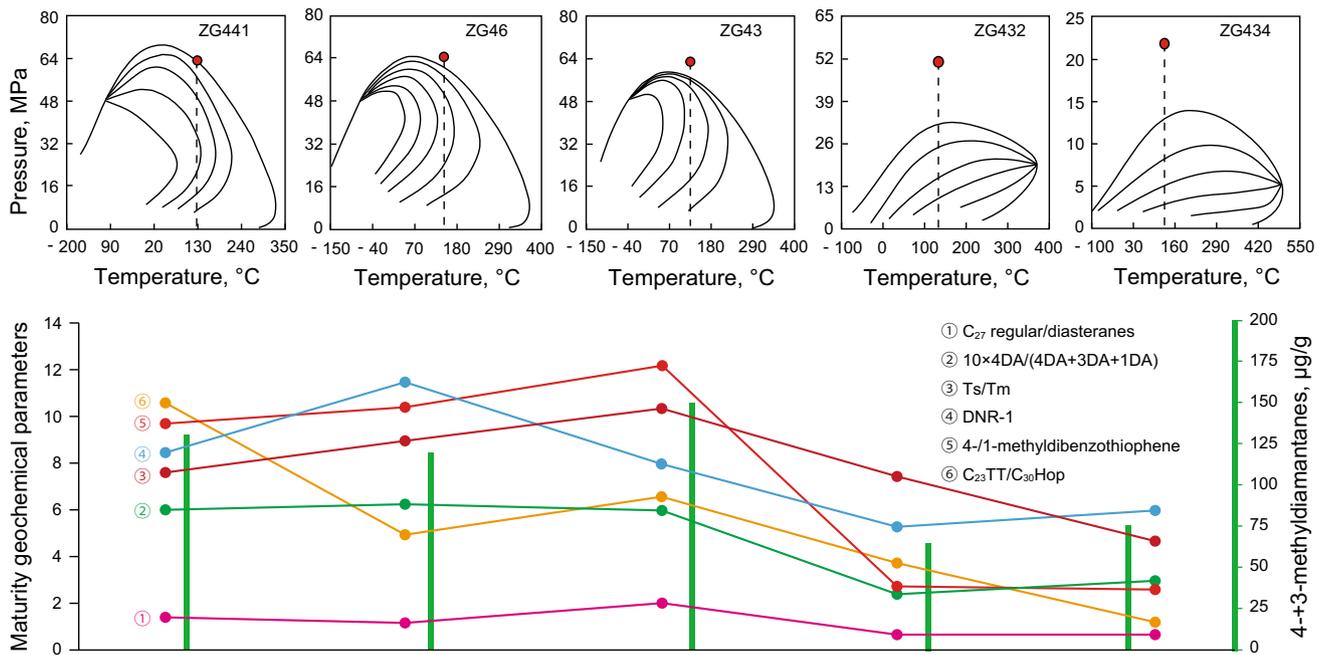
Fig. 4 Comparison of phase and maturity between condensate and normal oils in the ZG-43 block of the Yingshan Formation in the Tazhong Uplift

far away from faults have low oil/gas yields and low GOR. This indicates that the strike-slip faults might act as pathways for gas charging. The intensity of gas charging has been proved to be main mechanism by which the early oil reservoir transferred to the coexisting condensate and oil reservoirs (Zhang et al. 2011). The analysis on the relative concentrations of individual compound in condensates shows that the maturity of condensates is evidently higher than that of the oils (Fig. 4). In particular, the concentration of diamantanes reflects the extent of oil cracking (Dahl et al. 1999; Zhang et al. 2011). The concentration of diamantanes is 150 µg/g in the condensates of well ZG43 with an H_2S concentration of 36.537 mg/m^3, which is much higher than that in conventional oil. So, it is indicated that high concentrations of H_2S may originate from oil cracking or thermal chemical alteration, which have also led to the higher maturity of condensates compared with conventional oil.

The oil cracking commonly includes two main processes, i.e., thermal cracking of oil and thermochemical sulfate reduction (TSR). It is revealed that the well bottom temperature of O_1y condensate reservoirs does not exceed 160°C. Previous research considered that thermal cracking would not occur unless the temperature exceeds at least 190°C (Price 1980; Zhang et al. 2008). So, it could be concluded that the high maturity of condensates and high concentration of H_2S in the O_1y reservoirs were not due to liquid hydrocarbon thermal cracking. So, it can be inferred that the high concentration of diamantanes and H_2S in the condensate reservoirs is likely to derive from the TSR.

Further detailed analyses on the composition of the Ordovician formation water would be needed to diagnose whether the geochemical conditions in the Tazhong Uplift were suitable to trigger the TSR and accumulate H_2S of TSR-origin.

4.2 Relationships between H_2S-origin and formation water in the condensate reservoirs

According to the statistics, the formation water of the lower Ordovician—Cambrian differs from that of the upper Ordovician in the concentration of principal ions (Fig. 5). In particular, the concentrations of SO_4^{2-} in the O_3l formation water are higher than those in the lower Ordovician—Cambrian formation water. On the contrary, the Mg^{2+} concentration is higher in the formation water of O_1y-Cambrian. Both of SO_4^{2-} and Mg^{2+} are significant for thermochemical sulfate reduction (Zhang et al. 2011). It has been noted that the SO_4^{2-} commonly exists in the form of contact ion-pairs, which are the actual oxidant of TSR at geological temperatures. The decrease in SO_4^{2-} concentration in the lower Ordovician to Cambrian formation water may be due to the consumption of SO_4^{2-} in the TSR (Su et al. 2016). The concentration of Mg^{2+} and Ca^{2+} is lower than 1.1 and 20 g/L in the upper Ordovician formation water and much higher in the lower Ordovician to Cambrian formation water. In particular, the concentration of Mg^{2+} goes up beyond 1.5 g/L, which is proposed to activate TSR in actual geochemical conditions. Therefore,
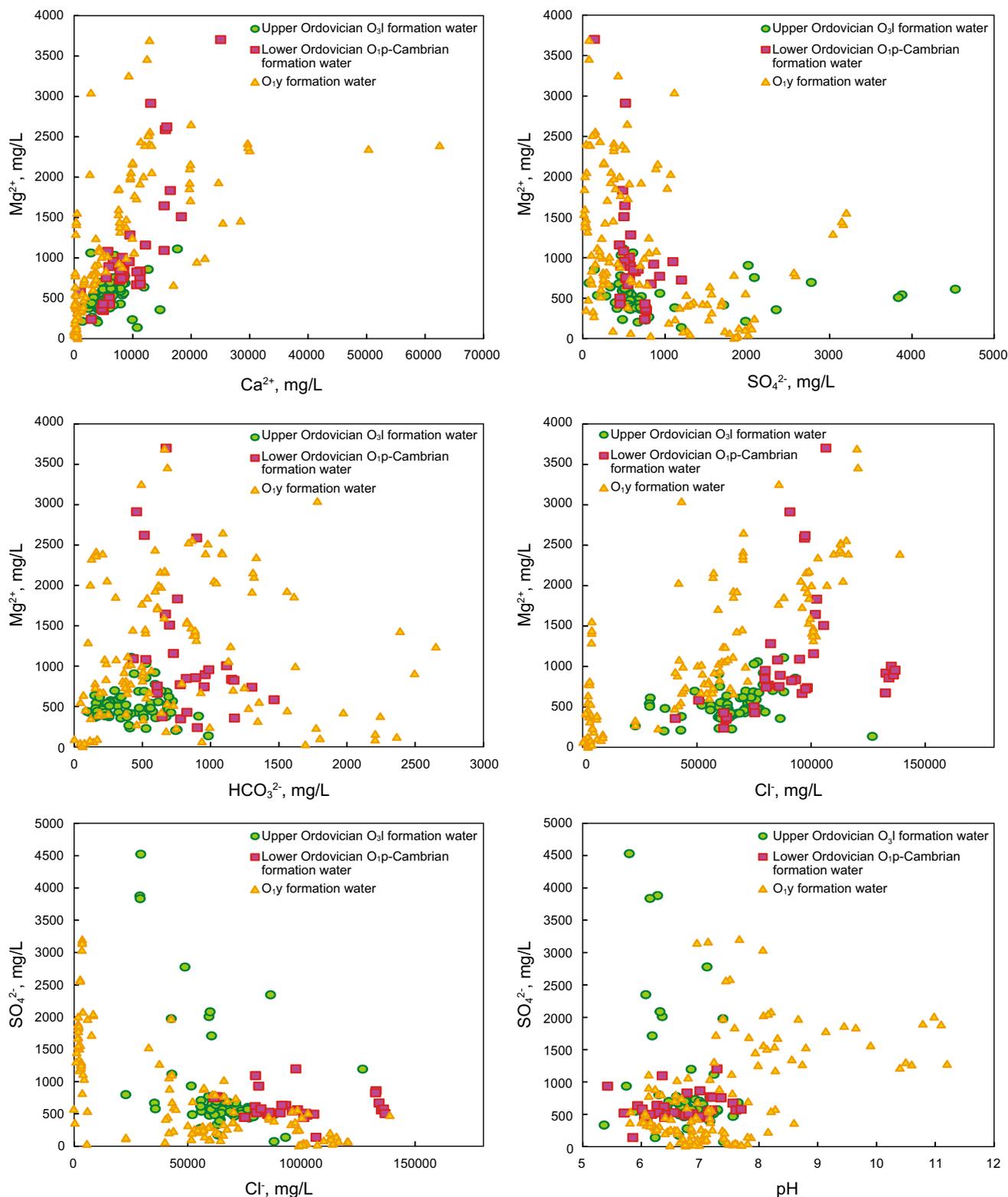
Fig. 5 Comparison of formation water ion concentration between the upper Ordovician Lianglitage Formation and the lower Ordovician Penglaiba Formation—Cambrian in the Tazhong Uplift
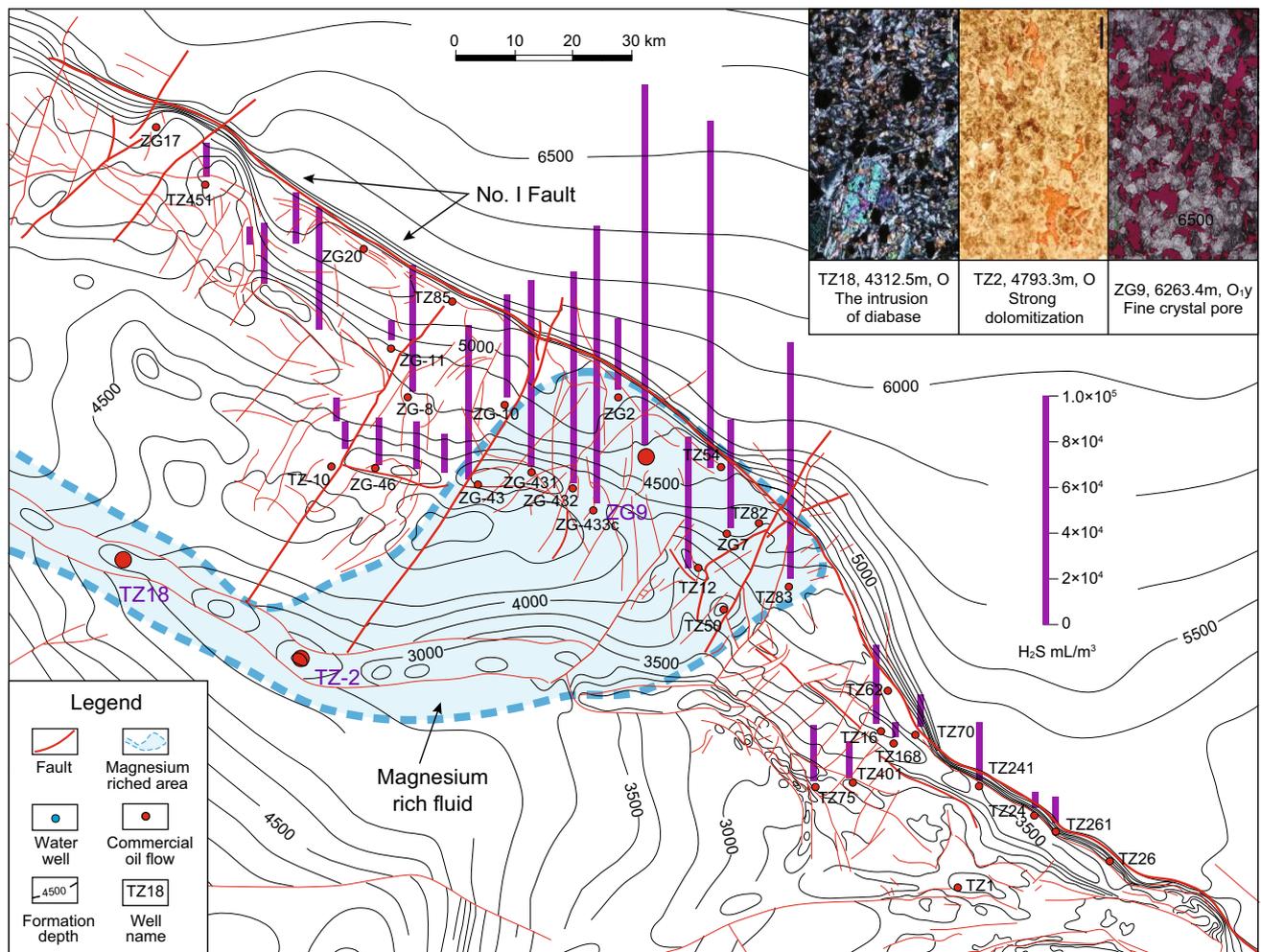
Fig. 6 Relationship between the content of H_2S in the condensate reservoirs and Mg^{2+}-enriching fluid in the Ordovician of Tazhong Uplift

the deep dolomite reservoirs of lower Ordovician could provide a favorable setting for TSR.

The Tazhong Uplift has experienced multi-period hydrothermal invasion and dolomitization. So that Mg^{2+} is rich in the formation water of the tectonic area experiencing strong dolomitization and hydrothermal activity, which provides the geochemical conditions for the TSR of sulfate-CIPs in the Tazhong Uplift. Intrusive diabases are seen in well TZ-18, strong dolomitization happened in well Tazhong-2, and a number of fine crystalline porous dolomites have been found in the lower Ordovician Yingshan Formation of well ZG-9 (Fig. 6). The most active region of magnesium-rich fluid was mainly located in the Tazhong Uplift and the middle section of the No. 1 fault zone (Fig. 6). On the other hand, the highest concentration of H_2S in the Tazhong area is also mainly distributed in the same zone as the magnesium-rich fluid. The concentration of H_2S was more than 5% (m^3/m^3), coinciding with the region of reservoirs with strong dolomitization (Fig. 6).

This indicates a very close relationship between the formation of H_2S and the activity of Mg^{2+}-enriching fluid in the lower Ordovician Yingshan Formation.

4.3 The formation mechanism of high H_2S in the condensate reservoirs

The production data have shown that the concentration of H_2S is not clearly related to the gas volume of condensate reservoirs in O_1y reservoirs, but correlated to the volume of formation water and the content of condensates. In the condensate reservoirs of Well-ZG7 and ZG9 blocks with the highest production volume of formation water, the H_2S concentration is up to 600 g/m^3 (Table 3). Through comparing the properties and distribution of formation water in the Tazhong Uplift, it is found that the formation water in the O_1y dolomite reservoirs connects with the fluids in the Cambrian formations. The Tazhong No. 1 fault and strike-slip faults of Tazhong Uplift may act as the major

Table 3 Statistics of fluid production and H_2S content in the Yingshan condensate reservoir of the Tazhong Uplift

Well	Formation	GOR, m^3/m^3	Output			H_2S content, mg/m^3
			Oil, 10^3t	Water, 10^3t	Gas, 10^3t	
ZG9	O_1y^1	0	0.000	3.497	0.256	616,000
ZG501	O_1y^1	237	8.392	0.000	0.283	32,200
ZG51	O_1y^2	1500	1.791	0.337	0.269	55,100
ZG6	O_1y^1	245	1.521	3.310	0.037	593,000
ZG7	O_1y^2	2024	3.503	2.332	0.594	47,500
ZG10	O_1y^2	2372	28.984	0.931	6.616	36,500
ZG102	O_1y^1	1688	1.403	0.000	0.195	77,800
ZG103	O_1y^1	2049	8.448	0.000	1.723	3870
ZG11	O_1y^2	3300	8.771	2.398	2.586	5300
ZG111	O_1y^2	2815	18.089	0.193	5.126	3400
ZG12	O_1y^2	13,500	0.029	0.045	0.040	640
ZG13	O_1y^1	185	10.596	1.921	0.594	6080
ZG14	O_1y^2	1800	8.536	0.512	1.526	5100
ZG14-1	O_1y^2	3064	4.849	0.002	1.955	3600
ZG21	O_1y^2	886	0.057	0.031	0.005	19
ZG22	O_1y^2	2300	3.385	0.123	0.671	23,100
ZG23CH	O_1y^2	0	1.282	0.009	0.047	42
ZG8	O_1y^2	1168	18.97	0.030	2.409	46,300
TZ201C	O_1y^3	3900	2.881	0.010	1.144	20,700
ZG43	O_1y^3	1205	26.556	1.545	3.689	36,500
ZG431	O_1y^3	589	7.627	0.286	0.458	82,100
ZG432	O_1y^3	176	6.054	0.003	0.102	89,400
ZG433C	O_1y^3	307	16.197	0.07	0.368	116,000
ZG441	O_1y^3	3008	2.939	0.032	0.962	10,100
ZG44C	O_1y^3	3260	0.073	0.011	0.024	10,600
ZG45	O_1y^3	778	7.079	0.817	0.583	15,900
ZG46	O_1y^3	10,572	0.609	0.451	0.641	18,400
ZG462	O_1y^3	1924	7.274	0.014	1.329	120
ZG48	O_1y^4	4294	0.860	0.767	0.373	1000

migration pathway for the formation water in gas condensate reservoirs, and contribute high H_2S in the condensate reservoirs around the faults.

Much previous research has proved TSR between hydrocarbons and sulfate could induce oil-cracking processes in actual geological conditions (Worden and Smalley 1996; Wei et al. 2012). It is generally agreed that the sulfate contact ion-pair would be the dominant mechanism to trigger thermochemical sulfate reduction (Rudolph et al. 2003; Amrani et al. 2008). So, samples of formation water were collected to test the concentration of ions at ambient temperature. Then, the measured ionic concentrations had been converted to in situ conditions by thermodynamic modeling, in order to discuss the TSR reaction mechanism with the oxidant of sulfate-CIPs in the highly sulfuretted condensate reservoirs (Table 3). Mg^{2+} with high ionic strength is encircled completely by water molecules in aqueous systems, so SO_4^{2-} could not be bound with Mg^{2+} directly and would form contact ion-pairs (CIPs) to accelerate TSR reactions (Azimi et al. 2007; Leusbrock et al. 2008). Based on the theory of CIPs, good correlation between the concentration of H_2S and Mg^{2+} in formation water (Fig. 7) has indicated the TSR-origin of H_2S in the condensate reservoirs. In addition, the concentration of principal negative ions, i.e., Cl^- and HCO_3^-, is separately lower than 100 and 1.0 g/L in the upper Ordovician formation water and higher than 100 g/L and 1.0 g/L in the lower Ordovician—Cambrian formation water. It has shown that the concentration of H_2S in the O_1y gas condensates has increased with the alkalinity of formation water (Fig. 7), which demonstrated that the pH of formation water may drop down in the process of forming CIP from magnesium sulfate (He et al. 2014). Alkaline formation water would guarantee the rightward reaction
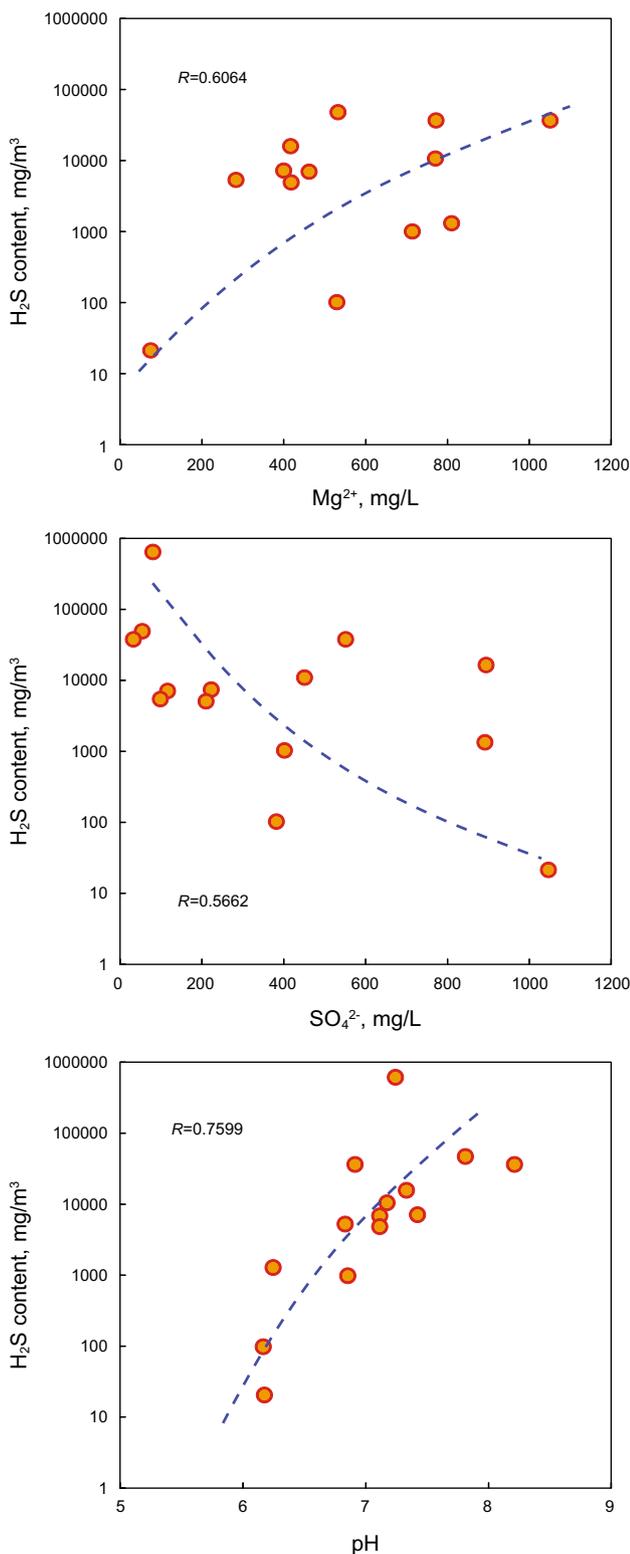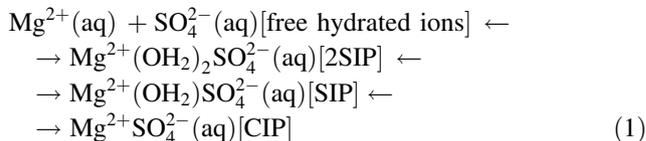
Fig. 7 Scatter point correlation between H$_2$S content in condensate reservoirs and ion concentration of underground water

expressed in Eq. (1) to generate sufficient ion-pairs and activate reaction in Eq. (1) as well to produce sulfate with various structures which would promote the TSR reaction

to form H$_2$S in large amounts. Therefore, it could be inferred that TSR with sulfate-CIPs might also occur in the deep Cambrian dolomite reservoirs.

$$
\begin{aligned}
\mathrm{Mg^{2+}(aq)} + \mathrm{SO_4^{2-}(aq)}[\text{free hydrated ions}] \; &\leftarrow \\
\rightarrow \mathrm{Mg^{2+}(OH_2)_2SO_4^{2-}(aq)}[2\mathrm{SIP}] \; &\leftarrow \\
\rightarrow \mathrm{Mg^{2+}(OH_2)SO_4^{2-}(aq)}[\mathrm{SIP}] \; &\leftarrow \\
\rightarrow \mathrm{Mg^{2+}SO_4^{2-}(aq)}[\mathrm{CIP}] \quad &(1)
\end{aligned}
$$

With the initiation of TSR, the concentration of H$_2$S increases and concentration of SO$_4^{2-}$ decreases. Therefore, it could be demonstrated that H$_2$S in the condensates of lower Ordovician dolomite reservoirs does originate from redox reaction between hydrocarbons and sulfate-CIPs.

5 Conclusions

The condensates in the dolomite reservoirs of the lower Ordovician in the Tazhong Uplift are generally characterized by various properties and phases of hydrocarbons. The concentration of H$_2$S in the condensate reservoirs increases with the production volume of formation water. Both the Mg^{2+} concentration and pH in the O$_1$y formation water are all higher than those in the upper Ordovician reservoirs and correlate well with the H$_2$S concentration in the gas condensate reservoirs. The decrease in SO$_4^{2-}$ concentration in the O$_1$y condensates is due to the consumption of SO$_4^{2-}$ during TSR, which is the formation mechanism of H$_2$S in the O$_1$y condensates. The pH values of the formation water are positively correlated with the H$_2$S concentration in the condensate of the lower Ordovician dolomite reservoirs, which shows that high alkalinity of the formation water is another important factor to initiate and promote the TSR of sulfate-CIPs. It is thus inferred the deep dolomite reservoirs have favorable geological conditions for TSR. The properties of the formation water in the Cambrian are similar to those of the high H$_2$S-bearing condensate in the O$_1$y reservoirs. This indicated that the sulfur condensates of the O$_1$y reservoirs originated from the Cambrian source rocks based on triaromatic dinosterane and 4-methyl-24-ethyl cholestane. Therefore, it can be inferred that the H$_2$S concentration of Cambrian dolomite reservoirs might be higher than that of the O$_1$y reservoirs.

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