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Research Article

Occurrence and Origin of H_2S from Volcanic Reservoirs in Niudong Area of the Santanghu Basin, NW China

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A series of samples including natural gas, formation water, and rocks were collected from volcanic rock reservoirs in the Niudong area of the Santanghu Oilfields and analyzed for their mineral and/or chemical compositions and sulfur and carbon isotopes in order to investigate the occurrence and origin of hydrogen sulfide (H_2S). H_2S was mostly dissolved in the formation water along with petroleum production in the study area. The $\delta^{34}S$ values of on-well H_2S samples varied in a range of 9.2‰ to 20.5‰, probably indicating thermochemical sulfate reduction (TSR) and/or thermal decomposition of organic sulfur-bearing compounds (TDS) as the genetic process for H_2S. However, the chemical composition of formation waters from the Kalagang Formation (C_2k) and their coefficient of desulfurization also revealed that TSR could be the main principle for H_2S formation. Considering the regional geological background, especially the tectonic structures and thermal evolution features of the basin, it was concluded that H_2S in the study area was dominantly produced by thermal genesis with TSR as a domain through interactions between hydrocarbons and aqueous sulfate dissolved from sulfate minerals.

1. Introduction

Hydrogen sulfide (H_2S) is one of the most perilous constituents of natural gases and also hazardous in several aspects such as diluting the proportion of hydrocarbons in natural gas, gravely altering its economic vitality, and being extremely lethal and corrosive to equipment used for oil and gas exploration and development [1, 2]. It is significantly important to study and get a better understanding of H_2S's occurrence and its origin for the reduction of health-related risks and to ensure safety, proper management of reservoirs, suitable construction facilities, and drilling-well design [3–5]. According to the literature, there are four major sources in geology for H_2S from a viewpoint of genesis: (1) inorganic (volcanic) source [6], (2) bacterial sulfate reduction (BSR) [7, 8], (3) thermal decomposition of organic sulfur-bearing compounds (TDS) in oil or kerogen [5, 9], and (4) thermochemical sulfate reduction (TSR) [7, 10, 11]. Inorganic (volcanic) H_2S genesis always occurs through volcanic activities and leads to a higher concentration of H_2S, whose sulfur isotope is normally in a range of −1‰ to −6-7‰ V-CDT [6, 11]. BSR is the typical and important source of H_2S genesis in sediments and many gas and oil reservoirs, being common in a low proportion of H_2S contribution (sulfur

concentration < 3–5%). The BSR source for H_2S genesis is generally considered to be active at temperatures below 80–100°C, and their sulfur isotopic ratios are mostly in a range of -5‰ and +5‰ V-CDT [7, 8, 11]. TDS normally takes place in the heating periods of organic matters and following petroleum formation. However, the H_2S contribution of TDS is very low and the isotopic ratios of sulfur range from 4‰ to 12‰ V-CDT, being always related to the secondary recovery of petroleum by using steam and/or hot water [7, 11]. Finally, the most influential source for H_2S production is TSR, contributing massive proportions of H_2S in natural gases and presenting in numerous petroliferous basins and even in some metal sulfide deposits [5, 7, 9, 12, 13]. Their sulfur isotopic ratios are normally between 8‰ and 25‰ V-CDT [3, 14]. The TSR reactions often occur along with interactions between hydrocarbons and aqueous sulfate which is always derived from the dissolution of sulfate minerals (primarily anhydrite and also barite and celestite). Both experimental studies and field inspections have revealed that the TSR process was kinetically practicable at outset temperatures > 10 $0^{\circ}C$. Suitable temperature and pH values are the important essential factors to control the reaction rate and degree of TSR [8, 15–21]. A common chemical reaction of TSR can be summarized as follows [22].

$$\text{sulphate} + \text{petroleum} \longrightarrow \text{calcite} + H_2S \pm H_2O \pm CO_2 \pm S \pm \text{altered petroleum} \quad (1)$$

With the progression of petroleum exploitation, unconventional oil and gas resources are the vital sources for exploration. Besides clastic and carbonate rocks, volcanic rocks as reservoirs are a potential target for oil and gas exploration as well in recent times [23]. Therefore, in the current scenario, the occurrence and origin of H_2S in volcanic reservoirs should be an important topic for exploration and as a supplement to the basic theory. About 100 ppm of H_2S was found in several wellheads in the Niudong area, Santanghu Basin, during the oil and gas development in 2010. Since then, growing concerns on the influence of H_2S on workers' health have led to the study on H_2S and measures were set up to reduce the negative influences on health and equipment. However, before controlling H_2S in these reservoirs, its occurrence and origin should be properly revealed. Therefore, a series of samples, including oil and gas, formation water, drilling core rocks, and on-well H_2S precipitant were collected and analyzed for this purpose.

2. Geological Settings

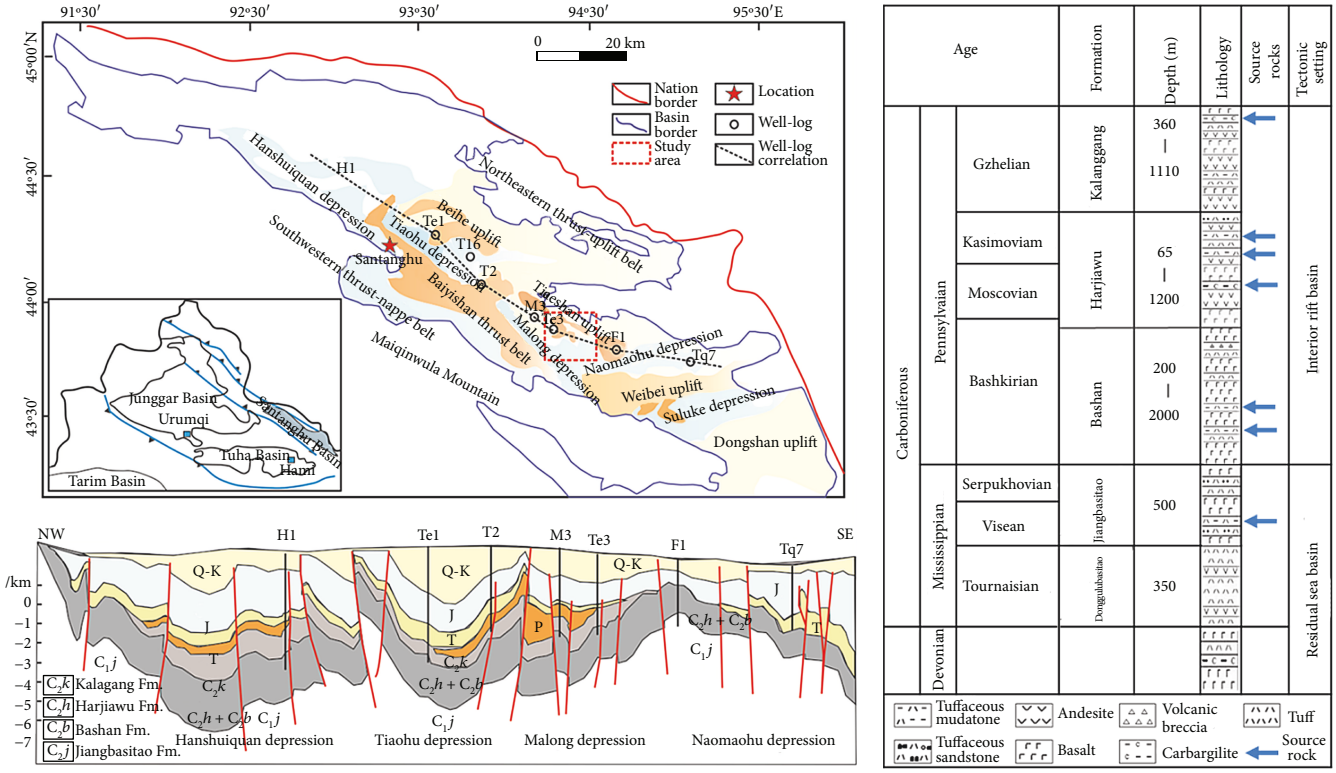
The Santanghu Basin, bordered by the Junggar Basin to the west, the Tuha Basin to the south, and the Mongolia Gebi to the northeast, is a special petroleum-bearing basin with volcanic rocks as reservoirs in NW China (Figure 1(a)). The basin in an area of $2.3 \times 10^4\,km^2$ and with accumulative petroleum reserves of more than 3×10^8 tons has been discovered at present. Since the initial formation in the Silurian period, this basin has experienced several tectonic movements, inducing well-developed regional faults and strongly weathered local rocks [23–25]. Volcanic eruptions frequently occurred in and around the basin during the late Palaeozoic era which probably produced some fracture channels by faulting. However, the process of volcanism was extremely intensive during the Middle Permian period. A basalt layer in a thickness of 200–600 m was developed in several parts of the basin, mainly due to crustal thinning, lithospheric subsidence, and asthenosphere upwelling [25]. The present tectonic units of the Santanghu Basin can be divided into the northern thrust uplift zone, central depression zone, and southern thrusting nappe zone. The Niudong area belongs to the central depression in the front edge of the Tiaoshan uplift and pitches the Malang depression in the northwest-southeast direction with an area of $260\,km^2$.

The Carboniferous sequences in the study area can be classified into five formations (from bottom to top, Figure 1(b)): the Donggulubasitao Formation (C_1d), Jiangbasitao Formation (C_1j), Bashan Formation (C_2b), Harjiawu Formation (C_2h), and Kalagang Formation (C_2k). The Kalagang Formation is primarily composed of fundamental intermediate volcanic lava that is incorporated within basalt, andesite, and transitional rock types [24]. Beneath the Kalagang Formation is the Haerjiawu Formation which contains hydrocarbon source rocks. Hydrocarbons from these source rocks migrated vertically into the weathered volcanic crust through faults. Reservoirs developed oil wells in the areas where there were abundant faults, and the hydrocarbons are distributed mainly in the weathered volcanic crust near the faults. The volcanic rocks of the Haerjiawu Formation alternate with source rocks. Hydrocarbons were generated from these source rocks, migrated into the weathered volcanic crust directly or through the faults, and then accumulated to construct the petroleum reservoir in the study area [23].

The maximum burial depth of the Kalagang Formation reached 1637 m in the study area, and the present strata temperature is about 55°C [26]. Since the Santanghu Basin is just located at the junction of several major tectonic belts such as the Tianshan and Altai Mountains tectonic zones, the geothermal conditions should be changed in geological evolution history. The ancient geothermal gradient could be higher than that at present [27]. The geothermal history of the study area indicates the Middle Permian magmatism which caused locally thermal anomalies, and both the Late Indosinian movement (Late Triassic and Early Jurassic period) and Late Yanshan movement (Late Jurassic period) contributed to the increase of ancient geothermal gradients in the basin and led to the maturation of organic matters in the source rocks [26]. The temperature in oil and gas reservoirs of the Kalagang Formation (C_2k) reached more than 110°C during the Permian-Triassic period [26, 27].

3. Samples and Analysis

3.1. Sample Collection. Seventeen rock samples were selected from drilling cores of the Niudong area for the present study on geochemical and mineralogical characteristics of the volcanic rocks (Table 1). All the cored samples were rocks in the reservoir of Kalagang formation (C_2k), including 9 basalts, 4 andesites, 2 volcanic breccia, and 2 tuff samples.



(a) (b)

Figure 1: (a) Location of the study area, structure units, and section map of the Santanghu Basin. (b) Lithological column and sedimentary evolution of the Carboniferous (modified after Song et al. [24]).

Table 1: General property of study samples from the Kalagang Formation in the Santanghu Basin.

Sample no.	Depth (m)	Description
NDYX-01	1401.59-1401.80	Dark grey basalt
NDYX-02	1402.25-1402.39	Dark grey basalt with oil infected
NDYX-03	1403.38-1403.51	Tauro fluorescence basalt
NDYX-04	1410.81-1411.07	Tauro fluorescence basalt
NDYX-05	1416.44-1416.59	Purple basalt
NDYX-06	1420.84-1420.94	Brown basalt with oil infected
NDYX-07	1423.48-1423.62	Greyish-green breccia
NDYX-08	1429.38-1429.61	Purple oil spot andesite
NDYX-09	1429.61-1429.72	Purple oil spot andesite
NDYX-10	1430.05-1430.20	Purple oil spot andesite
NDYX-11	1433.82-1433.91	Taupe oil spot basalt
NDYX-12	1437.36-1437.51	Purple oil spot andesite
NDYX-13	1439.38-1439.49	Greyish-green breccia
NDYX-14	1444.68-1444.85	Brown-grey fluorescent basalt
NDYX-15	1447.23-1447.37	Brown-grey fluorescent basalt
NDYX-16	1508.63-1508.75	Taupe tuff
NDYX-17	1509.48-1509.56	Taupe tuff

The basalts were characterized by greyish-green and brownness and contained oil spots, air holes, and cracks. The andesites contained few and small purple oil spots and holes. The volcanic breccia and tuff were pyroclastic rocks with

Table 2: General properties of fillings in the crack of core samples obtained from the Kalagang Formation in the Santanghu Basin.

Sample no.	Depth (m)	Filling feature	Core
NDCT-01	1457.56-1457.68	Taupe	Dark grey basalt
NDCT-02	1552.85-1553.00	Transparent	Greyish-green basalt
NDCT-03	1540.69-1540.93	Greyish-green	Grey-brown basalt
NDCT-04	1508.63-1508.75	White	Taupe tuff
NDCT-05	1509.48-1509.56	White vein	Taupe tuff
NDCT-06	1430.05-1430.20	Milky white	Purple andesite

greyish-green and taupe, respectively. Six samples with clear veins were selected, and the vein fillings were extracted by indoor drilling for sulfur and carbon isotope analysis (Table 2 and Figure 2). The veins were in white color and transparent, some of which were characterized in an *X*-type of joints.

The samples for H_2S isotopes were obtained from twelve production wells and one gas gathering station. For sampling, the mixture of natural gases was introduced into a pre-prepared cadmium acetate solution (Cd $(CH_3COO)_2 \cdot 3H_2O$), and then the precipitant of cadmium sulfide (CdS) was collected in situ by filtration for laboratory analysis.

3.2. Analytical Methods. All the rock samples without chemical pretreatment were crushed into powder by using an agate mortar and pestle. Mineralogical measurements were carried

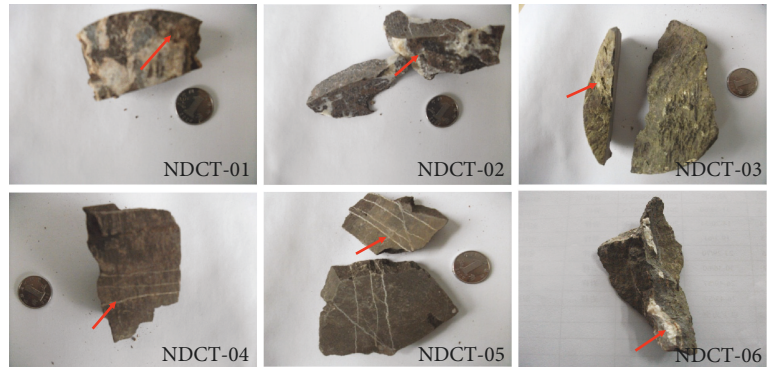


Figure 2: Photos showing the veins of cored samples.

out by the powder X-ray diffraction (XRD) method, using a D/Max-3B X-ray diffraction (XRD) Bruker diffractometer equipped with a graphite monochromator and operated at 40 kV and 100 mA using Cu Kα radiation. A small portion of finely powdered sample crushed again in a clean mortar was properly mounted on a plastic holder (ϕ25 mm, depth 1 mm). Scanning of samples was performed over an interval of 2–60° (2θ) at a scanning speed of 2°/min for every 0.03° (2θ) step. Divergence, scattering, and receiving slits were 0.5°, 0.5, and 0.10 mm, respectively.

Sulfur K-edge XANES analysis of well-crushed either cored rock or drilled vein samples were performed at beamline 4B7A of the Beijing Synchrotron Radiation Facility (BSRF), Beijing. Both the beam path and samples were positioned in a vacuum to overcome the scattering of X-ray and their absorption by air when the crushed samples were exposed to the X-ray beam with an incident angle of 45°. The X-ray fluorescence emitted during analysis was quantified by using a solid-state detector (Si). As a reference, the spectrum of the blank filter was also measured for the comparison purpose and the absorption of sulfur was negligible [28].

The isotopic composition of sulfur (S) was analyzed by using an isotope mass spectrograph (Model MAT271) produced by Finnigan MAT Company. The mass range is 1 to 700 amu, and the mass resolution is 220 to 3000 used for gas composition and stable isotope analysis. CdS and CuO (copper oxide) obtained through precipitation were mixed in a 1 : 3 weight ratio into a quartz tube and rapidly heated to 850°C inside the reaction furnace for 30 minutes. Subsequently, the released gas was collected inside the cold trap by using liquid nitrogen for freezing the gas, and the vacuum pump was started to eliminate the impurities and pure SO_2 was released. The obtained gas was introduced into the instrument for isotope analysis and the $\delta^{34}S$ value of sulfide was ultimately obtained by using an international standard (CDT), with an accuracy of ±0.5‰.

Calcite presented inside the vein fillings of rock samples was extracted by using a small driller and was subjected to carbon and oxygen isotopic analysis. About 50–100 mg of calcite samples was treated with pure phosphoric acid for 4 hours at 72°C under a vacuumed container. The released CO_2 was analyzed for carbon and oxygen isotopes by using a Finnigan MAT253 plus mass spectrometer standardized with GBW04416. The obtained data of carbon and oxygen were reported in units/mL relative to the V-PDB standard. The precision for both $\delta^{13}C$ and $\delta^{18}O$ measurements was ±0.5‰.

The composition of formation water and the concentration of H_2S were measured by the Sangtanghu Oil Production Plant of Tuha Oilfield Company. A portable hydrogen sulfide detector was used to monitor the H_2S concentration at the wellhead of Oilfield, the precision being better than 5%.

4. Results and Discussion

4.1. Occurrence of H_2S. During the first recovery of oil in the Santanghu Oilfield, the H_2S content was reported in the oil-wellhead as 10–120 ppm/m^3air in 2010, and the relative content of H_2S in the dissolved air of formation water reached 0.19%. The average pressure value of reservoir strata C_2k in the study area was 10.5 MPa, of which the H_2S-bearing wells were mostly located in the area with low pressure (3–9 MPa) [29], and fractures were strongly developed in the surrounding rocks. Furthermore, the oil-wells containing H_2S more than 100 ppm were always characterized with a higher water cut (65–100%) while other oil-wells in lower H_2S concentration (<30 ppm) were assigned to a lower water cut (<60%). Thus, H_2S was mainly distributed in oil-wells with low formation pressure, high water cut, and fractures developed and mostly dissolved in formation water.

4.2. Minerals and Sulfur Characteristics of Reservoir Rocks. The reservoir rocks of the Santanghu Oilfields are typical volcanic rocks of the Carboniferous Kalagang Formation, which are dominated by basalt, andesite, volcanic breccia, and tuff [23]. The SiO_2 content of the volcanic rocks is 44% to 65%. There are a number of air holes and almond constructs in the rocks so that these rocks have relatively high porosity and proper connectivity; the porosity is 6% to 11% [23]. Weathering and leaching during the cessation of deposition should be the major controlling factor of favorable reservoirs in the Carboniferous volcanic rocks, and the secondary minerals such as clay minerals could be largely formed. The hydrolysis belt was mainly composed of mudstone and tiny volcanic grains, most of which were broken down into clay minerals [23]. The cracks or vein fillings in the

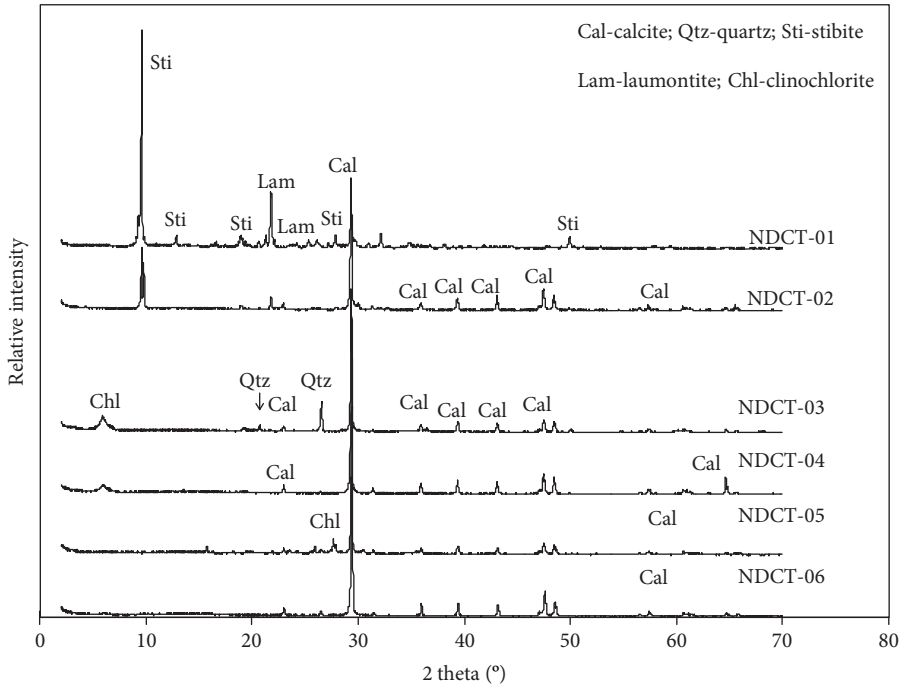


Figure 3: Powder X-ray diffraction patterns for the study samples.

core of volcanic rocks were widely developed and mainly consisted of volcanic zeolites, quartz, and/or calcite (Figure 3).

Sulfur species were herein referred to as the chemical status of sulfur, which was identified using XANES in this study by comparison of the obtained spectra for samples with those of selected sulfur-containing reference materials such as pyrite (FeS_2), pyrrhotite (FeS), calcium sulfate ($CaSO_4$), and sulfur (S^0). The impact of self-absorption associated with reference materials was investigated by using well-crushed mixtures of boron nitride in various concentrations of sulfur. The self-absorption impact was not detected in sulfur concentration < 0.5 wt.% [28]. The peak positions obtained from the cored samples were mostly positioned at two series of comparable energy range to those presented in the spectra of pyrite, pyrrhotite, and calcium sulfate, signifying that the foremost sulfur species were sulfide and sulfate, respectively. The absorbing peaks presented on the left (in range of 2.470–2.474 keV) indicate the presence of S^{2-}, S_2^{2-}, and also possibly elemental sulfur (S^0). On the other hand, the peak presented on the right (in range of 2.481–2.484 keV) denotes SO_4^{2-} species (Figure 4). The spectra thus obtained for all samples are shown in Figure 4, in which several composite variations within numerous sulfur species are displaced based on their spectrum structures as well as the location of the peak that is signified as sulfides and/or sulfate, respectively. In this study, it was found that both the sulfate (more than 90%) and sulfide minerals widely coexisted in the reservoir rocks, which could provide an effective sulfur source for the genesis of H_2S gas within the reservoirs.

4.3. Characteristics of Formation Water. The chemical compositions of formation water are shown in Table 3 and Figure 5. Relatively most samples belong to the group of Na(K)-Cl or Ca-Cl_2 water while the existence of Ca(Mg)-SO_4 waters indicates possible evolutionary trends toward SO_4-enriched waters. There are no samples belonging to the Ca(Mg)-HCO_3 and Na(K)-HCO_3 groups in the study area. In particular, the Na^++K^+ concentration of formation water in Kalagang Formation (C_2k) was in a range of 69–1008 mg/L and the Cl^- concentration in a range of 309–1955 mg/L, respectively. The range of Mg^{2+} concentration of C_2k formation water was from 1 to 291 mg/L with an average of 56.6 mg/L. Generally, the higher the Mg^{2+} concentration, the higher would be the H_2S yields, because ion Mg^{2+} could play a catalysis role in TSR [30–32]. The range of SO_4^{2-} concentration was from 27 to 1288 mg/L. The coefficient of desulfurization ($100 \times r\ SO_4^{2-}/Cl^-$) was in a range of 2–160 with a mean value of 30. This coefficient could be used to reflect consumption of SO_4^{2-} during TSR and the redox conditions of formation water. The low mark means reduced condition and active TSR reactions [32]. The H_2S contraction rose with a decrease in the coefficient of desulfurization (Figure 6), exhibiting that TSR really occurred in the study reservoirs. The CO_3^{2-} concentration in most water samples was low (mostly not detected), and the average of HCO_3^- was 335.8 mg/L. In addition, the concentration of HCO_3^- decreased with the process of TSR reactions, strongly indicating the dilution of additional water under TSR conditions. This kind of dilution might be lowering the concentration of CO_3^{2-} and HCO_3^- in formation waters of volcanic reservoirs.

4.4. Sulfur Isotopes of H_2S. The sulfur isotopes of sulfates and/or sulfides presented in the volcanic rocks from wells ND89-9 and ND89-10 are quite close to each other, being 9.2‰ and 10.3‰, respectively. The natural gases at the

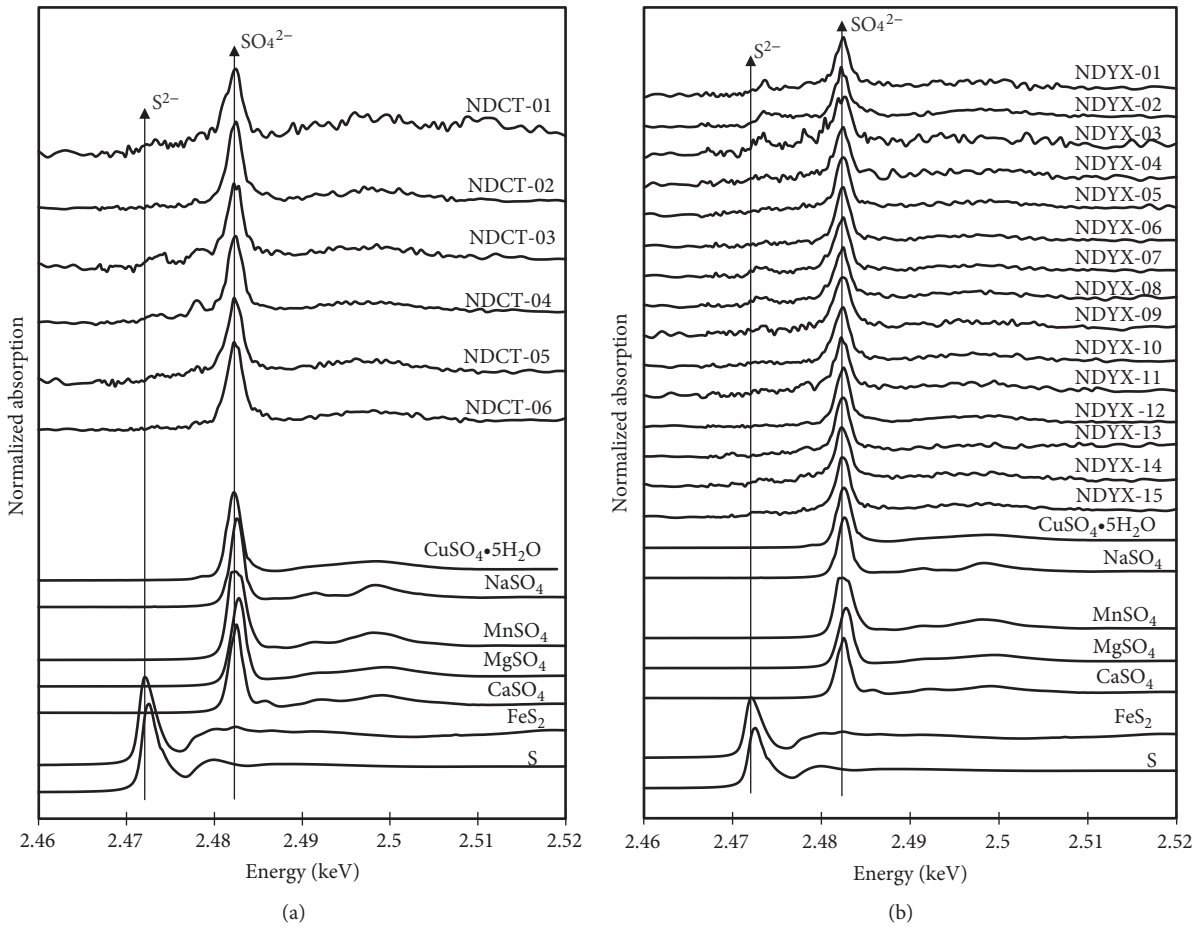


Figure 4: Spectra of sulfur species in the study samples. (a) Filling materials in the veins of cored rocks and (b) core samples. The absorbing peak on the left with a lower energy range corresponds to sulfides whereas the peak on the right with a higher energy range corresponds to sulfate.

Table 3: Hydrochemistry of the formation water from the Niudong area, Santanghu Basin.

Sample no.	Stratum	Sampling date	H_2S (ppm/m^3 air)	mg/L									
				K^++Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}	Total salinity	Type	pH
ND8-14	C_2k	2008/8/7	n.d.	410	864	291	1755	920	710	268	5218	$CaCl_2$	9.3
ND78-9	C_2k	2008/8/6	115	592	545	1	1652	32	164	n.d.	2986	$NaCl_2$	7.3
ND78-812	C_2k	2010/8/7	6	371	123	10	512	283	168	n.d.	1467	NaCl	6.0
ND89-10	C_2k	2010/10/8	44	647	442	24	1375	329	397	n.d.	3214	$CaCl_2$	7.0
ND8-11	C_2k	2008/8/7	35	1008	683	67	1955	434	1171	n.d.	5318	NaCl	6.5
ND89-9	C_2k	2008/11/4	31	592	521	14	1544	349	123	n.d.	3143	$NaCl_2$	6.0
ND8-111	C_2k	2010/5/1	13	194	566	98	1272	47	482	n.d.	2659	$CaCl_2$	7.0
ND89-812	C_2k	2010/8/24	25	69	315	21	309	495	85	n.d.	1294	$CaSO_4$	6.0
ND9-9	C_2k	2010/3/7	50	547	384	15	1393	188	57	n.d.	2584	$CaCl_2$	7.0
ND89-91	C_2k	2010/6/5	44	869	369	15	1324	495	596	n.d.	3668	NaCl	6.0
ND 8-71	C_2k	2007/12/21	120	386	396	7	1264	27	36	10	2126	$CaCl_2$	9.0
ND8-10	C_2k	2007/10/16	13	394	873	122	1475	1288	143	n.d.	4295	$CaCl_2$	7.7
ND8-8	C_2k	2008/8/7	10	537	404	51	1368	255	234	n.d.	2849	$NaCl_2$	6.5

Note: these data were provided by the Santanghu Oil Production Plant of Tuha Oilfield Company. pH was tested at room temperature.

Niudong pumping station have undergone a series of technological operations such as separation of oil and gas, whose sulfur isotopic ratios reached 20.5‰ (Table 4). As shown in Figure 7, the $\delta^{34}S_{V\text{-}CDT}$ values for TSR-H_2S in this study were comparable with those in the Sichuan Basin (main frequency: 8‰ to 26‰) [14], the Tarim Basin (14‰ to 19‰) [17, 33],

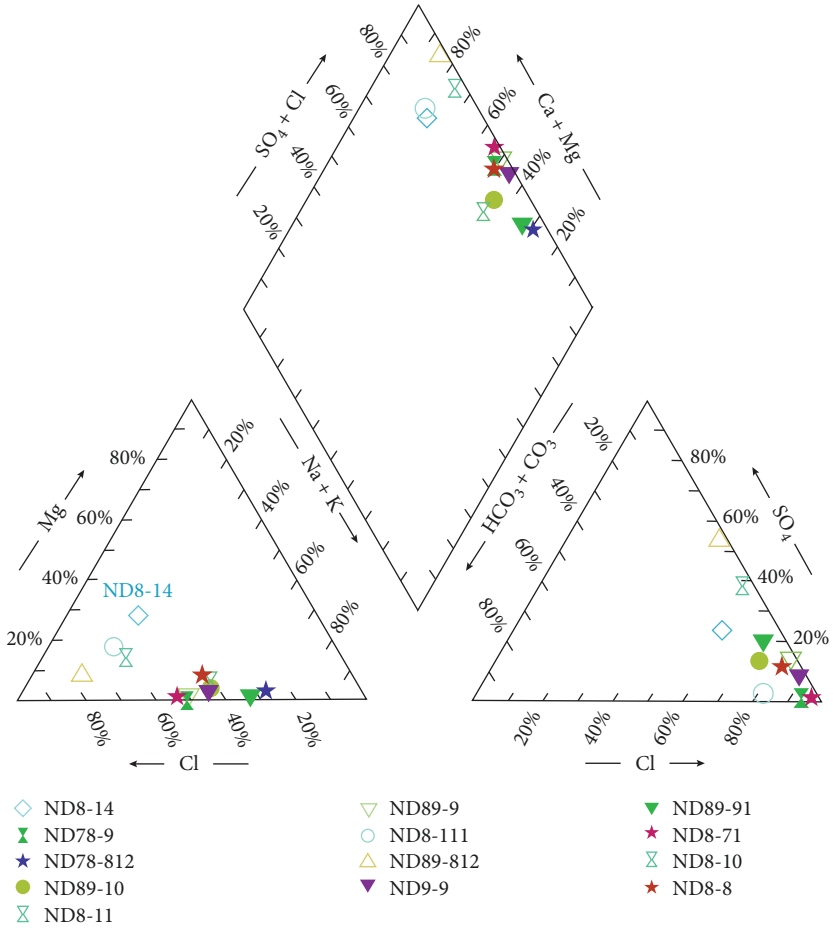


Figure 5: Pipe diagram for ion composition of study formation waters.

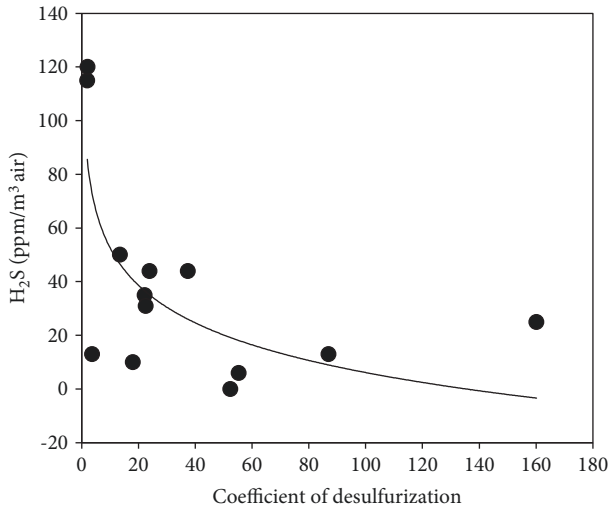


Figure 6: Relationship between the coefficient of desulfurization ratios and H_2S concentrations of oil wells.

and the Ordos Basin (16‰ to 20‰) [14]. Such comparison may indicate that H_2S presented in the oil wells of the Niudong area could probably be derived from TSR. $\delta^{34}S_{V\text{-}CDT}$ of TDS-H_2S in crude oils is usually from 3‰ to 15‰ [5]; thus, H_2S in the Niudong area could also be due to TDS. However, there is lack of meaningful evidence for the possibility of inorganic (volcanic) origin and BSR involvement for H_2S in the study area.

4.5. Carbon Isotopes of Calcite. The isotopic data of the calcite matrix from the Kalagang Formation exhibited a relatively wider range of carbon isotopic values between -10.7‰ and -3.3‰ V-PDB and a narrower range of oxygen isotopic values between -21.8‰ and -18.6‰ V-PDB, respectively (Table 4). These relatively negative carbon isotopic values may suggest a possible contribution of organic carbon into calcite, but the carbon and oxygen isotopic values failed on the boundary of TSR calcite [22] which was formed through TSR reactions. In addition, these carbon and oxygen isotopic values of vein calcite were also similar to those of primarily igneous carbonatite ($\delta^{13}C_{V\text{-}PDB}$‰: -5.0‰ to -8.0‰, $\delta^{18}O_{V\text{-}PDB}$‰: -21.7‰ to -23.7‰) [34], indicating the calcite formation with fluids from deep layers under low hydrothermal temperatures (<167°C) [35]. Therefore, calcite in the rock veins was mostly of magmatic origin and very less produced due to TSR reactions.

4.6. Origin of H_2S. As for the low concentration of H_2S in crude oils and natural gases, the BSR origin is always regarded as the first originating mechanism that may be

Table 4: Sulfur and carbon isotope of samples obtained from the Kalagang Formation in the Santanghu Basin.

Well or sample no.	Type	$\delta^{34}S_{V\text{-}CDT}$‰	$\delta^{13}C_{V\text{-}PDB}$‰	$\delta^{18}O_{V\text{-}PDB}$‰	Note
Gas pumping station	Gas	20.5			
ND89-9	Gas in water	9.2			
ND89-10	Gas in water	10.3			
NDCT-03	Rock		-10.7	-20.6	Calcite
NDCT-04	Rock		-5.8	-21.8	Calcite
NDCT-05	Rock		-5.7	-18.6	Calcite
NDCT-06	Rock		-3.3	-21.4	Calcite

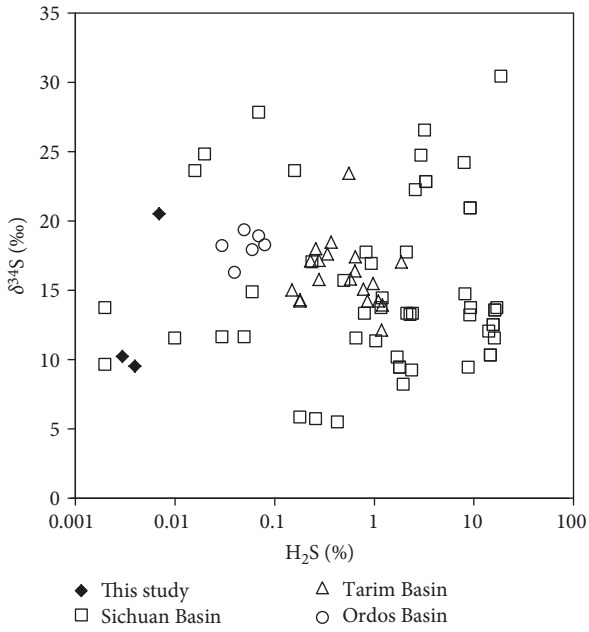


Figure 7: Correlation between $\delta^{34}S$ values and H_2S contents of samples from the Santanghu Basin and other referenced TSR H_2S-bearing basins in China (data of Sichuan Basin, Tarim Basin, and Ordos Basin are from Zhu et al. [14] and Jiang et al. [22]).

caused by bacterial loadings during water injection. The sulfur isotopes of H_2S in the study area were 9.2‰ to 20.5‰, suggesting that BSR was probably not the most possible source in the Niudong Oilfield, where H_2S was found in the first recovery of oil without water injection in early oil and gas exploration. Additionally, the values of sulfur isotopes are not in favor of volcanic sources for the genesis of H_2S. Therefore, TSR and TDS should be their possible origins that were supported by the sulfur isotopic data. However, TDS usually occurred during the secondary recovery of oil under a relatively higher temperature than under the initial temperature of TSR [5], but no steam and/or hot water was utilized during the secondary recovery of heavy oils in the study reservoir and the heavy oils was typically low in sulfur content (about 0.17%). Based on these facts, either TDS should not be the origin or slightly contributed if TDS occurred. As for TSR, although gypsum and/or anhydrite in the cored rocks was not observed by naked eyes, trace sulfate and sulfide were detected by XANES. Such sulfur-bearing materials in the reservoir rocks could supply enough sulfur for TSR reactions due to the huge volume of rocks. Secondly, the local geothermal temperature (>110°C) reached the reaction conditions for TSR during the Permian-Triassic period as for the volcanic activity [27]. Finally, some increase in H_2S concentration was observed with a decrease in desulfurization coefficient, which confirmed the occurrence of TSR. Such formed H_2S in the reservoir of volcanic rocks is easily dissolved in the formation water. On the other hand, CO_3^{2-} and HCO_3^- concentrations in most samples were relatively low, indicating that the additional water formed along with TSR may dilute the concentrations of both CO_3^{2-} and HCO_3^-. Considering all the evidences above, TSR should be the main source for H_2S in the natural gases of the Niudong Oilfield, but the TDS origin could not also be excluded.

5. Conclusions

The volcanic reservoir rocks of the Carboniferous Kalagang Formation are dominated by basalt and andesite, whose cracks or vein fillings in the core are mainly composed of volcanic zeolites, quartz, and/or calcite. Both sulfate (more than 90%) and sulfide minerals extensively existed in the reservoir rocks, which could provide a potential sulfur source for H_2S gas formation through TSR in the reservoirs.

H_2S was distributed in the producing wells with low formation pressure and high water cut of the oil wells, which was mostly dissolved in the formation water. The sulfur isotopic data and ion compositions of formation water indicated that TSR should be the main source for H_2S genesis. The geological structures of the basin, the mineral compositions of the reservoir rocks, and the evolution characteristics of the paleogeothermal temperatures provided effective conditions for TSR reactions in the study area.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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