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Original Paper

Geochemistry and origins of hydrogen-containing natural gases in deep Songliao Basin, China: Insights from continental scientific drilling

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ABSTRACT

The different reservoirs in deep Songliao Basin have non-homogeneous lithologies and include multiple layers with a high content of hydrogen gas. The gas composition and stable isotope characteristics vary significantly, but the origin analysis of different gas types has previously been weak. Based on the geochemical parameters of gas samples from different depths and the analysis of geological settings, this research covers the diverse origins of natural gas in different strata. The gas components are mainly methane with a small amount of C_{2+}, and non-hydrocarbon gases, including nitrogen (N_2), hydrogen (H_2), carbon dioxide (CO_2), and helium (He). At greater depth, the carbon isotope of methane becomes heavier, and the hydrogen isotope points to a lacustrine sedimentary environment. With increasing depth, the origins of N_2 and CO_2 change gradually from a mixture of organic and inorganic to inorganic. The origins of hydrogen gas are complex and include organic sources, water radiolysis, water-rock (Fe^{2+}-containing minerals) reactions, and mantle-derived. The shales of Denglouku and Shahezi Formations, as source rocks, provide the premise for generation and occurrence of organic gas. Furthermore, the deep faults and fluid activities in Basement Formation control the generation and migration of mantle-derived gas. The discovery of a high content of H_2 in study area not only reveals the organic and inorganic association of natural-gas generation, but also provides a scientific basis for the exploration of deep hydrogen-rich gas.

1. Introduction

Hydrogen (H_2), as a non-polluting energy source with high energy density, has attracted more and more attention as the world moves away from its dependence on fossil fuels (Boreham et al., 2021). Currently, artificially produced is the main way to get hydrogen, and is used almost entirely for industrial purposes (It is mainly used for ammonia production and oil recovery and refining), with approximately 70 million metric tons produced globally each year (Nikolaidis and Poullikkas, 2017). In addition to hydrogen production from fossil energy reforming and industrial by-product purification ("grey hydrogen"), it can also be produced using steam reforming from natural gas with carbon capture and storage ("blue hydrogen") and by water electrolysis using renewable energy ("green hydrogen") (Chi and Yu, 2018; Nuttall and Bakenne, 2020; Oni et al., 2022). However, the cost of green hydrogen needs to be reduced, and the technology of blue hydrogen has not yet achieved key breakthroughs. Perhaps, the natural hydrogen found subterranean is an alternative energy source for promoting the replacement of grey hydrogen by blue hydrogen and green hydrogen.

H_2 has the physicochemical characteristics of high reactivity, high mobility, and small molecular size, so the traditional view is that hydrogen is easily oxidized and is difficult to exist in elemental form on the surface. But the distribution of hydrogen on the surface further confirms the existence of free hydrogen in nature, its content in nature varies greatly from one region to another (Vacquand et al., 2018). H_2 with a purity of up to 98% was found in northern

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Mali (Prinzhofer et al., 2018). The CFA oil company drilled the Scott well in the North American rift system valley in 1982 and obtained gas with an H_2 content of approximately 50% (Goebel et al., 1983). Gas with more than 40% hydrogen has been found in New Caledonia, located in the structurally active belt of the Indo-Australian plate (Vacquand et al., 2018). The occurrence of high-purity H_2 in nature is significant for helping to reduce the consumption of non-renewable resources. Nevertheless, the current understanding of geological H_2 is still rather limited, and the main reaction mechanisms and contributions to the geochemistry process of H_2 generation are not clear, and the migration and fractionation of H_2 in different lithology are missing.

Hydrogen has been discovered in different areas of the Songliao Basin. The hydrogen content in the Xujiaweizi fault depression is particularly significant and varies widely. The strata have good natural-gas cap-rock conditions, which are conducive to the preservation of a high hydrogen content. Stable isotope characteristics are essential for the study of sedimentary environments, deep source rocks, and natural gas origins (Whiticar, 1999; Etiope et al., 2009). In this study, the well Songke 2 (SK-2) of the International Continental Scientific Drilling Program (ICDP) and the adjacent region are adopted as the study area, using the chemical composition and stable isotopic characteristics of different gases to determine the origin of hydrocarbon and non-hydrocarbon gases. The research of the origin and content variation of H_2 provides a geochemistry explanation for H_2 accumulation in deep strata and a practical basis for the exploration and development of deep hydrogen-rich natural gas.

2. Geological setting

The Songliao Basin, located in northeast China, is a very large lacustrine basin with the world's longest development history in Cretaceous time (Wang et al., 2013), and has a total area of about 2.6×10^5 km^2 (Fig. 1a). It is adjacent to the Da Xing'an mountains in the west, the Xiao Xing'an mountains in the northeast, the Zhang Guangcai mountains in the southeast, and the Kangping-Faku hill region in the south. In its multi-stage tectonic evolution, Songliao Basin has formed a complex mosaic of superimposed tectonic belts and deposited Mesozoic-Cenozoic continental strata, mainly lacustrine and clastic deposits (Feng et al., 2010; Yang et al., 2021). There are six first-order tectonic units: the north tilting zone, the west slope zone, the central depression zone, the northeast uplift zone, the southeast uplift zone, and the southwest uplift zone. The main oil and gas producing area is located in the central depression (Meng et al., 2016; Cai et al., 2017). SK-2 is situated in the Xujiaweizi fault depression in the northern Songliao Basin and has reached a drilling depth of 7018 m. A complete Cretaceous continental stratum has been revealed, and provides important basic data for the study of deep natural gas resources in Songliao Basin (Fig. 1b).

SK-2 has drilled sedimentary rocks, volcanic rocks, and metamorphic rocks, and the lithology varies with depth. The Denglouku Formation is fluvial sedimentary facies, mainly shale and silty shale, followed by conglomerate and glutenite. The Yingcheng Formation began to deposit at the end of the fault basin, and has undergone the stage of fault-depression transformation. The sedimentary facies are mainly fluvial facies, alluvial fan facies, and volcanic facies, and the lithology shows shale, conglomerate, and rhyolite tuff. The Shahezi Formation was deposited in the intense period of the fault basin, and experienced continued deposition and burial for a long time. It developed mainly fan delta sedimentary facies, characterized by multi-stage superposition (Liu et al., 2021). The Shahezi Formation is characterized by rock layers, and the reservoir lithology is relatively complex: it is mainly shale, sandstone, and siltstone, interspersed with coal seams. The bottom of Shahezi Formation is bounded by Basement Formation and is mostly glutenite and sandstone. The lithology of Basement Formation includes principally low-metamorphic glutenite, metamorphic rock, and andesite. Hydrocarbon and non-hydrocarbon gases were detected by logging at different depths, and abnormal gas logging occurred many times. The Denglouku Formation and Basement Formation have shown abnormal H_2 gas logging, with a logging value as high as 2.39% (Fig. 1b). The gas is distributed in various lithologies such as shale, sandstone, volcanic rock, and metamorphic rock. In the Xujiaweizi fault depression, natural gas wells such as Shengshen Geng 2 (SS-G2), Xushen 9 (XS-9), and Fangshen 7 (FS-7) are found to have widely varying content of H_2 (Fig. 1a). The H_2 content is more than 10% in FS-7 (Dai et al., 2009; Han et al., 2022). These findings provide an ideal basis for pursuing a series of scientific investigations of H_2-rich natural gas in Songliao Basin.

3. Samples and methods

Using the continental scientific drilling sampling standard and collection process for natural gas samples, 30 gas samples at different depths were collected continuously from SK-2 in this study. The sampling covered strata of about 4 km from Denglouku Formation to Basement Formation and is the basis for studying geochemical characteristics of deep natural gas in Songliao Basin. An Agilent7890A gas chromatograph was used for gas component analysis. According to the China GB/T 13610-2014 analysis and test standard, gas samples were separated into six chromatographic columns with a high-purity carrier gas. The molecular compositions of natural gases (CH_4, C_{2+} (including ethane and propane), CO_2, N_2, He, and H_2) were determined. CH_4, CO_2, H_2, and N_2 were analyzed by a MAT-253 gas isotope mass spectrometer. According to V-PDB and V-SMOW standards, five isotopes ($\delta^{13}C_{CH_4}$, $\delta^{13}C_{CO_2}$, δD_{CH_4}, δD_{H_2}, and $\delta^{15}N$) were analyzed. The measurement precision of the stable carbon isotope is estimated to be ±0.5‰. Those of stable hydrogen and nitrogen isotope are estimated to be ±3‰ and ±0.4‰, respectively. He, as a noble gas, was isolated by Ti–Zr getters at approximately 800 °C, and was analyzed by a Fisons Instrument VG 5400 sector-type mass spectrometer.

4. Results and discussion

4.1. Gas composition characteristics

The hydrocarbon gas content of SK-2 is more than 70.19%, some non-hydrocarbon gases, such as CO_2, H_2, N_2, and the rare gas He are also present (Table 1). Hydrocarbon gas is dominated by methane, with a content ranging from 60.42% to 89.68%, its average being 77.80%. The content of ethane and propane is small, and the content of C_{2+} lies between 0.74% and 3.89%, with an average of 1.75%. The percentage of methane content has no significant relationship with depth, while the content of C_{2+} gradually decreases as depth increases (Fig. 2). The lacustrine shale in SK-2 is deeply buried, varying from high maturity to over-maturity. A large number of gases such as ethane, propane, and butane have been cracked, resulting in the production of dry gas.

CO_2 content of the SK-2 gas ranges from 0.28% to 26.70%, with an average value of 7.34%. In the 4079–4500 m interval, CO_2 is somewhat enriched, with an average content of more than 13% and a maximum content of 26.70%. In the 6225–6630 m interval, the CO_2 content is above 9% on average. The abnormally high content of CO_2 in Basement Formation is attributable to mantle-derived gas of inorganic origin, mainly associated with deep fault activities and hydrothermal fluids (Lu et al., 2009; Zhang et al., 2010). The N_2 content is between 1.05% and 8.47%, with an average of 3.45%. The 3630–3810 m interval of Shahezi Formation and the 6110–6230 m

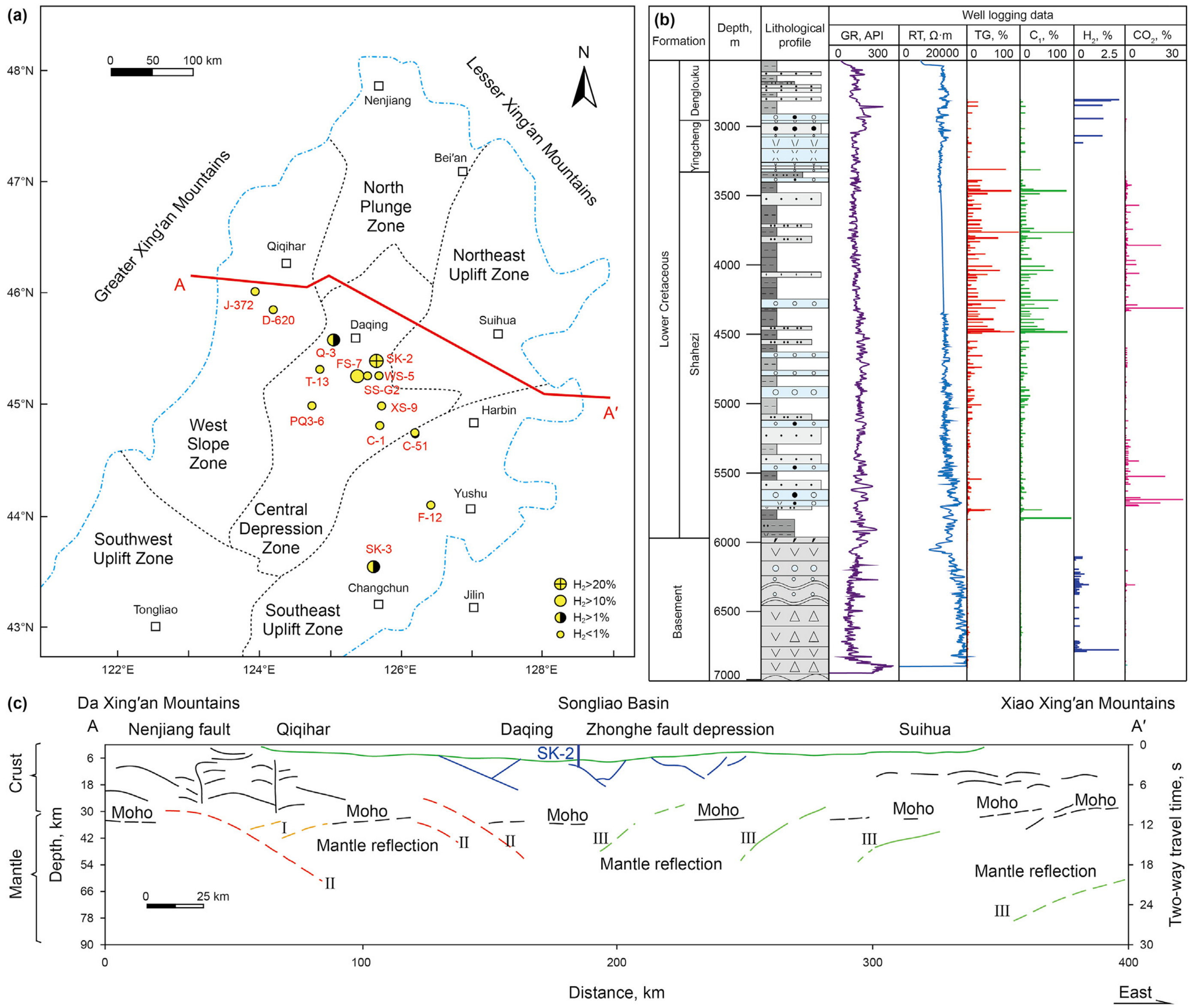

Fig. 1. The location, tectonic units and distribution of hydrogen-rich wells in Songliao Basin (a), lithologic profile and gas logging of SK-2 well in Songliao Basin (b), and geological profile of SK-2 well in Songliao Basin (c). The (a) modified after Han et al. (2022). The (c) modified after Hou et al. (2018).

interval of Basement Formation have high N_2 content, with an average in the former of 5.69%, and an average in the latter of 8.14%. N_2 is of both organic and inorganic origin. The organic origins are mainly thermal ammonification and thermal degradation/thermal cracking in the high maturity stage. The inorganic origins are mainly mantle-derived gas and high-temperature metamorphism of nitrogen-bearing rocks (Liu, 2017).

The deep stratum of SK-2 contains some He gas resources. The 6110–6630 m interval of the Basement Formation is relatively rich in He, with a maximum of 0.13%; the He gas content in this interval reaches the standard of industrial He gas reservoirs (Dai et al., 2017). The content of He is generally high at deeper levels, mainly from the deep crust and upper mantle. The decay of radioactive elements produces large amounts of additional He in the crustal environment. He is mostly of crustal origin, associated with natural gas (Liu et al., 2022). As shown in Fig. 2, there is a positive correlation between the concentration trends of H_2 and He in all gases present. This may indicate that they are generated, migrated, and saved in a similar pattern.

The deep interval of SK-2 also contains a large amount of H_2. During the drilling, hydrogen gas anomalies were found in different formations. On the whole, there is no sharp trend that H_2 content increases or decreases with the increase of underground depth. The H_2 content in the deep interval of SK-2 shows the distribution characteristics of “high-low-high”. In the 2808–3150 m interval, H_2 is present with an average content of 11.78% and a maximum of 20.16%. H_2 content in the middle of Shahezi Formation is slightly lower, ranging from 1.36% to 5.45%. In the 6110–6807 m interval, the average H_2 content is 18%, and the highest value is 26.89%. The origins of H_2 are complex and diverse, both inorganic and organic. Inorganic origins include earth degasification of deep fluids, water-rock reactions between deep fluids and rock minerals, and radiolysis between radioactive elements and water in the continental crust (Reeves and Fiebig, 2020). Organic origins include microbial action in the shallow layer and the pyrolysis of organic matter of high maturity (Boreham et al., 2021; Han et al., 2021). The SK-2

Table 1
H_2-containing gas composition and isotope data results.

Depth, m	CH_4, %	C_{2+}, %	CO_2, %	N_2, %	He, %	H_2, %	$\delta^{13}C_{CH_4}$, ‰	$\delta^{13}C_{CO_2}$, ‰	δD_{CH_4}, ‰	δD_{H_2}, ‰	$\delta^{15}N$, ‰	*R/Ra*
2808	71.74	2.46	0.28	5.34	0.021	20.16	43.8	−14.4	−208.2	−685	4.4	0.071
2874	75.92	3.89	0.69	4.19	0.032	15.28	−44.8	−13.6	−205.4	−667	3.2	0.037
2940	77.42	2.92	0.92	3.26	0.042	15.44	−42.8	−11.4	−202.2	−678	3.8	0.112
3010	88.08	1.28	/	4.15	0.025	6.05	−43.1	/	−196.4	−691	4.5	0.482
3080	87.77	2.18	0.66	/	0.007	8.07	−46.1	−10.3	−195.4	−656	/	0.214
3150	89.67	2.01	0.55	2.08	0.013	5.68	−41.9	−9.9	−190.5	−662	5.9	0.693
3639	80.48	2.18	5.98	6.12	0.033	5.21	−41.8	−12.6	−213.4	−687	5.6	0.246
3810	82.4	3.09	7.84	5.25	0.058	1.36	−39.5	−11.7	−212.4	−672	5.1	1.124
3944	85.4	2.36	5.78	3.34	0.035	3.08	−41.5	−11.4	−209.6	−699	4.8	1.692
4079	83.29	1.2	12.12	1.2	/	2.17	−35.2	−9.4	−208.4	−684	6.1	/
4281	82.62	1.23	10.62	2.33	0.015	3.18	−40	−8.8	−205.5	−646	7.2	0.728
4415	87.86	2.27	4.63	3.05	0.036	2.15	−37.5	−8.6	−204.5	−657	5.5	0.284
4500	60.42	2.13	26.7	/	0.017	3.39	−44.2	−8.4	−202.2	−661	/	0.535
4830	89.68	1.21	2.71	1.44	0.082	4.88	−39.5	−8.2	−200.5	−690	6.7	0.788
5287	85.27	3.15	/	4.05	0.106	5.45	−39.5	/	−199.3	−706	5.3	0.175
5488	87.46	1.27	3.09	3.07	0.031	5.08	−35.9	−7.1	−198.7	−626	4.6	1.321
5600	86.27	2.23	7.63	1.05	/	2.8	−41.9	−6.3	−197.5	−639	4.7	/
5760	76.77	1.11	18.92	1.4	0.029	1.77	−39.5	−6	−196.4	−703	5.1	0.285
5830	70.99	2.17	22.7	2.09	0.026	2.02	−40	−5.9	−190.4	−660	4.7	0.075
5890	82.14	1.15	13.44	1.84	0.037	1.39	−44.9	−5.1	−188.5	−712	4.3	0.431
6110	70.22	1.69	4.57	8.47	0.091	14.96	−33.9	−11.2	−209.1	−669	1.7	2.921
6225	64.11	1.09	6.99	7.81	0.132	19.87	−27.1	−10.4	−206.4	−694	0.9	3.962
6292	66.62	0.74	5.24	/	0.062	20.9	−30.7	−9.4	−205.7	−723	/	2.521
6324	67.97	1.43	3.67	3.82	0.044	23.06	−35.7	−8.5	−204.5	−711	3.6	1.172
6396	73.63	1.06	1.98	5.58	/	17.73	−33.5	−7.1	−200.1	−730	3.1	/
6560	68.41	0.92	11.25	1.33	0.055	18.03	−24.8	−6.6	−199.8	−701	0.8	1.894
6630	73.42	0.78	8.46	2.44	0.105	14.79	−27.6	−6.5	−198.4	−695	1.4	0.792
6694	72.88	1.21	/	3.9	0.083	19.36	−30.6	/	−196.3	−761	3.8	1.462
6761	62.48	1.09	7.51	1.91	0.125	26.89	−38.1	−5.7	−194.4	−753	2.2	0.165
6807	82.67	0.99	3.23	2.67	0.068	10.38	−35.8	−4.2	−190.3	−702	2.7	0.129

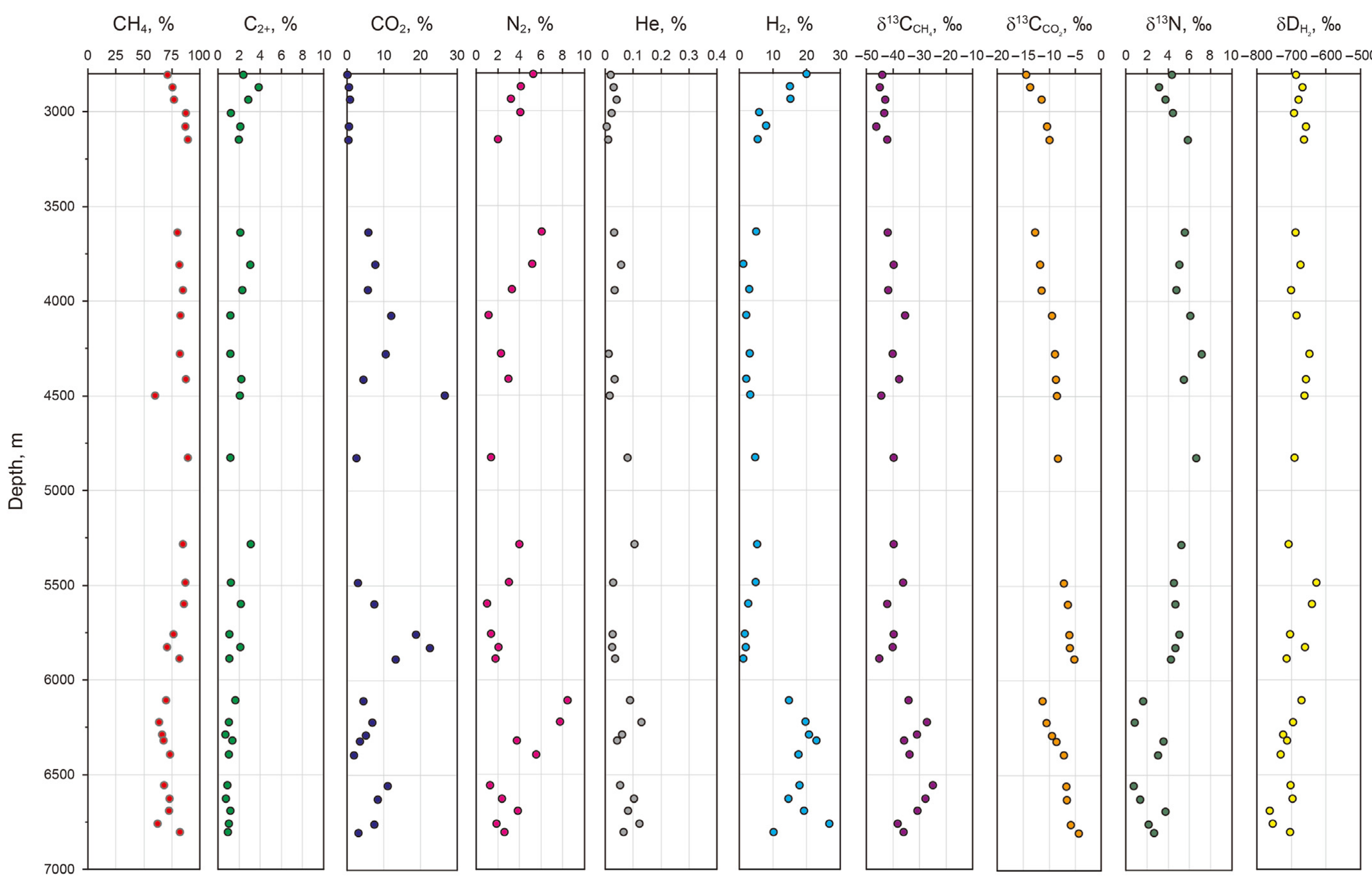

Fig. 2. Natural gas components, including specific isotopes, as functions of depth.

strata have a long geological age, various reservoir conditions, and a wide distribution of H_2 content. Accordingly, the origins of H_2 in SK-2 need to be further identified.

4.2. Origin of alkane gases

The stable carbon isotope of methane ($\delta^{13}C_1$) is an important parameter reflecting the geochemical characteristics of alkane gas. Its identification is of great significance for studying the origins of shale gas (Strąpoć et al., 2007; Cesar et al., 2022). The amount of $\delta^{13}C_1$ is usually determined by the type of hydrocarbon-generating parent material and the degree of thermal evolution (Shi et al., 2020). The $\delta^{13}C_1$ value of alkane gas gradually increases with an increase of organic matter evolution in hydrocarbon source rock. The $\delta^{13}C_1$ values show an increasingly heavy distribution trend in vertical range of SK-2. The $\delta^{13}C_1$ values in Denglouku Formation range from −46.1‰ to −41.9‰, with an average value of −43.8‰. The $\delta^{13}C_1$ values in Shahezi Formation range from −44.9‰ to −35.2‰, with an average value of −40.0‰. The ones in Basement Formation range from −38.1‰ to −24.8‰, with an average value of −31.8‰.

The hydrogen isotope composition of methane (δD_{CH_4}) is influenced not only by thermal evolution maturity of organic matter, but also by source-rock strata environment (Zumberge et al., 2009). The light hydrogen isotopes are relatively enriched in a freshwater environment, while the heavy hydrogen isotopes are relatively enriched in a saline environment. Because the C—C bond affinity of $-CH_2D$ functional group of methane is stronger than that of $-CH_3$ functional group, hydrogen isotopes have the largest stable isotope values, ranging from −250‰ to −150‰ (Ni et al., 2011). The boundary for dividing the methane formed in marine and lacustrine environments is $\delta D_{CH_4} = -190‰$ (Schoell, 1983; Moore et al., 2022). The δD_{CH_4} values in Denglouku Formation range from −208.20‰ to −190.50‰, with an average value of −199.60‰. Their values in Shahezi Formation range from −213.40‰ to −190.30‰, with an average value of −200.50‰, and in Basement Formation from −209.10‰ to −190.30‰, with an average value of −200.50‰. Unlike with carbon isotopes, the vertical distribution of methane hydrogen isotopes in SK-2 differs significantly from linearity, but overall is less than −190‰, which points to a lacustrine sedimentary environment.

The carbon and hydrogen isotopic characteristics of methane can be used to identify the origin of alkane gas, and can be combined with molecular components to achieve better application effect (Whiticar, 1999; Liu et al., 2021). As shown in Fig. 3, the hydrocarbon gases of different strata samples have their own genesis characteristics in SK-2. The C_1/C_{2+3} ratio shows that their drying coefficients (C_1/C_{2+} ratio) are relatively high, which is related to the thermal degradation/thermal cracking at high-over-maturity of Songliao Basin as a whole. The alkane gases in Denglouku Formation are concentrated and point to standard thermogenic gases; their source material tends to be kerogen type II. The alkane gases in Shahezi Formation are relatively scattered and mostly of thermogenic origin; a small part is scattered outside the contour of thermogenic gases. Most of the alkane gases in Basement Formation are scattered outside the thermogenic gas outline, because their $\delta^{13}C_1$ values are relatively large (>−40‰).

Carbon and hydrogen isotopic characteristics of methane can be used to further identify alkane gases (Fig. 4). The identification results of alkane gases in Denglouku Formation are consistent with the previous results shown in Fig. 3, and still show absolute thermogenic origin. The alkane gases in Shahezi Formation are distributed according to geothermal, hydrothermal, and crystallization locations, indicating that their origin may be influenced by a mixture of mantle-sourced genesis and thermal genesis. The alkane

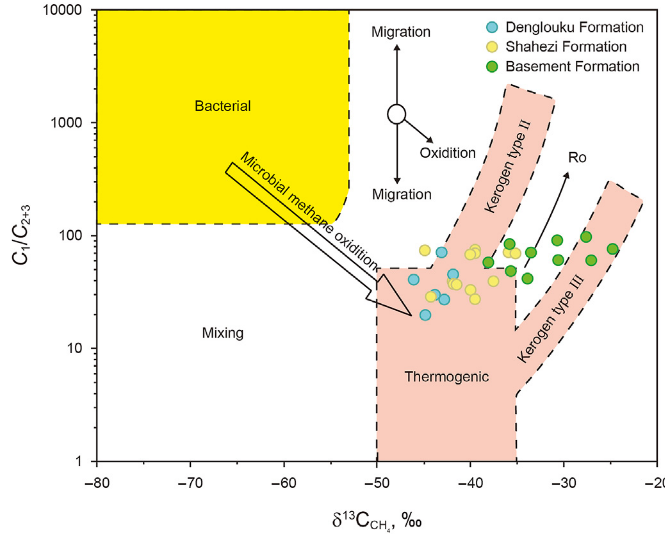

Fig. 3. Origin identification of alkane gas by $\delta^{13}C_{CH_4}$ value and C_1/C_{2+3} ratio (base map patterned after Bernard et al., 1976).

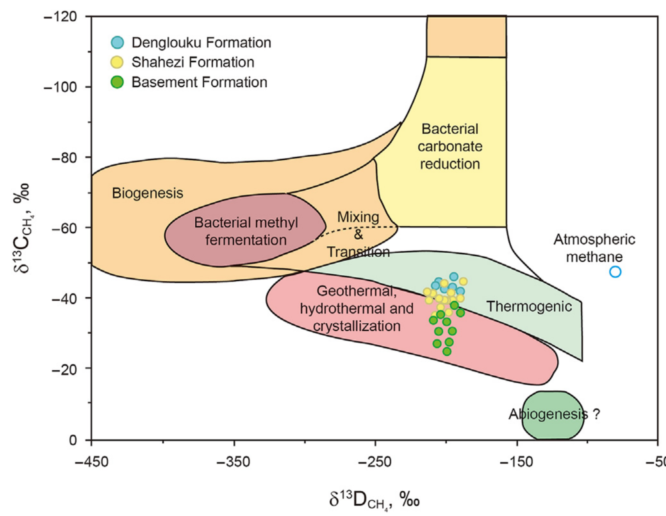

Fig. 4. Origin identification of alkane gas by $\delta^{13}C_{CH_4}$ and δD_{CH_4} (base map patterned after Whiticar, 1999)

gases in Basement Formation are mainly affected by geothermal, hydrothermal, and crystallization effects, indicating that their origins were dominated by mantle-sourced genesis. Overall, the origin of alkane gas in SK-2 gradually shifts from thermal genesis of organic matter to genesis from the mantle source as the depth increases.

4.3. Origins of nitrogen and carbon dioxide

The study of nitrogen and its compounds in oil and gas exploration is of great significance for tracing evolution and migration of these fossil fuels. The origins of N_2 in natural gas are complex and diverse, and include the atmosphere, nitrogen-bearing rocks in the crust formed under high-temperature metamorphism, degassing of mantle materials, and generation of organic matter during thermal evolution (Zhu et al., 2000; Su et al., 2019). As indicated in Fig. 2, there is a small amount of N_2 in the natural gas in study area. Due to the overlapping distribution ranges of nitrogen isotope ($\delta^{15}N$)

values in different types of nitrogen, sources cannot be accurately identified by using only $\delta^{15}N$. Moreover, the crust and mantle origins of noble gases provide a certain indication of N_2 origins (Li et al., 2017), so *R/Ra* was selected (*R* represents $^3He/^4He$ ratio in the sample, and *Ra* is $^3He/^4He$ ratio in the atmosphere). *R/Ra* and $\delta^{15}N$ were used to identify the origin of nitrogen in natural gas samples (Fig. 5). ^3He has been generated in the Big Bang, and it is relatively enriched in the mantle (Byrne et al., 2018). The crust-derived helium has an *R/Ra* value between 0.01 and 0.1, and the mantle-derived helium has *R/Ra* values greater than 0.1 (Jenden et al., 1993).

The *R/Ra* and $\delta^{15}N$ values of gas samples in SK-2 are in the ranges of 0.037–3.962 and 0.8‰–7.2‰, respectively. These break down by formations as follows: for Denglouku Formation the *R/Ra* value is between 0.01 and 1, the $\delta^{15}N$ value is between 3.2‰ and 5.9‰; for Shahezi Formation, the *R/Ra* value is generally greater than 0.1 and the $\delta^{15}N$ value is between 4.3‰ and 7.2‰; for Basement Formation, the *R/Ra* value is greater than 0.1 and the $\delta^{15}N$ values are distributed between 0.8‰ and 3.8‰. Through $\delta^{15}N$–*R/Ra* values, identification figure judgment, and analysis (Fig. 4), N_2 of Denglouku Formation and Shahezi Formation are both found to be mainly of mixed organic and inorganic origin of crustal genesis, while N_2 in Basement Formation is of volcanic-mantle inorganic genesis. As depth increases, the origin of N_2 gradually transitions from the crustal source to the mantle source, and the organic-inorganic mixed origin gradually transitions to inorganic genesis.

The CO_2 content of natural gas samples is relatively rich, and its source is identified mainly by the content of CO_2 components, carbon isotopes ($\delta^{13}C_{CO_2}$), and rare gas isotope indicators (*R/Ra*) (Meng et al., 2015; Dai et al., 2016). Based on a comprehensive analysis of a large number of CO_2-related identification data and gas components (Dai et al., 2016), it is proposed that the $\delta^{13}C_{CO_2}$ value of inorganic CO_2 is greater than −8‰, mainly between −8‰ and 3‰ and the CO_2 content is greater than 60%. The $\delta^{13}C_{CO_2}$ value of organic CO_2 is less than −10‰ and the CO_2 content is less than 15%. The $\delta^{13}C_{CO_2}$ value is between −10‰ and −8‰ in the coexisting mixture area of organic and inorganic CO_2. The $\delta^{13}C_{CO_2}$ value of CO_2 derived from the magma mantle is mostly distributed at −6‰ ± 2‰. According to the analysis of CO_2 content and $\delta^{13}C_{CO_2}$ (Fig. 6), the $\delta^{13}C_{CO_2}$ value of Denglouku Formation is between −14.4‰ and 9.9‰, and is mainly of organic origin. The $\delta^{13}C_{CO_2}$ value of Shahezi Formation is between −12.6‰ and −5.1‰, and is mainly of mixed organic and inorganic origin. The $\delta^{13}C_{CO_2}$ value of Basement Formation is between −11.2‰ and −4.2‰, and is mainly caused by inorganic CO_2.

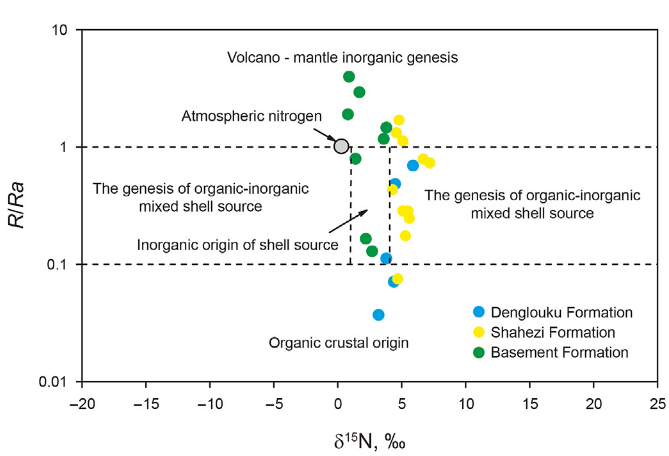

Fig. 5. Origin identification of N_2 by $\delta^{15}N$ and *R/Ra* (base map patterned after Li et al., 2017).

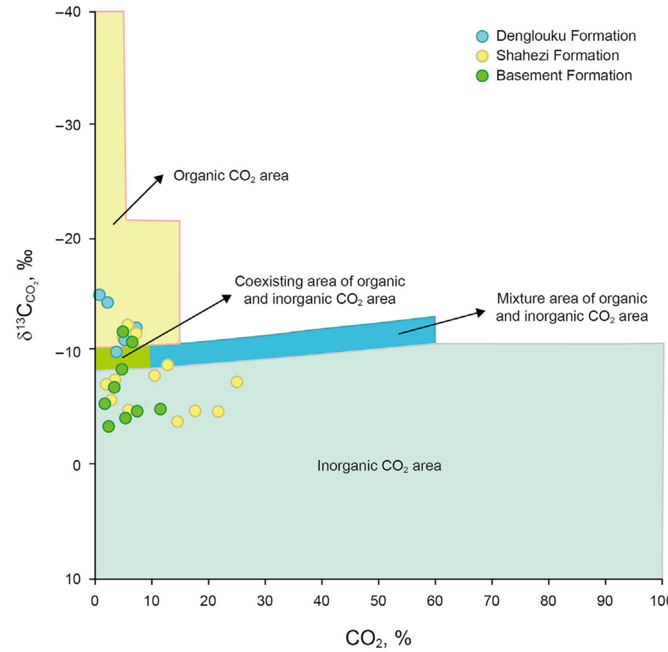

Fig. 6. Origin identification of CO_2 by $\delta^{13}C_{CO_2}$ and CO_2 (base map patterned after Dai et al., 2016).

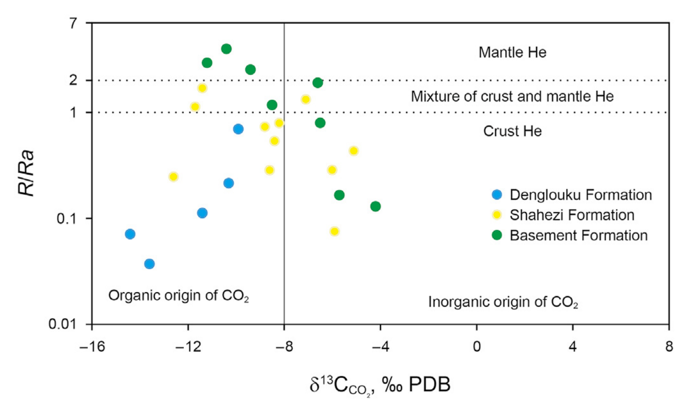

Fig. 7. Origin identification of CO_2 by *R/Ra* and $\delta^{13}C_{CO_2}$ (base map patterned after Meng et al., 2015).

The map of *R/Ra* and $\delta^{13}C_{CO_2}$ (Fig. 7) provides further identification of origins. The samples of Denglouku Formation are located in organic origin region; the samples of Shahezi Formation are located in both organic and inorganic origin regions; and the samples of Basement Formation are located mainly in mantle origin region and crust-mantle mixed-origin region. It is concluded that the CO_2 of Denglouku Formation is mainly organic, produced during the pyrolysis of organic matter; the CO_2 of Shahezi Formation is both organic and inorganic, produced during the pyrolysis of organic matter and degassing of basement fracture and igneous rock; and the source of CO_2 in Basement Formation is related to intrusive rock body and volcanic lava following the Late Jurassic (Li et al., 2011), and is mainly from volcanic mantle, the result of mantle-derived degassing.

4.4. Origin of hydrogen gas

H_2 is widely distributed on Earth and exists in stable sedimentary basins and basic volcanic rocks (Woolnough, 1934; Neal and

Stanger, 1983; Truche et al., 2018). Areas of deep fluid activity also provide favorable geological conditions for the development of high-content H_2 (Abrajano et al., 1988). The H_2 generation process is complex, including not only biological origin from the crust, earth degassing, and serpentinization from the mantle, but also thermal origin from both the mantle and the crust (Han et al., 2021). Hydrogen generally consists of two stable isotopes, ^1H (protium) and ^2H (deuterium, δD_{H_2}). The half-life of ^3H (tritium) is only 12.43 years, which cannot be used as a criterion for identification. Due to the small sample data of hydrogen isotopes in natural gas and the possible overlap of hydrogen isotopes from different origins, hydrogen isotopes from formation water are easy to exchange with hydrogen isotopes in hydrogen, and are affected by temperature-dependent equilibrium isotope fractionation and hydrodynamics (Löffler et al., 2022; Ricci et al., 2022). There are still problems in determining the more specific H_2 generation mechanism. Consequently, identifying the source of H_2 is difficult.

As an important component of natural gas, H_2 is often produced along with other gases, such as He and CH_4. Therefore, the geochemical characteristics of associated gases can be used to determine origins of H_2 and to some extent can reduce the uncertainty of hydrogen isotope tracing. Because the isotope (^3He) can effectively point to the mantle source, previous studies have identified H_2 origin by using the isotopes of an associated gas (He), and calculating the geochemical characteristics of H_2 in natural gas from different regions. It is considered that the upper limit of $H_2/^3He$ ratio is about 2×10^7 for mantle-derived H_2, which is distinguished from crust-derived H_2. There is also a mixing region of mantle-derived H_2 and crust-derived H_2 (Jin et al., 2007), where the mantle-derived H_2-rich fluid enters the natural gas and mixes with the organic natural gas. As shown in Fig. 8 (data sourced from Han et al., 2022), the $H_2/^3He$ ratio of Denglouku Formation is larger than the upper limit of the mantle-derived H_2, indicating that the H_2 at a shallow depth of SK-2 is of crustal origin and is not the result of earth degassing. A small part of H_2 in Shahezi Formation is of crustal origin, and the majority has features of mantle-crust mixed origin (Fig. 8). It is possible that the H_2-rich fluid generated by mantle source entered Shahezi Formation and mixed with the natural gas of organic origin, and some H_2 may also be produced by organic reactions in shale intervals. The H_2 in Basement Formation is more discrete in *R/Ra* range, which is characteristic of mantle source and mixing source.

Based on He isotope identification and previous data analysis of H_2 origins in different geological settings (Jeffrey and Kaplan, 1988; Meng, 2022), further discrimination was carried out combined with the hydrogen isotope of H_2 (δD_{H_2}) and the relationship between CH_4 and H_2 content. As shown in Fig. 9, both zone C and zone D are mantle-crust mixed source regions, but there are some differences between them. In zone C, hydrogen in deep-source CO_2-rich fluids is oxidized during its upward migration, and the main geochemistry characteristics are that the isotopic composition of hydrogen is heavier than −700‰, while the value of $\ln(CH_4/H_2)$ is greater than −8. Zone D is the remaining hydrogen of deep source H_2-rich fluid after being oxidized. The main feature of zone D is that hydrogen still retains the deep source characteristics, but the content of methane and the value of $\ln(CH_4/H_2)$ decrease, and its main geochemistry characteristics are that the isotopic composition of hydrogen is less than −700‰, while the value of $\ln(CH_4/H_2)$ is less than −4.

All samples of Denglouku Formation are located in zone C, $\ln(CH_4/H_2)$ of the samples in Denglouku Formation range from 1.26 to 2.76, indicating a higher H_2 content. The δD_{H_2} values of samples were more than −700‰ and relatively enriched between −650‰ and −700‰. It indicates that the samples in Denglouku Formation have the characteristics of mixing origin. According to the analysis of anomaly intervals of natural gamma-ray data in well logging, it is possible that H_2 is produced by the radiolysis of water from a crustal source, and may also be produced by the pyrolysis of organic matter.

The $\ln(CH_4/H_2)$ of samples in Shahezi Formation ranges from 2.74 to 4.10, indicating a low H_2 content, with δD_{H_2} values of more than −700‰ in most samples and less than −700‰ in a small number of samples. Therefore, most samples of Shahezi Formation are located in zone C, and a few samples are located in zone B, it can be concluded that most of Shahezi samples have the characteristics of mantle-crust mixing origin and a few of them only have mantle-derived characteristics. Due to the long-term deposition and burial of Shahezi Formation, some intervals are mainly of shale and mixed with coal seams, which are typical source rocks. Therefore, its crustal origin includes the source of hydrogen generation from pyrolysis of organic matter. During the thermal evolution of organic matter, the H/C element ratio generally decreases, and the degree of

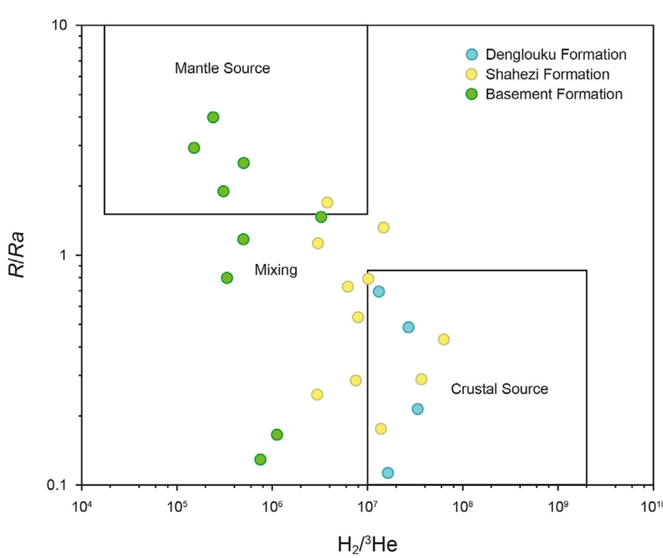

Fig. 8. Origin identification of H_2 by *R/Ra* and $H_2/^3He$ (base map patterned after Jin et al., 2007).

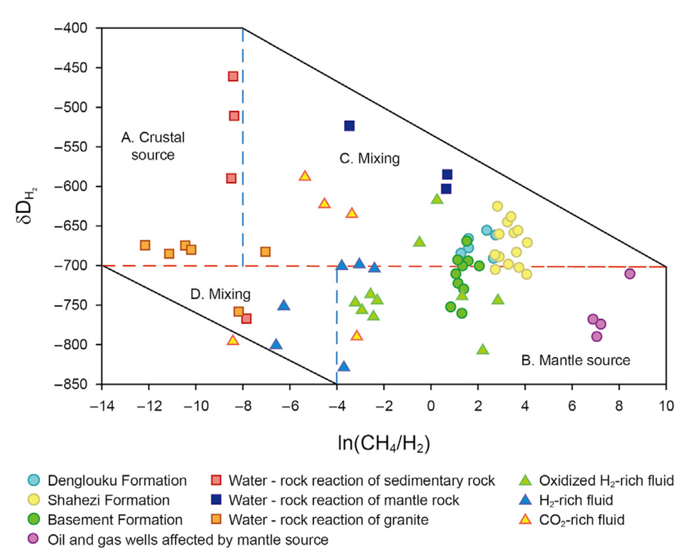

Fig. 9. Origin identification of H_2 by δD_{H_2} and $\ln(CH_4/H_2)$ (base map patterned after Meng, 2022).

aromaticity increases, especially in high-over-mature stage. The original organic matter will release a large number of hydrogen radicals, which are redistributed and reacted, and generation of H_2 may be accompanied by hydrocarbons. Compared with methane, the pyrolysis temperature of deep shale organic matter pyrolysis to generate hydrogen is higher, the generation temperature range is larger, and the temperature node of mass generation is relatively lagging behind. There is usually only one peak for methane in source rocks, but the hydrogen generation models are more complex and can be divided into four patterns (Fig. 10, data sourced from Horsfield et al., 2022): model 1 and model 2 are both single peak, but the peak temperature of hydrogen generation in model 1 is earlier than that in model 2; model 3 shows double peaks and model 4 shows three peaks.

In Basement Formation, $\ln(CH_4/H_2)$ of the samples are relatively concentrated, ranging from 0.84 to 2.07, indicating a relative enrichment of H_2, and the characteristics of δD_{H_2} and *R/Ra* are dispersed. Some of the samples in Basement Formation were lighter than −700‰, located in zone B, suggesting a typical mantle origin. Some were heavier than −700‰, located in zone C, suggesting a mixing origin. Under the microscope it was found that most of the rock slices of Basement Formation were affected by hydrothermal alteration, and Fe^{2+}-containing minerals (such as pyroxene and amphibole) were once developed (Fig. 11). The altered andesites all show a porphyritic structure, the component of porphyritic crystal is mainly feldspar, and the groundmass is cryptocrystal and vitreous. The groundmass of sample (a) was chloritized during the alteration process of the wall rock; the surface of feldspar phenocryst of sample (b) was sericite and muscovite, and the surface of feldspar phenocryst of sample (c) was epidoted. The hydrothermal alteration of pyroxene and amphibole (arfvedsonite) in Basement Formation may be the main factor for the increase of its hydrogen content, and it shows part of the crustal origin.

Combining the identification of hydrogen origins in Figs. 8 and 9, it is found that the source characteristics of hydrogen in Shahezi Formation and Basement Formation samples are consistent, while the source characteristics of hydrogen in Denglouku Formation are contradictory. The Shahezi Formation samples show that some are of single origin and some are of mixed origin; the Basement Formation samples show that some are of mantle origin and some are of mixed origin. The Denglouku Formation samples are shown as crustal-derived in Fig. 8 and mixed in Fig. 9. It can be seen that there is still controversy in identifying the more specific H_2 generative mechanism based on the isotopic composition, which needs to be combined with the actual geological environment to make a detailed judgment.

5. Geological implications

In this study, the main components of natural gas (CH_4, C_{2+}, H_2, N_2, and CO_2) and isotopes were found to vary greatly among gas samples (Fig. 2), reflecting the diverse sources of gases in different strata. In the samples of Denglouku Formation, CH_4 and H_2 are the principal components, with a small amount of N_2 also being present. The GR value in Denglouku Formation is abnormally high (Fig. 1b) and this result indicated that the shale has high clay content, large specific surface area and strong radioactive elements such as uranium (U), thorium (Th) and potassium (K), and created favorable conditions for the radioactive decomposition of water. According to the analysis of gas origins, the physical and chemical interactions are complex for the inorganic gas origins, attributable mainly to the radiolysis of water and the pyrometamorphism of nitrogen-bearing rocks. The radiolysis of water can lead to high δD_{H_2} values, ranging from −348‰ to −539‰ (Lin et al., 2005a, 2005b), while the δD_{H_2} values of Denglouku Formation samples are lower, not exceeding −650‰. This data discrepancy may be the result of a rapid exchange of isotopes between H_2 and groundwater.

Since coal seams have not developed in Denglouku Formation, the shale interval is most likely to be the source rock for organic gas

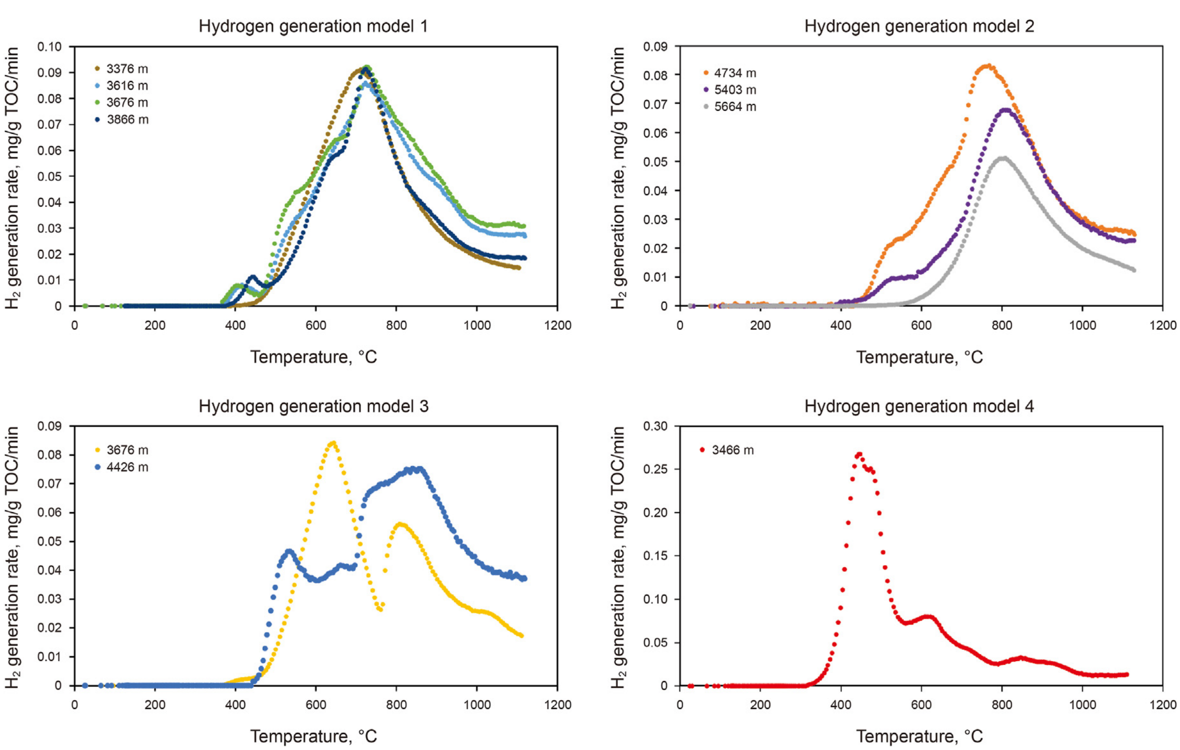

Fig. 10. Organic hydrogen generation models of Songliao Basin.

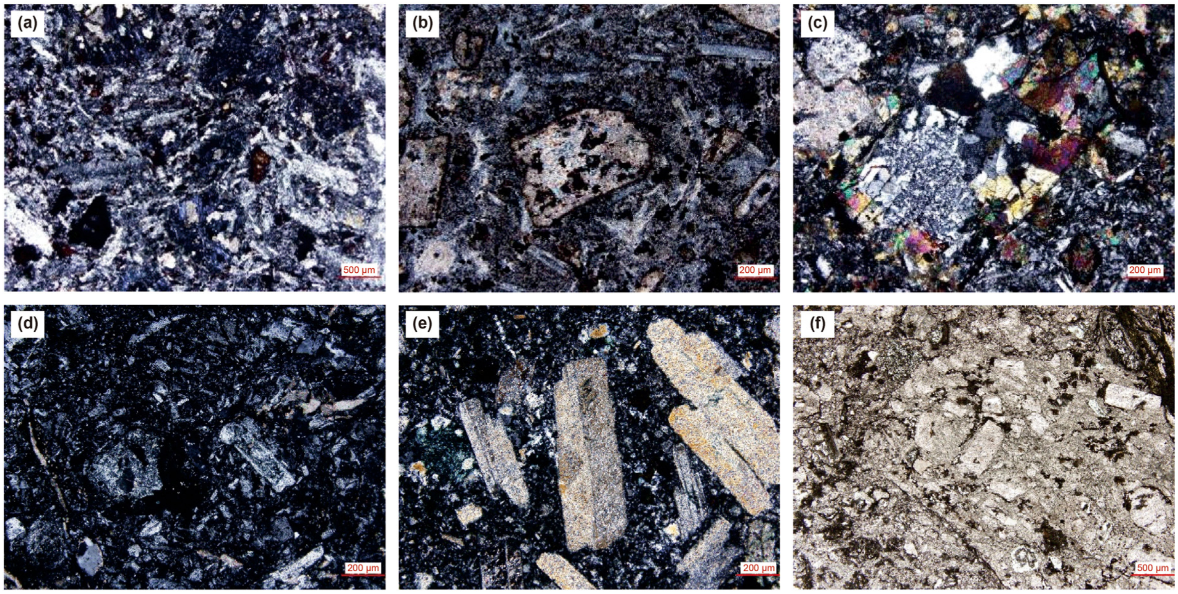

Fig. 11. Microscopic slice observation. (a) Altered andesite, 6514 m; (b) altered andesite, 6522.6 m; (c) altered andesite, 6537 m; (d) altered trachyandesite, 6628 m; (e) altered trachyte, 6718 m; (f) altered coarse andesitic volcanic breccia, 6751 m.

generation. In the samples of Shahezi Formation, CH_4, H_2, N_2, and CO_2 are all measured. The upper part of the lithology of Shahezi Formation is a shale reservoir with thick deposits and good continuity, and there are multiple sections of shale-coarse sandstone interbeds. The lower part is a glutenite-shale reservoir, with thin coal seams interposed. As the source rock, shale is at high-over maturity (measured R_o is 1.33%–4.24%, with an average of 2.61%). According to the gas origin analysis, CH_4, H_2, N_2, and CO_2 are produced partly by the process of organic matter pyrolysis. The δD_{H_2} value of organic origin is −810‰ ~ −629‰ (Suzuki et al., 2017), which overlaps with the sample data of Shahezi Formation. The inorganic gases in Shahezi Formation come from mantle sources, which were affected by deep faults in Basement Formation and migrated upward along the deep fault activity and nonuniform surfaces. As shown in Fig. 12, the SK-2 passes through two regional seismic reflection layers of T_4 (top interface of faulted sequence) and T_5 (bottom interface of faulted sequence) and local seismic reflection layers of $T_{4\text{-}1}$, $T_{4\text{-}a}$, and $T_{4\text{-}2}$, which provides a seismological basis for the source of deep inorganic gas in Songliao Basin. The former layers represent a regional tectonic basin-forming event; the latter layers represent the change of filling process and sequence in basin or rift scale. There is a distinct discontinuity of Moho surface in the deep basin (Fig. 1c), indicating that this is a mantle-scale magmatic activity zone. There is a lot of magmatic activity, which may be mixed with a large amount of inorganic gases upward migration. However, the temperature and pressure conditions were changed during the up transport, causing part of the mantle-driven CH_4 and H_2 to be lost, and the H_2 content is now

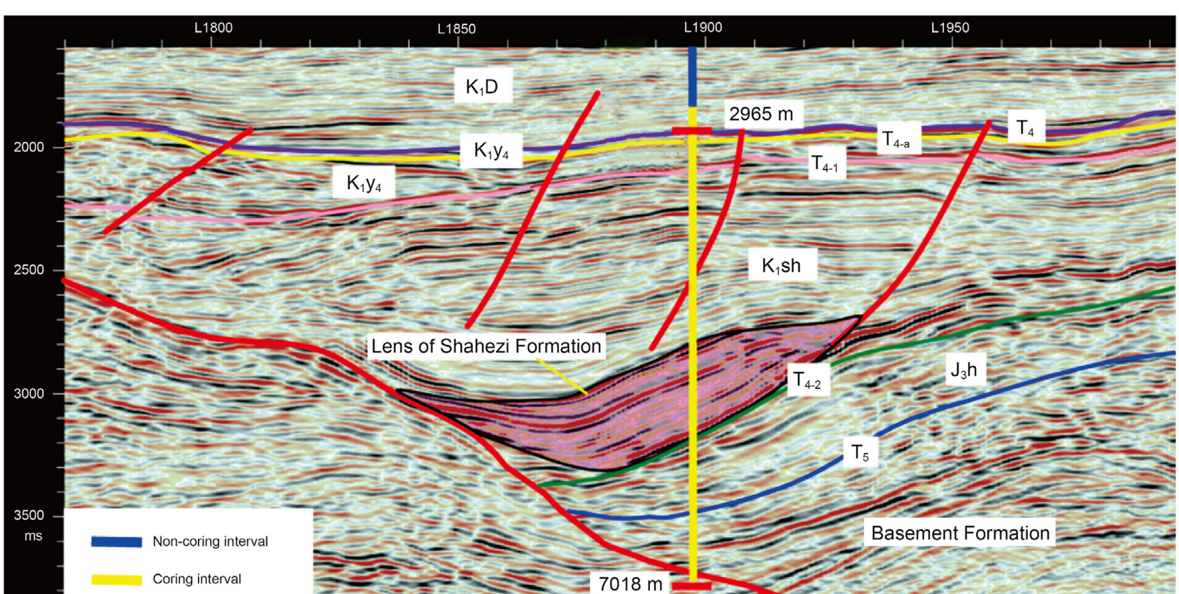

Fig. 12. The north-south seismic section image of study area.

relatively small.

The Basement Formation is composed mainly of tuff rock, with low metamorphic characteristics below. A small amount of altered andesite has developed, with large rock pore structure. The CH_4 occurring in Basement Formation is mantle-derived, and CO_2 and N_2 are mixed gases of the mantle and crust. The deep faults controlled the migration and mixing of gases from different formations. In Basement Formation, part of the H_2 is of mantle genesis, and part is of mantle and crust mixed genesis. The former H_2 is mainly affected by mantle degassing, and the latter H_2 is the result of the water-rock reaction of Fe^{2+}-containing minerals (such as pyroxene and amphibole). The δD_{H_2} value of H_2 produced by serpentinization reaction is about −715‰ (Milkov, 2022), which is exactly close to the sample data of Basement Formation. Although the content of hydrogen produced by serpentinization of ultramafic rocks is large, under the influence of deep faults, hydrogen is easy to escape. Therefore, compared with the typical areas with better preservation conditions (Mali serpentinized hydrogen gas with content of 98%, Prinzhofer et al., 2018), the hydrogen content in Basement Formation of study area is relatively low.

In the discussion above, we found that the genetic types of hydrogen are mixed sources in Shahezi Formation, and are strongly related to mantle origin in Basement Formation. This may be due to the very strong reducibility of hydrogen itself. H_2 is widely distributed in the petroliferous basins, and it not only has many origins, but also has many consumption pathways (Meng, 2022). The complexity of petroliferous basins has a profound influence on the generation, migration, and storage of H_2 (Han et al., 2022). Active H_2 can easily participate in the hydrocarbon-generation reactions of organic matter thermal evolution in source rocks, and has the effect on increasing hydrocarbon production by hydrogenation (Zhang et al., 2017). Therefore, H_2 provides a bridge between organic and inorganic hydrocarbon generation theories. The study area in Songliao Basin is rich in alkane gas, and due to plate collision and subduction, it has the geological conditions for high-content H_2 generation. International continental scientific drillings (SK-2 and SK-3), along with several oil and gas wells, show significant hydrogen gas anomalies. The occurrence of high hydrogen content may affect the lower-limit depth of gas generation in sedimentary basins. These implications can not only assist in the further development of gas resources in petroliferous basins, but also contribute to the exploration and development of deep H_2-rich natural gas.

6. Conclusions

The alkane gas content of study area is above 70.19%, and the main composition is CH_4. The $\delta^{13}C_1$ of CH_4 tends to be heavier on the vertical range. The δD_{CH_4} of CH_4 is lighter than −190‰, indicating a lacustrine environment. The origin of CH_4 in different strata varies. The CH_4 of Denglouku Formation is mainly of thermogenic origin; in Shahezi Formation it is a mixture of mantle and thermogenic origins; and in Basement formation it is dominated by mantle origin.

Working from both isotopes and gas components, the generation of N_2 and CO_2 is found to change from crust to mantle genesis with an increase of depth, and transitions from mixed (organic and inorganic) origin to inorganic origin. The N_2 and CO_2 in Basement Formation are the mixed gas of mantle and crust, and mainly produced by mantle-derived degassing.

Using the analysis of geological settings, the origin of H_2 was identified through various parameters. In Denglouku Formation and Shahezi Formation, H_2 is mainly associated with the radiolysis of water and pyrolysis of organic matter. In Basement Formation, H_2 content is determined not only by mantle-derived degassing, but also by the water-rock reaction of Fe^{2+}-containing minerals (such as pyroxene and amphibole) to produce hydrogen.

The gases of CH_4, C_{2+}, H_2, N_2, and CO_2 are present in diverse extents in different strata of Songliao Basin. The deep faults and unconformity surfaces in study area control the upward migration of mantle-derived gas. H_2 has high content in Denglouku and Basement Formations. The occurrence of high-content H_2 may affect lower-limit depth of natural gas generation in sedimentary basins, and it is of great significance for opening up a new field of deep H_2-rich natural gas exploration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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