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Review

Occurrence of Global Natural Hydrogen and Profitable Preservation

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ABSTRACT: Occurrence and abundance of molecular hydrogen in natural geologic reservoirs are enigmatic, due to its various sources, diverse migration pathways and complicated biological and chemical reactions. Natural gas samples containing hydrogen from producing wells in several sedimentary basins in China were collected in this study, and gas abundances and isotopic compositions of these gases were compared with those in global petroliferous basins and deep intrusive rocks. Several geochemical indicators were suggested for identifying sources, migration and accumulation mechanisms of hydrogen in the subsurface environment. Hydrogen contents in natural gas deposits have contributions from various sources with the following high-to-low order: microbial degradation > serpentinization > deep mantle volatile release > radiation-induced water decomposition > thermal cracking of organic matter. A hydrogen-rich reservoir in Kansas, USA, is specifically analyzed to determine its formation mechanism. This study suggests that future exploration of geological hydrogen resources may focus on the igneous rock bodies with overlying dense sedimentary rocks in the continental rift systems.

KEY WORDS: “white” hydrogen, hydrogen storage, genetic identification, enrichment and preservation, geological distribution.

0 INTRODUCTION

With the increasing concerns on the environment and energy on a global scale, many countries have successively proposed the development goals for carbon emission peak and carbon neutrality. Hydrogen (H_2) is receiving increasing attention from various organizations as the most environmentally friendly “green” energy source. Although hydrogen is the ultimate green energy, different sources of H_2 have different values of energy. Hydrogen produced artificially from petroleum, coal and other fossil sources is termed as gray hydrogen (Stiegel and Ramezan, 2006; Kim, 2003), because it consumes a certain amount of energy and produces greenhouse gases. Hydrogen produced by re-pyrolysis of natural gas is termed as blue hydrogen, owing to energy consumption, greenhouse gases release, and the raw natural gas itself as a clean energy. Hydrogen prepared by renewable energy such as wind energy, solar energy, water energy, biomass energy, and other non-fossil energy is termed as green hydrogen, since renewable energy is a green and low-carbon energy, with no greenhouse gas being produced in the process of H_2 generation. However, it is required to consume a certain amount of energy. The molecular hydrogen which occurs naturally in geological formations in underground deposits is termed as gold hydrogen, because H_2 in the geological bodies is exploited using economic and low-carbon techniques with no energy consumption. The calorific value of hydrogen combustion is 2.56 times of that of methane, and the combustion product is pure water, therefore, molecular hydrogen is an efficient, green, low-carbon and clean energy (Rigollet and Prinzhofer, 2022). According to the prediction of the International Hydrogen Energy Commission, if the global temperature increase is controlled at 2 °C, the global demand for hydrogen energy will reach 0.55×10^9 t by 2050, which will lead to reduce CO_2 emissions by 6×10^9 t (Hydrogen Council, 2017). At present, the development and utilization of hydrogen energy in the world is at an early stage, and H_2 is mainly used as a secondary energy source. Processes of hydrogen production cause secondary energy consumption, greenhouse gas emission

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and pollution. Therefore, exploration and development of natural hydrogen as a primary energy source in geological bodies has received great attention (Cheng et al., 2023; Hand, 2023).

Discovering hydrogen resources under natural conditions can be a milestone in filling the gap in hydrogen energy demand, reducing the consumption of non-renewable resources, and promoting the conversion of gray and blue hydrogen into green hydrogen. With the continuous development of exploration technology and analytical techniques, molecular hydrogen has been found in various geological scenarios, and it has successively been discovered in onshore sedimentary basins, plate active zones, and rift zones (Wang et al., 2024; Hassan et al., 2024; Etiope, 2023, 2017; Han et al., 2022; Horsfield et al., 2022; Jin and Wang, 2022; Cathles and Prinzhofer, 2020; Deronzier and Giouse, 2020; Klein et al., 2020, 219; McCollom et al., 2020; Zgonnik, 2020; Bougault, 2019; Etiope and Whiticar, 2019; Guélard et al., 2017; Meng et al., 2015; Sherwood Lollar et al., 2014; Etiope et al., 2011; Bradley and Summons, 2010; Allen and Seyfried, 2004; Abrajano et al., 1988; Jeffrey and Kaphlan, 1988; Coveney et al., 1987; Goebel et al., 1983; Neal and Stanger, 1983; Welhan and Craig, 1983, 1979; Craig and Lupton, 1976; Hawkes, 1972). Mendeleev first discovered hydrogen molecule in a fault within a coal mine in Eastern Europe in 1888 (Zgonnik, 2020); Kravtsov (1967) measured the H_2-bearing gas in a basic volcanic complex on the Kola Peninsula in Russia for three consecutive years, and the H_2 content was in the range of 2.8%–3.8%, which had not changed significantly in three years between 1969 and 1971 (Hawkes, 1972). The gas measurement for the drilling flushing fluid in the world's deepest Kola ultra-deep drilling SG-3 well with 12 263 m depth showed abnormal levels of H_2 molecule in the layers deeper than 5 000 m The H_2 content in the rock drilled out is 4.9–32.5 m^3 per cubic meter, and the H_2 content in the deep part is higher than that in the shallow part (Zgonnik, 2020). The hydrogen content in the natural gas drilled near the axis of the continental rift in the Hengill area in the southwestern Iceland was as high as 37% (Marty et al., 1991). The flames in the Chimaera area of Türkiye, where the first Olympic fire was collected, were almost produced by underground hydrogen combustion that have been active for 2 500 years, and still contain the hydrogen content in the range of 7.5% – 11.3% (Etiope, 2017; Etiope et al., 2011). The daily production of H_2 molecule is about 1.5×10^3 m^3 in Well Gazbongou-1 in Mali, West Africa (Prinzhofer et al., 2018). Well 42 of Yudaknaya Diamond Mine in Russia found an initial daily hydrogen production of about 10^5 m^3 in kimberlite dikes (Zgonnik, 2020). Therefore, hydrogen resource has huge exploration and development potential in geological bodies.

Due to active chemical properties of hydrogen itself, molecular H_2 is prone to secondary transformation during the enrichment process after formation, making its geochemical characteristics very complex. The content distribution and isotope fractionation of H_2 in different scenarios vary significantly (Etiope, 2023; Milkov, 2022), making the determination of the genetic origin and source of H_2 molecule very challenging (Liu et al., 2024). It is also difficult to understand the hydrogen enrichment in geological bodies. In order to determine the hydrogen accumulation in various scenarios, we collected the gas composition, carbon and hydrogen isotope and noble gas isotope data of natural gases in H_2-bearing sedimentary basins, deep intrusive rock mass gases and hot spring gases in China, and compared them with reported H_2 data around the world. By combining the geological background of H_2-bearing gases, we demonstrate the origin and source of molecular H_2, and establish geochemical indicators to identify different sources of molecular H_2 in various scenarios. In addition, the main geological factors controlling the accumulation of H_2-bearing natural gas in the Kansas Basin, USA were illustrated to clarify the distribution and enrichment of natural hydrogen in geological bodies. These understandings not only reduce the risk of hydrogen exploration in geological bodies, but also provide the support for the effective development and efficient utilization of hydrogen in geological bodies as well as the sustainable and low-cost development of hydrogen.

1 DISTRIBUTION OF MOLECULAR HYDROGEN IN GEOLOGICAL BODIES ON LAND

Molecular hydrogen is widely distributed in various geological scenarios on land, including oil-gas-bearing cratonic basins, fault zones, subduction zones, and rift zones controlled by deep faults (Figure 1). The rocks in which molecular H_2 is present include sedimentary rocks in basins, igneous rocks (e. g., basalt, ophiolite, peridotite) and metamorphic rocks in deep intrusions. The formation and distribution of hydrogen gas are affected by structural background, lithology and water contact, and the hydrogen gas often coexists with CO_2, N_2 and alkane gases in geological bodies.

Well Gazbongou-1, located on the graben structure of Taoudenni Meganbasin in Mali, West Africa, is an exploration well with the highest H_2 content discovered in natural gas so far. The drilled well encountered the Proterozoic sedimentary strata, and the Triassic diabase bedrock is observed in interlayer, and the gas production flow is about 1 500 m^3/d. Subsequently, a total of 5 sets of carbonate and sandstone reservoirs reaching as deep as 1 800 m were surveyed through a large number of drilled wells. The H_2 reservoir is composed of multi-layered diabase bedrock and sedimentary rock layers, and an aquifer blocks the upward migration and leakage of H_2. The best enrichment of molecular hydrogen occurs in carbonate reservoirs, because the molecular hydrogen forms a "gas lift" barrier under action of water and is sealed in the carbonate reservoir (Prinzhofer et al., 2018). The H_2 content in the test gas reaches 98%, accompanied by trace amounts of CH_4 (~1%) and N_2 (~1%), in which the δ^2H-H_2, $\delta^{13}C_1$, and δ^2H-C_1 values are -702‰, -40.4‰, and -249‰, respectively (Briere and Jerzykiewicz, 2016; Prinzhofer et al., 2018). The $^3He/^4He$ ra-

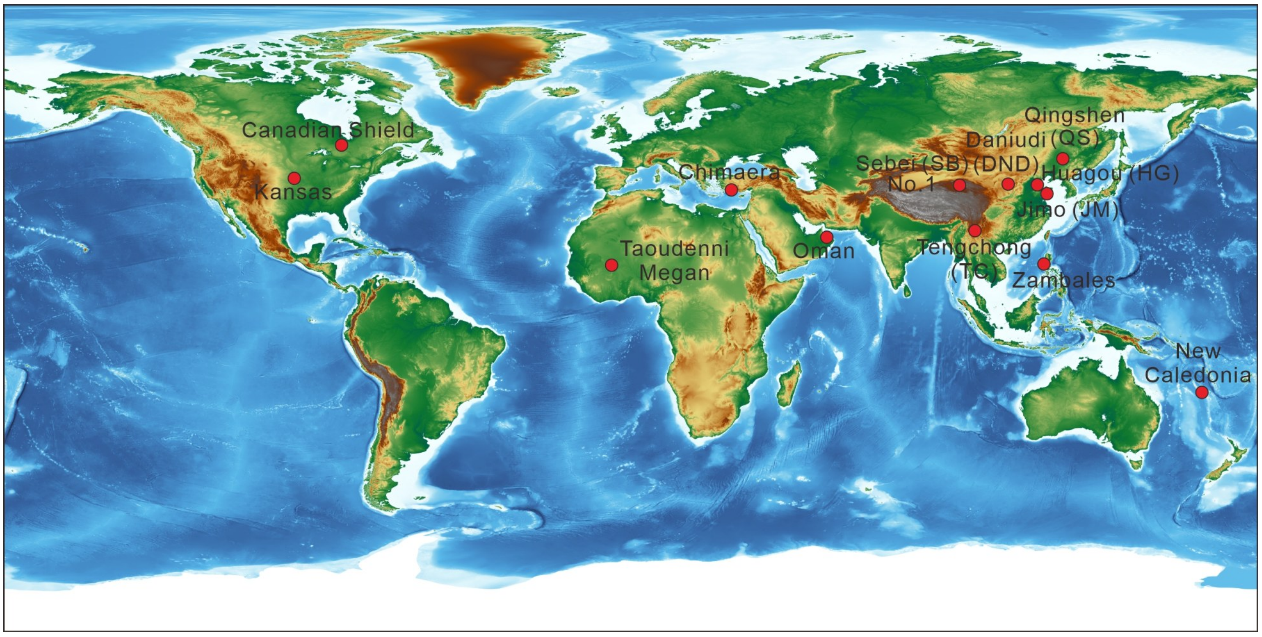

Figure 1. Distribution of typical hydrogen-bearing gases around the world.

tio is 8.2 × 10^{-8} (0.058 6 Ra) with $^{40}\mathrm{Ar}/^{36}\mathrm{Ar}$ ratio of 384, indicating the characteristics of crust-derived gas.

Since the 1980s, the Henis and Scott wells drilled by the Kansas Branch of the US Geological Survey and the CFA Petroleum Company in the Kansas Basin have produced H_2 with a stable content at 34% in sedimentary rock and at 90% in Precambrian basement volcanic rock, which is mainly composed of basalt. The H_2 production was about 93.2 and 370 m^3 per day, respectively, and the production has continued for more than 30 years (Newell et al., 2007). In 2008, the Well Sue Duroche 2 was drilled into the fractured basement of Precambrian basic-ultrabasic volcanic rocks. During the drilling, the molecular hydrogen was detected in Late Precambrian feldspar sandstone, Devonian – Mississippian Chattanooga marine shale, Silurian-Devonian Hunton limestone aquifer, and Pennsylvanian sandstone (Guélard et al., 2017), and the H_2 content in natural gas reached as high as 91.8%. The formation water of the gas reservoir is fresh-salt water, whereas the sedimentary formation water is saline water, and the water in the basement volcanic body is fresh water. The fresh water in the basement layer may be attributed to the uplift of the western part of the basin, which caused the meteoric water to pass through fractures and infiltrate into the basin basement (Guélard et al., 2017). The chemical composition of natural gas is mainly H_2, CH_4 and N_2, with a small amount of He and CO_2 (Guélard et al., 2017; Newell et al., 2007; Coveney et al., 1987). The H_2 content ranges from 0.1% to 91.8%, with an average value of 18.9%, and the $\delta^2\mathrm{H}\text{-}\mathrm{H}_2$ value ranges from -826‰ to -717‰, with an average value of -768%. The CH_4 content ranges from 0.04% to 53.8%, with an average of 15.42%, and the $\delta^{13}\mathrm{C}_1$ value ranges from -52.9‰ to -20.1‰, with an average of -35.0%. Most of the carbon isotope value of methane are distributed at both ends. The $\delta^2\mathrm{H}\text{-}\mathrm{C}_1$ value ranges from -438‰ to -423‰, with an average of -431‰, and the distribution of hydrogen isotope values of methane is concentrated. The nitrogen content ranges from 4.7% to 96.0%, with an average of 69.19%. The He content ranges from 0.002% to 3.10%, with an average value of 1.248%, and the $^3\mathrm{He}/^4\mathrm{He}$ ratio ranges from 0.009 4 Ra to 0.32 Ra, with an average value of 0.049 1 Ra, indicating that the gas is crust-derived.

Several H_2-bearing oil and gas reservoirs and hot spring gas have been discovered along the Tancheng-Lujiang extra-large deep fault zone and its surrounding areas in eastern China, including Qingshen (QS) gas field in the Songliao Basin, Huagou (HG) gas field in Jiyang Depression in the Bohai Bay Basin, and the Jimo (JM) hot spring gas. The JM hot spring is located in the Muping-JM fault zone in the southern part of the Jiaodong Peninsula along the Tancheng-Lujiang extra-large deep fault zone, and the hot spring gas is mainly produced from Cretaceous sandstone and basalt body which is rich in pyroxene and olivine, and the hot spring water is alkaline saline (Hao et al., 2020). The main component of hot spring gas is N_2, and its content ranges from 83.81% to 89.44%, with an average value of 86.56%. The H_2 content ranges from 2.38% to 12.45%, with an average of 7.20%, and the $\delta^2\mathrm{H}\text{-}\mathrm{H}_2$ value ranges from -822‰ to -709‰, with an average of -756‰. The CH_4 content ranges from 0.27% to 3.81%, with an average of 1.36%, and the $\delta^{13}\mathrm{C}_1$ value ranges from -41.5‰ to -33.2‰, with an average value of -37.0‰. The $\delta^2\mathrm{H}\text{-}\mathrm{C}_1$ values range from -428‰ to -221‰, with an average value of -279‰. The CO_2 content ranges from 0.05% to 1.89%, and the He content ranges from 0.01% to 0.53%, with an average of 0.138 6%. The $^3\mathrm{He}/^4\mathrm{He}$ ratios range from 0.55 Ra to 0.65 Ra, with an average value of 0.60 Ra. The Jiyang Depression in the Bohai Bay Basin is affected by the strike-slip action of the Tancheng-Lujiang extra-large deep fault, with frequent tectonic activities and creating a series of deep faults and recessive fault zones, and there are extensive Tertiary diabase intrusions. The formation water is fresh-brackish water. The natural gas layers in the HG gas field in Jiyang Depression of Bohai Bay Basin are clastic and volcanic rocks, and natural gas components are mainly CH_4, CO_2 and N_2 (Meng et al., 2015). Although H_2 content is low (< 0.01%), it is widely distributed. The overall distribution of δ^{2}H-H_2 ranges from -759‰ to -635‰, with an average of -690‰. The methane content ranges from 1.31% to 97.69%, with an average of 75.42%. The $\delta^{13}C_1$ values range from -54.8‰ to -43.4‰, with an average of -50.4‰, which is a typical thermal cracking gas formed by thermal decomposition of organic matter. The δ^{2}H-C_1 values range from -277‰ to -144‰, with an average of -245‰, and the CO_2 content ranges from 0.16% to 88.60%, with an average value of 18.68%. The He content ranges from 0.002 3% to 0.145 0%, with an average value of 0.040 6%, and the ^{3}He/^{4}He ratio ranges from 0.036 5 Ra to 3.262 0 Ra, indicating a mixing of crust and mantle endmembers. The Songliao Basin is located on the outward accretionary fold belts between Siberia Plate and Tarim-China-Korea Plate, on the northern edge of the Tancheng-Lujiang extra-large deep fault zone. Structurally, it belongs to the Mesozoic half-graben continental rift basin, with basement, depression layer, and fault layer from bottom upward, showing a style of fault-depression double structure (Hu et al., 1998). The basement of the basin is composed of pre-Paleozoic and Paleozoic metamorphic and volcanic rocks, produced during the Hercynian orogeny (Feng, 2008). In the basin, there is a large positively buried structural belt formed by central uplift and fault-depression belts on the east and west edges. The fault depressions of Xujiaweizi, Gulong, Meilisi and Yingtai are developed in the western fault-depression belt. Gas fields, such as Wangjiatun, Songfangtun, Changde and Nong’ancun, have been discovered in the Xujiaweizi fault depression and its surrounding areas. CH_4 is reatively enriched in ^{13}C ($\delta^{13}C_1 > -30$‰) and the alkane gases have the characteristics of negative carbon isotope sequence (i.e., $\delta^{13}C_1 > \delta^{13}C_2 > \delta^{13}C_3$) with high ^{3}He/^{4}He ratios (> Ra) of accompanied helium gas, which is a feature of gas of abiogenic origin (Liu et al., 2016; Jin et al., 2009; Dai et al., 2005a). The QS gas field is located in the middle of the Xujiaweizi fault depression, with proven geological natural gas reserves of 252.271 × 10^9 m^3 at the end of 2018. The production layers are mainly volcanic and sandstone rocks of the Cretaceous Yingcheng Formation, and the formation water is mainly fresh water. The main component of natural gas in the QS gas field is methane, with trace amount of H_2. CH_4 content ranges from 92% to 95%, and $\delta^{13}C_1$ value ranges from -29.7‰ to -17.4%, with an average of -26.1‰. The δ^{2}H-C_1 value ranges from -204‰ to -197‰, with an average of -202‰. The H_2 content ranges from 0.05% to1.94%, and δ^{2}H-H_2 value ranges from -792‰ to -708%, with an average value of -762‰. The N_2 content is between 0.33% and 5.03% and the CO_2 content in the gas reservoir varies greatly. In the central part of the gas reservoir, it is dominated by alkane gas, with the CO_2 content less than 2%, whereas the CO_2 content at the western part of gas field is higher than 80% (i.e., wells FS9 and FS701) (Liu et al., 2016). $\delta^{13}C_{CO2}$ values range from -16.5‰ to -5.9‰, with an average value of -10.8‰. He contents ranges from 0.007 6% to 0.034%, with an average value of 0.02%, and the ^{3}He/^{4}He ratio ranges from 1.04 Ra to 5.84 Ra, with an average value of 2.28 Ra, showing the characteristics of mantle-derived gas.

The Qaidam Basin is located inside the Qinghai-Tibet Plateau. As a product of mutual extrusion of Eurasian Plate and Indian Ocean Plate, the Qinghai-Tibet Plateau develops several deep and large faults, however, these faults are undeveloped in the Sanhu area in the east of the Qaidam Basin, with weak volcanic activity (Pang et al., 2005). The Quaternary source rocks deposited in this area are enriched in organic matter available for microorganisms, and the formation water is either weakly acidic or freshwater deposits (Tuo and Philp, 2003). Abnormally high H_2 content was detected in the tank top gas collected from Well Xinse 3-4 (XS3-4) in the Sebei (SB) No. 1 gas field of Sanhu area and Well Senan 2 (SN2) in the Senan structural belt in the eastern Qaidam Basin (Shuai et al., 2010). The H_2 content ranges from 47.7% to 95.4%, with an average value of 74.5%, and the δ^{2}H-H_2 value ranges from -831‰ to -720‰, with an average value of -772‰. The CH_4 content ranges from 3.60% to 51.30%, with an average of 24.46%, and $\delta^{13}C_1$ value ranges from -68.0‰ to -64.0‰, with an average value of -66.0‰. The $\delta^{13}C_1$ value is less than -55‰, suggesting a typical bacterial gas. The δ^{2}H-C_1 value ranges from -237‰ to -201‰, with an average of -223‰. ^{3}He/^{4}He ratio in the gas layers ranges from 3.47 × 10^{-8} to 4.97 × 10^{-8} with the ^{40}Ar/^{36}Ar ratio from 318 to 381.6 (Pang et al., 2005), and the $\delta^{13}C_{CO2}$ value of associated CO_2 ranges from -17‰ to -3.2‰ (Shuai et al., 2010), indicating the characteristics of typical crustal source.

The Ordos Basin is located on the western edge of the North China Craton, with a mean thickness of sedimentary rocks of 5 000 m. Among them, the source rock series in Carboniferous–Permian Shanxi Formation, Taiyuan Formation and Benxi Formation were developed (Hanson et al., 2007; Xiao et al., 2005). They are mainly composed of coal seams, dark mudstone, and biological limestone. The sedimentary water is freshwater-brackish water(Liu et al., 2015, 2008). The uranium (U) content in basement and source rocks is generally high, ranging from 8.42 ppm to 1 897 ppm. Natural gas components in the Daniudi (DND) gas field of the Ordos Basin are dominated by CH_4, which has a content ranging from 87.91% to 94.36% with an average of 90.18%; $\delta^{13}C_1$ value ranges from -37.9‰ to -33.3‰, with an average of -36.2‰; δ^{2}H-C_1 value ranges from -204‰ to -179‰, with an average value of -192.9‰. CO_2 content ranges from 0.41% to 2.11%; H_2 content ranges from 0.02% to 0.24%, with an average value of 0.06%; δ^{2}H-H_2 value ranges from

-758‰ to -607‰, with an average value of -673‰. The hydrogen isotopic compositions of H_2 and CH_4 in this area have a significant positive correlation (Liu et al., 2015), implying that there could be a certain relationship between H_2 and CH_4. The He content ranges from 0.028 7% to 0.127 3%, with an average of 0.044 9%, and the $^3He/^4He$ ratio ranges from 0.006 5 Ra to 0.460 Ra, with an average value of 0.023 9 Ra (Liu et al., 2022), showing a typical crustal origin.

The structure of Kidd Creek Shield in Canada is stable, and the Precambrian granite crystalline basement was intruded by basic-ultrabasic igneous rocks (Macgeehan and Hodgson, 1980). Serpentinized and altered ultramafic rocks are widely found in this area, and the formation water is brackish (Sherwood Lollar et al., 1993). The CH_4-rich natural gas reservoir occurs mostly associated with H_2 and He (Warr et al., 2019). The H_2 content ranges from 0.01% to 26.0%, with an average of 2.58%. The δ^2H-H_2 value at the CCS4000 station is -637‰ (Sherwood Lollar et al., 1993). The methane content ranges from 0.21% to 82.30%, with an average of 51.03%, and the $\delta^{13}C_1$ value ranges from -47.3‰ to -25‰, with an average value of -36‰. δ^2H-C_1 value ranges from -419‰ to -184‰, with an average value of -317‰, and the distribution of carbon and hydrogen isotope values of CH_4 is relatively wide, indicating that the process of methane isotope fractionation would be complex. The He content ranges from 1.98% to 11.6%, and the $^3He/^4He$ ratio in this area ranges from 0.014 Ra to 0.018 Ra. The $^3He/^4He$ ratios are less than 0.02 Ra, demonstrating the typical characteristic of crust-derived gases. Although $^3He/^4He$ ratios are < 0.02 Ra, He content is > 1.0%, indicating that He is sourced from the radioactive decay of uranium (U) and thorium (Th) elements in minerals and rocks (Ozima and Podosek, 2004; Sherwood Lollar et al., 1993). The N_2 content varies greatly, ranging from 3.48% to 87.00%, with an average of 36.60%, and the CO_2 content ranges from 0.02% to 2.52%, with an average of 0.47%.

The Oman rock mass is located near the subduction zone of the Indian Ocean Plate. The rock mass is mainly composed of Cretaceous peridotite complexes which intruded into the ancient oceanic crust of sedimentary rocks such as carbonates. The gas in the Oman rock mass is mainly produced in the alkaline saline groundwater, and both H_2 and N_2 are the main components of the gas (Vacquand et al., 2018; Neal and Stanger, 1983). The H_2 content ranges from 1.0% to 99.0%, with an average of 59.9%. The δ^2H-H_2 value ranges from -745‰ to -697‰, with an average of -713‰, and most of the values are distributed around -700‰. CH_4 content is generally low, ranging from 0.10% to 15.90%, with an average of 4.80%. $\delta^{13}C_1$ value ranges from -12.8‰ to 7.9‰, with an average of -3.9‰, and $\delta^{13}C_1$ values > -20‰ implies the CH_4 has abiogenic characteristics; δ^2H-C_1 value ranges from -428‰ to -234‰, with an average value of -331‰. Although the range of $\delta^{13}C_1$ values in Oman peridotite complexes gas is relatively concentrated and higher than -20‰, the δ^2H-C_1 value has a large variation. Even though the gas is produced in the saline layer, the δ^2H-C_1 value is still less than -180‰. The CO_2 content is very low, basically less than 0.05%, while the N_2 content varies greatly, ranging from 1.0% to 78.0%, with an average of 33.6%. The He content is generally less than 0.1%, and the $^3He/^4He$ ratios range from 0.17 Ra to 1.25 Ra with an average value of 0.70 Ra, showing the mixing of crust and mantle sources.

The Chimaera ophiolites in Türkiye is located on the collision zone between African Plate and Eurasian Plate. To the north of the rock mass is the Cretaceous ophiolite, and to the south is the Triassic clastic rock. Natural gas components are mainly CH_4 and H_2, and the H_2 content ranges from 7.5% to 11.3%, with an average of 9.8%, whereas δ^2H-H_2 value ranges from -748‰ to -720‰, with an average of -735‰. The methane content ranges from 65.2% to 93.2%, with an average of 84.9%. The $\delta^{13}C_1$ value ranges from -12.6‰ to -7.9‰, with an average value of -11.5‰, whereas the $\delta^{13}C_1$ value is > -20‰, showing characteristics of abiogenic CH_4. δ^2H-C_1 value ranges from -129‰ to -97‰, with an average value of -123‰. Although the $\delta^{13}C_1$ value is higher than -20‰, showing the characteristics of abiogenic CH_4, the δ^2H-C_1 value is less than -160‰, which is different from the hydrogen isotope composition of CH_4 in the Oman ophilite complexes. The CO_2 content ranges from 0.01% to 0.18%, with an average of 0.07%, and $\delta^{13}C_{CO2}$ value ranges from -20.4‰ to -15.1‰, with an average of -18.1‰. The He content in this area is very low, ranging from 0.000 079% to 0.02%, with an average value of 0.005%, and the $^3He/^4He$ ratio ranges from 0.31 Ra to 4.35 Ra, with an average value of 1.64 Ra, showing the characteristics of crust-mantle mixing. It was considered that CH_4 in this area was mainly synthesized by the Fischer-Tropsch reaction between H_2 and CO_2 dissolved in water, and the continuous supply of molecular H_2 cannot be completely consumed by Fischer-Tropsch synthesized hydrogen, therefore, the H_2-enriched natural gas was formed (Vacquand et al., 2018; Etiope et al., 2007; Hoşgörmez, 2007; Hoşgörmez et al., 2005). The higher $^3He/^4He$ ratio indicates that there is a contribution from the deep mantle in this area, and the $\delta^{13}C_1$ value which is higher than -20‰ suggesting that the contribution of methane from thermal cracking of organic matter in Triassic sedimentary rocks would be limited.

The Zambales ophiolotes in Philippines is an ophiolite body located in the subduction zone of Philippine Sea Plate and Pacific Plate. There are two sets of ophiolite bodies, namely the Jurassic – Cretaceous ophiolite and the Eocene peridotite. There are several hot spring gas and gas seeps above the Zambales rock mass in the Philippines (Abrajano et al., 1988). The development of multiple sets of fault systems in the rock mass provide channels for material exchange and chemical reactions between surface layer and deep plate. The hot spring water is alkaline and the ground temperature is about 110–150 °C (Vacquand et al., 2018). The gas components in this area are mainly H_2 and CH_4, of which H_2 content ranges from 35.1% to 58.5%, with an average of 44.6%, and the δ^2H-H_2 value ranges from -756‰ to -581‰, with an average of -650‰. The methane content ranges from 16.7% to 55.3%, with an average of 43.5%. The $\delta^{13}C_1$ value ranges from -7.5‰ to -5.6‰, with an average of -6.6‰, and it is higher than -20‰, which is a typical feature of abiogenic CH_4. The δ^2H-C_1 value is distributed between -175‰ and -118‰, with an average value of -145‰. In the statistics of CH_4-H_2-rich sites, it is found that there is a significantly negative correlation between methane and hydrogen contents, indicating that both of them have a direct relationship, see discussion in text below. The CO_2 content is basically less than 0.1%. The He content is less than 0.1%, and the $^3He/^4He$ ratios range from 0.49 Ra to 4.35 Ra, with an average value of 3.22 Ra, showing the characteristics of crust-mantle mixing.

The New Caledonia ophiolites in the east of Australia is located near the collision zone between Australia-India Plate and Pacific Plate, where a large number of Eocene ophiolites (mainly peridotite) with a large number of deep faults are exposed (Deville and Prinzhofer, 2016). The ultra-alkaline hot spring gas in the rock mass contains a large amount of H_2, CH_4, N_2, and He (Deville and Prinzhofer, 2016; Woolnough, 1934). The H_2 content ranges from 0.01% to 36.07%, with an average of 26.34%. Among them, the H_2 content in Baie du Carenage and Source des Kaoris is highly concentrated, ranging from 26.81% to 36.07%, with an average of 31.59%. The CH_4 content in the New Caledonia pohiolite gas ranges from 2.65% to 15.74%, with an average of 9.16%, and the $\delta^{13}C_1$ value ranges from -39.2‰ to -12.1‰, with an average of -30.36‰. The CO_2 content is very low and generally less than 0.1%. The He content ranges from 0.01% to 0.1%, with an average value of 0.03%, and $^3He/^4He$ ratio ranges from 0.06 Ra to 1.76 Ra, with an average value of 0.944 Ra, showing the characteristics of crust-mantle mixing. The N_2 content is very high, ranging from 50.3% to 97.3%, with an average of 73.0%. The N_2 was sourced mainly from mantle degassing and peridotite metamorphism by means of gas components, noble gas isotopes and N isotopes in the rock mass gas, and a small part of N_2 was dissolved by shallow atmospheric precipitation (Vacquand et al., 2018; Sano et al., 1993).

The Tongchong (TC) hot spring gas is located at the junction of Eurasian Plate and Indian Plate. Since the Cenozoic, the Indian Plate has continued to squeeze northeastward and caused frequent tectonic activities. Most of the gas in TC hot springs is produced from the basic-ultrabasic volcanic rocks, and the water body is acidic. The hot spring gas component is mainly CO_2, and its content ranges from 57.49% to 96.64%, with an average of 90.24%. The $\delta^{13}C_{CO2}$ value ranges from -5.8‰ to -1.9‰, with an average of -4.0‰, showing that it is of abiogenic origin. Other gases in the hot spring include N_2, and a small amount of H_2, CH_4, and He (Dai, 1989). The H_2 content ranges from 0.015% to 5.15%, with an average of 0.78%, and the δ^2H-H_2 value ranges from -804‰ to -583‰, with an average of -711‰. CH_4 content ranges from 0.001% to 0.820%, with an average of 0.152%. The $\delta^{13}C_1$ value ranges from -32.6‰ to -16.4‰, with an average value of -22.4‰, whereas the δ^2H-C_1 value is distributed from -267‰ to -130‰, with an average value of -191‰. The He content ranges from 0.01% to 5.2%, with an average value of 1.635%, and the $^3He/^4He$ ratio ranges from 1.094 Ra to 5.280 Ra, with an average value of 3.196 Ra (Shangguan and Hou, 2002), showing the characteristics of mantle-derived gas.

Based on the gas composition and stable isotope data in various geological settings, a general summary is that the H_2 content in the hot spring gas system is mainly affected by deep faults, and it is also significantly affected by the volcanic bedrock or surrounding rock. The H_2 content is generally high in ophiolites and peridotites, while the H_2 content is relatively low in oil and gas reservoirs in sedimentary basins, however, it is abnormally high under the action of microorganisms in sedimentary basins. Therefore, the key way to clarify the source of molecular H_2 is to identify the source of H_2-bearing gas in geological bodies. In this study, the authors intend to illustrate the geochemical characteristics of molecular H_2 and asociated gases and use them to reveal the source and formation mechanisms of molecular H_2 in various geological scenarios.

2 SOURCES OF MOLECULAR HYDROGEN IN GEOLOGICAL SCENARIOS

2.1 Geochemistry of Molecular Hydrogen and Its Associated Gas in Geological Scenarios

As an important component in natural gas, molecular hydrogen is often associated with gases such as methane and helium. The origin and sources of molecular hydrogen can be inferred by the geochemical characteristics of its associated gases (Figures 2, 3).

2.1.1 Relationship between H_2 content and R/Ra

During volcanic activity, a large amount of deep gas can be released. The gas is mainly composed of CO_2, H_2, and CH_4, and it also contains a trace amount of noble gases including He, Ne and Ar (Welte et al., 1988). Due to chemical inertness of noble gases, their abundances and isotope ratios during geological processes are hardly affected by complex chemical and biological reactions, but mainly depend on physical processes, such as diffusion, dissolution, adsorption, and nuclear reactions (Prinzhofer and Battani, 2003; Ballentine and Burnard, 2002). Noble gases do not accumulate in a free state, and they mix with other natural gases and display the contents generally not higher than 1% (Xu et al., 1998). Mantle-derived helium in natural gas is mainly controlled by deep fault zones, volcanic activities, and magmatic activities, and the migration of mantle-derived volatiles is through channels directly connected to the mantle (Ding et al., 2005; Xu Y C et al., 1997a, b; Xu S et al., 1995a, b). ^3He is of primitive origin, which is mainly related to the deep mantle (Caffee et al., 1999; Craig and Lupton, 1976), whereas ^4He is mainly produced by α-decay of radioactive elements such as U and Th in rocks and minerals,

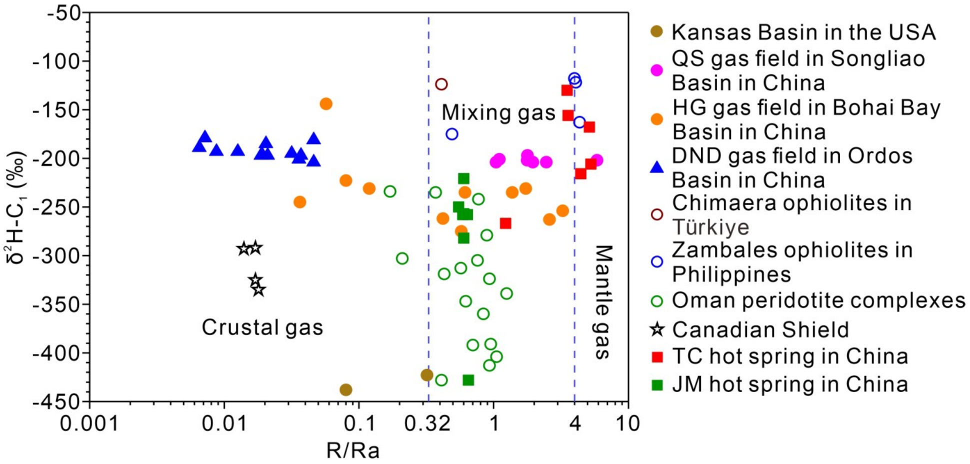

Figure 2. Correlation between $^3He/^4He$ ratios (R/Ra) and $\delta^2H\text{-}C_1$ values in various geological settings.

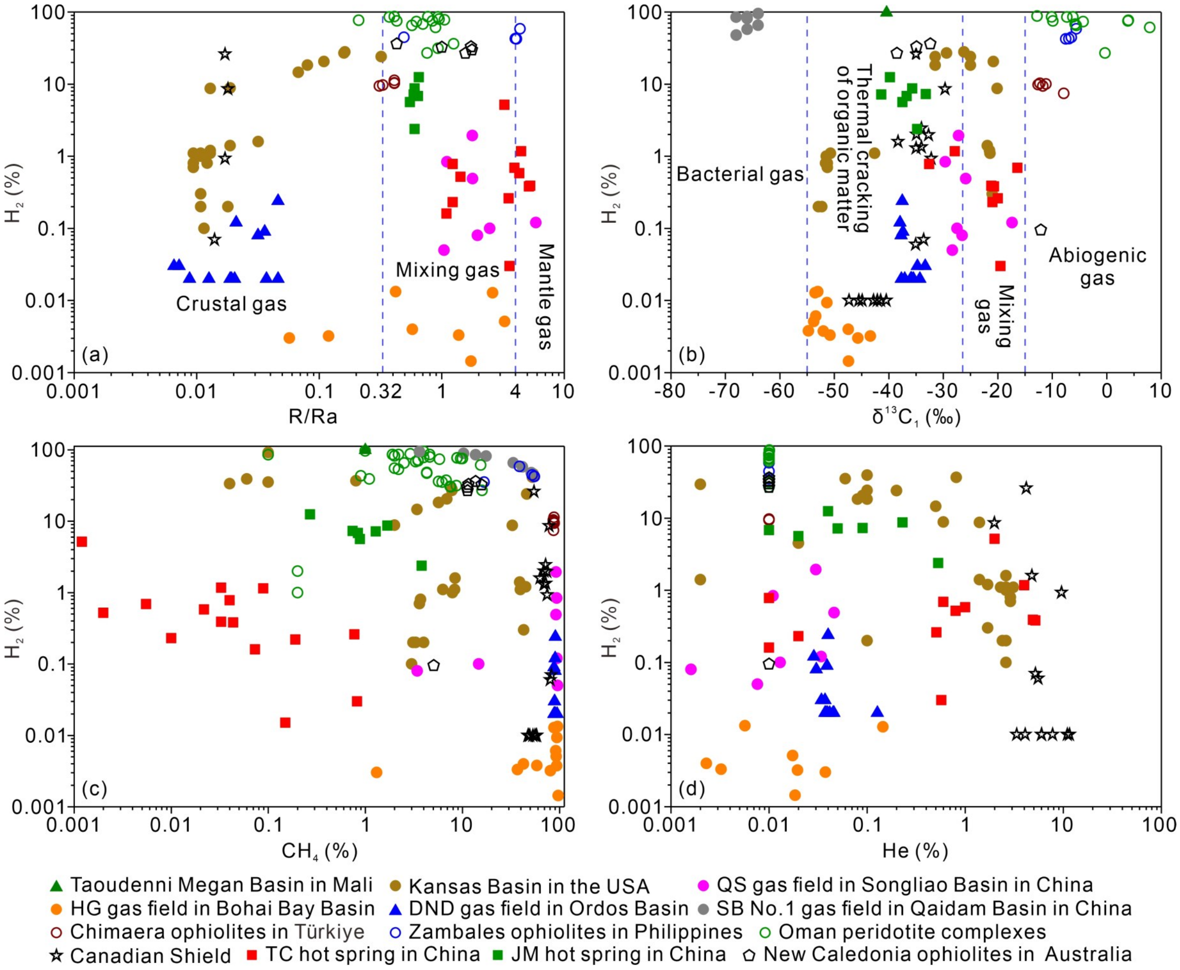

Figure 3. (a) Correlation diagrams of H_2 (%) versus $^3He/^4He$ ratios (R/Ra) (modified after Liu et al., 2024); (b) $\delta^{13}C_1$ (‰) (modified after Liu et al., 2024); (c) CH_4% and (d) He% in various geological scenarios.

and its source rocks are mainly granite, volcanic rock, and mudstone, etc. The $^3He/^4He$ (R) ratio in the gas can indicate the origin and source of helium. The He content in the air is extremely low, generally less than 5 ppm, and the atmospheric $^3He/^4He$ (Ra) value is 1.4×10^{-6} (Mamyrin and Tolstikhin, 1984; Mamyrin et al., 1970). The He content in crust-derived natural gas varies widely, and the typical crust-derived $^3He/^4He$ value (R) is 2×10^{-8}; the He content in mantle-derived gas also varies greatly, and the typical mantle-derived $^3He/^4He$ (R) is 1.1×10^{-5} (Ballentine et al., 2001; Xu et al., 1995a; Allègre et al., 1987; Poreda et al., 1986; Lupton, 1983). Although the R/Ra value is 8.0 for typical mantle-derived helium, and that of typical crust-derived helium is 0.02, the crust-derived thermogenic natural gas collected from Ordos Basin and Sichuan Basin as a cratonic basin (Liu et al., 2022, 2015; Peng et al., 2022; Ni et al., 2014; Xu et al., 1995a) as well as the gas from the Scott ophiolite in Kansas (Vacquand, 2011; Guélard et al., 2017), has a $CH_4/^3He$ ratio of $10^9–10^{12}$ and the $CO_2/^3He$ ratio of $10^8–10^{10}$, with the R/Ra value lower than 0.32. The typical mantle-derived gas reported in the world has a $CH_4/^3He$ ratio of $10^5 – 10^7$, a $CO_2/^3He$ ratio of $10^{10} – 10^{13}$, and a R/Ra ratio > 4.0, while the gas from the hot spring and hydrothermal system in the mid-ocean ridge of East Pacific has the R/Ra ratio > 1.0 (Wang et al., 2022; Chavrit et al., 2016; Graham, 2002; Poreda and Craig, 1989; Jenden et al., 1988; Craig et al., 1978). Here, R/Ra > 4.0 can be assumed to be of typical mantle origin, whereas R/Ra < 0.32 is of typical crust origin.

Previous studies show that gases from the Daniudi (DND) gas field in the Ordos Basin, the Canadian Shield volcanic-metamorphic rock basement, and the basic-ultrabasic volcanic rock basement in the Kansas Basin of the United States have R/Ra ratios < 0.32, indicating that they are typical crustal gas (Figures 2, 3a). Therefore, the associated molecular H_2 in these fields is presumed to be of crustal origin. The gas in the Zambales ophiolites in Philippines has R/Ra ratio > 4.0, characterizing as a typical mantle-derived gas, and this suggests that the molecular H_2 in this area is of mantle origin. Some gas samples from the Tengchong (TC) hot spring have R/Ra ratios > 4.0, and other samples have R/Ra ratios of 0.32–4.0, suggesting two sources of molecular H_2 from both mantle and crust in these gases. The R/Ra ratios in samples from the Qingshen (QS) gas field in Songliao Basin, the Huagou (HG) gas field in Jiyang Depression of Bohai Bay Basin, the Oman peridotite complexes, the New Caledonia ophiolites, and the Chinese Jimo (JM) hot spring range from 0.32 to 4.0, indicating that He in these samples is a mixture of crust-derived and mantle-derived gases. Therefore, molecular H_2 in these areas is considered as a mixture of crust-derived and mantle-derived H_2.

Deep faults or channels for the input of mantle-derived volatiles have been developed in Zambales ophiolites in Philippines, New Caledonia ophiolites in Australia, QS gas field in the Songliao Basin, HG gas field in Jiyang Depression of Bohai Bay Basin, Chimaera ophiolites in Türkiye, Oman peridotite complexes, TC hot spring, and JM hot spring. In contrast, deep faults were undeveloped in American Kansas Basin, Chinese Ordos Basin, and Canadian Shield, and both He and H_2 from these regions are typical crustal-derived gases rather than mantle-derived ones in these regions.

2.1.2 Relationship between H_2 content and $\delta^{13}C_1$ value

Methane in geological bodies is generally classified into biogenic and abiogenic methane in terms of its origin. Abiogenic methane is also termed as inorganic methane referring to CH_4 formed by non-organic matter, including CH_4 from deep mantle in the earth, and synthesized via Fischer-Tropsch reaction in special geological setting. Abiogenic CH_4 has relatively heavy carbon isotope compositions, generally with $\delta^{13}C_1$ values higher than -20‰ (Abrajano et al., 1988; Welhan, 1988; Javoy et al., 1986; Welhan and Craig, 1983, 1979). Biogenic methane refers to CH_4 formed from organic matter by microorganisms or via thermally physicochemical reactions. The $\delta^{13}C_1$ values of biogenic gas are usually less than -55‰ (Xu et al., 2006; Whiticar, 1999; Whiticar et al., 1986; Coleman et al., 1981; Schoell, 1980). The content of heavy hydrocarbons (C_{2+}) in biogenic gas is very low. Thermogenic CH_4 is formed by thermal cracking of organic matters (including hydrocarbon cracking) under thermally physicochemical reaction, and the $\delta^{13}C_1$ value of thermogenic gas ranges from -55‰ to -30‰, with varying contents of heavy hydrocarbons (C_{2+}) (Liu et al., 2019, 2008; Dai et al., 2005b; Schoell, 1988, 1980). As shown in Figure 3b, the $\delta^{13}C_1$ value in the Sebei (SB) No. 1 gas field in the Qaidam Basin was obviously less than -55‰, indicating that the gas was a typical biogenic gas (Whiticar, 1999; Whiticar et al., 1986), and the molecular H_2 in natural gas could also be formed under the action of microorganisms. The gas in Zambales ophiolites in Philippines, Oman peridotite complexes, and Chimaera ophiolites in Türkiye has $\delta^{13}C_1$ values higher than -20‰, suggesting that the gas could be typically abiogenic. Therefore, its associated molecular H_2 could be abiogenic in origin. The $\delta^{13}C_1$ values of natural gas from the basic-ultrabasic volcanic basement of Kansas Basin in USA, the New Caledonia ophiolite in Australia, the TC hot spring, and part of the QS gas field in the Songliao Basin range from -30‰ to -20‰, indicating that these gases are likely the mixture of thermogenic and abiogenic CH_4. This suggests that the molecular H_2 in these regions could also belong to the mixture of biogenic and abiogenic hydrogen.

The $\delta^{13}C_1$ values in the HG volcanic/sandstone gas field of Jiyang Depression of Bohai Bay Basin, the DND sandstone gas field in the Ordos Basin, the basic-ultrabasic volcanic rocks in the Taoudenni Megan Basin in Mali, the volcanic-metamorphic rock basement of the Canadian Shield, and the JM hot spring range from -55 ‰ to -30‰. As Dai et al. (2005b) considered that methane in natural gas with $\delta^{13}C_1$ values less than -30‰ was derived from thermal cracking of organic matters, CH_4 gases in these regions were formed by thermal cracking of organic matter. Therefore, molecular H_2 in these regions could also be related to organic thermal cracking. Although CH_4 formed by thermal cracking of organic matter is relatively more enriched in ^{13}C than bacterial gas, it does not mean that all of CH_4 with relatively enriched ^{13}C would be formed by thermal cracking of organic matter. The $\delta^{13}C_1$ value in the gas produced from volcanic-metamorphic rock basement of Canadian Shield was less than -30‰, however, Sherwood Lollar et al. (2002) believed that the alkane gas in this area was abiogenic according to the carbon and hydrogen isotope compositions. That means the molecular H_2 in the volcanic-metamorphic rock basement gas of Canadian Shield may also be abiogenic.

2.1.3 Relationship between R/Ra ratio and δ^{2}H-C$_1$ value

Since the hydrogen isotope of CH_4 has inheritance effect of precursor depositional environment, the hydrogen isotope composition of CH_4 can effectively identify the depositional environment of natural gas precursors (Liu et al., 2019, 2008; Wang et al., 2015; Dai et al., 2012; Mastalerz and Schimmelmann, 2002; Yeh and Epstein, 1981; Schoell, 1980). The gas precursors in the freshwater environment are relatively more enriched in ^{1}H, whereas those in the saline environment are relatively more enriched in ^{2}H. Therefore, natural gas sourced from the precursors under freshwater depositional environment has the δ^{2}H-C$_1$ values less than -180‰, whereas the δ^{2}H-C$_1$ values for natural gas from precursors under marine or saltwater deposition environment are higher than -160‰, and natural gas from the transitional facies precursors has the δ^{2}H-C$_1$ values ranging from -180‰ to -160‰ (Liu et al., 2008; Shen et al., 1988; Schoell, 1980). In addition to depositional environment of gas precursor, the hydrogen isotope composition of CH_4, similar to its carbon isotope composition, is affected by thermal maturity of organic matter, and methane becomes isotopically more enriched in ^{2}H with the increase of thermal maturity (Liu et al., 2019, 2008; Wang et al., 2015; Ni et al., 2012, 2011).

The highest hydrogen isotope value of methane was reported to be from a CO_2 well in the Salton Lake area (shallow thermal wells in the Salton Sea region, California), USA, with δ^{2}H-C$_1$ value of -16‰ (Welhan, 1988), and the lowest hydrogen isotope value of methane in samples collected from N256-1985 of Norita (Canadian Shield), Quebec, Canada, is -470‰ (Schoell, 1988). The main factors affecting methane hydrogen isotope are the participation of external hydrogen source in gas formation and the hydrogen isotope exchange between organic matter and water. Water plays an important role in the formation of hydrocarbons and participates in the chemical reactions (Reeves et al., 2012; Horita et al., 2002; Schimmelmann et al., 2001). H in water becomes part of biogenic hydrogen, and undergoes reversible isotope exchange reactions with H in kerogen. Hydrogen is mainly connected to heteroatoms, such as hydrogen in N-H, S-H, O-H, etc. However, after the generation of alkane gas, hydrogen isotope will not or rarely undergo isotope exchange with hydrogen atoms in other substances such as water (Schimmelmann et al., 1999).

From the correlation between ^{3}He/^{4}He ratios and δ^{2}H-C$_1$ values (Figure 2), it can be seen that the mantle-derived gas with ^{3}He/^{4}He ratios > 4.0 Ra in Zambales ophiolites in Philippines, TC hot spring and QS gas field in the Songliao Basin has δ^{2}H-C$_1$ value between -216‰ and -118‰, indicating that δ^{2}H-C$_1$ values of mantle-derived CH_4 would be different from δ^{2}H-C$_1$ values of CH_4 thermally formed by organic matter in the freshwater or saline sedimentary environment in the sedimentary basins. The hydrogen isotope values of mantle-derived CH_4 can be higher than those of CH_4 formed by organic matter in a saltwater depositional environment (-160‰), or lower than those of CH_4 formed by organic matter in a freshwater depositional environment (-180‰) (Liu et al., 2014, 2008; Dai et al., 2012; Shen et al., 1988).

The δ^{2}H-C$_1$ values for crustal gas with ^{3}He/^{4}He ratios < 0.32 Ra in DND sandstone gas field of Ordos Basin, HG volcanic sandstone gas field in Jiyang Depression of Bohai Bay Basin, ophiolites in the American Kansas Basin, and volcanic-metamorphic rock basement in Canadian Shield, are less than -180‰, indicating that the gas precursors were in a freshwater depositional environment, which is consistent with the depositional environment of source rocks in DND gas field of Ordos Basin and HG gas field in the Jiyang Depression of the Bohai Bay Basin (Liu et al., 2022; Meng et al., 2015). The δ^{2}H-C$_1$ values of some gas samples in the HG gas field in the Jiyang Depression of the Bohai Bay Basin are higher than -160‰, which is mainly associated with the saline water environment by transgression when the source rock was formed. δ^{2}H-C$_1$ values for gas produced from the ophiolites in American Kansas Basin, and saline water in the volcanic-metamorphic basement in Canadian Shield, are less than -180‰, which indicates that the δ^{2}H-C$_1$ values produced by deep intrusive rock mass could be less than -180‰ in stable cratonic regions.

In the region where ^{3}He/^{4}He ratios are from 0.32 Ra to 4.0 Ra, the hydrogen isotope values of CH_4 in the Zambales ophiolites in Philippines and the Chimaera ophiolites in Türkiye are generally higher than -180‰ and even higher than -160‰, whereas the hydrogen isotope values of CH_4 in the volcanic reservoir of QS gas field in Songliao Basin, the HG volcanic and sandstone gas field in Jiyang Depression of Bohai Bay Basin, Oman peridotite complexes, and JM hot spring gas are less than -180‰. For sedimentary basins where the hydrogen isotopic composition of CH_4 is mainly controlled by the salinity of methane precursors, CH_4 formed from organic matter in a saline environment has a δ^{2}H-C$_1$ value higher than -160‰, while the δ^{2}H-C$_1$ value of methane formed from organic matter in a freshwater environment is less than -180‰ (Liu et al., 2019, 2008; Shen et al., 1988). For deep intrusive rock bodies such as ophiolite, peridotite and volcanic rock, and hot spring gas where the δ^{2}H-C$_1$ value is more complex, and some of them has δ^{2}H-C$_1$ values higher than -160‰, suggesting the saltwater environment, and there are also δ^{2}H-C$_1$ values less than -180‰, indicating the freshwater sedimentary environment. Meanwhile, the hydrogen isotope composition of CH_4 within various geological scenarios tends to become lighter with the increase of ^{3}He/^{4}He ratios. For example, the correlation between ^{3}He/^{4}He ratios and δ^{2}H-C$_1$ values in the DND sandstone gas field of Ordos Basin and Oman peridotite complexes are negative. If it is assumed that ^{3}He/^{4}He ratios would roughly reflect the stability of a regional structure (Xu et al., 1995a), the regional thermal energy increases with the ^{3}He/^{4}He ratios. The negative correlation between ^{3}He/^{4}He ratios and δ^{2}H-C$_1$ values suggests that methane would not isotopically more enriched in ^{2}H rather than ^{1}H with increase of regional thermal energy in the DND sandstone gas field of Ordos Basin and Oman peridotite complexes. This variation trend is completely different from the CH_4 which becomes isotopically more enriched of ^{2}H with the increase of thermal evolution in sedimentary basins (Wang et al., 2015; Liu et al., 2008).

2.1.4 Relationship between H_2 content and CH_4 content

Molecular H_2 is one of the main associated gases of alkane gases such as CH_4, and the correlation between contents of CH_4 and H_2 reflects the intrinsic genetic relationship between the two gases. For the molecular H_2 produced by the thermal pyrolysis of organic matter, the change of H_2 content usually has a certain correspondence with the hydrocarbon gaseous components, and the peak of CH_4 generation often corresponds to the peak generation of H_2. For the molecular H_2 generated from water-rock reaction (such as serpentinization) or decomposition of H_2O by radioactive decay, it occurs that molecular H_2 would be consumed to generate abiogenic CH_4 when it chemically reacts with carbon-oxygen-containing chemical groups under certain conditions, resulting in the decrease of H_2 content and increase of CH_4 content. There is a negative correlation between H_2 and CH_4 contents (McCollom et al., 2020; Etiope, 2017; McCollom and Seewald, 2001; Coveney et al., 1987; Thayer, 1966). As shown in Figure 3c, the slightly positive correlation between CH_4 and H_2 contents is observed in the QS gas field of Songliao Basin, the DND gas field of Ordos Basin, and the HG gas field in Jiyang Depression of Bohai Bay Basin. Since these gas reservoirs in sedimentary basins are predominantly alkane gases, such as CH_4 formed by thermal cracking of organic matter, and the content of molecular H_2 is very low. The molecular H_2 in these gas reservoirs could be a production of thermal cracking of organic matter, however, the existence of abiogenic molecular H_2 cannot be ruled out in these areas. For example, the gas with ^{3}He/^{4}He ratios > 1.0 Ra in the QS gas field of Songliao Basin contains a certain amount of abiogenic molecular CH_4 (Liu et al., 2016), indicating a possible contribution of abiogenic molecular H_2.

In the SB No. 1 gas field in Qaidam Basin, there is a good negative correlation between CH_4 and H_2 (Figure 3c). According to carbon isotope values of methane mentioned above, the methane in the SB No. 1 gas field in the Qaidam Basin is bacterial gas formed under the action of microorganisms. Therefore, molecular H_2 in this basin could also be generated by the activity of microorganisms. The good negative correlation between CH_4 and H_2 contents may be related to the degradation of organic matter under the action of microorganisms to produce molecular hydrogen, and then the molecular hydrogen is converted into CH_4 afterwards. Shuai et al. (2010) considered that microorganisms produced molecular H_2 by degrading organic matter, thus providing a material for the formation of bacterial CH_4. Although there is no obvious correlation between CH_4 and H_2 in gas produced by deep intrusive rock mass and hot spring gas, overall there is a trend of decreasing H_2 content with the increase of CH_4 content. For example, there is a good negative correlation between CH_4 and H_2 contents in the Zambales ophiolites in Philippines. According to ^{3}He/^{4}He ratios (> 4.0 Ra) and CH_4 carbon isotopic values (> -20‰), CH_4 in the Zambales ophiolites in Philippines is a typical deep mantle-derived abiogenic CH_4. Therefore, there may also be a process of conversion of abiogenic H_2 to abiogenic CH_4 in the deep mantle. In the gas and hot spring gas produced by intrusive rock bodies with ^{3}He/^{4}He ratios ranging from 0.32 Ra to 4.0 Ra, such as the gas produced from Oman peridotite complexes, Chimaera ophiolites in Türkiye as well as hot spring gas of TC and JM, the H_2 content showed a decreasing trend with an increase of CH_4 content. The $\delta^{13}C_1$ value in the Oman peridotite complexes and the Chimaera ophiolites in Türkiye is higher than -20‰, suggesting typical abiogenic CH_4, and its associated molecular H_2 is also of abiogenic origin. However, the gas in these areas has the ^{3}He/^{4}He ratios < 4.0 Ra, indicating that the abiogenic CH_4 and H_2 in these areas are not completely from deep mantle source, and there may exist abiogenic molecular H_2 formed by serpentinization and abiogenic CH_4 formed by Fischer-Tropsch synthesis.

In the gas with ^{3}He/^{4}He ratios < 0.32 Ra produced from the igneous rock basement of Kansas Basin and New Caledonia ophiolites, the $\delta^{13}C_1$ value ranges from -30‰ to -20‰, indicating that it would be a mixture of biogenic and abiogenic CH_4. The negative correlation between CH_4 and H_2 in the igneous rock basement of Kansas Basin and New Caledonia ophiolites indicates that there is also a mixture of biogenic and abiogenic molecular hydrogen, and even part of molecular H_2 has been converted to CH_4.

2.1.5 Two-endmemer mixing between crust and mantle and H_2 conversion to CH_4

As mentioned above, there are not only biogenic hydrogen produced by thermal cracking of organic matter and microbial action in geological bodies, but also abiogenic H_2 produced by deep mantle source, radioactivity, and water-rock reaction (such as serpentinization). Biogenic molecular H_2 usually coexists with methane and other alkane gases sourced from organic matter. Mantle-derived abiogenic molecular H_2 is generally released through deep faults. Radioactive abiogenic molecular hydrogen is a product of water decomposition by α, β, γ particle radiation. Abiogenic molecular H_2 produced in water-rock reaction, such as serpentinization, refers to reaction between mafic and ultramafic rocks containing olivine and pyroxene and water to form serpentine and release molecular H_2 (Coveney et al., 1987; Barnes and O'Neil, 1969; Thayer, 1966). The serpentinization is generally expressed as follows.

$$3Fe_2SiO_4\text{(fayalite)} + 2H_2O = 2Fe_3O_4\text{(magnetite)} + 3SiO_2\text{(aq)} + 2H_2\text{(aq)}$$

$$3FeSiO_3\text{(iron pyroxene)} + H_2O = Fe_3O_4\text{(magnetite)} + 3SiO_2(aq) + H_2(aq)$$

Mantle-derived abiogenic gas generally has typical mantle-derived $^3He/^4He$ ratios (> 4 Ra) and heavy carbon isotopes in CH_4 ($\delta^{13}C_1$ > -20‰), whereas the abiogenic molecular H_2 formed by radioactivity and serpentinization is launched within the radioactive or catalytic geological conditions, and part of molecular H_2 would be converted into CH_4 by Fischer-Tropsch synthesis or catalytic hydrogenation (Anderson et al., 1984; Salvi and Williams-Jones, 1997). Therefore, there is a certain correlation between $^3He/^4He$ ratios and $\delta^2H\text{-}C_1$ values as indicated in Figure 2. Meanwhile, radioactive He is formed during the radioactive process of producing α, β, and γ particles to form the radioactive molecular H_2, i. e., ^4He is formed through α decay of ^{235}U, ^{238}U, and ^{232}Th, and ^3He is radioactively produced through ^6Li reacting with nutron ($^6Li(n,\alpha)\,^3H(\beta^-)^3He$) (Basu et al., 2006; Oxburgh et al., 1986; Mamyrin and Tolstikhin, 1984). Natural gas in typical cratonic basins and mid-ocean ridges representing the mantle has significantly different $^3He/^4He$, $CO_2/^3He$ and $CH_4/^3He$ ratios. Natural gas in cratonic basins generally has $^3He/^4He$ < 0.02 Ra, $CO_2/^3He$ between 10^8 and 10^{10}, and $CH_4/^3He$ between 10^9 and 10^{12}, while in gases from mid-ocean ridges, $^3He/^4He \approx 8.0$ Ra, $CO_2/^3He$ is 10^9–10^{10}, and $CH_4/^3He$ is 10^5–10^7. According to two-endmember mixing between crust-derived and mantle-derived gases (Figure 4a), the gas in the DND sandstone gas field of Ordos Basin is at the crust-derived endmember, in which CH_4 and CO_2 were formed by thermal cracking of organic matter, and He is mainly crust-derived formed by U and Th radioactivity. The gases in the volcanic rock basement of American Kansas Basin, the HG volcanic and sandstone gas field in Jiyang Depression of Bohai Bay Basin, the Chimaera ophiolites in Türkiye, the Oman peridotite complexes, and the hot spring gas of TC and JM, fall within the mixing region of crust-derived and mantle-derived gases.

For the gases from volcanic basement in American Kansas Basin, volcanic and sandstone reservoir of QS gas field of Songliao Basin, HG volcanic and sandstone gas field in Jiyang Depression of Bohai Bay Basin, Chimaera ophiolites in Türkiye, Oman peridotite complexes, New Caledonia ophiolites, and hot spring gases of JM and TC, the $CO_2/^3He$ ratios in some gas samples are below the area of typical two-endmember mixing between crust-derived and mantle-derived gases (Figure 4b), while their $CH_4/^3He$ ratios are above the typical two-endmember mixing between crust-derived and mantle-derived gases (Figure 4a). Therefore, it is possible that there could be conversion of CO_2 by Fischer-Tropsch synthesis to CH_4, so that the CO_2 content decreases and the CH_4 content increases. In the process of Fischer-Tropsch synthesis, a certain amount of molecular H_2 must be consumed. The abiogenic gas with $^3He/^4He$ ratios > 4.0 Ra and $\delta^{13}C_1$ values > 20‰ from the Zambales ophiolites in Philippines is a mixture of mantle-derived and Fischer-Tropsch synthesized CH_4.

The gases with $^3He/^4He$ ratios < 0.02 Ra in the volcanic-metamorphic basement of Canadian Shield and some basic volcanic rocks in American Kansas Basin, have typically crust-derived helium, but the ratios of $CO_2/^3He$ and $CH_4/^3He$ are below the typical crustal endmember, and this may be related to the high He content in these areas. When the $CH_4/^3He$ ratios in gases produced from the volcanic-metamorphic rock basement in Canadian Shield and the basic volcanic rocks in American Kansas Basin are less than 10^9, the He content range from 4.19% to 9.61%, and from 0.5% to 3.1%, respectively. Therefore, the ratios of $CO_2/^3He$ and $CH_4/^3He$ in gases produced from the volcanic-metamorphic basement of Canadian Shield and some basic volcanic basements of American Kansas Basin could be all less than the typical endmember of crust-derived gas, which may be related to the significantly high He content in these areas. Although the $^3He/^4He$ ratios in the cratonic region is significantly lower than that of the mantle source, in

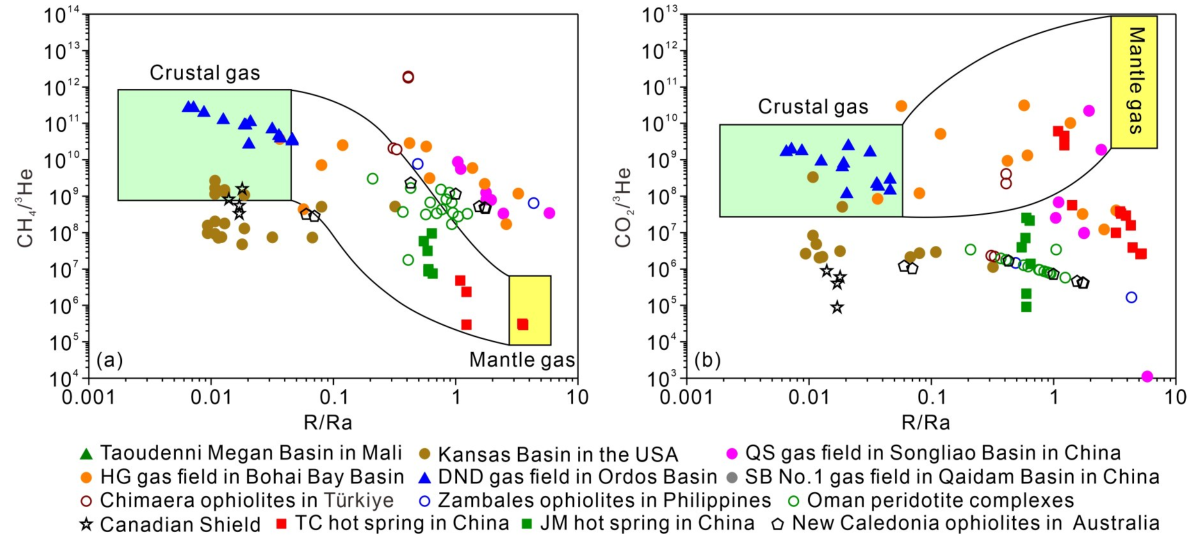

Figure 4. Correlation of the $^3He/^4He$ ratios (R/Ra) versus $CH_4/^3He$ (a) and $CO_2/^3He$ (b).

which He in cratonic region is mainly sourced from the radioactive decay of U- and Th-bearing minerals to form ^{4}He, the high He content would also inevitably lead to a relative increase of ^{3}He content, resulting in the ratios of $CO_2/^3He$ and $CH_4/^3He$ in the volcanic-metamorphic rock basement of Canadian Shield and some basic volcanic rock basements in American Kansas Basin, below the typical endmember of crust-derived gas (Figures 4a, 4b).

In cratonic basins, He is formed by α decay of U- and Th-bearing minerals, while molecular hydrogen can be produced through H_2O decomposition caused by radiation of subsurface α, β, and γ particles, such as U (^{238}U, ^{235}U), Th (^{232}Th), and K (^{40}K) in the basement rocks (Dzaugis et al., 2016; Lin et al., 2005; Vovk, 1987). Sherwood Lollar et al. (2014) suggested that the rate of H_2 production in the continental region can reach (0.36–2.27) × 10^{11} mol/y. If He was formed by radioactive decay of U- and Th-bearing minerals, then molecular hydrogen must also be produced through H_2O decomposition caused by radioactive decay during this process.

From the correlation between He and H_2 content in Figure 3d, the positive correlation between He and H_2 content in the gas with $^3He/^4He$ ratios < 0.02 Ra in the basic volcanic basement of American Kansas Basin and the volcanic-metamorphic rock basement of Canadian Shield cannot be observed, while both regioins have relatively high He and H_2 contents. There is a coarse decreasing trend of H_2 content with increasing He content, which may also reflect that molecular H_2 would be converted to form abiogenic CH_4 through Fischer-Tropsch synthesis. It is well known that Fischer-Tropsch synthesis was first proposed by German chemists Franz Fischer and Hans Tropsch in 1926. It is an abiogenic catalytic chemical reaction that can convert CO into liquid hydrocarbons (Fischer and Tropsch, 1926) and is widely used in the petroleum industry (Mahmoudi et al., 2017; Taran et al., 2007). The Fischer-Tropsch synthesis in the geological conditions has been used to explain the synthesis of abiogenic CH_4 during serpentinization of mafic and ultramafic rocks such as mid-ocean ridges. The reaction is generally expressed as follows.

$$nCO_2 + (3n + 1)H_2 = C_nH_{2n+2} + 2nH_2O \text{ or}$$

$$nCO + (2n + 1)H_2 = C_nH_{2n+2} + nH_2O$$

Therefore, molecular H_2 is not only produced by serpentinization, but also consumed to form abiogenic CH_4 via Fischer-Tropsch synthesis in the mineral enriched in U (^{238}U, ^{235}U), Th (^{232}Th) and K (^{40}K) in cratonic regions and the olivine and pyroxene-bearing mafic and ultramafic basement rocks in deep igneous bodies, such as the basic volcanic basement of American Kansas Basin and the volcanic-metamorphic basement of Canadian Shield.

2.1.6 Genetic sources of CH_4 in geological bodies

The pattern of carbon and hydrogen isotopes can be used to identify genetic origin of methane under different geological backgrounds (Whiticar, 1999). In Figure 5, CH_4 from SB No. 1 gas field in the Qaidam Basin is located in the area of bacterial gas formed under the activity of typical microorganisms.

The isotope data for the HG volcanic/sandstone gas field of Jiyang Depression of Bohai Bay Basin are within the area of early mature, thermal associated and humic gas. Considering the gas in the HG volcanic/sandstone gas field of Jiyang Depression of Bohai Bay Basin is associated with oil, the gas is prone to the early mature CH_4 from thermal cracking of organic matter. The isotope compositions of gas from the DND sandstone gas field of Ordos Basin are located in the area of geothermal, hydrothermal and crystalline gas, but the deep faults were undeveloped in the Ordos Basin with $^3He/^4He$ ratios less than 0.32 Ra. Therefore, the contribution of mantle volatile to gas is excluded. The reasonable explanation is that there is a small contribution of abiogenic CH_4 formed by Fischer-Tropsch synthesis to the gas generated from organic matter, since the formation of Fischer-Tropsch synthesized methane occurred at low temperature less than 150 ºC, which had lighter carbon and hydrogen isotope composition than that of biogenic CH_4 (Suda et al., 2014). The carbon and hydrogen isotope compositions of CH_4 in the QS volcanic gas field of Songliao Basin are mainly located in regions of

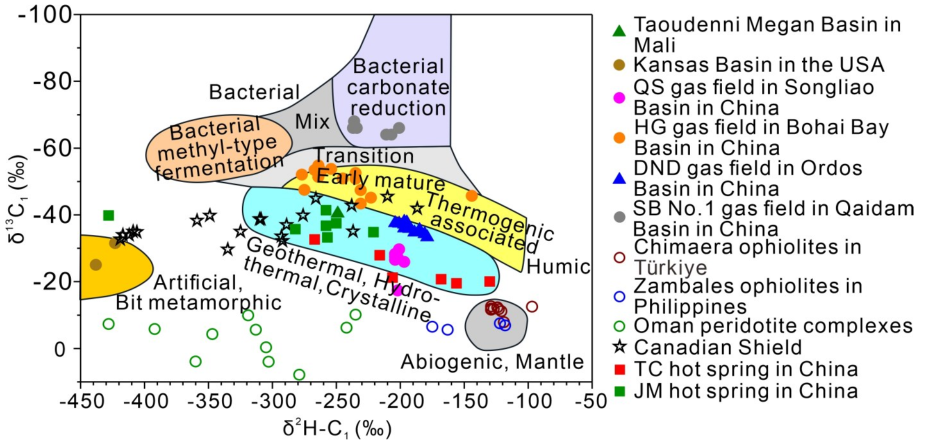

Figure 5. Pattern of carbon and hydrogen isotopes of methane in various geological scenarios (modified after Whiticar, 1999).

CH_4 formed by geothermal, hydrothermal or crystallization. Liu et al. (2016) suggested that CH_4 in the QS gas field of Songliao Basin was a mixture of gases from thermal cracking of organic matter, deep mantle and Fischer-Tropsch synthesis, based on tectonic evolution, potential source rock, thermal maturity, and gas geochemistry. Mixing of triple-sourced CH_4 led to the carbon and hydrogen isotopes of CH_4 fall within the area of geothermal, hydrothermal or crystalline CH_4 in the chart proposed by Whiticar (Suda et al., 2014).

The isotopic compositions of methane in the basic volcanic basements of American Kansas Basin and the volcanic-metamorphic rocks in Canadian Shield are located within the areas of geothermal, hydrothermal, crystalline gas, even in the area of artificial, bit metamorphic gas (Figure 5), suggesting a typical crustal feature and little contribution from deep mantle in consideration of $^3He/^4He$ ratios < 0.02 Ra. Methane in the basic volcanic basements of American Kansas Basin, is mainly related to the Fischer-Tropsch synthesis of Precambrian basement (Guélard et al., 2017), while methane in the volcanic-metamorphic basements of Canadian Shield is mainly formed by Fischer-Tropsch synthesis under high geothermal gradients (Sherwood Lollar et al., 2008).

Although isotopes of methane in the Zambales ophiolites in Philippines, the Chimaera ophiolites in Türkiye, and the Oman peridotite complexes falls into the area of typical abiogenic mantle-derived gas (Figure 5), the gas with $^3He/^4He$ ratios > 4.0 Ra in the Zambales ophiolites in Philippines is mainly mantle-derived. Therefore, CH_4 in the Zambales ophiolites in Philippines is dominated by deep mantle-derived CH_4, and the contribution of CH_4 from Fischer-Tropsch synthesis in the two-endmember mixing of crust-derived and mantle-derived gas also existed. Although the carbon and hydrogen isotopes of CH_4 in the Chimaera ophiolites in Türkiye suggested that methane would be formed by geothermal, hydrothermal or crystalline processes (Figure 5), two-endmember mixing of crust-derived and mantle-derived gas supported the mixing gas formed from crust and mantle sources. The $^3He/^4He$ ratio is about 0.32 Ra in this area characterized by crustal sources, and there is no significant contribution of deep mantle source to the Chimaera ophiolite gas in Türkiye. Therefore, CH_4 in the Chimaera ophiolites is dominated by Fischer-Tropsch synthesized CH_4. Hoşgörmez (2007) and Etiope et al. (2011) believed that CH_4 in the Chimaera ophiolites in Türkiye were formed by Fischer-Tropsch synthesis within ultrabasic rocks under low temperature. Although the carbon and hydrogen isotope compositions of CH_4 in the Oman peridotite complexes fall in area of mantle-derived gas, the hydrogen isotope of methane is significantly lighter than that of Zambales ophiolite gas as a typical mantle-derived CH_4. Moreover, the $^3He/^4He$ ratio in the Oman peridotite complexes gas ranges from 0.17 Ra to 1.25 Ra, with an average value of 0.697 Ra, indicating that the contribution from deep mantle is limited. Furthermore, the $CH_4/^3He$ ratio for Oman peridotite complexes gas is in the mixing of crust-derived and mantle-derived gas, and the $CO_2/^3He$ ratio is obviously in the lower part of the mixing of crust-derived and mantle-derived gas, indicating that there was a significant loss of CO_2. Therefore, CH_4 in the Oman peridotite complexes was mainly converted through the Fischer-Tropsch synthesis in which the molecular H_2 was formed by ophiolite (Vacquand et al., 2018).

Although the reported highest H_2 content was higher than 90% in the mafic-ultramafic volcanic rocks in Taoudenni Megan Basin in Mali, the carbon and hydrogen isotopes of CH_4 indicated that methane would be sourced from geothermal, hydrothermal or crystalline processes (Figure 5). It is impossible to determine the mantle contribution exists due to the lack of He content and $^3He/^4He$ ratio.

Isotope compositions of both TC and JM hot spring gases are located in the area of geothermal, hydrothermal or crystalline background (Figure 5), however, there is low contribution of mantle-derived CH_4 and Fischer-Tropsch synthesized CH_4 based on two-endmember mixing of crust-derived and mantle-derived gas. Considering that the $^3He/^4He$ ratios in the JM hot spring gas range from 0.5 Ra to 0.65 Ra, the contribution of mantle-derived CH_4 is limited, and the $CO_2/^3He$ ratio of the JM hot spring gas is below the two-endmember mixing zone of crust-derived and mantle-derived gas. This suggested that a large portion of CO_2 would be converted to abiogenic CH_4 by Fischer-Tropsch synthesis in the JM hot spring gas. However, the $^3He/^4He$ ratios in the TC hot spring gas range from 1.0 Ra to 5.28 Ra, indicating that the contribution of mantle-derived CH_4 would be significantly higher than that in JM hot spring gas.

2.2 Origin of Molecular Hydrogen and Geochemical Identification

Since molecular H_2 is generally associated with CH_4 and He, the genetic sources of CH_4 and He must also reflect the genetic source of molecular H_2. Therefore, the genetic sources of molecular H_2 can be determined by parameters such as gas components (CH_4, He), carbon and hydrogen isotopic compositions in methane, and $^3He/^4He$ ratios. In this study, the geochemical characteristics of molecular hydrogen under various geological scenarios are established through the geochemical characteristics of CH_4 and He from different sources (Figures 6, 7). Identifying the different sources of molecular H_2 in geological bodies is also the key to evaluating the prospect of H_2 resources.

2.2.1 Correlation between $\delta^{13}C_1$ value and δ^2H-H_2 value

The abiogenic and biogenic methane is usually classified using carbon isotope of methane higher than -20‰ and lower than -30‰, respectively. It can be seen from the relationship between $\delta^{13}C_1$ and δ^2H-H_2 values, that the δ^2H-H_2 values vary in the formation process of both abiogenic and biogenic CH_4 (Figure 6). Gases produced from Zambales ophiolites in Philippines, Oman peridotite complexes, Chimaera ophiolites in Türkiye, and TC hot spring, have $\delta^{13}C_1$ values higher than -20‰, suggesting that CH_4 is of abiogenic origin, and δ^2H-H_2 values in these gases range from -792‰ to -581‰ (Figure 6). Although CH_4 is of abiogenic gas in the Zambales ophiolites in Philippines, the Oman peridotite complexes, and the Chimaera ophiolites in Türkiye, δ^2H-H_2 values vary differently. The gas in the Zambales ophiolites in Philippines has a narrower range of $\delta^{13}C_1$ values from -7.5‰ to -5.6‰ and a wide range of δ^2H-H_2 values from -756‰ to -581‰, while the gas in the Oman peridotite complexes and the Chimaera ophiolites in Türkiye has a wide range of $\delta^{13}C_1$ values from -12.6‰ to -7.9‰ and a narrow range of δ^2H-H_2 values from -745‰ to -710‰. $^3He/^4He$ ratios in the Zambales ophiolites in Philippines are higher than 4.0 Ra, suggesting a typical deep mantle source, while $^3He/^4He$ ratios in the Oman peridotite complexes and the Chimaera ophiolites in Türkiye range from 0.32 Ra to 1.0 Ra, suggesting that the gas could be a mixing of crust-derived and mantle-derived gases. Since CH_4 in the Oman peridotite complexes and the Chimaera ophiolites in Türkiye is abiogenic gas, it is likely that the abiogenic CH_4 in the Oman peridotite complexes and the Chimaera ophiolites in Türkiye is dominated by Fischer-Tropsch synthesis, and the contribution of mantle-derived CH_4 is limited. Therefore, for mantle-derived abiogenic gases in the Zambales ophiolites in Philippines, the range of $\delta^{13}C_1$ values is relatively narrow, while the range of δ^2H-H_2 values is relatively wide. On the contrary, the crustal-derived abiogenic gas has the narrow range of δ^2H-H_2 values and the relatively wide $\delta^{13}C_1$ values (Figure 6). The $\delta^{13}C_1$ values in gases from basic-ultrabasic volcanic rocks in Taoudenni Megan Basin in Mali, HG volcanic/sandstone gas field of Jiyang Depression in Bohai Bay Basin, DND sandstone gas field of Ordos Basin, SB No. 1 sandstone gas field of Qaidam Basin, volcanic-metamorphic rock basement in Canadian Shield, and JM hot spring, are less than -30‰, showing the characteristics of biogenic CH_4. The δ^2H-H_2 values of these gases range from -831‰ to -608‰ (Figure 6), and the range covers the δ^2H-H_2 of crust-derived abiogenic molecular hydrogen in Oman peridotite complexes and Chimaera ophiolites in Türkiye and mantle-derived molecular hydrogen in Zambales ophiolites in Philippines. $\delta^{13}C_1$ values in gases from QS volcanic/sandstone gas field in Songliao Basin, basic-ultrabasic volcanic rocks in American Kansas Basin, and TC hot spring gas range from -30‰ to -20‰, showing a mixing of biogenic and abiogenic CH_4, whereas δ^2H-H_2 values range from -800‰ to -600‰ (Figure 6), displaying a similar range with the hydrogen isotope value of H_2 associated with typical abiogenic CH_4 and biogenic CH_4. Therefore, whether methane is abiogenic or biogenic, or

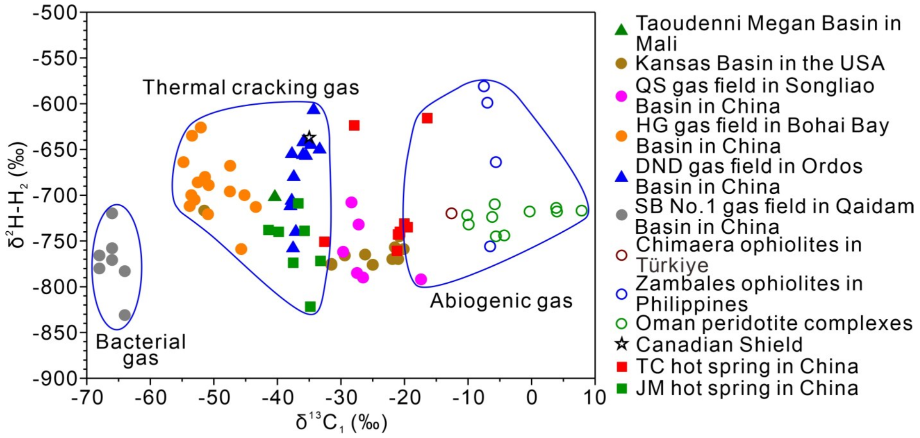

Figure 6. Correlation between δ^2H-H_2 and $\delta^{13}C_1$ values in various geological scenarios.

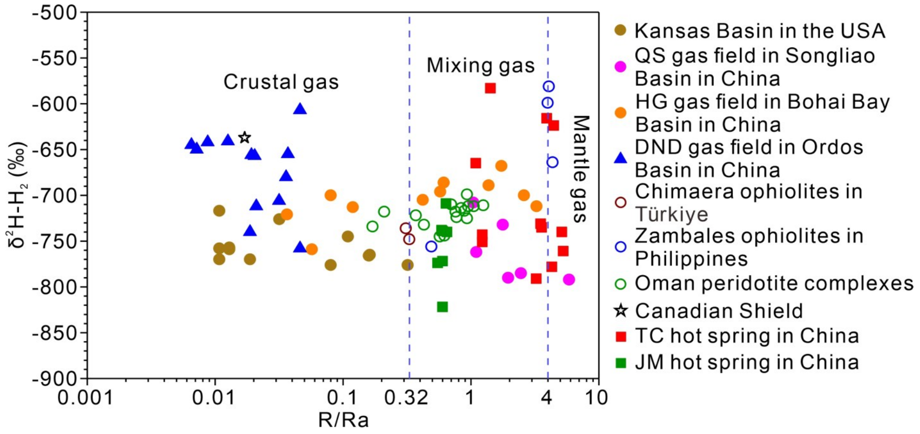

Figure 7. Relationship between $^3He/^4He$ ratios (R/Ra) and δ^2H-H_2 values in various geological scenarios.

a mixing of gases from both sources, the δ^2H-H_2 values of molecular hydrogen associated with methane in different geological scenarios range from -800‰ to -600‰. The range of δ^2H-H_2 values from mantle-derived H_2 molecule is relatively wide, whereas the range of δ^2H-H_2 value of crust-derived abiogenic H_2 is relatively narrow.

2.2.2 Relationship between R/Ra ratio and δ^2H-H_2 value

Gases in different spheres and tectonic environments of the earth have different $^3He/^4He$ ratios. Therefore, the specific distribution of $^3He/^4He$ ratios in the Earth's spheres can be used to trace the sources of various fluids. The stable continental crust is enriched in ^4He, associated with low $^3He/^4He$ ratio, while the Cenozoic magmatic activities and mantle uplift Introduce the mantle-derived ^3He excess in the continental crust and have a high $^3He/^4He$ ratio. Generally, the $^3He/^4He$ ratio of typical mantle-derived helium is about 8.0 Ra, while $^3He/^4He$ ratios of typical crust-derived helium is about 0.02 Ra (Xu et al., 1995a; Oxburgh et al., 1986). Statistics of sample data show that $^3He/^4He$ ratios are larger than 4.0 Ra in gas from mid-ocean ridge and hydrothermal system in the eastern Pacific (Basu et al., 2006; Graham, 2002; Lupton et al., 1999; Marty and Tolstikhin, 1998; Poreda and Craig, 1989; Welhan and Craig, 1983; Wakita and Sano, 1983), and $^3He/^4He$ are less than 0.32 Ra in gas from cratonic basins such as Sichuan and Ordos basins (Peng et al., 2022; Liu et al., 2015; Ni et al., 2014; Xu et al., 1995a). In these cases, the gas can be assumed to be of typical mantle-derived gas when $^3He/^4He > 4.0$ Ra, while the gas with $^3He/^4He$ ratios < 0.32 Ra is of typical crustal origin. The relationship between $^3He/^4He$ ratios and δ^2H-H_2 values (Figure 7) shows that δ^2H-H_2 values range from -792‰ to -581‰ in the active region of mantle-derived volatile with $^3He/^4He$ ratios higher than 4.0 Ra, such as Zambales ophiolite in Philippines and TC basic-ultrabasic volcanic hot spring gas, while δ^2H-H_2 values range from -776‰ to -607‰ in structurally stable areas with $^3He/^4He$ ratios less than 0.32 Ra, such as DND sandstone gas field in Ordos Basin, basic volcanic basement of Amerasian Kansas Basin, volcanic-metamorphic basement of Canadian Shield, Chimaera ophiolites in Türkiye. The range of δ^2H-H_2 value in the mantle-derived volatile is slightly wider than that in the structurally stable area. δ^2H-H_2 values range from -822‰ to -583‰ in structural sub-stable areas with $^3He/^4He$ ratios between 0.32 Ra and 4.0 Ra, such as QS volcanic /sandstone gas field in Songliao Basin, HG volcanic/sandstone gas field in Bohai Bay, Oman peridotite complexes, JM basalt hot spring gas, TC basic-ultrabasic volcanic hot spring gas. The δ^2H-H_2 values in the structurally sub-stable area overlap with those from the area of mantle-derived volatile and the structurally stable area. They are even higher than the δ^2H-H_2 values of the two. Therefore, there is insignificant difference in the variation range of δ^2H-H_2 regardless of whether they are from mantle-derived volatile, structurally stable area or the structurally sub-stable area.

Despite there are no data on helium content and $^3He/^4He$ ratios in the samples from Qaidam Basin, the $^3He/^4He$ ratios in the gas layer of SB No. 1 structural belt in the Qaidam Basin range from 3.47×10^{-8} to 4.97×10^{-8}, corresponding to $^3He/^4He$ ratios ranging from 0.025 Ra to 0.036 Ra. $^{40}Ar/^{36}Ar$ ratios range from 318 to 381.6 (Shuai et al., 2010), indicating that the gas is a typical crustal source, while δ^2H-H_2 values in SB No. 1 gas field in Qaidam Basin range from -831‰ to -720‰, and $\delta^{13}C_1$ values are less than -55‰, showing a typical bacterial gas (Figure 8). δ^2H-H_2 values also have a similar range of hydrogen isotopes with mantle-derived volatile and gases from structurally stable area. Therefore, whether the geological background is an active area of deep mantle-derived volatile or the structurally stable area, the δ^2H-H_2 values are almost in similar range, which is mainly distributed from -800‰ to -600‰.

2.2.3 Relationship between ln(CH_4/H_2) and $\delta^{13}C_1$ value

The sources of molecular hydrogen in geological bodies can be abiogenic and biogenic. Abiogenic molecular hydrogen is sourced from mantle-derived volatile, serpentinization, and water decomposition caused by radioactivity, while biogenic molecular hydrogen is from thermal cracking and microbial degradation of organic matter. Due to chemical property of molecular H_2, it may be

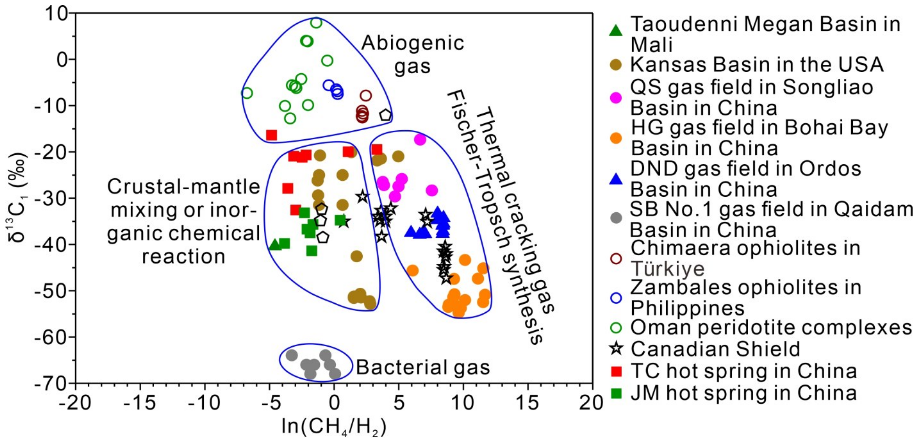

Figure 8. Diagram of ln(CH_4/H_2) versus $\delta^{13}C_1$ values in various geological scenarios (modified after Liu et al., 2024).

converted into CH_4 under certain conditions, such as Fischer-Tropsch synthesis, which means that CH_4 associated with H_2 can not only come from mantle, thermal cracking of organic matter, and microbial degradation, but also from Fischer-Tropsch synthesis by H_2 consumption. If the occurrence of Fischer-Tropsch synthesized CH_4 in geological bodies widely existed in H_2-bearing gas systems, it would definitely affect the identification of H_2 sources in geological bodies. $\ln(CH_4/H_2)$ is negatively correlated with $\delta^{13}C_1$ values in HG volcanic/sandstone gas field in Jiyang Depression of Bohai Bay Basin, the DND sandstone gas field in Ordos Basin, and QS volcanic/sandstone gas field in Songliao Basin (Figure 8). Since the increase trend of thermal maturity of natural gas from HG gas field, DND gas field to QS gas field is observed as indicated by $\delta^{13}C_1$ value, $\ln(CH_4/H_2)$ values gradually decreased from 11.53 to 3.86, that is, the CH_4 content decreases relatively, while the H_2 content of increases relatively. Although there is mantle-derived methane and Fischer-Tropsch synthesized methane in the QS gas field of Songliao Basin based on $^3He/^4He$ ratios and carbon isotope values in CH_4, methane from thermal cracking of organic matter is a dominant component (Liu et al., 2016). Thus, the relationship between $\ln(CH_4/H_2)$ and $\delta^{13}C_1$ values shows that the H_2 content in the gas from thermal cracking of organic matter in sedimentary basins is relatively enriched at low-mature stage, and the H_2 content tends to decrease as the thermal maturity increases. The decrease of H_2 content may be related to relative increase in the CH_4 content formed by greatly thermal cracking of organic matter as the thermal maturity increases, or H_2 conversion to CH_4 through Fischer-Tropsch synthesis. The distribution of CH_4 and H_2 contents formed under the action of microorganisms in SB No. 1 gas field of Qaidam basin displays relatively small variation, associated with isotopically more enriched in ^{12}C for CH_4 ($\delta^{13}C_1$ < -55‰). The $\ln(CH_4/H_2)$ ranges from -3.28 to -0.07, and the relationship between $\ln(CH_4/H_2)$ and $\delta^{13}C_1$ value is insignificant. Therefore, organic matter should preferentially form H_2 under the action of microorganisms. Shuai et al. (2010) suggested that molecular H_2 produced by degradation of organic matter under action of microorganisms could provide a substance for formation of bacterial CH_4.

A weak positive correlation between $\ln(CH_4/H_2)$ and $\delta^{13}C_1$ values occurs in Zambales ophiolites in Philippines, Oman peridotite complexes, Chimaera ophiolites in Türkiye, and New Caledonia ophiolites (Figure 8). The $\ln(CH_4/H_2)$ values range from -6.75 to 4.0 and the $\delta^{13}C_1$ values are higher than -20‰ as a typical abiogenic CH_4, indicating that both CH_4 and H_2 in the gases from Zambales ophiolites in Philippines, Oman peridotite complexes, Chimaera ophiolites in Türkiye, and New Caledonia ophiolites are of abiogenic origin. Moreover, the $^3He/^4He$ ratios in the Zambales ophiolite gas in Philippines is higher than 4.0 Ra, which shows a typical mantle signature, indicating both CH_4 and H_2 are of mantle origin with $\ln(CH_4/H_2)$ values range from -0.41 to 0.28, showing a very narrow range. The abiogenic CH_4 in the Oman peridotite complexes and the Chimaera ophiolites in Türkiye is dominated by methane synthesized by Fischer-Tropsch reaction, and the contribution of mantle-derived CH_4 is limited. Molecular H_2 in the Oman peridotite complexes and the Chimaera ophiolites in Türkiye could be formed by inorganic chemical reactions, and $\ln(CH_4/H_2)$ values vary widely, ranging from -6.75 to 2.46. Therefore, the abiogenic CH_4 and abiogenic H_2 derived from deep mantle have a very narrow range of $\ln(CH_4/H_2)$ values, indicating that the contents of abiogenic CH_4 and abiogenic H_2 derived from deep mantle are relatively stable, while both abiogenic CH_4 and abiogenic H_2 formed by inorganic reaction have a wide range of $\ln(CH_4/H_2)$ values, suggesting that both abiogenic CH_4 and abiogenic H_2 formed by inorganic chemical reactions would be complicated in different ways.

There is a negative correlation between $\ln(CH_4/H_2)$ and $\delta^{13}C_1$ values in gases from the basic volcanic basement of American Kansas Basin, New Caledonia ophiolites, TC basic-ultrabasic volcanic hot spring, and JM sandstone/rhyolite hot spring (Figure 8). $\delta^{13}C_1$ values tend to decrease with the increase of $\ln(CH_4/H_2)$ values, while $\ln(CH_4/H_2)$ values range from -3.83 to 4.96 with $\delta^{13}C_1$ values ranging from -55‰ to -20‰. The $^3He/^4He$ ratios in these areas range from 0.32 Ra to 4.0 Ra, indicating that gases could be a mixture of crust-derived and mantle-derived gas, and in combination with the result of abiogenic CH_4 having $\ln(CH_4/H_2)$ values less than 4.0 in Zambales ophiolites in Philippines, Oman peridotite complexes, Chimaera ophiolites in Türkiye, and New Caledonia ophiolites. Both CH_4 and H_2 in the basic volcanic rock basement of American Kansas Basin, the New Caledonia ophiolite, as well as TC basic-ultrabasic volcanic hot spring and JM sandstone-rhyolite hot springs are of abiogenic origin. At the same time, there is a conversion of H_2 to CH_4 through Fischer-Tropsch synthesis in these regions, and the more molecular H_2 is converted to abiogenic CH_4, the more negative $\delta^{13}C_1$ value becomes. The conversion of H_2 to CH_4 through Fischer-Tropsch synthesis is a process where the carbon isotopes of abiogenic CH_4 are more enriched in ^{12}C. According to $^3He/^4He$ ratios which are less than 0.32 Ra, the gas in the volcanic-metamorphic rock basement of Canadian Shield is from a typical crustal source. The $\ln(CH_4/H_2)$ values have a certain negative correlation with $\delta^{13}C_1$ values, and $\ln(CH_4/H_2)$ values range from 0.47 to 8.46 with $\delta^{13}C_1$ values ranging from -45.5‰ to -29.7‰. The gas in the volcanic-metamorphic basement of Canadian Shield is rich in He, ranging from 1.51% to 19.1%, and high He content is considered to be produced by radioactive α-decay of U- and Th-bearing minerals. If the U- and Th-bearing minerals can produce He through radioactive α-decay, molecular H_2 will be produced by groundwater decomposition under radioactivity. In fact, the H_2 content in the volcanic-metamorphic rock basement of Canadian Shield varies greatly, ranging from 0.01% to 26.0%. This indicates that part of molecular H_2 has been consumed by Fischer-Tropsch synthesis and converted to abiogenic CH_4. Sherwood Lollar et al. (2014) suggested that the gases in the volcanic-metamorphic basement of Canadian Shield were abiogenic based on carbon and hydrogen isotopes of alkane gases. Since there is no contribution of mantle-derived gas, abiogenic CH_4 in this area can only be formed through inorganic chemical reactions, in which Fischer-Tropsch synthesis is an important route. However, $\delta^{13}C_1$ values in the volcanic-metamorphic rock basement of Canadian Shield range from -45.5‰ to -29.7‰, covering the range of carbon isotope composition of CH_4 formed by thermal cracking of organic matter. Therefore, the carbon isotope composition of abiogenic CH_4 formed by inorganic chemical reactions may also overlap with that of CH_4 formed by thermal cracking of organic matter. There is no data of He content or $^3He/^4He$ ratios in the basic-ultrabasic volcanic rocks in Taoudenni Megan Basin in Mali, but both $\ln(CH_4/H_2)$ and $\delta^{13}C_1$ values are distributed within the area of gas in the volcanic-metamorphic basement of Canadian Shield, the basic volcanic basement in American Kansas Basin, the New Caledonia ophiolites, the TC basic-ultrabasic volcanic hot spring and JM sandstone/rhyolite hot spring (Figure 8). Therefore, gases could be a mixture of crust-derived and mantle-derived gases, or abiogenic gas formed by inorganic chemical reaction.

In addition, the mantle-derived abiogenic gas and crust-derived abiogenic gas can be identified by correlation of $\delta^{13}C_1$ and δ^2H-H_2 values (Figure 6). Therefore, the carbon isotope composition of abiogenic CH_4 from mantle volatile is completely different from that of the gas generated by thermogenic cracking of organic matter and bacterial activity. Although the carbon isotope composition of abiogenic CH_4 formed by inorganic chemical reactions has a wide range, even covering the range of carbon isotope of CH_4 formed by thermal cracking of organic matter, there is a certain difference of CH_4/H_2 ratio between thermal cracking of organic matter and inorganic chemical reaction.

2.2.4 Relationship between $\ln(CH_4/H_2)$ and δ^2H-C_1 value

The relationship between $\ln(CH_4/H_2)$ and δ^2H-C_1 values (Figure 9a) shows that the distribution of $\ln(CH_4/H_2)$ and δ^2H-C_1 values in the HG volcanic/sandstone gas field in the Jiyang Depression of Bohai Bay Basin, the DND sandstone gas field in Ordos Basin, and the QS volcanic/sandstone gas field of Songliao Basin is relatively narrow, but there is a certain positive correlation between $\ln(CH_4/H_2)$ and δ^2H-C_1 values in these basins with $\ln(CH_4/H_2)$ values ranging from 3.76 to 11.68 and δ^2H-C_1 values ranging from -277‰ to -179‰. Since source rocks in the HG gas field in the Jiyang Depression of the Bohai Bay Basin, the DND gas field in Ordos Basin, and the QS gas field in Songliao Basin were deposited in fresh water, the positive correlation between $\ln(CH_4/H_2)$ and δ^2H-C_1 values indicated that H_2 and CH_4 contents and δ^2H-C_1 values were obviously controlled by the evolution of thermal maturity, as the thermal maturity increased, the CH_4 content also increased, while the H_2 content decreased relatively, and the δ^2H-C_1 value gradually increased. As the gradual increase of thermal maturity from the HG gas field in the Jiyang Depression of Bohai Bay Basin, the DND gas field in Ordos Basin, and the QS gas field in Songliao Basin was observed, CH_4/H_2 ratios gradually decreased, while the δ^2H-C_1 values gradually increased, they indicated that the formation of CH_4 and H_2 was mainly controlled by the hydrocarbon generation process of organic matter, while δ^2H-C_1 values were affected by thermal evolution. Although the thermal maturity of source rocks in the QS gas field of Songliao Basin is higher than that of the DND gas field of Ordos Basin (Liu et al., 2016, 2015; Zhou et al., 2008), the δ^2H-C_1 values (from -204‰ to -197‰) are slightly smaller than that of the DND gas field of Ordos Basin (from -204‰ to -179‰), and the very small range of δ^2H-C_1 values in the QS gas field in the Songliao Basin is mainly related to intrusion of deep mantle-derived volatile (Liu et al., 2016). The $^3He/^4He$ ratios indicated that natural gas in the DND gas field of Or-

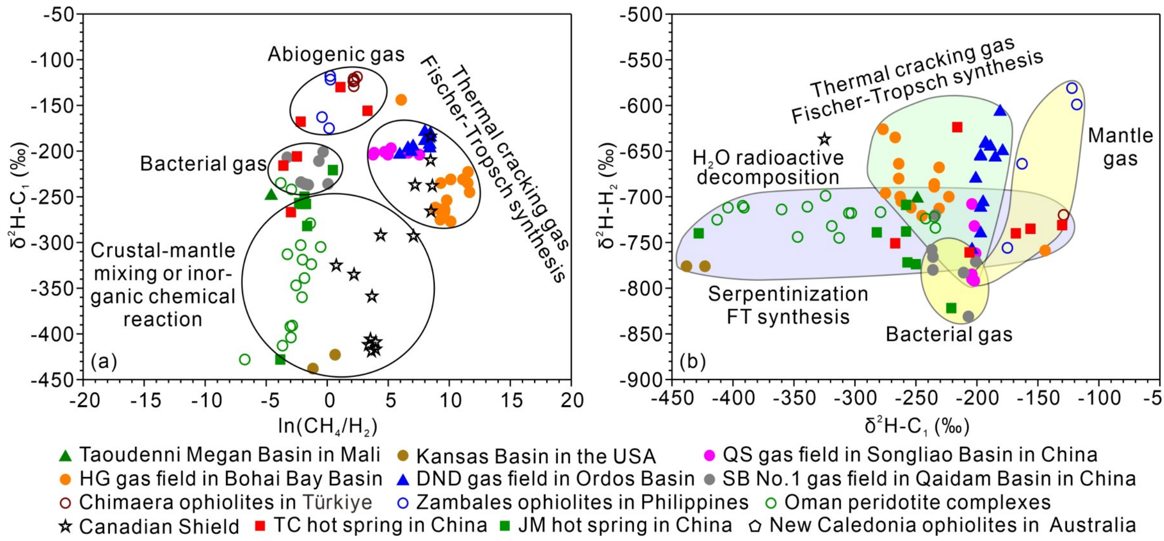

Figure 9. Correlation of the δ^2H-C_1 values versus $\ln(CH_4/H_2)$ (a) and δ^2H-H_2 (b) in various geological scenarios (modified after Liu et al., 2024).

dos Basin was typically crust-derived, whereas the natural gas in the QS gas field of Songliao Basin and the HG gas field in Jiyang Depression of Bohai Bay Basin had deep mantle-derived fluid intrusion. There could be more mantle-derived fluids in the QS gas field of Songliao Basin than that in the HG gas field in Jiyang Depression of Bohai Bay Basin, and more deep mantle-derived fluids could lead to the smaller range of δ^2H-C_1 values in the QS gas field of Songliao Basin.

The degradation of organic matter by microorganisms caused little variation of both ln(CH_4/H_2) and δ^2H-C_1 values in the SB No. 1 sandstone gas field of Qaidam Basin with ln(CH_4/H_2) values ranging from -3.28 to -0.07, and δ^2H-C_1 values ranging from -237‰ to -201‰, indicating that microorganisms had not differentiated degradation and translation in the degradation process of organic matter.

There is a positive correlation between ln(CH_4/H_2) and δ^2H-C_1 values for gases from Zambales ophiolites in Philippines, Chimaera ophiolites in Türkiye, and TC basic-ultrabasic volcanic hot spring gas with ln(CH_4/H_2) values ranging from -3.68 to 3.31 and δ^2H-C_1 values ranging from -216‰ to -118‰ (Figure 9a). Despite the contribution of crust-mantle mixing gas and Fischer-Tropsch synthesized abiogenic CH_4 in Zambales ophiolites in Philippines, Chimaera ophiolites in Türkiye, and TC basic-ultrabasic volcanic hot spring gas occurred based on ^{3}He/^{4}He ratios and two-endmember mixing of crust-derived and mantle-derived gas, both ^{3}He/^{4}He ratios and $\delta^{13}C_1$ values indicate that CH_4 was mainly of abiogenic origin. The gas in Zambales ophiolites in Philippines is mantle-derived abiogenic gas, with ln(CH_4/H_2) values ranging from -0.74 to 0.27, and δ^2H-C_1 values ranging from -175‰ to -118‰, while the gas in Chimaera ophiolites in Türkiye and part of TC basic-ultrabasic volcanic hot spring is a mixture of mantle-derived and Fischer-Tropsch synthesized gases.

The gas in the Oman peridotite complexes is abiogenic gas based on ^{3}He/^{4}He ratios and $\delta^{13}C_1$ values. There is a significant positive correlation between ln(CH_4/H_2) and δ^2H-C_1 values (Figure 9a). The ln(CH_4/H_2) values range from -6.75 to -0.53, and δ^2H-C_1 values range from -428‰ to -282‰. Since the distribution range of carbon and hydrogen isotope composition of mantle-derived abiogenic gases in the Zambales ophiolite in Philippines is very narrow, the abiogenic gases in the Oman peridotite complexes should be dominated by abiogenic gases formed by inorganic chemical reactions, in which H_2 is converted to CH_4 through Fischer-Tropsch synthesis, causing the relative increase of CH_4 content and the relative decrease of H_2 content, and the gradual increase of δ^2H-C_1 values.

Both ln(CH_4/H_2) and δ^2H-C_1 values for the gases from basic-ultrabasic volcanic rocks in Taoudenni Megan Basin in Mali, basic volcanic basement of American Kansas Basin, New Caledonia ophiolites, and TC basic-ultrabasic volcanic hot spring and JM sandstone-rhyolite hot spring have a similar variation range with those of Oman peridotite complexes, where ln(CH_4/H_2) values range from -4.58 to 0.47, and δ^2H-C_1 values range from -428‰ to -206‰. Considering that ^{3}He/^{4}He ratios for gases from basic volcanic basement of American Kansas Basin, New Caledonia ophiolites, TC basic-ultrabasic volcanic hot spring and JM sandstone-rhyolite hot springs range from 0.32 Ra to 4.0 Ra, these gases are formed by inorganic chemical reactions such as Fischer-Tropsch synthesis. Therefore, the initial CH_4 isotopically enriched in ^{1}H would be gradually more enriched in ^{2}H as the Fischer-Tropsch synthesis reaction proceeds. Since the gas has typical crustal origin in the volcanic-metamorphic basement of Canadian Shield with ^{3}He/^{4}He ratios less than 0.32 Ra, molecular H_2 is formed by water decomposition caused by radioactive decay, and ln(CH_4/H_2) values have a positive correlation with the δ^2H-C_1 values with ln(CH_4/H_2) values ranging from 0.74 to 8.63 and δ^2H-C_1 values ranging from -417‰ to -184‰. However, the variation ranges of ln(CH_4/H_2) and δ^2H-C_1 values are different from that of gases from the basic-ultrabasic volcanic rocks in Taoudenni Megan Basin in Mali, New Caledonia ophiolites, and TC basic-ultrabasic volcanic hot spring and JM sandstone/rhyolite hot spring. Therefore, molecular H_2 from the basic-ultrabasic volcanic rocks in the Taoudenni Megan Basin in Mali, New Caledonia ophiolites, TC basic-ultrabasic volcanic hot spring, and JM sandstone-rhyolite hot spring should be mainly serpentinized, whereas molecular H_2 in the volcanic-metamorphic basement of Canadian Shield was produced by H_2O decomposition through radioactive decay.

There were only two data collected from the basic volcanic basement in American Kansas Basin, which are distributed between the regions of serpentinization and H_2O decomposition caused by radioactive decay. Therefore, two sources of molecular H_2 in basic volcanic basement in American Kansas Basin may exist.

The sources of molecular H_2 in geological bodies mainly include deep mantle, thermal cracking and microbial degradation of organic matter, serpentinization and H_2O decomposition caused by radioactive decay. Since molecular H_2 is converted to CH_4 by inorganic chemical reactions under certain conditions, hydrogen isotope fractionation between CH_4 and H_2 must exist. Meanwhile, there is also hydrogen isotope fractionation of associated H_2 in the process of thermal cracking of organic matter to natural gas.

2.2.5 Relationship between δ^2H-H_2 value and δ^2H-C_1 value

The relationship between δ^2H-C_1 and δ^2H-H_2 values in SB No. 1 sandstone gas field of Qaidam Basin indicated that the range of hydrogen isotope values of CH_4 and H_2 formed by microbial decomposition of organic matter was narrow (Figure 9b). The δ^2H-C_1 values range from -237‰ to -201‰ and δ^2H-H_2 values range from -831‰ to -758‰, and there was no obvious correlation between them, suggesting that the undifferentiated degradation of organic matter by microorganisms did not cause significant hydrogen isotope fractionation between CH_4 and H_2. Shuai et al. (2010) suggested that molecular H_2 produced by microbial degradation of organic matter had relatively stable hydrogen isotopic composition, generally ranging from -800‰ to -700‰.

In the HG volcanic/sandstone gas field in the Jiyang Depression of Bohai Bay Basin, the DND sandstone gas field in Ordos Basin, and the QS volcanic/sandstone gas field in Songliao Basin, the relatively narrow range of hydrogen isotopes of CH_4 occurs, with δ^2H-C_1 values ranging from -277‰ to -179‰. However, the wide range of hydrogen isotope composition of molecular H_2 is observed, with δ^2H-H_2 values ranging from -792‰ to -607‰, and the distribution of δ^2H-C_1 values and δ^2H-H_2 values appears as an inverted triangle (Figure 9b), reflecting that the thermal cracking of organic matter in the sedimentary basins would cause significant hydrogen isotope fractionation of molecular H_2. A certain negative correlation between δ^2H-C_1 and δ^2H-H_2 values in the HG gas field in Jiyang Depression of Bohai Bay Basin occurs, whereas there is a positive correlation in the QS gas field of Songliao Basin and the DND gas field of Ordos Basin. This observation can be interpretated as the thermal maturity of source rocks in the Jiyang Depression of Bohai Bay Basin is lower than that of the QS gas field of Songliao Basin and the DND gas field of Ordos Basin (Liu et al., 2016, 2015; Meng et al., 2015; Zhou et al., 2008; Jin et al., 2002). Both organic matter and H_2O jointly participate in the hydrocarbon generation process in sedimentary basins, and the rate of H_2 production reaches the highest at the peak of hydrocarbon generation, accompanied by H_2 formation and hydrogen isotope fractionation. The thermal maturity of natural gas in QS gas field in Songliao Basin is higher than that in DND gas field in Ordos Basin, but its hydrogen isotope composition of molecular hydrogen (from -792‰ to -712‰) is isotopically more enriched in ^1H than that in DND gas field in Ordos Basin (from -758‰ to -607‰). This suggests that the conversion of H_2 to CH_4 during the process by Fischer-Tropsch synthesis in QS gas field would be more intensive than that in DND gas field.

It is well known that the gases in the Zambales ophiolites in Philippines, the Oman peridotite complexes, and the Chimaera ophiolites in Türkiye have abiogenic CH_4 and abiogenic H_2 based on $^3He/^4He$ ratios, $\delta^{13}C_1$ values, δ^2H-C_1 values, and CH_4/H_2 ratios. The molecular H_2 in the Zambales ophiolites in Philippines is sourced from deep mantle, while the molecular H_2 in the Oman peridotite complexes and the Chimaera ophiolites in Türkiye was mainly produced by serpentinization, where part of molecular H_2 would be converted to CH_4 through Fischer-Tropsch synthesis. The relationship between δ^2H-C_1 value and δ^2H-H_2 value has a certain positive correlation in the Zambales ophiolites in Philippines. The δ^2H-C_1 values range from -175‰ to -118‰, and δ^2H-H_2 values range from -756‰ to -581‰. Therefore, δ^2H-H_2 values increase with increasing of δ^2H-C_1 values for abiogenic CH_4 and abiogenic H_2 which were mainly derived from deep mantle with significant fractionation of hydrogen isotope for molecular H_2. No significant linear correlation between δ^2H-C_1 values and δ^2H-H_2 values is observed in the Oman peridotite complexes and the Chimaera ophiolites in Türkiye, where molecular H_2 was produced by serpentinization and CH_4 was formed by Fischer-Tropsch synthesis with a narrow variation ranges of δ^2H-H_2 values (from -725‰ to -699‰) and a wide variation range of δ^2H-C_1 values (from -413‰ to -129‰). Therefore, molecular H_2 formed by serpentinization has a relatively narrow distribution of hydrogen isotope values, while CH_4 produced by Fischer-Tropsch synthesis has a wide range of hydrogen isotope values. In the correlation diagram between δ^2H-C_1 values and δ^2H-H_2 values (Figure 9b), the gases in basic-ultrabasic volcanic rocks of the Taoudenni Megan Basin in Mali, basic volcanic rock basement of American Kansas Basin, New Caledonia ophiolites, TC basic-ultrabasic volcanic hot spring, and JM sandstone-rhyolite hot spring, are located within the gases in Oman peridotite complexes and Chimaera ophiolites in Türkiye. Therefore, the gases in basic-ultrabasic volcanic rocks of the Taoudenni Megan Basin in Mali, basic volcanic rock basement of American Kansas Basin, New Caledonia ophiolites, TC basic-ultrabasic volcanic hot spring, and JM sandstone-rhyolite hot spring have a similar origin with that of Oman peridotite complexes and Chimaera ophiolites in Türkiye. The hydrogen isotopes of H_2 produced by inorganic chemical reactions have a wide range. As the temperature increases, the hydrogen isotopes of H_2 become heavier (Proskurowski et al., 2006), which is related to the fact that molecular H_2 was consumed and converted into CH_4, thus making present molecular H_2 more isotopically enriched in ^2H and CH_4 isotopically more enriched in ^1H. Thus, methane produced by Fischer-Tropsch synthesis is more isotopically enriched in ^1H than that of thermal cracking of organic matter. Despite there are not much data of δ^2H-H_2 values to illustrated the origin of molecular H_2 in the volcanic-metamorphic rock basement gas in Canadian Shield, the geochemical parameters of $^3He/^4He$ ratios (< 0.32 Ra), $\delta^{13}C_1$ values, δ^2H-C_1 values, and CH_4/H_2 ratios indicated that molecular H_2 in the volcanic-metamorphic rock basement gas in Canadian Shield was a typical crust-derived abiogenic gas. Only one datum of δ^2H-C_1 value showed that molecular H_2 would be formed by H_2O decomposition caused by radioactive decay, since its hydrogen isotope value (δ^2H-H_2 = -637‰) is obviously higher than that of molecular H_2 formed by serpentinization in the Chimaera ophiolites in Türkiye. The water in volcanic-metamorphic rock basement in Canadian Shield is alkaline saline type which has heavy hydrogen isotope. Lin et al. (2005) used ^{60}Co as a radioactive source to understand the ability of H_2O decomposition in generating molecular H_2 under excitation of radioactive substances. The results showed that the production of molecular H_2 generated by H_2O decomposition under excitation of radioactive substances was related to the dose of radioactive energy, when the H_2O with a δ^2H-H_2O value of -44‰ is excited by radioactive energy, the hydrogen isotope values of molecular H_2 range from -520‰ to -490‰, and is not affected by the dose of radioactive substances, the pH value of water, salinity or oxygen. The hydrogen isotope of molecular H_2 generated from H_2O decomposition of radioactive decay is mainly controlled by hydrogen isotope fractionation between H_2O and H_2.

Molecular H_2 in geological bodies includes mantle volatile, thermal cracking of organic matter, microbial degradation of organic matter, serpentinization of olivine and pyroxene in mafic and ultramafic rock, and H_2O decomposition of radioactive decay by radioactive elements of U (^{238}U, ^{235}U), Th (^{232}Th), K (^{40}K) in the basement rock (Dzaugis et al., 2016; Lin et al., 2005; Vovk, 1987). Due to chemical activity of molecular H_2, various inorganic chemical reactions make the hydrogen isotope fractionation of H_2 and CH_4 under certain geological conditions. It can be assumed that the rate of H_2 production from serpentinization or H_2O decomposition caused by radioactivity under the geological condition was basically constant. Gases from areas where Fischer-Tropsch synthesis was relatively weak have relatively high H_2 content, associated with the wide range of hydrogen isotope fractionation of molecular H_2, since the low content of CH_4 was formed by Fischer-Tropsch synthesis and its hydrogen isotope is more isotopically enriched in ^1H than that of CH_4 produced by thermal cracking or microbial degradation of organic matter. On the contrary, gases from areas with relative strong Fischer-Tropsch synthesis have a relatively low content of molecular H_2, since a certain amount of molecular H_2 was consumed and converted into CH_4, causing the high content of CH_4 generated by Fischer-Tropsch synthesis. As a result, the hydrogen isotope of CH_4 was relatively enriched in ^2H, distributed in a similar range with that of CH_4 formed by thermal cracking of organic matter and microbial degradation.

According to occurrence of molecular H_2 under different geological conditions, in combination with $^3He/^4He$ ratios as well as carbon and hydrogen isotopes of CH_4, the formation environments and co-evolution of H_2 and CH_4 under different geological conditions can be identified as shown in Table 1. Due to the mixing of gases from different sources, the threshold of constrained parameters for molecular H_2 is not constant, and the sources of molecular H_2 is identified in combination with its geological backgrounds and formation processes.

3 ACCUMULATION OF MOLECULAR HYDROGEN IN GEOLOGICAL SCENARIOS

3.1 A Case of H_2-Bearing Gas Reservoirs in Kansas Basin, North America

Since the early 1980s, H_2, N_2, and He gases, as well as a small amount of hydrocarbon gases, have been found in oil wells in the continental rift system in Kansas, USA (Guélard et al., 2017; Newell et al., 2007; Coveney et al., 1987; Goebel et al., 1983). Among them, the conti-

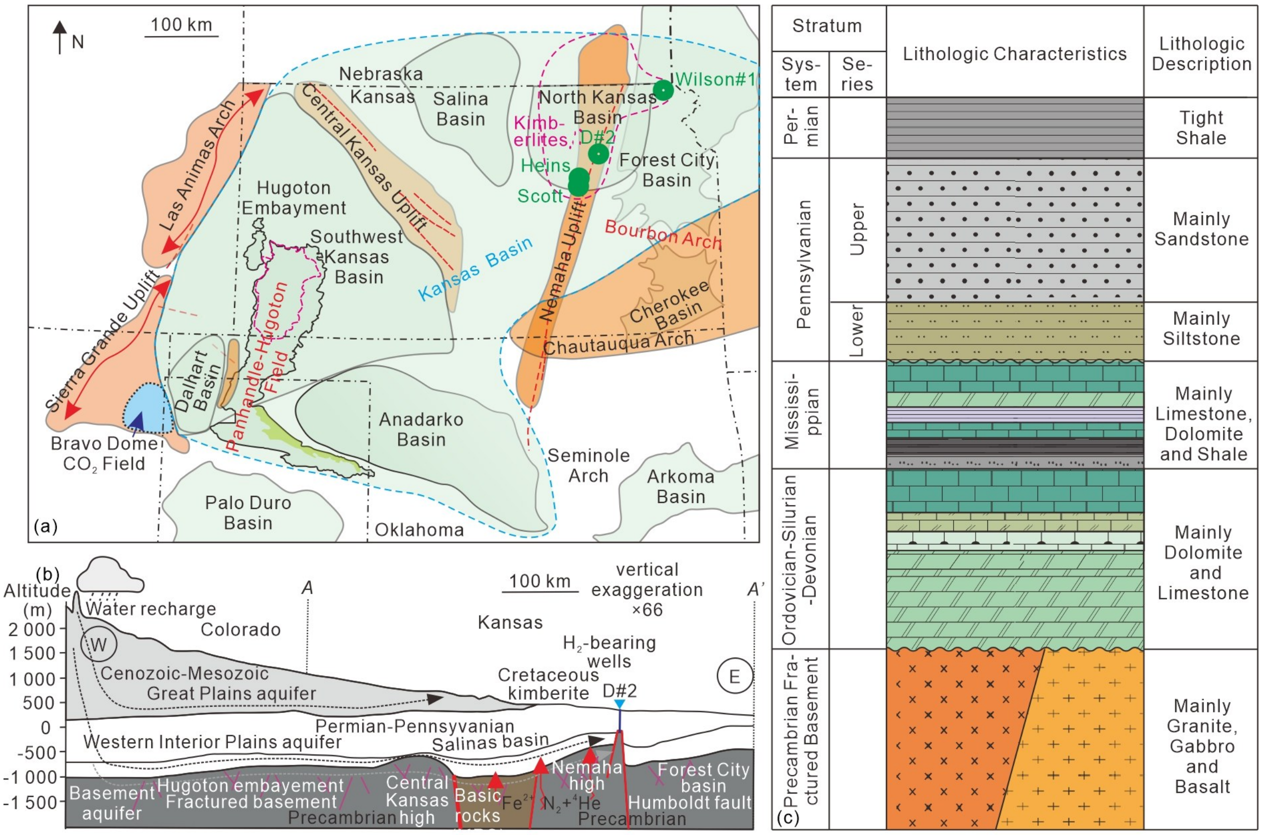

Figure 10. (a) Schematic diagram of structural units and drilled wells in Kansas Basin, USA (modified from Coveney et al., 1987; Guélard et al., 2017); (b) geological sections of the basin; (c) lithology of the basin.

nental rift is the main distribution area of high-content molecular H_2. For example, the H_2 content in natural gas in Well Scottt 1 reached about 50% at the time of discovery (Goebel et al., 1983), and then the H_2 content decreased with time, varying between 24% and 43% (Coveney et al., 1987; Goebel et al., 1983). During 2005–2006, the H_2 content in natural gas drilled by WTW Petroleum Company in the Forest City Basin of Kansas area reached 17%, and heavy hydrocarbon components were detected (Newell et al., 2007). In 2008, Kansas Branch of the US Geological Survey carried out drilling targeting for molecular H_2 in this area, and the natural gas was discovered in the Precambrian basement of D#2-1 Well, with H_2 content as high as 91.8%, showing a good prospect for molecular H_2 exploration and development (Figure 10).

The H_2 wells in the Kansas Basin are distributed on the Nemaha anticline, which is located several miles west of Humboldt fault. The Nemaha anticline was formed by deformation in the Early Pennsylvania Period (Goebel et al., 1983). Humboldt fault, which cuts Precambrian basement rocks and Paleozoic strata, is a low energy seismic zone, and coincides with the continental rift system. The basement of the basin is mainly affected by tension, resulting in the development of a fault system. The pre-Cambrian basement gas reservoir is unconformably overlaid by the Ordovician series, and the pre-Cambrian basement rock is mainly composed of igneous or metamorphic rocks, of which igneous rocks are mainly composed of granite, gabbro, and basalt, etc. (Newell et al., 2007; Coveney et al., 1987). A series of Devonian–Ordovician sedimentary strata, mainly composed of limestone and sandstone, were deposited above the basement. The overlying Ordovician formation developed a dense set of carbonate rocks, mainly consisting of dolomite and limestone, which form a good cap for the basement gas reservoir. Therefore, the central rift system is the area where H_2 is mostly enriched. The Carboniferous period is characterized by the development of Mississippi-Pennsylvanian sandstones, and coal measures. The lower section of the Pennsylvanian series developed dense carbonate rocks, which are the cap rocks for the underlying Mississippi series sandstones (Coveney et al., 1987). The Pennsylvanian sandstone series is in conformity with the overlying thick Permian marine dense shale, which is a good cap rock for gas reservoirs (Schulmeister et al., 2019).

The molecular H_2 in the Kansas Basin was mainly produced from Fe-rich mafic mass in Precambrian basement-ultrabasic volcanic rocks. The H_2 reservoir in the Kansas Basin is mainly distributed in the mafic volcanic basement and sedimentary rocks, mainly in the pre-Cambrian basement fractures, the Honton limestone of the Silurian–Devonian Period, the Kinderhookian sandstone of the Mississippi – Devonian Period, and the Indian cave sandstone of the Pennsylvania Period (Guélard et al., 2017; Coveney et al., 1987). Due to large number of dense fractures in the volcanic basement, it is an important H_2 producing layer, and the overlying limestone and sandstone also produce a certain amount of H_2, but the H_2 content in the sedimentary layer is significantly lower than that in the volcanic basement (Guélard et al., 2017). At the same time, a small amount of H_2 is also produced in the tiny pores of the carbonate rocks.

According to $^3He/^4He$ ratios and two-endmember mixing of crust-derived and mantle-derived gases, natural gas in the Kansas Basin has $^3He/^4He$ ratio < 0.32 Ra, which is of crustal origin. From the perspective of the natural gas production and lithology of the Kansas Basin reported in previous studies, there is no contribution of thermal cracking or microbial degradation of organic matter. The He in the gas is mainly produced by the α-decay of uranium and thorium-rich minerals in mafic and ultramafic rocks, while the H_2 is mainly generated by the reaction of water with olivine and pyroxene in mafic and ultramafic rocks to form serpentine, and by the decomposition of water induced by α, β, and γ radiation. The Kimberlite and hidden layered mafic and ultramafic rocks in the Kansas Basin's volcanic basement are important sources for the generation of H_2 by the serpentinization process (Guélard et al., 2017; Newell et al., 2007; Coveney et al., 1987). In addition, U- and Th-rich granitic rocks in the pre-Cambrian basement of the region also provide favorable conditions for the formation of He through radioactive decay and the production of H_2 through radiation-induced water decomposition. The coexistence of gases such as ^4He, ^{40}Ar, and N_2 (with an average $\delta^{15}N$ value of +2.5‰) indicates a radioactive origin, and the $^3He/^4He$ values are less than 0.02 Ra, which show characteristic crustal source with a radioactive origin (Guélard et al., 2017).

The correlation between He and H_2 contents in Figure 11a suggests that the Heins and Scott regions of the Kansas basin are dominated by serpentinization, while the D and Wilson regions are dominated by radioactive He and H_2. This is because the H_2 content is high in the Heins and Scott regions, while He is generally low. Although the variation of H_2 content in D and Wilson regions is large, the content of He is generally higher than 0.5%, and the high He content may be attributed to the production of He through U and Th radioactive decay. The large variation in H_2 content is likely due to the H_2 being consumed through the Fischer-Tropsch synthesis of CH_4. It shows in the relationship between $\ln(H_2/He)$ and $\ln(CH_4/CO_2)$ that natural gas has a certain negative correlation between $\ln(H_2/He)$ and $\ln(CH_4/CO_2)$ in regions where gases are of radiogenic origin (Figure 11b), while region with serpentinization mainly show that $\ln(H_2/He)$ values have a small range of variation, while there has a large range of variation in $\ln(CH_4/CO_2)$ values, and there is no obvious correlation between the two, indicating that for regions of radiogenic origin, not only H_2 and He are formed, but also the consumption of H_2 through Fischer-Tropsch synthesis could increase the CH_4 content significantly. In contrast, serpentinization only generates serpentine and releases H_2 through the reaction of olivine and pyroxene with water, without producing He. High levels of H_2 are not necessarily accompanied by high levels of He in this case.

From the relationship between the δ^2H-C_1 and δ^2H-H_2 values in Figure 11c, it can be inferred that although data are limited for both the radioactive and serpentinite regions, the hydrogen isotope composition of CH_4 in the radioactive region is significantly heavier than that in the serpentinite region. In the serpentinite region, the δ^2H-C_1 values range from -450‰ to -350‰, while in the radioactive region, they range from -300‰ to -250‰. According to the relationship between H_2 contents and δ^2H-H_2 values (Figure 11d), there is a certain positive correlation between the δ^2H-H_2 values and the H_2 contents of natural gas in the serpentinization area. This suggests that, with the increase of the H_2 content, the δ^2H-H_2 values show an increasing trend, while there is no significant correlation between the two in the radioactive area. Therefore, it is inferred that high levels of H_2 are more easily formed in the serpentinite region, while in the radioactive region, some H_2 is easily transformed into CH_4 through Fischer-Tropsch synthesis, resulting in a relatively low H_2 content, but a relatively high He content can be formed in the radioactive region.

The study of well D#2-1 showed that the H_2 content reached 91.8% at the bottom when the well was initially drilled, while the CH_4 content was only 0.1%. However, in the later stages, the H_2 content sharply decreased while the CH_4 content sharply increased, and the hydrogen isotope of H_2 became heavier, while the carbon isotope of CH_4 became abnormally lighter ($\delta^{13}C_1$ < -55‰), indicating typical characteristics of biogenic gas, which may be due to the consumption of H_2 by microorganisms to produce methane, leading to changes in H_2 content and isotopes (Guélard et al., 2017). H_2 is easily consumed by subsurface microbial activity. For example, H_2 is consumed to generate CH_4 or acetate by microorganisms in the presence of CO_2, whereas H_2 is consumed to generate H_2S in the presence of SO_4^{2-}. In an underground storage facility in Robodis, Czech Republic, 45%–60% of H_2 was transformed into CH_4 or H_2S through microbial reactions (Šmigáň et al., 1990). The Vaux-en-Bugey condensate gas field in France has 5% of natural gas at the beginning of exploration, about 1.1 × 10^6 m^3, and a sharp decrease in H_2 content was detected later, which was attributed to oxidation by sulfur bacteria (Deronzier and Giouse, 2020). At the same time, H_2 is an electron donor for some microorganisms, including archaea and bacteria, thereby promoting microbial metabolism and the formation of substances such as acetate, which in turn affects reservoir permeability and porosity (Ebigbo et al., 2013). Therefore, compared with other components in natural gas, H_2 is more susceptible to loss due to microbial or inorganic reactions (Lin et al., 2005; Telling et al.,

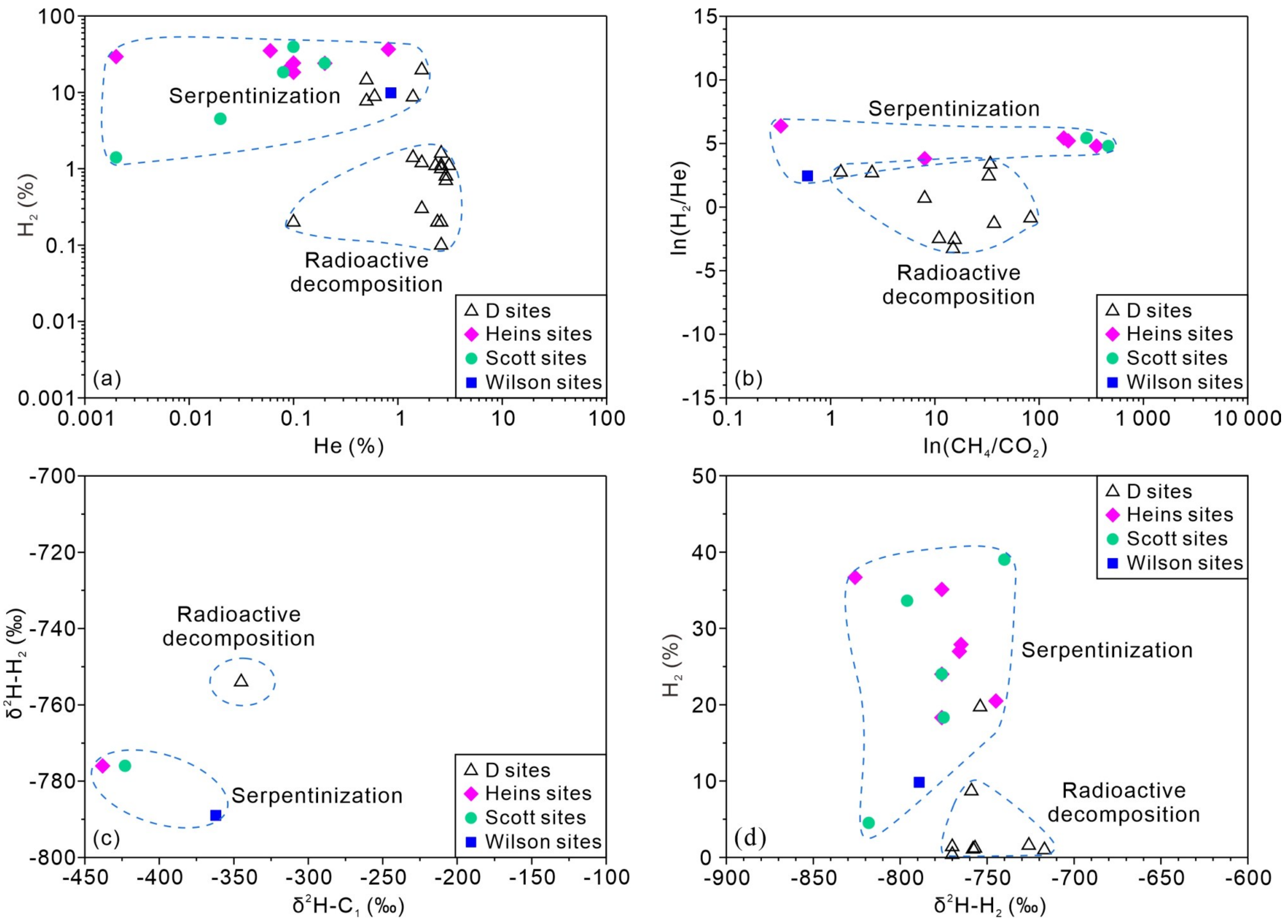

Figure 11. Diagrams of (a) He% versus H_2%; (b) δ^2H-C_1 versus δ^2H-H_2; (c) ln(CH_4/CO_2) versus ln(H_2/He); (d) H_2% versus δ^2H-H_2 in various regions in Kansas Basin, USA.

2015).

The gas with the H_2 content higher than 25% in the Kansas Basin is mainly distributed in the basic-ultrabasic volcanic rocks in the central rift area, which is either deeply fractured or influenced by deep faults. Although there is also a certain amount of H_2 production in the sedimentary layers overlying the basement in the Kansas Basin, the H_2 content in the sedimentary reservoirs is significantly lower than that in the basement volcanic rocks, indicating that H_2 in the Kansas Basin is mainly enriched in the near-source area (Figure 12). Due to the development of fractures at the edge of the Kansas Basin, which provide channels for groundwater infiltration, groundwater flows into the sedimentary layer and dense fractures of the volcanic basement of the basin along the fractures, and the aquifers are mainly distributed in the sandstone layer at the top of the Carboniferous Pennsylvanian and Devonian systems. The capillary force generated by the water affinity of minerals in dense shale or siltstone plays a good protective role by blocking the production, migration and diffusion of H_2, and inhibiting the loss of H_2.

In summary, the enrichment of H_2 requires a continuous supply of H_2, as H_2 consumption and loss are ongoing processes. The basement of the Kansas Basin is composed of extensive basic-ultrabasic volcanic rocks overlain by thick sedimentary deposits. These basic-ultrabasic volcanic rocks are not only rich in U, Th and other radioactive elements, but also develop mafic and ultramafic rocks containing olivine and pyroxene, which are the main source of high-abundance H_2 and He. Furthermore, because of the active chemical properties of H_2, its enrichment not only requires in situ accumulation or short-distance migration and aggregation in adjacent strata (Coveney et al., 1987), but also depends on the sealing ability of the overlying and surrounding rocks to ensure that the H_2 accumulation rate exceeds the H_2 loss rate (Deronzier and Giouse, 2020; Zgonnik, 2020). The well-developed fractures in basement rocks in Kansas Basin not only increased the contact area with reactive fluid, but also provided a larger storage space. Meanwhile, the tight sedimentary rocks overlying the basement effectively prohibited the diffusion of molecular H_2 from the basement reservoir, and the detection of different concentrations of H_2 in the crust suggests that H_2 has a sustained supply (Etiope, 2023; Prinzhofer et al., 2019), thus establishing a dynamic balance between continuous supply and diffusion of molecular H_2. Therefore, the enrichment of H_2 in geological bodies requires a comprehensive evaluation based on the different mineral compositions of rocks and the physical properties of surrounding rocks (Sherwood Lollar et al., 2014). In future, H_2 resources that can be commercialized are more likely to be obtained from the geological structures in the continental rift systems. The Bohai Bay Basin in China is located within the Cathaysian Rift System and shares a similar geological background with the Kansas Basin Rift System. Both areas exhibit basic and ultra-basic volcanic activities, representing significant regions for the abundant distributions of basic and ultra-basic magmas. The upper part of the rift features the development of thick sedimentary layers, which serve as valuable reservoirs for the storage and accumulation of hydrogen gas under appropriate geological conditions. Therefore, the region of the eastern Bohai Bay Basin in China, characterized by the development of alkaline and ultra-alkaline volcanic rocks and stable sedimentary layers, holds substantial value for geological exploration focused on molecular hydrogen. It is considered a key area for future exploration efforts targeting hydrogen gas as a resource.

3.2 Sealing Properties of Caprock and Surrounding Rock

3.2.1 Effects of surrounding rocks on physical and chemical characteristics of molecular H_2

Compared with conventional natural gas reservoirs, the distribution of H_2 enrichment in geological bodies in

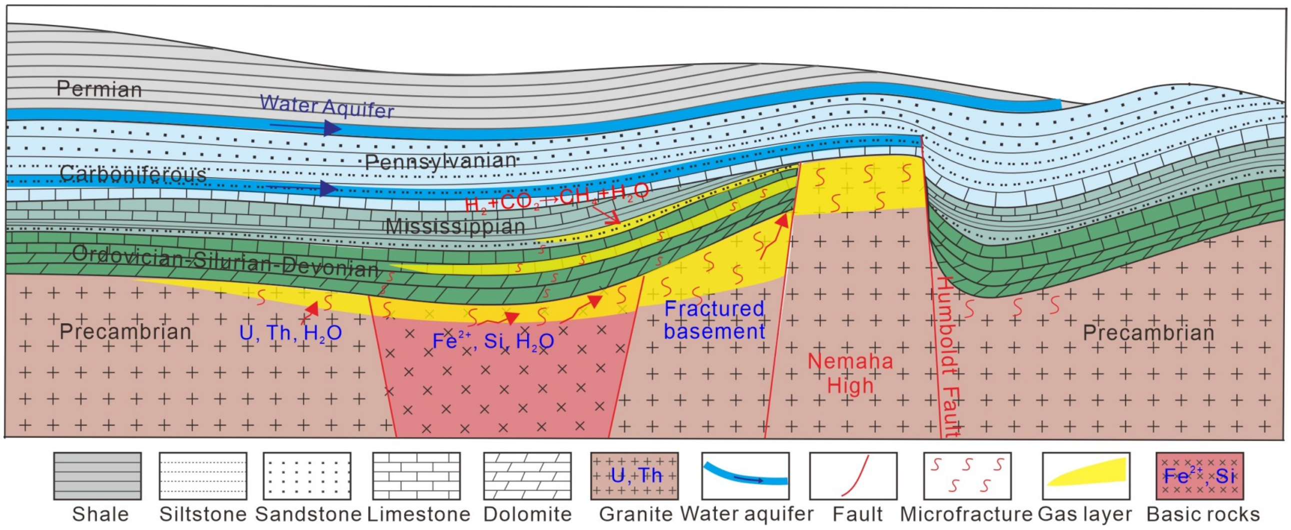

Figure 12. Schematic diagram of H_2 accumulation in Kansas Basin, USA.

the world is less due to small molecular size and active chemical properties of molecular H_2. However, the accumulation of molecular H_2 is similar to conventional natural gas reservoirs, which requires sufficient gas supply, good storage space and safe sealing. The high reactivity and consumption of molecular H_2 required the relatively available supply in geological scenarios. Molecular H_2 is also a very diffusible gas, and the detection of molecular H_2 in varying amounts in geological scenarios indicated a continuous supply of molecular H_2 (Etiope, 2023; Prinzhofer et al., 2019).

Due to active physical and chemical properties, molecular H_2 is generally enriched in situ or undergoes short-distance migration and accumulates in adjacent layers (Coveney et al., 1987). In addition to proximity to source of H_2-enriched interval, the sealing ability of cap rock and surrounding rock is an important factor for the H_2 enrichment (Deronzier and Giouse, 2020; Zgonnik, 2020). When molecular H_2 migrates to water-rock interface of cap rock, it will be blocked by capillary pressure. As long as the threshold pressure does not exceed, molecular H_2 will be kept tightly sealed and act as a geological barrier to the underlying gas (Reitenbach et al., 2015). If the gas pressure exceeds the capillary threshold of cap rock, molecular H_2 will escape and leak through cap rock, and thus it is fate for H_2 enrichment to the capillary sealing efficiency of cap rock and surrounding rock. The capillary sealing efficiency is mainly affected by different lithology of cap rocks. For example, the sealing effect of shale and evaporite is mainly affected by the interface, and the interface affects the parameters of the capillary sealing efficiency of the cap rock (water-H_2-rock pores, wettability). The wettability of molecular H_2 increases with pressure, surface concentration of organic matter, and TOC value, but it decreases with temperature. The sealing efficiency of shale for molecular H_2 decreases with increasing temperature (Aftab et al., 2022; Reitenbach et al., 2015). In addition, evaporites with small pore sizes provide the most effective seals. The physicochemical reactions between surrounding rock and fluid have an important impact on the porosity-permeability evolution of reservoirs, which in turn affects the gas flow process and rock barrier properties.

3.2.2 Mineralogical or microbial modification in the surrounding rocks

During the process of migration and accumulation, molecular H_2 in geological bodies will undergo a series of physicochemical reaction with minerals in surrounding rocks or participate in the process of bioheterotrophy, resulting in H_2 consumption. Generally, molecular H_2 chemically reacts with S-containing minerals to produce H_2S. Under normal pressure, no catalyst and below 100 °C, the chemical reaction between H_2 and rocks is slow, but the chemical reaction accelerates as pressure increases. When molecular H_2 interacts with clay minerals, it causes that the dissolution of carbonate and sulfate minerals of chlorite group, feldspar and clay minerals, and the precipitation of illite, iron sulfide and pyrrhotite (Klein et al., 2020; Heinemann et al., 2018). The dissolution and precipitation of minerals affects the migration and diffusion of molecular H_2.

Molecular H_2 as an electron donor for certain microorganisms (including archaea and bacteria), has ability to promote microbial metabolism and formation of substances such as acetic acid, which in turn affects the permeability and porosity of reservoir (Ebigbo et al., 2013). Molecular H_2 is easily consumed under action of microorganisms. In the presence of CO_2, molecular H_2 is consumed by microorganisms and produces CH_4 or acetate, or in the presence of SO_4^{2-}, molecular H_2 is consumed and produces H_2S. In an underground storage of gas in Roberdis of Czech Republic, 45%–60% of molecular H_2 was converted into CH_4 or H_2S through microbial reaction (Šmigáň et al., 1990). When the Vaux-en-Bugey condensate gas reservoir in France started to be explored, the H_2 content in natural gas was 5% with a total gas amount of 1.1×10^6 m^3, and then a sharp decrease in H_2 content was detected, which might be related to oxidation and consumption of S-bearing bacteria (Deronzier and Giouse, 2020).

Therefore, compared with other components in natural gas, molecular H_2 is more susceptible to loss due to microbial action or abiogenic reaction (Telling et al., 2015; Sherwood Lollar et al., 2006; Lin et al., 2005), such as abiogenic synthesis of CH_4, sulfur reduction reaction or oxidation reaction. Since H_2 consumption is a continuous process, only does the continuous supply of molecular H_2 keep the H_2 enrichment. At the same time, due to active chemical properties of molecular H_2, the section of H_2 enrichment is required to be close to H_2 source, and the amount of H_2 generation is larger than the amount of H_2 diffusion. Therefore, the enrichment of molecular H_2 in geological bodies needs to be comprehensively evaluated in combination with mineral composition of source-reservoir-caprock and the physical properties of surrounding rocks (Briere and Jerzykiewicz, 2016; Sherwood Lollar et al., 2014).

4 CONCLUSIONS

Molecular H_2 is widely distributed and enriched in various geological scenarios, and different genetic origins of molecular H_2 have distinct geochemical characteristics. According to the origin and source of molecular H_2, it can be classified into several groups, including deep mantle, thermal cracking of organic matter, microbial degradation, serpentinization and H_2O decomposition caused by radioactive radiation. Due to active chemical properties of molecular H_2, it is easily consumed by biological and chemical reactions under certain geological conditions. Fischer-Tropsch synthesis is one of the most common ways for molecular H_2 to be consumed and converted into abiogenic CH_4 in geological bodies.

The Fischer-Tropsch synthesis not only consumes molecular H_2, but also causes the isotope fractionation of hydrogen in H_2 and CH_4. Therefore, abiogenic CH_4

formed by the inorganic chemical reaction has a similar distribution of hydrogen isotope composition to that of the CH_4 formed by thermal cracking of organic matter and microbial degradation.

Among different genetic sources of molecular H_2 in geological bodies, the most abundant molecular H_2 is from the indiscriminate degradation of organic matter by microorganisms, followed by H_2 from serpentinization and mantle-derived H_2. The amount of molecular H_2 from decomposition of H_2O under radioactive radiation depends on the amount of H_2 consumed by the Fischer-Tropsch synthesis. The amount of molecular H_2 formed by thermal cracking of organic matter is the lowest among all sources. Radioactivity not only decomposes H_2O to produce molecular H_2, but also forms high content of He.

The accumulation of molecular H_2 in geological bodies is mainly constrained by continuous supply from H_2 sources, migration distance, and dynamic balance between H_2 supply and loss. If the supply is larger than the loss, it is easier for the molecular H_2 to enrich. The continental rift system can be the area with a high chance of discovery and commercial development of H_2 resources in the future.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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