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Short Communication

Integrated geochemical identification of natural hydrogen sources

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Owing to heightened environmental and energy concerns, countries worldwide are setting carbon peak and carbon neutrality goals. Natural hydrogen gas (H_2) is considered a clean energy source and is often referred to as “gold” or “white” hydrogen. Discovering natural hydrogen reserves could be critical for meeting the demand for hydrogen energy.

Hydrogen has been discovered in various geological settings [1,2]. However, the active chemical properties of hydrogen pose considerable challenges in identifying H_2 sources [3,4]. Multiple sources of natural hydrogen have been identified using gas geochemistry, including mantle volatiles, serpentinization, radiolytic decomposition of water (H_2O), and organic matter reactions (see Supplementary Materials online for a detailed discussion). However, there are no integrated geochemical criteria for identifying natural hydrogen, and such criteria are necessary for accumulation and resource evaluation. We analyzed the gas compositions, carbon and hydrogen isotopes, and $^3He/^4He$ of natural gases and hot springs to acquire representative H_2 data (Fig. S1, Table S1 online) in order to elucidate the genetic source of natural hydrogen. These insights not only mitigate the risks to economic challenges in hydrogen exploration in geological bodies but also support the effective and efficient development and utilization of hydrogen.

Sources of methane (CH_4) and helium (He) can be correlated with H_2 sources, given their common association. Typical mantle-derived gas has $R/Ra \approx 8.0$, whereas gases from hot springs and hydrothermal systems in the East Pacific mid-ocean ridge have $R/Ra > 1.0$ [5,6]. A value of $R/Ra > 4.0$ is typical of a mantle origin. Although typical crust-derived helium has $R/Ra = 0.02$, crust-derived gases from cratonic basins such as the Ordos, Sichuan, and Kansas basins have $R/Ra < 0.32$ [7–9]. Consequently, $R/Ra < 0.32$ is consistent with a crustal origin. Gases in the Daniudi (DND) gas field in the Ordos Basin, the Canadian Shield, and the American Kansas Basin are typical crust-derived gases, with $R/Ra < 0.32$ and H_2 concentrations of 0.1%–27.9% (Fig. 1a). Gas in the Zambales Ophiolite in the Philippines has $R/Ra > 4.0$ (Fig. 1a), indicative of typical mantle-derived H_2, with concentrations ranging from 35.1% to 58.5%. Samples from the Qingshen (QS) gas field in the Songliao Basin, the Huagou (HG) gas field in the Bohai Bay Basin, Oman peridotite complexes, New Caledonia ophiolites, and the Jimo (JM) hot springs of China yield R/Ra of 0.32–4.0 (Fig. 1a), indicating mixing of crust- and mantle-derived H_2, with H_2 concentrations ranging from 0.0014% to 99%. Similarly, gas samples from the Tengchong (TC) hot springs yield R/Ra of 0.32–4.0, consistent with H_2 derived from both mantle and crustal sources, although some samples have $R/Ra > 4.0$ and H_2 concentrations of 0.015%– 5.15%, consistent with mantle-derived gas (Fig. 1a).

Methane in geological bodies is commonly categorized as biogenic or abiogenic. Abiogenic CH_4 typically exhibits heavier carbon isotopes, with $\delta^{13}C_1$ values greater than $-20‰$ [10], whereas biogenic CH_4 originating from organic matter typically yields $\delta^{13}C_1$ values of less than $-55‰$ for bacterial gas and $-55‰$ to $-30‰$ for thermogenic gas [11] (see Supplementary Materials online for a detailed discussion). Gas in the Sebei (SB) No.1 gas field in the Qaidam Basin is typically bacterial, with $\delta^{13}C_1 < -55‰$ and H_2 concentrations of 47.7 %–95.4 % (Fig. 1b). Abiogenic gas can be derived from both the deep mantle and inorganic chemical reactions (ICRs) in the crust; as a result, crust-mantle mixing (CMM) gas can also be abiogenic. It is extremely difficult to determine the type of abio-

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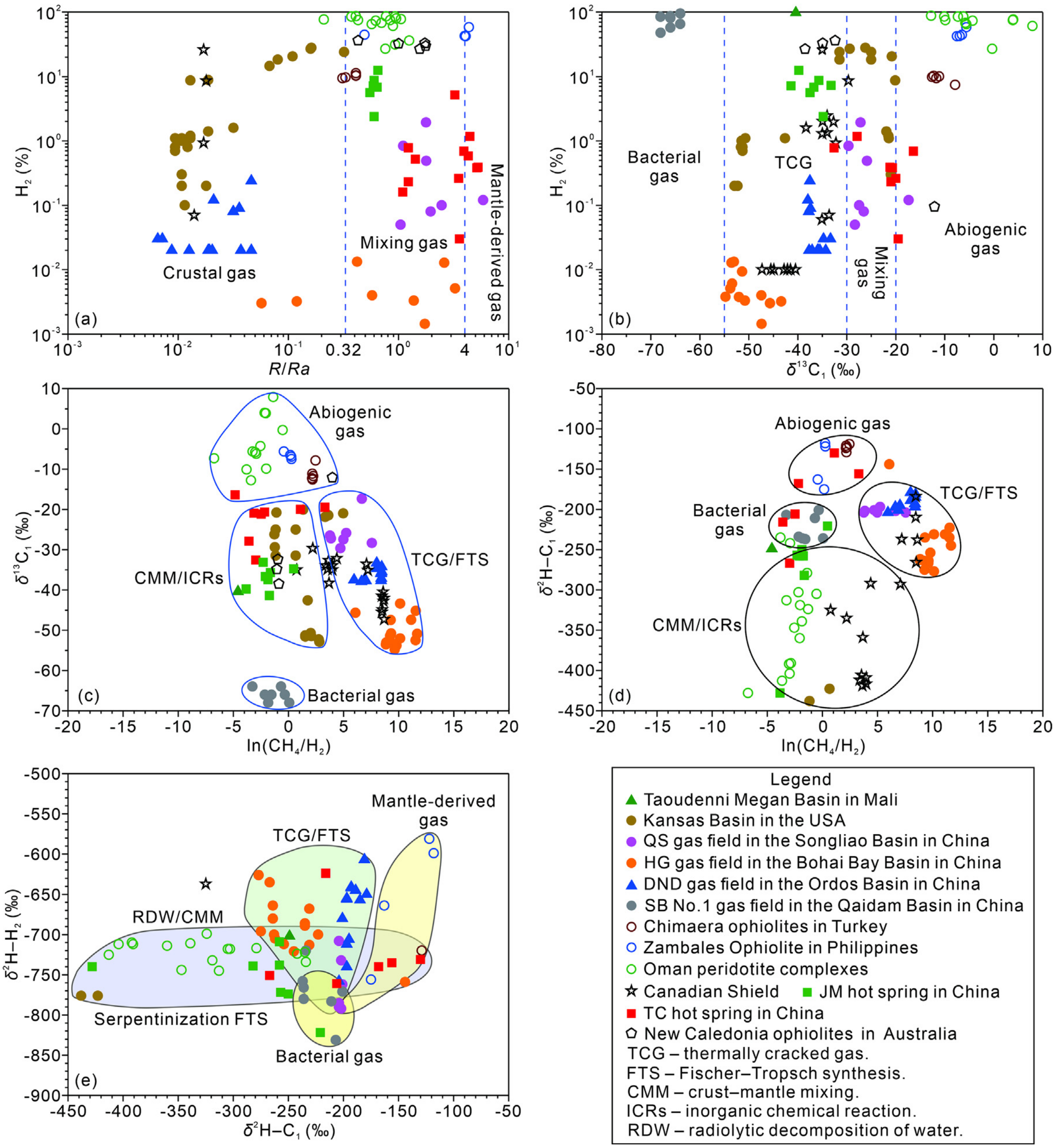

Fig. 1. Diagrams of (a) H_2 (%) *versus* R/Ra, (b) H_2 (%) *versus* $\delta^{13}C_1$ (‰), (c) $\delta^{13}C_1$ (‰) *versus* $\ln(CH_4/H_2)$, (d) $\delta^2H–C_1$ *versus* $\ln(CH_4/H_2)$, and (e) $\delta^2H–H_2$ *versus* $\delta^2H–C_1$ of natural gas in various geological settings.

genic gas using only carbon and hydrogen isotope compositions and gas compositions. Mantle-derived abiogenic gas generally has $\delta^{13}C_1$ values above −20‰ and can be more easily identified if R/Ra data are available. Gases in the Zambales Ophiolite, Oman peridotite complexes, and the Chimaera ophiolites in Turkey have $\delta^{13}C_1$ values above −20‰ and are typically abiogenic, with H_2 concentrations ranging from 7.46% to 87.3% (Fig. 1b). However, gases in the Oman peridotite complexes and Chimaera ophiolites have R/Ra < 4.0, suggesting that the abiogenic CH_4 and H_2 are not derived solely from a mantle source.

Abiogenic H_2 can also be formed by serpentinization. Gas from the Kansas Basin, New Caledonia ophiolites, TC hot springs, and part of the QS gas field have $\delta^{13}C_1$ values ranging from −30‰ to −20‰ (Fig. 1b), which likely represent a mixture of thermogenic and abiogenic CH_4. This suggests that the H_2 in these regions could also be a mixture of biogenic and abiogenic, with concentrations ranging from 0.03% to 36.07%. The $\delta^{13}C_1$ values of gases in the HG and DND gas fields, the Taoudenni Megan Basin in Mali, the Canadian Shield, and the JM hot springs range from −55‰ to −30‰ (Fig. 1b), suggesting that the hydrogen gas in these regions could be derived via thermal cracking of organic matter. However, the alkane gases of the Canadian Shield are abiogenic [12], so the H_2 may also be abiogenic, with H_2 concentrations of 0.01%–26%.

The $\ln(CH_4/H_2)$ values of natural gas derived via thermal cracking and Fischer-Tropsch synthesis (FTS) decrease with increasing $\delta^{13}C_1$ values (Fig. 1c). In the SB No.1 gas field, headspace gas samples collected from two wells had high concentrations of H_2 (Fig. 1b), in contrast to the CH_4-dominated gas collected from the wellheads. The minimal variations in the H_2 concentrations (Fig. 1b) and $\ln(CH_4/H_2)$ values (Fig. 1c) of natural gas indicate that

H_2 may be preferentially derived from organic matter owing to certain types of microorganisms. In the HG, DND, and QS gas fields, a negative correlation is observed between $\ln(CH_4/H_2)$ and $\delta^{13}C_1$ values (Fig. 1c). As the thermal maturity increases from the HG to QS gas fields, $\ln(CH_4/H_2)$ values decrease from 11.53 to 3.86, indicating a relative increase in H_2 concentrations. In the QS field, despite the presence of mantle- and FTS-derived CH_4, thermal cracking is dominant [13]. A weak positive correlation is observed between the $\ln(CH_4/H_2)$ and $\delta^{13}C_1$ values of gases from the Zambales Ophiolite, Oman peridotite complexes, Chimaera ophiolites, and New Caledonia ophiolites (Fig. 1c), with $\ln(CH_4/H_2)$ values of −6.75 to 4.0 and $\delta^{13}C_1$ values above −20‰, indicating that the CH_4 and H_2 are both abiogenic. Hydrogen in these areas is formed by inorganic chemical reactions, resulting in a wide range of $\ln(CH_4/H_2)$ values. A negative correlation is observed between the $\ln(CH_4/H_2)$ and $\delta^{13}C_1$ values of gases from the New Caledonia ophiolites and the TC and JM hot springs (Fig. 1c), with $\ln(CH_4/H_2)$ values of −3.83 to 4.96 and $\delta^{13}C_1$ values of −55‰ to −20‰, indicating a mixture of crust- and mantle-derived gas.

Gases in the Kansas Basin have similar $\ln(CH_4/H_2)$ and $\delta^{13}C_1$ values to gases from the TC and JM hot springs; however, the low R/Ra values are consistent with a crustal origin with a limited mantle contribution (Fig. 1a), which suggests that the gases were mainly derived from inorganic chemical reactions (Fig. 1c). In addition, the presence of abiogenic CH_4 with $\ln(CH_4/H_2) < 4.0$ in the Zambales Ophiolite, Oman peridotite complexes, Chimaera ophiolites, and New Caledonia ophiolites further supports an abiogenic origin for both CH_4 and H_2 in these locations.

Hydrogen is converted to CH_4 through FTS, and $\delta^{13}C_1$ values become increasingly negative with ongoing conversion. Gas in the Canadian Shield is crustal in origin and rich in He (1.51%–19.1%), and it was most likely produced by radioactive α-decay of U- and Th-bearing minerals; the variations in H_2 concentration suggest consumption through FTS, leading to the formation of abiogenic CH_4 [14].

Gases in the HG, DND, and QS gas fields have $\ln(CH_4/H_2)$ values ranging from 3.76 to 11.68 and δ^2H–C_1 values of −277‰ to −179‰ (Fig. 1d). As the source rocks in these gas fields were deposited in fresh water, the negative correlation between $\ln(CH_4/H_2)$ and δ^2H–C_1 values indicates that H_2 and CH_4 concentrations and δ^2H–C_1 values were controlled by thermal maturity. With the gradual increase in thermal maturity through the HG, DND, and QS gas fields, $\ln(CH_4/H_2)$ values gradually decrease while δ^2H–C_1 values increase, indicating that the formation of CH_4 and H_2 was mainly controlled by their generation processes. The narrower range of δ^2H–C_1 values in the QS gas field indicates a higher proportion of mantle-derived fluids, emphasizing the impact of mantle-derived fluids on hydrogen isotopic compositions. The $\ln(CH_4/H_2)$ and δ^2H–C_1 values of gases from the Zambales Ophiolite, Chimaera ophiolites, and TC hot springs are positively correlated (Fig. 1d). Mantle-derived abiogenic gas from the Zambales Ophiolite has $\ln(CH_4/H_2)$ values between −0.74 and 0.27 and δ^2H–C_1 values from −175‰ to −118‰. Given the narrow ranges of $\delta^{13}C_1$ and δ^2H–C_1 values for the mantle-derived abiogenic gases of the Zambales Ophiolite, it is inferred that the abiogenic gases of the Oman peridotite complexes were also formed mainly by inorganic chemical reactions. During this process, H_2 is progressively converted to CH_4 via FTS, leading to decreasing H_2 and increasing CH_4 concentrations and δ^2H–C_1 values. The Chimaera ophiolites and the TC hot springs host a mixture of mantle- and FTS-derived gases. The $\ln(CH_4/H_2)$ and δ^2H–C_1 values of the gases from the Taoudenni Megan Basin, Kansas Basin, New Caledonia ophiolites, TC hot springs, and JM hot springs are similar to those of the Oman peridotite complexes, which have $\ln(CH_4/H_2)$ and δ^2H–C_1 values of −4.58 to 0.47 and −428‰ to −206‰, respectively (Fig. 1d). Gases in the Kansas Basin, New Caledonia ophiolites, TC hot springs, and JM hot springs, which formed through inorganic chemical reactions such as FTS, have R/Ra values between 0.32 and 4.0. Consequently, initial CH_4 is isotopically enriched in ^1H but becomes gradually more enriched in ^2H with ongoing FTS. In contrast, the gas in the Canadian Shield with $R/Ra < 0.32$ is crust-derived, and the H_2 was probably formed through radiolytic decomposition of water. The $\ln(CH_4/H_2)$ values of gas from the Canadian Shield exhibit a positive correlation with δ^2H–C_1 values, with values ranging from 0.74 to 8.63 and −417‰ to −184‰, respectively.

The relationship between δ^2H–C_1 and δ^2H–H_2 values in the SB No.1 gas field reveals a narrow range of hydrogen isotope values for CH_4 and H_2 in bacterial gas (Fig. 1e). The δ^2H–C_1 and δ^2H–H_2 values range from −237‰ to −201‰ and −831‰ to −758‰, respectively. Bacterial H_2 typically has relatively stable δ^2H–H_2 values ranging from −800‰ to −700‰. In the HG, DND, and QS gas fields, a relatively narrow range of δ^2H–C_1 values from −277‰ to −179‰ is observed, whereas δ^2H–H_2 values range widely from −792‰ to −607‰ (Fig. 1e). A negative correlation exists between δ^2H–C_1 and δ^2H–H_2 values for the HG gas field, whereas a positive correlation is observed for the QS and DND gas fields.

The $\delta^{13}C_1$ values of natural gas increase with the thermal maturity of the source rocks [15], and $\delta^{13}C_1$ values can be used to indicate thermal maturity. The $\delta^{13}C_1$ values of natural gas from the QS gas field are significantly higher than those from the DND gas field (Fig. 1b, Table S1 online), suggesting a higher level of thermal maturity for natural gas in the QS gas field compared with the DND gas field, whereas the H_2 is isotopically more enriched in ^1H than that in the DND gas field (Fig. 1e). This suggests that the conversion of H_2 to CH_4 during FTS in the QS gas field is more intensive than that in DND gas field. A positive correlation is observed between δ^2H–C_1 and δ^2H–H_2 values for gas from the Zambales Ophiolite, with values ranging from −175‰ to −118‰ and −756‰ to −581‰, respectively (Fig. 1e), indicating an increase in δ^2H–H_2 values with increasing δ^2H–C_1 values for mantle-derived CH_4 and H_2. Hydrogen formed by serpentinization in the Oman peridotite complexes and Chimaera ophiolites has a relatively narrow range of δ^2H–H_2 values (from −725‰ to −699‰), whereas CH_4 produced by FTS has a wide range of δ^2H–C_1 values (from −413‰ to −129‰). This suggests that H_2 formed by serpentinization has a relatively narrow distribution of δ^2H–H_2 values, whereas CH_4 produced by FTS has a wide range of δ^2H–C_1 values. Gases of the Taoudenni Megan Basin, Kansas Basin, New Caledonia ophiolites, TC hot springs, and JM hot springs have similar origins to those of the Oman peridotite complexes and Chimaera ophiolites, which have a wide range of δ^2H–H_2 values for H_2 produced by inorganic chemical reactions. Consequently, methane produced by FTS is more isotopically enriched in ^1H than methane produced by thermal cracking of organic matter (Fig. 1e). Although there are insufficient δ^2H–H_2 data to evaluate the origin of H_2 in the Canadian Shield, the $^3He/^4He$ ratios ($R/Ra < 0.32$), $\delta^{13}C_1$ values, δ^2H–C_1 values, and $\ln(CH_4/H_2)$ indicate that the H_2 is a typical crust-derived abiogenic gas. The only available δ^2H–C_1 value indicates that the H_2 was formed by radiolytic decomposition of water, as its δ^2H–H_2 value (−637‰) is markedly higher than that of H_2 formed by serpentinization in the Chimaera ophiolites.

Table 1 summarizes the formation and co-evolution of H_2 and CH_4 under different geological conditions based on gas composition, $^3He/^4He$, and δ^2H–C_1 and $\delta^{13}C_1$ values. It is important to note that the threshold of constrained parameters for H_2 is not constant due to the mixing of gases from different sources. Sources of H_2 can be identified by considering geological backgrounds and formation processes in combination with relevant compositional and isotopic data. The present summaries are empirical, and the boundary values of the identification indexes may vary as the amount of data increases; however, the general rules and trends are believed to be consistent.

Table 1
Thresholds of different indicators for H_2 and associated gases in geological deposits.

H_2 source	H_2 (%) (Min.–Max./Avg.)	$\ln(CH_4/H_2)$	δ^2H–H_2 (‰, VSMOW)	δ^2H–C_1 (‰, VSMOW)	$\delta^{13}C_1$ (‰, VPDB)	*R*/*Ra*
Mantle	0.12–58.50/18.26	−0.5 to 0.5	≤−700	>−180	>−20	≥4.0
Thermal cracking	0.02–0.24/0.056	>5	−750 to − 600	−280 to −180 (freshwater) or >−160 (saltwater)	−55 to −30	<0.32
Microbial degradation	47.70–95.40/74.54	−5 to 0	−850 to − 750	−240 to −200 (freshwater)	<−55	<0.32
Serpentinization	0.0007–99.00 /28.16	<5	−780 to − 700	−450 to −200	>−55	0.32 to 4.0
Radiolytic decomposition of water	0.01–26.00/1.76	>0	≤−700	−450 to −180	−50 to −30	<0.02

Conflict of interest

The authors declare that they have no conflict of interest.

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Author contributions

Quanyou Liu and Zhijun Jin conceptualized the study; Quanyou Liu and Xiaoqi Wu performed the methodology; Quanyou Liu, Xiaoqi Wu, Xiaowei Huang, Qingqiang Meng, Dongya Zhu, and Jiayi Liu performed the investigation; Qingqiang Meng, Quanyou Liu, Pengpeng Li, and Kaiqiang Zhang performed the visualization; Zhijun Jin, Zheng Zhou, and Kaiqiang Zhang were responsible for supervision; Quanyou Liu, Zhijun Jin, and Xiaoqi Wu wrote the original draft; Quanyou Liu, Zhijun Jin, Zheng Zhou, and Kaiqiang Zhang carried out the review and editing.

Appendix A. Supplementary materials

Supplementary materials to this short communication can be found online at https://doi.org/10.1016/j.scib.2024.07.004.

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