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Global distribution, genesis, and enrichment characteristics of high-concentration natural hydrogen

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Under the global decarbonization initiative, natural hydrogen has garnered significant attention as a green, high-calorific-value, zero-carbon emission clean energy source in marine and continental contexts. Previous research on natural hydrogen systems remains nascent. This study systematically synthesized the distribution characteristics, genetic mechanisms, and enrichment processes of high-concentration natural hydrogen globally, yielding four key insights: (1) Natural hydrogen originates from complex processes broadly categorized as organic and inorganic, predominantly including deep-Earth degassing, waterrock reactions, and radiolysis of water. (2) Hydrogen-rich accumulations exhibit widespread distribution, primarily occurring in rift systems, plate collision zones, subduction zones and their peripheries, as well as Precambrian iron-rich formations. (3) Natural hydrogen reservoirs form through dynamic accumulation processes requiring: high-quality source supply, favorable migration pathways and preservation conditions, and sustained influx exceeding leakage rates. (4) Favorable exploration targets should avoid microbial active zones and deep hydrogenation/hydrocarbon generation regions; current evidence suggests promising reservoirs occur in ultra-deep settings, peripheral areas of convergent zones, and shallow strata proximal to deep-seated faults. Exploration of natural hydrogen should prioritize evaluating the hydrogen anomalies to identify potential reservoirs and advance systematic comprehension of this emerging energy play.

KEYWORDS

natural hydrogen, global distribution, geological conditions, genesis, enrichment characteristics

1 Introduction

In the context of green development and the global "dual carbon" goals (carbon peak and carbon neutrality), the world is undergoing its third energy transition—moving from fossil fuels to low-carbon energy sources. Hydrogen, with its renewability and potential for net-zero emissions, is rapidly gaining prominence in the clean energy sector. Due to its significantly higher calorific value compared to conventional fuels like oil and natural gas, hydrogen energy stands as a critical pathway for achieving decarbonization (Zou et al., 2014; Dou et al., 2024). Currently, hydrogen is primarily produced artificially through processes such as coal gasification, steam methane reforming (SMR), industrial by-product purification, and water electrolysis. Hydrogen generated via these methods is classified as a "secondary energy" source, with types including: Grey Hydrogen (produced from fossil fuels), Blue Hydrogen (produced through steam reforming coupled with carbon capture and storage), and Green Hydrogen (produced via renewable-powered water electrolysis) (Meng et al., 2024; Zhang et al., 2024). However, these conventional production methods rely on fossil resources, generate significant CO2 emissions, incur high costs (Chen et al., 2022), and face persistent technical challenges in large-scale implementation (Cao et al., 2021). In contrast, Natural Hydrogen, also referred to as "white hydrogen" or "gold hydrogen," is hydrogen generated geologically within Earth's natural systems, including the atmosphere, crust, and mantle (Dou et al., 2024; Jin, 2023; Liu et al., 2025). This purely abiogenic hydrogen, detectable at or near the Earth's surface, presents a vast, untapped energy resource.

Hydrogen (H₂) is the simplest atomic structure, consisting of a nucleus with a single proton. As the lightest and most abundant element in the solar system, hydrogen accounts for approximately 90% of all atoms by number (Grochala, 2015). Scientific evidence supports the existence of a vast deep-Earth hydrogen reservoir. During Earth's early formation, the primordial atmosphere was predominantly composed of hydrogen and helium, with trace amounts of methane and carbon dioxide (Young et al., 2023). Hydrogen, a crucial component of this primordial mix, played an essential role in the origin of life and in biological processes, as well as the formation of abiotic hydrocarbons (Young et al., 2023; McCollom et al., 2022; Milkov, 2022; Wang et al., 2025). Over time, through planetary accretion, primordial hydrogen became trapped within the Earth's interior. Under high pressures and temperatures, it stabilized in solutions and compounds (Wang et al., 2025; Olson and Sharp, 2018). As Earth evolved and its surface cooled, portions of this deep-seated hydrogen were eventually released into the atmosphere (Martin, 2012; Jiang and Liu, 2025).

The existence of natural hydrogen has been documented for centuries. Approximately 200 years ago, a naturally burning gas seep in the Philippines was found to contain 41.4–44.5% hydrogen (Jin, 2023). However, constrained by traditional geological paradigms and the inherent properties of hydrogen—its low molecular weight, high reactivity, and strong reducing capacity—

most scholars dismissed the possibility of large-scale, economically viable subsurface hydrogen accumulations (Hand, 2023; Meng, 2022; Wei et al., 2024). As a result, systematic research on natural hydrogen remained limited for many decades. Over the past decade, hydrogen has gained increasing recognition as a critical clean energy carrier. This was further catalyzed by a series of dedicated international conferences on natural hydrogen (Dou et al., 2024), and the "quest for natural hydrogen sources" was acknowledged as the second breakthrough of 2023 by Science magazine (Couzin-Frankel, 2023). This recognition spurred a surge in research, with over 40 energy companies globally initiating natural hydrogen exploration programs by late 2023. Significant breakthroughs have been achieved in countries such as the United States, Australia, Mali, Russia, and Brazil. Although China's natural hydrogen research started relatively late, it has made significant progress in this emerging energy field.

Global natural hydrogen resources are estimated to be vast. The U.S. Geological Survey (USGS) suggests potential resources on the order of 1×10^{12} tons (Meng et al., 2024). As momentum for natural hydrogen research continues to grow, numerous countries have reported promising exploration outcomes. Dedicated resource assessment programs and exploration initiatives are currently underway in the United States, Canada, Australia, and various European Union countries. Canada's Hydroma Inc. commissioned the world's first commercial natural hydrogen power plant in Mali in 2011, which also supplies hydrogen for fuel cells to provide local electricity (Prinzhofer et al., 2018). Additionally, Natural Hydrogen Energy LLC (USA) and HyTerra Ltd (Australia) successfully drilled and tested hydrogen flow from the HoartyNE3 well—the world's first dedicated natural hydrogen exploration well—in Nebraska, USA (2023) (Dou et al., 2024). NH²³ LLC (founded 2013 in USA) conducted natural hydrogen surveys across multiple countries, drilling the first U.S. natural hydrogen well in a Kansas cornfield in late 2019 (Wei et al., 2024). Gold Hydrogen Ltd in Australia secured exploration licenses (2021) for the Yorke Peninsula and Kangaroo Island (South Australia). Their dedicated hydrogen exploration well Ramsay 1 (the world's second) encountered 73.3% hydrogen by volume, alongside 3.6% helium (Ogilvie, 2023).

Beyond these developments, surface hydrogen seeps exhibiting "fairy circle" features have been documented in North Carolina, USA (Zgonnik et al., 2015), São Francisco Basin, Brazil (Prinzhofer et al., 2019), Perth Basin, Western Australia (Prinzhofer et al., 2019) and Central Russia (Larin et al., 2015). In Russia's Podovoye region, thousands of elliptical to semi-circular depressions (ranging from hundreds to thousands of meters in diameter) demonstrate hydrogen fluxes of (2.1-2.7) × 10⁴ m³/day (Larin et al., 2015). Similar seeps in the Northern Perth Basin show elevated soil hydrogen concentrations along feature margins (Emanuelle et al., 2021). 45–8 Energy in France identified high-potential natural hydrogen prospects in 2020, planning Europe's first test production by 2023 (Zgonnik, 2020). In May 2023, a giant natural hydrogen accumulation was confirmed in the Lorraine Mining Basin with estimated reserves of 46 million tons.

Concentrations increase with depth (Boschee, 2023), reaching 15% at 1,093m and 20% at 1,250m - representing Europe's largest "white hydrogen" discovery to date.

As a latecomer to natural hydrogen research, China's efforts remain nascent. While not yet systematically studied as a standalone energy resource, sporadic hydrogen occurrences have been reported during other resource explorations (Wei et al., 2024). Based on comprehensive field reconnaissance, preliminary investigations have identified multiple promising natural hydrogen surface manifestations across China. Hydrogen seeps with concentrations ranging from 0.32% to 5.15% have been detected in thermal springs within the Tengchong volcanicgeothermal system, Yunnan Province (Shangguan and Huo, 2001); Hydrogen seeps with concentrations ranging from 2.4% to 12.5% by volume have been documented in the fault-controlled hydrothermal system of Jimo, within the Sulu Orogenic Belt of coastal East China (Hao and Pang, 2020); Trace hydrogen concentrations have been detected within coal-bearing strata and associated wellbores in the Qinshui Basin, Shanxi Province (Zhou et al., 2006); Drill cuttings from Well 2 in the Sanhu Area, Qaidam Basin, yielded measured hydrogen concentrations up to 99% by volume, interpreted as originating from biodegradation processes within shallow biogenic gas reservoirs (Shuai et al., 2010); Minor natural hydrogen occurrences have been detected peripheral to fault zones in the Jiyang Depression, Bohai Bay Basin, with geochemical signatures suggesting a deep mantle-derived degassing origin (Meng et al., 2024); The Songliao Basin exhibits widespread natural hydrogen occurrences. Trace hydrogen concentrations have been documented within conventional gas accumulations in the Fuyu, Chaoyanggou, and Putaohua fields (Guo et al., 2007). Notably, elevated but highly variable hydrogen contents (reaching economically significant thresholds) occur in individual wells penetrating volcanic reservoirs of the Xujiaweizi area (Dai et al., 2009). Most significantly, the SK-2 scientific borehole and surrounding region have revealed an extensive hydrogen-bearing zone with concentrations up to 26.9%, demonstrating substantial resource potential (Han et al., 2022).

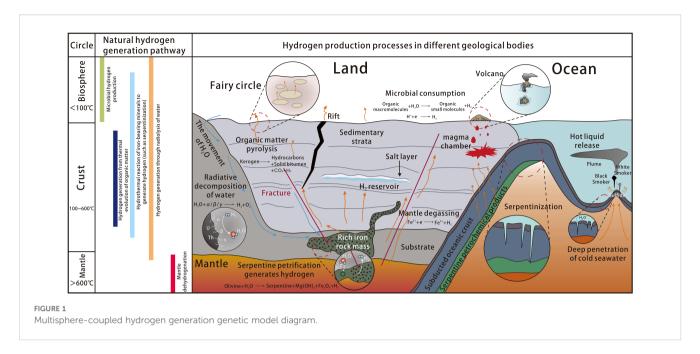
Owing to hydrogen's strong reducing capacity and high diffusivity, the widespread existence of commercially viable natural hydrogen accumulations remains uncertain-despite existing commercial hydrogen wells and demonstrated geological hydrogen-generation potential (Wang et al., 2025). Natural hydrogen exhibits diverse origins and highly variable distribution patterns with significant disparities in accumulation scales (Chen et al., 2015; Wang et al., 2021). Advancements in hydrocarbon generation theory and exploration technologies have enabled the integration of surface satellite imaging, geochemical gas analysis and soil microseepage detection, geophysical methods (gravity, magnetic, electrical, and seismic surveys) and downhole logging (primarily neutron and acoustic tools) for natural hydrogen exploration (Wei et al., 2024). However, extreme spatial and temporal heterogeneity in hydrogen concentrations (Satake et al., 1985), evidenced by orders-of-magnitude fluctuations at single locations, poses fundamental challenges to resource assessment and development.

The increasing global energy demand and environmental imperatives have heightened the focus on subsurface hydrogen systems. Expanding research has challenged traditional petroleum paradigms, confirming Earth's potential for large-scale hydrogen accumulation. Although dedicated exploration wells have been drilled in several regions, significant barriers remain, such as an incomplete understanding of hydrogen distribution patterns, the high complexity of exploration and development, and the underdeveloped state of extraction technologies. These challenges continue to keep natural hydrogen research in its early stages.

China's theoretical framework for natural hydrogen is significantly underdeveloped compared to the well-established knowledge of petroleum systems. While considerable research has been devoted to understanding the genetic mechanisms of natural hydrogen, a comprehensive synthesis of key aspects such as the identification and characterization of premium hydrogen source rocks, migration pathways through geological substrates, critical accumulation dynamics, and long-term preservation conditions remains lacking. Additionally, differing interpretations of tectonic settings complicate the development of universally applicable accumulation models across diverse structural contexts. To address these gaps, this paper builds upon previous research and presents an extensive review of both domestic and international literature on natural hydrogen. It delves into the genetic types and geological significance of natural hydrogen, while also examining the favorable geological conditions for the formation of highcontent natural hydrogen reservoirs. Furthermore, it systematically summarizes the current status of exploration and development, including the basic geological characteristics and formation-distribution patterns of natural hydrogen. Ultimately, the goal is to offer valuable insights to guide the exploration and development of natural hydrogen reservoirs in China.

2 Genetic types of natural hydrogen

The estimated hydrogen reserves on Earth are vast, highlighting the potential of this resource. Understanding the genetic mechanisms and reservoir-forming conditions of natural hydrogen is essential for advancing geological research and resource exploration. Given that hydrogen has been detected across diverse geological environments, it is likely the product of multiple genetic processes, with its sources and types exhibiting considerable diversity and complexity. These varied origins result in significant differences in the occurrence states of natural hydrogen (Zgonnik, 2020). In ophiolites, natural hydrogen often exists in a "free state," a key condition for enriching high-concentration hydrogen in shallow formations. Within rocks, hydrogen is commonly found in an "adsorbed state," with certain minerals exhibiting a notable capacity for adsorption. The adsorption potential is influenced by the mineral's properties and pore structures. In rift systems and along deep, major faults, hydrogen is frequently observed in a "dissolved state," where it exists in groundwater in dissolved form. Regarding the sources of natural hydrogen, some researchers classify it into primordial and



secondary types. Primordial hydrogen primarily refers to hydrogen released directly from the mantle or core to the Earth's surface, while secondary hydrogen is generated through various geological reactions occurring in the mantle or crust. The genesis of natural hydrogen can also be further categorized based on its organic and inorganic origins (Meng et al., 2024; Han et al., 2021; Simon et al., 2019; Suzuki et al., 2017; Rumyantsev, 2016). Figure 1 provides a comprehensive illustration of the multiple origins and occurrence contexts of hydrogen: Organically derived hydrogen includes hydrogen produced through the decomposition of organic matter and microbial processes. During organic matter decomposition, hydrogen radicals are generated, which then combine to form molecular hydrogen. Hydrogen-producing microorganisms further transform hydrocarbon source rocks and coals with high organic content, leading to the formation of hydrogen at relatively high concentrations. In contrast, inorganically derived hydrogen originates from processes such as water-rock reactions, degassing of mantle-derived fluids, and radiolytic decomposition of water. Among these, water-rock reactions include processes like serpentinization, interactions between water and fresh rock surfaces, and reactions involving hydroxyl groups in minerals (Figure 1).

2.1 Subsection

2.1.1 Subsubsection

The Materials and Methods should be described with sufficient details to allow others to replicate and build on the published results. Please note that the publication of your manuscript implicates that you must make all materials, data, computer code, traditional geological theories hold that during Earth's formation, hydrogen almost completely escaped and there were no conditions for it to be preserved and accumulate into reservoirs. However, previous high-pressure experiments have confirmed that hydrogen

did not escape into the atmosphere (Rumyantsev, 2016); instead, it was trapped and accumulated in the core during the early stages of Earth's formation, and gradually accumulated in the deep Earth as the planet continued to evolve (Walshe et al., 2005; Gilat and Vol, 2012). Compared to the shallow crust, mantle fluids are overall reducing, making it easier for hydrogen to exist in molecular form (Smith et al., 2016; Yang et al., 2016; Frost and McCammon, 2008; Wadhwa, 2008). A large amount of deep fluids exist inside the Earth, with C, H, O, N, and S as the main constituent elements, along with some trace components such as alkaline elements. These fluids form the material basis for Earth's degassing (Yang and Jin, 2001; Tao et al., 2005). Among them, hydrogen is an important component of the mantle, and its concentration increases with depth (Coveney et al., 1987). Hydrocarbons are the main substances in the upper mantle, while hydrogen and hydrogen compounds dominate in the middle and lower mantles down to the core (Huang et al., 1995; Yu et al., 2023). Studies suggest that the hydrogen content in the mantle and core is approximately 80 times that in the oceans, highlighting the extreme importance of hydrogen in these deep Earth layers.

Deep Earth degassing is influenced by multiple geological processes, including tectonic movements and magmatic activities. Volatiles in deep fluids, along with mantle-derived and crust-derived thermogenic gases, serve as important carriers for the migration of deep hydrogen to the surface (Tao et al., 2005; Hu, 2016; Liu et al., 2019). In particular, gas components from the deep mantle, characterized by high temperatures, strong mobility, and high volatility, are highly prone to degassing (Yu et al., 2023). Deep degassing is often accompanied by large-scale tectonic activities, such as volcanic eruptions, seismic activities, and faulting (Dou et al., 2024). Therefore, areas with active deep fluids, such as regions with well-developed igneous rocks, are often favorable for hydrogen enrichment (Guélard et al., 2017). Currently, there are two main genetic types of deep Earth degassing. Previous studies have

classified deep Earth degassing into "thermal degassing" and "cold degassing" (Guélard et al., 2017; Feng et al., 2005). "Thermal degassing" mainly produces oxidizing gases and is closely related to volcanic eruption activities; in contrast, "cold degassing" primarily generates reducing gases, which seep out from surface depressions, depressions at the bottom of water bodies, or potholes through fractures and faults.

Given that hydrogen is highly susceptible to oxidation, the redox state of the tectonic environment plays a decisive role in determining whether deep hydrogen can migrate upward along faults to form reservoirs. In this context, the strongly reducing environment and low oxygen fugacity of the upper mantle provide favorable conditions for the migration of volatile substances such as carbon and hydrogen toward the surface. When mantle-derived gases migrate with deep fluids along major deep faults, mid-ocean ridges, or through volcanic and seismic activities (Yu et al., 2023), hydrogen components undergo degassing and are discharged upward to the surface (Shangguan et al., 2000; Li et al., 2007). Theoretically, the amount of hydrogen generated by deep fluid degassing is quite substantial. Relevant studies indicate that mantlederived igneous-magmatic activities in the Dongying-Huimin Depression of China could input approximately 44.1×109 m3 of hydrogen. Similarly, significant amounts of hydrogen can be emitted in mid-ocean ridge and ophiolite environments: high concentrations of hydrogen detected in the Heins well in Kansas, USA, are inferred to originate from deep fluid degassing based on isotopic comparisons of hydrogen and nitrogen (Prinzhofer et al., 2018; Goebel et al., 1984). Measurements of hydrogen concentrations in surface soils have revealed abrupt changes in hydrogen content within a short period before and after seismic activities, with variations reaching up to 106 times. Hydrogen manifestations near the San Andreas Fault in California, USA, are thought to be related to destructive seismic tectonic activities at continental margins (Motoaki et al., 1986).

Meanwhile, during the process of deep Earth degassing and upward migration of hydrogen, a series of hydrogen leakage phenomena inevitably occur. A number of hydrogen leakage phenomena observed on continental surfaces are primarily associated with circular depressions (Zgonnik et al.,2015; Larin et al., 2015; Myagkiy et al., 2020). Sustained hydrogen leakage occurs within these circular depressions, with maximum hydrogen concentrations detectable inside and at the boundaries of the depressions, while almost no hydrogen is found in soils outside the depressions. Such circular or elliptical depressions are termed "fairy circles" (Larin et al., 2015), and the hydrogen concentration and seepage within them are closely related to the geometric shape of the "fairy circles" (Myagkiy et al., 2020). "Fairy circles" with hydrogen leakage have been detected in various countries and regions worldwide, including the USA, Brazil, Australia, and Russia (Zgonnik et al., 2015; Prinzhofer et al., 2019; Emanuelle et al., 2021; Larin et al., 2015). Therefore, such anomalies in hydrogen concentration in near-surface soils indicate the presence of nearby hydrogen leakage and also suggest the existence of large-scale underground natural hydrogen reservoirs.

2.1.2 Water-rock interaction

The term "water-rock interaction" has a broad scope. In a general sense, it refers to the material exchange between fluids and rocks that occurs during all geological processes (Ding, 1989), spanning from the mantle to the Earth's surface. The water-rock interaction discussed in this paper specifically refers to a series of reactions related to hydrogen generation, primarily the physicochemical reactions between deep fluids and rock minerals. Among these, serpentinization is the most common and significant type of water-rock interaction. Serpentinization is a prevalent form of water-rock interaction, and depending on the composition and components of its reactants, it produces serpentine along with other distinct reaction products (Han et al., 2021; Ding et al., 2016). A large amount of hydrogen is generated during serpentinization; therefore, when referring to hydrogen generation through waterrock interaction, it generally denotes hydrogen production via serpentinization.

The essence of hydrogen generation through serpentinization lies in the reaction between Fe²⁺-rich minerals (olivine) in maficultramafic rocks and water to produce hydrogen. In nature, olivine commonly exists as a Mg-Fe binary solid solution [(Mg, Fe)₂SiO₄]. The reaction between the fayalite end-member (Fe₂SiO₄) and water is as follows:

$$3\text{Fe}_2\text{SiO}_4 + 2\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 2\text{SiO}_2 + 2\text{H}_2 \uparrow$$
 (1)

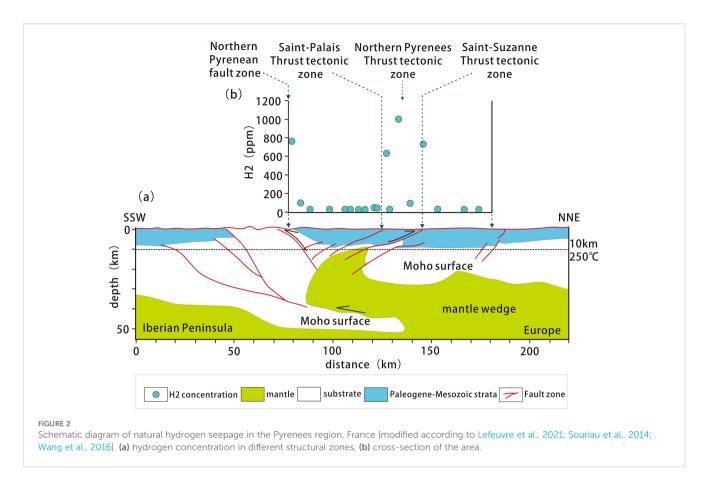
The reaction between the forsterite end-member (Mg_2SiO_4) and water occurs in two forms. The first is the direct reaction of forsterite with water to form serpentine and magnesium hydroxide:

$$2Mg_2SiO_4 + 3H_2O \rightarrow Mg_3Si_2O(OH)_4 + 2Mg^2 + 2OH^-$$
 (2)

The second is the reaction of forsterite with excess SiO_2 generated in Equation (1) to form serpentine $[Mg_3Si_2O_5(OH)_4]$:

$$3Mg_2SiO_4 + 4H_2O + SiO_2 \rightarrow Mg_3Si_2O_5(OH)_4$$
 (3)

Previous studies have suggested that under strongly reducing and closed system conditions, the products of olivine serpentinization mainly include serpentine (Mg₃Si₂O₅(OH)₄), brucite (Mg(OH)₂), magnetite (Fe₃O₄), methane, and hydrogen (Klein et al., 2019). Fe2+ in fayalite undergoes redox reactions, forming magnetite and SiO2-rich fluids, thereby generating hydrogen, as described in Equation (1). Meanwhile, when the reaction temperature is below approximately 400°C, forsterite reacts with water to form serpentine. When the temperature drops below 320-360°C, forsterite reacts with formation water, and brucite in the products becomes part of the equilibrium mineral assemblage, as shown in Equation (2). During serpentinization, the SiO₂-rich fluid generated in Equation (1) participates in the reaction, further promoting rock serpentinization and leading to the absence of brucite, as depicted in Equation (3) (Han et al., 2021; Zhang et al., 2016). Reactions (2) and (3) capture the overall serpentinization process of forsterite, which consumes water, creates alkaline fluids, and shifts the physicochemical regime. The critical hydrogen production, however, is driven by the oxidation of



Fe²⁺ in iron-bearing minerals [Reaction (1)]. This reaction subsequently promotes Reaction (3) by generating a silica-rich fluid and a reducing environment. Thus, serpentinization is an integrated sequence where Reaction (1) directly produces H_2 , supported by the mineralogical and fluid changes from Reactions (2) and (3) that enable continuous generation (McCollom and Bach, 2009).

Summarizing the above reaction processes, the essence of hydrogen generation through serpentinization is the reduction of Fe^{2+} to Fe^{3+} , which in turn reduces H_2O to H_2 . The fundamental hydrogen-generating reaction is as follows:

$$2(Fe^{2+}O) + H_2O \rightarrow (Fe_2^{3+}O_3) + H_2 \uparrow$$
 (4)

Take the Pyrenees as an example, natural hydrogen shows have been discovered in both France and Spain on either side of this suture zone (Figure 2). With the subduction and collision of the Iberian and Eurasian plates, mantle materials upwelled, forming ferromagnesian-rich peridotites in shallow layers, which then underwent serpentinization (McCollom and Bach, 2009). The generated hydrogen migrated along fault zones into sedimentary basins.

The amount of natural hydrogen generated is positively correlated with the degree of olivine serpentinization. Reaction temperature and the addition of catalysts are the main factors affecting the rate of hydrogen generation through serpentinization; the introduction of Ni²⁺ and other ions can significantly accelerate hydrogen production during serpentinization (Meng et al., 2024; Yu

et al., 2023). Many scholars argue that serpentinization is not limited to high-temperature conditions (T > 300°C); Fe²⁺ can also react with water to undergo serpentinization in relatively lowtemperature environments (Meng et al., 2024; Neal and Stanger, 1983; Deville and Prinzhofer, 2016). For example, hydrogen produced in ophiolites in Oman coexists with alkaline groundwater rich in Ca2+ and OH- (pH 10-12), and it is believed that this reaction occurs via redox processes in closed, lowtemperature groundwater systems (Neal and Stanger, 1983). In addition, reactions between water and basaltic mafic-ultramafic volcanic rocks can also generate substantial amounts of hydrogen. Previous estimates suggest that the annual hydrogen production from oceanic basaltic layers reaches up to 12.6×10⁶ tons (Dzaugis et al., 2016). However, as water further reacts with dissolved ions (Anderson et al., 1998), reaction products precipitate and adhere to the contact surface between water and rocks, thereby inhibiting the continuation of water-rock interactions and ultimately limiting hydrogen generation. Despite extensive research on hydrogen production through serpentinization in water-rock interactions, certain reaction mechanisms under natural geological conditions remain unclear. Consequently, the resource potential of hydrogen derived from this genesis may be severely underestimated.

2.1.3 Radiolytic decomposition of water

Radiolytic decomposition of water is regarded as an important source of hydrogen. Compared with other hydrogen generation mechanisms, the radiolytic decomposition of water to produce

hydrogen requires relatively simple reaction conditions, needing only water and radioactive elements (Klein et al., 2019). Natural radioactive elements mainly include potassium, thorium, and uranium. During their natural decay, K, Th, and U in minerals emit three types of particles: α , β , and γ . The generated radiation energy breaks the hydrogen-oxygen bonds in water molecules, producing hydrogen radicals and hydroxyl radicals. Two hydrogen radicals then react to form hydrogen (Yu et al., 2023; Klein et al., 2020; Wang, 2019), that is, water decomposes into H₂ and H₂O₂. Since H₂O₂ cannot exist stably, it rapidly decomposes further into H₂O and O₂ (Dou et al., 2024). Due to the differences in linear energy transfer (LET) rates generated during the decay of radioactive elements in minerals (Chupin et al., 2017), current studies suggest that α-radiation (heavy ion radiation) produces the largest amount of hydrogen, followed by β-radiation, and these two are important pathways in the hydrogen generation process (Han et al., 2021; Chupin et al., 2017). γ-rays, a type of high-energy electromagnetic radiation, mediate hydrogen production by transferring energy to water molecules via Compton scattering and the photoelectric effect, inducing ionization/excitation and ultimately forming H2 from H• radicals. Despite a lower Linear Energy Transfer (LET) and hence lower hydrogen yield per unit track compared to alpha particles, the markedly greater penetration depth of gamma rays allows for uniform hydrogen production across a substantial water volume, making it a significant radiolytic mechanism (Chupin et al., 2017; Klein et al., 2020).

Scholars detected trace amounts of hydrogen in Permian potassium salt samples from the Boulby Potash Mine in Yorkshire, UK (Parnell and Blamey, 2017). Some samples were irradiated under conditions without natural radiation sources, and hydrogen was detected in the products. It is thus believed that the potassium in the samples undergoes radioactive decay, during which water is radiolytically decomposed to generate hydrogen (Han et al., 2021; Parnell and Blamey, 2017; Barbara et al., 2014). Statistics show that the global annual hydrogen production from radiolytic decomposition of water is as high as 4.7×10^{10} mol, among which the hydrogen generated by radiolysis in the oceanic crust is 2×10^8 mol (Worman et al., 2016).

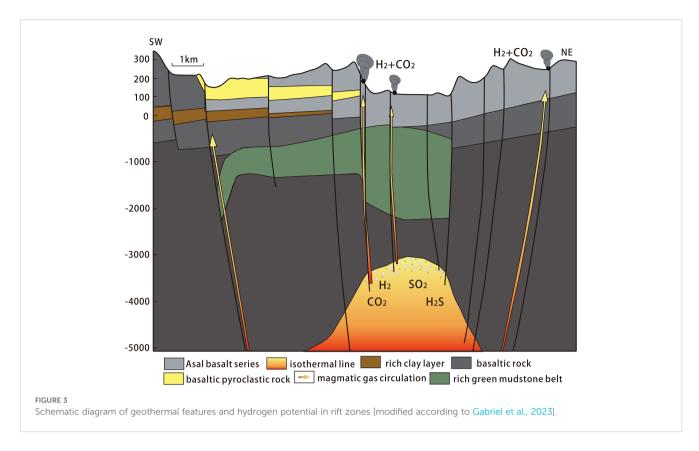
Since radiolytic hydrogen generation only requires a radiation source and water, it is considered that radiolytic decomposition of water can occur widely on Earth (Meng et al., 2024). Previous studies have shown that radiolytic hydrogen generation from pore water in rocks only needs to absorb 1% of the radiation energy released during element decay, and the remaining energy is converted into heat (Zgonnik, 2020). There are many factors affecting the reaction rate and yield of hydrogen generated by radiolytic decomposition of water, including the concentration of radioactive elements, the amount of water in fracture pores, pore space, and the concentration of anions and cations dissolved in fluids (Lippmann et al., 2003). When water in rock pores or fractures is radiolytically decomposed, such as pore water in sediments or crystalline rocks, the main limiting factors are the porosity and permeability of the rock (Meng et al., 2024; Lin et al., 2014). In addition, the existing state of water also affects the yield and rate of hydrogen generation. Compared with pure water, radiolysis of brine can produce more hydrogen (Dou et al., 2024; Klein et al., 2020). Due to the lack of systematic research on these influencing factors, there is still great uncertainty in the calculation of hydrogen yield from radiolytic decomposition of water.

In addition to hydrogen, some oxygen is also generated during the radiolytic decomposition of water. Because hydrogen itself is highly susceptible to oxidation, and both hydrogen and oxygen are prone to react with other substances, it is difficult to detect hydrogen and oxygen generated by water radiolysis simultaneously (Parnell and Blamey, 2017; Dubessy et al., 1988), making it hard to confirm whether water radiolysis truly occurs. Therefore, the mechanism of hydrogen generation through radiolytic decomposition of water still needs further research to clarify the specific process of this reaction.

2.2 Organic-origin hydrogen

Microbial activity and the thermal decomposition of organic matter are also crucial links in hydrogen production. When organic matter reaches the high - over mature evolutionary stage, the original organic matter will release a large number of hydrogen free radicals through a series of polycondensation reactions (Wang et al., 2012), and these hydrogen free radicals will redistribute and react. In this process, the generation of hydrogen is accompanied by the production of a large amount of hydrocarbon gases (Brian et al., 2022; Zhong et al., 2000; Xiong et al., 2004). In addition, in biological communities lacking photosynthesis, hydrogen is generally produced through processes such as fermentation and nitrogen fixation. Studies have shown that the fermentation of organic matter, nitrogen fixation by microbial communities, and the action of hydrogenase are the main pathways for hydrogen production through biological processes (Piche-Choquette and Constant, 2019). In moist and anoxic underground environments with sufficient organic carbon, large organic macromolecules are hydrolyzed into alcohols, fatty acids, and hydrogen under the action of fermentative bacteria, and are further degraded into various small molecular substances such as acetic acid, hydrogen, and carbon dioxide (Conrad, 1999). Under oxygen - sufficient conditions, nitrogen fixation is the primary way for microorganisms to produce hydrogen. Biological nitrogen fixation (BNF) consumes a large amount of energy, so it only occurs when there is no available nitrogen in the ecosystem (Burris, 1991). Microorganisms can also produce hydrogen under the action of hydrogenases. As a kind of metalloenzyme, hydrogenases differ in the arrangement sequence of internal amino acids. Among them, [FeFe] - hydrogenase is related to the generation of hydrogen. Under anaerobic metabolic conditions, hydrogenase, as an important biological catalyst, promotes the production of hydrogen (Armstrong and Albracht, 2005).

At present, the research on the genetic mechanism of organic - origin hydrogen is not yet clear. We believe that the thermal decomposition of organic matter may generate hydrogen, and the role of biological processes in promoting hydrogen accumulation is relatively weak. Firstly, biological hydrogen production mainly



occurs in strata shallower than 100 meters underground (Wang et al., 2025). At this depth, considering the highly diffusible nature of hydrogen itself, the hydrogen produced by this process is almost impossible to accumulate. Secondly, specific microbial communities in surface soils consume hydrogen, leading to a large amount of it being removed before entering the atmosphere (Constant et al., 2010). The rate of hydrogen production by microbial action is much lower than the rate of hydrogen consumption by soil, making it difficult for hydrogen to accumulate. However, in specific geological settings like well-sealed systems, its contribution to local hydrogen anomalies or particular play types cannot be overlooked, offering a crucial piece for understanding the full hydrogen source pedigree.

3 Global distribution of highconcentration natural hydrogen

Hydrogen-rich natural gas exhibits an extensive global distribution, with numerous reports documenting its presence across North America, the Asia-Pacific, Europe, Africa, and the Middle East. However, its content varies significantly, ranging from 0.1% to 99%. Natural hydrogen exhibiting a volume fraction exceeding 10% is classified as high-concentration natural hydrogen in this work. In contrast to the early formation stage of the Earth's surface atmosphere, the hydrogen content in the current atmosphere is extremely low, approximately 0.5 ppm. Natural hydrogen worldwide is characterized by a broad distribution, marked variations in content, and complex occurrence environments. To date, high-content natural hydrogen (with a

volume fraction exceeding 10%) has been primarily identified in specific geological settings, including rift tectonic systems, plate collision zones, subduction zones and their peripheral areas, as well as Precambrian iron-rich strata—consistent with insights from current natural hydrogen research, which integrates geological structural analysis, petrological characterization of iron-rich formations, and analogies to unconventional hydrocarbon accumulation patterns in tectonically active zones.

3.1 Rift tectonic systems

The development of rifts is closely linked to plate tectonic movements. In global intracontinental rift system development areas, the crust is generally thin. Their formation is accompanied by mantle upwelling and crustal stretching-fracturing (Mathooko and Kariuki, 2000), thus frequently involving persistent activity of deep and large faults. Mafic-ultramafic rocks typically develop along these deep and large fault zones, where substantial amounts of hydrogen, occurring in "inclusion forms," are hosted (Zgonnik, 2020) with an average concentration of 21.4%. Meanwhile, the presence of deep and large faults provides favorable conditions for hydrogen migration (Figure 3).

Natural hydrogen discovered in rift environments is mainly concentrated in mid-ocean ridge regions (Cannat et al., 2010). High-concentration hydrogen has been identified in black smokers at multiple sites. It is notably prominent along slow- and ultra-slow spreading ridges characterized by abundant ultramafics, such as the Mid-Atlantic Ridge—a paramount global locality for

seabed natural hydrogen. Serpentinization is the paramount process for hydrogen production during ocean crust alteration. At localities investigated via ocean drilling and hydrothermal vents, including the Rainbow and Lost City hydrothermal fields, measured hydrogen concentrations can reach volume fractions greater than 40% (Charlou et al., 2002). Average natural hydrogen volume fractions greater than 21.4% have also been detected in mid-ocean ridges (Zgonnik, 2020). Li et al (Li et al., 2025). first discovered a large deep-sea hydrogen-rich hydrothermal vent cluster on the subducting plate 80 km west of the Mussau Trench in the western Pacific Plate, naming it the Kunlun hydrothermal vent cluster. Previously, hydrothermal activities associated with serpentinization reactions were only found near mid-ocean ridges and plate boundaries. The Kunlun hydrothermal vent cluster consists of 20 giant circular pits with diameters of 450-1800 m and depths of 30-130 m. In-situ detection of four of these "pits" showed that the hydrothermal fluid is alkaline and hydrogen-rich, with hydrogen concentrations of approximately 5.9-6.8 mmol/kg and temperatures above 18°C, forming a hydrothermal system driven by deep-sea serpentinization reactions induced by subduction activity (Li et al., 2025). Using data from the Lost City hydrothermal field in the Mid-Atlantic Ridge as a reference (Deborah et al., 2001), the hydrogen end-member concentration in the Kunlun hydrothermal fluid was calculated to reach 13.2-22.1 mmol/kg, a value even exceeding the hydrogen concentrations observed in the Rainbow and Lost City hydrothermal fields (Seyfried et al., 2011).

Continental rift tectonic systems also possess geological conditions favorable for the development of hydrogen-rich fluids (Dou et al., 2024), with the U.S. Mid-Continent Rift Zone serving as an example. The North American Mid-Continent Rift System, formed approximately 1.1 billion years ago, extends 2000 km from Lake Superior in the U.S. to Oklahoma, spanning Kansas with a north-northeast to south-southwest strike (Guélard et al., 2017). Studies along the rift zone have identified multiple occurrences of natural hydrogen, especially in the Kansas Basin on the western side of the rift zone. Natural gas with relatively high hydrogen concentrations, accompanied by small amounts of nitrogen, has been found in over 10 wells near the rift zone within this region (Sherwood et al., 2007), with these exploration wells all located in anticlinal structures west of the rift zone (Guélard et al., 2017). Long-term monitoring of the Heis well in the axial area revealed that the hydrogen content initially stood at 34%, decreased in subsequent measurements, but recovered to over 30% when re-detected 30 years after exploration and development -indicating that natural hydrogen is in a continuous generation process (Guélard et al., 2017). In recent years, Kansas has emerged as a key block with natural hydrogen exploration potential, with multiple exploration prospects identified in the region. Additionally, Australia's HyTerra Company conducted natural hydrogen exploration in Nebraska, north of Kansas, in 2023 (Dou et al., 2024), drilling the world's first dedicated natural hydrogen exploration well, Hoarty NE3, which successfully produced hydrogen flow. Analysis of the raw gas from Hoarty NE3 showed

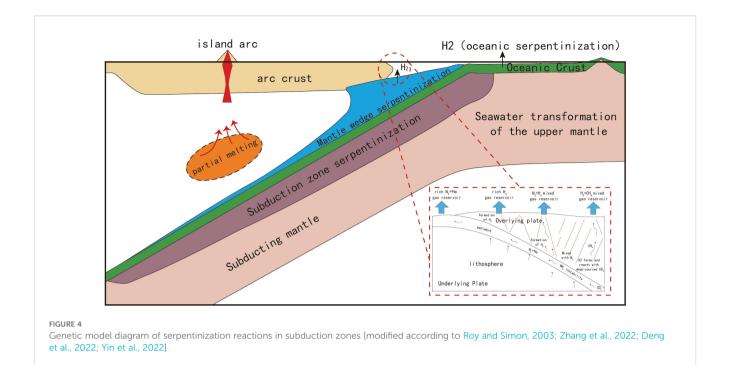
a hydrogen concentration as high as 44% and helium as high as 12.8% (Hoarty NE3, 2025).

The Pyrenean Rift System in northern France is another typical intracontinental rift system. Formed mainly during the Late Jurassic to Early Cretaceous, it strikes east-west and exhibits an irregular "double-wedge structure" overlying the Iberian continental lithosphere, which underwent intense extension during the Cretaceous. Studies have shown that relatively high hydrogen concentrations have been detected in soils around France and Spain on both the northern and southern sides of the Pyrenean Rift System (Lefeuvre et al., 2021; Saspiturry et al., 2024; Lefeuvre et al., 2022). Although the planar distribution of hydrogen concentrations is poorly homogeneous, it sufficiently confirms the presence of natural hydrogen accumulation in the subsurface of the rift system. High hydrogen concentrations, reaching up to 1000 ppm, have been detected in multiple thrust zones in northern Pyrenees, Saint-Palais, and Saint-Suzanne. In contrast, hydrogen concentrations near the Mauléon and Arzacq basins are mostly between 1-74 ppm. This phenomenon of orders-of-magnitude differences in hydrogen concentrations over short distances requires further research. However, in the three major fault zones of the Pyrenees with high hydrogen concentrations, the crust is thin, forming structurally weak zones, and deep and large faults reaching the surface exist—conditions that provide favorable pathways for the migration of natural hydrogen and deep fluids. Thus, the Pyrenean Rift System in France, like the North American Mid-Continent Rift System, has become a favorable area for natural hydrogen exploration and development.

3.2 Plate collision zones, subduction zones, and their peripheral areas

Within the framework of Earth's evolution and geodynamics, plate collision zones and subduction zones play a pivotal role (Dou et al., 2024; Yang et al., 2021). It serves as a channel for material communication between different layers, and are also sites of earthquakes, volcanic activities, and ophiolite belt formation (Zhu and Xu, 2019). Ophiolite belts, as key components of ancient convergent plate margins, represent lithospheric fragments of vanished ancient oceanic crust, primarily consisting of two parts: igneous rocks such as peridotite, gabbro, and basalt, and sedimentary rocks (Dou et al., 2024; Dilek and Furnes, 2011). During subduction, the oceanic crust at convergent plate margins undergoes continuous dehydration. The development of deep and large faults provides seepage channels for the upward migration and circulation of deep fluids. As deep fluids (including water) gradually permeate the entire forearc mantle wedge, large-scale hydrogengenerating serpentinization reactions occur, making plate collision zones, subduction zones, and their peripheral areas major sites for serpentinization (Figure 4) (Yu et al., 2023).

To date, occurrences of natural hydrogen have been identified in ophiolite belts of numerous plate collision zones and subduction zones worldwide. Statistical data indicate that natural hydrogen



associated with global ophiolite belts exhibits high content (Zgonnik, 2020), with annual global production reaching (0.18–0.36) \times 10⁶ tons. Previous studies on natural hydrogen in multiple global ophiolite belts have found that over 80% of samples have a natural hydrogen volume fraction exceeding 40%.

Taking the Tethys tectonic domain as an example, multiple occurrences of high-concentration natural hydrogen have been discovered in the region. The Tethys tectonic domain, spanning from the Alps in the west, through the Iranian and Turkish plateaus, to the Himalayas in the east, is a complex global tectonic system formed by the interaction and evolution of multiple plates across various geological periods (Wu et al., 2020; Zhu et al., 2023). Highconcentration natural hydrogen occurrences have been found in the Pyrenees at the western end of the domain, as well as in Oman, Turkey, and Algeria in the central part (Hosgormez et al., 2008; Laurent et al., 2024; James et al., 2023). Particularly in surface areas of ophiolite belt development zones in the Pyrenees, the leakage concentration of natural hydrogen can reach up to 1000 ppm (Lefeuvre et al., 2021). Additionally, in the Tethys tectonic domain of southwest China, favorable natural hydrogen shows have been observed in the Tengchong area (Shangguan et al., 2000), further highlighting the advantages of the Tethys tectonic domain in natural hydrogen accumulation environments.

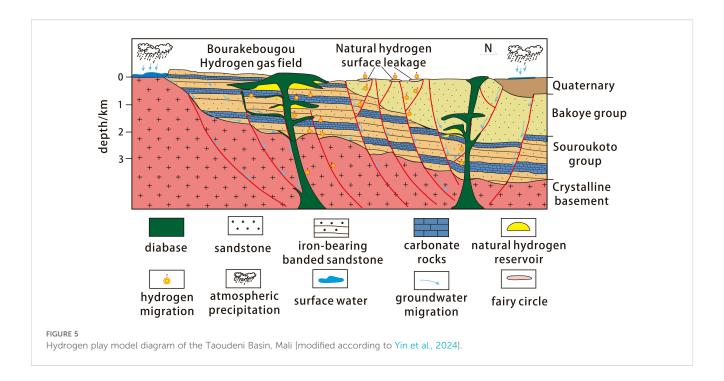
Hydrogen isotopes, noble gas isotopes (e.g., 20Ne/4He ratio) and R/Ra ratio can effectively identify hydrogen produced by serpentinization reactions. For example, δD values exhibit different variations and patterns under different environments and conditions. In marine environments, δD values decrease with increasing temperature (Yin et al., 2024; Giora et al., 2006), whereas in ophiolite belts, they increase with rising temperature (Neal and Stanger, 1983); Noble gas isotopes, especially the 3 He/ 4 He ratio (R/Ra), provide a robust tracer for deep-mantle contributions, where

R/Ra >> 1 is a key signature. The co-occurrence of N_2 , He, and H_2 is a common hallmark of deep degassing. Conversely, the CH_4/H_2 ratio and $\delta^{13}C\text{-}CH_4$ are critical for identifying the origin of methane —whether from organic, inorganic, or Fischer-Tropsch synthesis pathways (Milkov, 2022; Zgonnik, 2020). Furthermore, during the upward migration of hydrogen from depth along deep and large faults, deep hydrogen-bearing fluids with different concentrations and compositions randomly mix and interact, thereby giving rise to various types of gas accumulations (Meng et al., 2024).

In summary, ophiolite belts developed in plate subduction zones, influenced by tectonic evolution at different locations, exhibit variations in hydrogen concentration and associated gas components. During the upward migration of hydrogen from depth along deep and large faults, deep hydrogen-bearing fluids with different concentrations and compositions randomly mix and interact, forming various gas reservoir types. Therefore, clarifying different types of gas reservoirs, combined with geological evolution processes, and identifying hydrogen of different genetic types, holds significant guiding significance for exploring hydrogen reservoirs and summarizing favorable conditions for hydrogen accumulation.

3.3 Precambrian iron-rich formations

Precambrian iron-rich formations represent some of the oldest stratigraphic units with rock records on Earth, preserving abundant information about the early stages of planetary evolution. The Precambrian basement underlies approximately 70% of the Earth's continental crustal area (Liu et al., 2023). Geological and geochemical evidence indicates that Precambrian cratons generally existed in anoxic, iron-rich environments (Dou et al., 2024; Eric et al., 2018; Wang, 2022). Banded Iron Formations (BIFs), formed



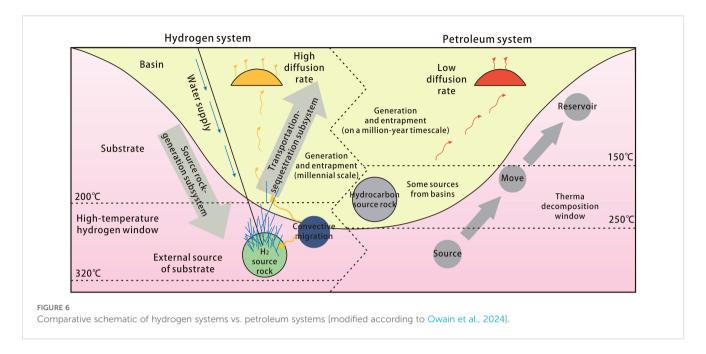
during the Precambrian, account for over 90% of global iron ore production and are primarily distributed across North America, Africa, Australia, and Asia (TiChadou et al., 2021). As a unique chemical sedimentary type exclusive to early Earth, BIFs record critical information about early planetary evolution (Dai et al., 2016), with statistics showing that approximately 60% of the world's iron ores belong to this category.

Hydrogen generation in Precambrian strata fundamentally involves the oxidation of Fe2+ ions, which occur predominantly in minerals such as magnetite (Fe₃O₄) and siderite (FeCO₃). Studies have confirmed high concentrations of Fe2+ in BIFs (Roche et al., 2024; Geymond et al., 2022), with metamorphosed BIFs exhibiting even higher Fe²+ contents (Roche et al., 2024; Lechte et al., 2019). Notably, numerous occurrences of natural hydrogen have been linked to Precambrian iron-rich formations. An example is the Taoudeni Basin in Mali, where iron-rich formation belts are widely developed in the Precambrian strata of the Bourakebougou area (Figure 5). Hydrogen generated via redox reactions between Fe²+ in these belts and water migrates and accumulates through deep, largescale faults in the surrounding area (Dou et al., 2024). In Australia, a dedicated natural hydrogen exploration well on the York Peninsula detected natural gas with a hydrogen concentration as high as 84%. In the United States, the Humboldt Fault Zone in Kansas penetrates into Paleozoic strata and extends to the Precambrian basement; two wells (Scott and Heins) drilled along this fault zone recorded hydrogen concentrations of 56% and 80%, respectively (David et al., 2007). Based on the regional geological setting, the Precambrian iron-rich formations are recognized as the primary source horizons for natural hydrogen in this area.

Statistical analysis of global drilling data reveals an inverse relationship between basement burial depth and hydrogen content: shallower basement depths correspond to higher hydrogen concentrations. Natural hydrogen contents detected in Precambrian strata are typically an order of magnitude higher than those in younger geological units (Parnell and Blamey, 2017), confirming that Precambrian iron-rich formations constitute a significant source of global natural hydrogen. Investigations into the isotopic and geochemical characteristics of hydrogen within these formations can help deduce hydrogen's genetic mechanisms, thereby shedding light on the composition and evolution of Earth's early atmosphere. Such research holds profound implications for understanding Earth's evolution, the origin of life, and planetary science—aligning with interdisciplinary advancements in geology, geochemistry, and natural hydrogen resource exploration, while mirroring analytical approaches used in unconventional hydrocarbon studies.

4 Favorable geological conditions for natural hydrogen enrichment

Similar to the challenges faced in the exploration and development of oil and natural gas, the traditional hydrocarbon theory factors of "generation, reservoir, cap, trapping, migration, and preservation" are also relevant to the exploration and development of natural hydrogen. However, there are notable differences. Hydrogen is chemically reactive, and its formation and distribution are influenced by a range of geological conditions and factors. Consequently, the conditions required for the migration and trapping of natural hydrogen to form reservoirs are more stringent. Therefore, high-quality hydrogen source conditions, along with favorable migration, accumulation, and preservation factors, represent the key geological conditions conducive to the enrichment of natural hydrogen (Figure 6).



4.1 High-quality hydrogen source conditions

The sources and genetic mechanisms of natural hydrogen are highly complex, encompassing both organic and inorganic origins. Formation processes include biological activity, thermal decomposition of organic matter, deep-Earth degassing, waterrock reactions, and radiolytic decomposition of water. Under the influence of varying geological conditions and stratigraphic evolution, the sources of hydrogen, as well as the compositions and relative contents of associated gases and carrier fluids, exhibit considerable diversity. Current research on natural hydrogen primarily identifies its sources as serpentinization reactions, mantle fluid degassing, and the radiolytic decomposition of water.

Similar to petroleum and natural gas studies, the hydrogen source remains one of the most elusive factors to identify, yet it is pivotal in determining the ultimate formation of hydrogen accumulations. Ultramafic rocks, iron-rich cratonic basements, and uranium-bearing rocks are recognized as three confirmed types of hydrogen source rocks (Dou et al., 2024; Jin, 2023; Zgonnik, 2020; Gaucher, 2020). These high-quality hydrogen source rocks are distributed across different locations, predominantly concentrated in plates such as North America, South America, Africa, Eastern Europe, Western Asia, India, North China, and Australia. They occur in diverse tectonic settings including oceanic crust, fault zones, subduction zones and their peripheries, mid-ocean ridges, igneous rocks, and orogenic belts. Synthesizing global hydrogen genesis and distribution patterns reveals that natural hydrogen sources are widely distributed across major plates and oceanic crust, with deep-seated sources dominating. For future research on natural hydrogen enrichment characteristics, it will be necessary to refine the occurrence characteristics of natural hydrogen under different geological conditions, continuously monitor hydrogen leakage and diffusion, draw on established geological exploration methodologies for conventional oil and gas, as well as insights from unconventional hydrocarbon studies, and develop geological evolution models tailored to natural hydrogen accumulation theory.

4.2 Favorable conditions for migration, accumulation, and preservation

Although primary hydrogen is mostly concentrated in the deep Earth, it exhibits strong migration capacity. Most hydrogen migrates upward with deep fluids along deep-seated major faults to shallow surface layers, and under suitable geological conditions, forms traps and further accumulates into reservoirs. Subsurface hydrogen has a close relationship with faults: faults and fractures are likely the main pathways for hydrogen migration. Since most deep-seated major faults can penetrate all sedimentary strata, they theoretically can reach any deep hydrogen source rocks. Meanwhile, mid-ocean ridges and rifts—products of crustal extension—are part of tectonically stressed weak zones, where the pressure of overlying strata is reduced. This facilitates the further exposure of deep mafic-ultramafic rocks such as peridotite and promotes the upward migration of deep fluids carrying large amounts of primary hydrogen along deep-seated major faults.

Natural hydrogen typically accumulates dynamically in the form of mixed gases. As noted earlier, during migration and production, natural hydrogen is accompanied by significant amounts of associated gases that accumulate simultaneously. Various gases originally present in the deep Earth—including hydrogen, methane, and helium—mix, continuously accumulate in reservoirs, and fill subsurface pores and fractures. Gas diffusion gradually occurs under the influence of geological activities, the influx of external gases, and changes in the original temperature and pressure conditions of preservation. Gases with lower mass, lower

solubility, and higher diffusion coefficients are more prone to diffusion (Liu et al., 2005). Hydrogen and helium have high diffusion coefficients and strong diffusion capacities, with their molecules easily passing through the pores of media. Thus, multiple factors—including the porosity and permeability of reservoirs and cap rocks, formation pressure, temperature, and the composition and relative content of mixed gases—affect the subsurface migration and accumulation of hydrogen, resulting in extremely complex mechanisms.

The preservation conditions for natural hydrogen are extremely stringent. Both in the geological evolution of hydrogen and in the field of traditional hydrocarbon theory, cap rocks and traps play a crucial role in the enrichment of hydrocarbon resources (Prinzhofer et al., 2018). Compared to oil and natural gas, hydrogen itself has stronger migration and diffusion capabilities; cap rocks that can form perfect traps for oil and natural gas may fail to enable hydrogen to accumulate in significant quantities. Therefore, the enrichment of deep natural hydrogen requires intact cap rocks with relatively high sealing capacity to further form natural hydrogen traps.

To identify specifically favorable cap rocks for natural hydrogen, we can explore and summarize from the cap rocks and traps of discovered high-concentration, high-content natural hydrogen reservoirs. Studies suggest that salt diapir structures may provide excellent cap rocks for natural hydrogen. Evidence shows that hydrogen concentrations in gas reservoirs with gypsumsalt rock as cap rocks can reach 20%–30% (Smith et al., 2005), which is closely related to the physicochemical properties of gypsum-salt rocks. As evaporites, gypsum-salt rocks have extremely low porosity and permeability, dense structures, strong sealing capacity, and high capillary breakthrough pressure.

Additionally, gypsum-salt rocks exhibit strong fluidity and plasticity. At burial depths exceeding 2000 m, they undergo dehydration, releasing half their volume in water and transforming into anhydrite, which enhances the sealing capacity of the cap rock. Simultaneously, the released water, unable to flow out, accumulates in rock pores—on one hand, inhibiting further diffusion of hydrogen, and on the other hand, causing formation overpressure, which further strengthens the sealing of natural hydrogen by the gypsum cap rock and consolidates trap formation.

In natural hydrogen discovered in the Pyrenean foothills, the ranges of hydrogen concentrations and other associated gases (including methane and carbon dioxide) that exceed abnormal thresholds are mostly concentrated near the Salies salt diapir (Lefeuvre et al., 2021). The top of the Salies salt diapir is located 70 meters below the surface (Lefeuvre et al., 2021). Although the natural hydrogen trap in the Pyrenean foothills has not yet been confirmed, the excellent sealing capacity of this salt diapir and its inertness relative to H₂ are considered to make it a "sweet spot" for the formation of large-scale natural hydrogen reservoirs—consistent with current insights from natural hydrogen research, which integrates petrological analysis of cap rock properties and analogies to seal mechanisms in unconventional hydrocarbon reservoirs.

4.3 Dynamic accumulation of natural hydrogen reservoirs

The natural hydrogen system shares numerous similarities with petroleum and natural gas systems, allowing for the reference of traditional hydrocarbon system frameworks in terms of hydrogen source rocks, reservoirs, cap rocks, migration, and preservation conditions. However, the formation of natural hydrogen reservoirs differs significantly from that of oil and natural gas reservoirs (Emanuelle et al., 2021; Lefeuvre et al., 2021).

Unlike the generation models of hydrocarbon reservoirs, the accumulation process of natural hydrogen reservoirs is dynamic. Firstly, across numerous geological environments, hydrogen production and consumption are often highly coupled in both time and space, hydrogen generation and consumption occur simultaneously. The diverse genesis of natural hydrogen and the abundance of source rocks ensure that hydrogen production far exceeds consumption. While hydrogen generated in source rocks continuously replenishes the reservoir, the natural hydrogen already accumulated in the reservoir is constantly escaping, leaking, or being consumed by other subsurface reactions. This replenishment and escape of natural hydrogen in the reservoir is a continuous process: when the replenishment rate exceeds the escape rate, hydrogen in the reservoir accumulates, and the reservoir expands; conversely, when replenishment lags behind escape, hydrogen in the reservoir diminishes, and the reservoir shrinks or even depletes. It is this persistent dynamic state that causes the accumulation status and enrichment degree of the reservoir to change continuously. The dynamics of natural hydrogen—its generation/ replenishment versus its loss/consumption—hinge on numerous factors. The generation rate is dictated by source rock reactivity (e.g., serpentinization rate), fluid flux, and PT conditions. The loss rate is primarily controlled by seal integrity, fault connectivity, microbial activity, and reservoir properties. Crucially, a positive hydrogen balance, leading to accumulation, requires a sustained generation rate that surpasses the loss rate (Guélard et al., 2017).

Secondly, long-term monitoring and calculations of hydrogen leakage from "fairy circles" in multiple regions have revealed that while deep primary hydrogen undergoes a series of tectonic evolutionary movements and physicochemical reactions—continuously generating and migrating to reservoirs through processes such as deep fluid degassing, serpentinization, and water radiolysis—near-surface hydrogen leakage occurs simultaneously. Some microorganisms in shallow soils obtain energy by reducing gases such as hydrogen and hydrogen sulfide (Jacob et al., 2021), further consuming the hydrogen leaking to the surface.

Additionally, long-term monitoring of hydrogen concentrations in wells indicates that dynamic migration and accumulation of hydrogen is a relatively short-term process. In the Scott well area of Kansas, USA, on a decadal measurement scale, the concentration of natural hydrogen gradually rises after a period of recovery following extraction (Guélard et al., 2017) (Donzé et al., 2020). suggest that as pressure gradually decreases toward the

surface, hydrogen reservoirs become increasingly unable to maintain stable conditions, and transient accumulation may even be observed at near-surface depths. This indicates that once a hydrogen reservoir is formed and available for development, its current reserves are subject to constant change, with the specific resource quantity depending on the total regional resources—aligning with current insights from natural hydrogen research, which integrates dynamic geological process analysis, geochemical monitoring of hydrogen fluxes, and analogies to transient fluid behavior in unconventional reservoirs.

5 Conclusions

Based on a comprehensive synthesis of global natural hydrogen distribution, genesis, and enrichment characteristics across marine and continental contexts, we have reached the following key conclusions:

5.1 Complex genesis

Natural H_2 originates from diverse pathways. Organic mechanisms include biological activity and organic matter thermolysis. Inorganic sources encompass deep degassing, waterrock reactions, and aqueous radiolysis. Understanding these mechanisms is crucial for subsurface H_2 resource exploration.

5.2 Widespread distribution

Globally, high-concentration natural H₂ primarily occurs within rift systems, plate collision zones, subduction zones and their peripheries, and Precambrian iron-rich formations.

5.3 Dynamic accumulation

 $\rm H_2$ enrichment depends on high-quality sources and favorable migration-pathway-seal conditions. Due to its dynamic nature, forming significant accumulations requires effective traps coupled with a continuous $\rm H_2$ supply where influx exceeds loss.

5.4 Significant consumption

Natural H₂ production is counterbalanced by consumption processes. Major sinks include microbial metabolism and deep subsurface hydrogenation for hydrocarbon formation. Regions with high consumption are unfavorable for large-scale H₂ reservoirs; prospecting should focus elsewhere. Current hypotheses suggest ultra-deep strata (especially near major convergent zones) and shallow layers adjacent to deep-seated faults represent promising accumulation targets.

As an emerging exploration frontier, natural hydrogen holds significant resource potential and research value. The establishment of a natural hydrogen system theory will build upon the welldeveloped conventional oil and gas theoretical framework, which has evolved over more than a century, and is expected to yield theoretical advances and practical applications in a relatively short time. Although China started relatively late in the field of natural hydrogen, a considerable number of researchers have now engaged in related disciplines. Therefore, within the current natural hydrogen energy development plan, China should first increase the emphasis on natural hydrogen, accelerate the initiation of general surveys, and gradually refine the natural hydrogen system, with a focus on enhancing research related to its formation mechanisms and reserve potential. Hydrogen component detection could be added to routine compositional analysis programs in relevant industries or sectors to promptly identify its presence. Simultaneously, re-evaluating existing well data and reinterpreting old well logs may reveal new, promising natural hydrogen accumulations. Furthermore, China possesses complex geological settings and, given the diverse origins and sources of natural hydrogen, represents a vast "sweet spot" area with enormous potential awaiting exploration. This is particularly true for region types aligning with the high-concentration natural hydrogen criteria discussed in this paper, which merit further indepth study. Promising areas include: The Songliao Basin and its periphery, especially zones like the Xujiaweizi Fault Depression, which features deep-seated faults, volcanic reservoirs, and where the SK-2 well has already indicated high hydrogen concentrations. The periphery of the North China Craton, including the Jiyang Depression in the Bohai Bay Basin and the Jimo area in the eastern Sulu Orogen. These regions, characterized by deep faults, mantle-derived fluid activity, and Precambrian basements, are favorable for upward migration of deep-sourced hydrogen. The Southwest Tethyan tectonic domain, primarily the Tengchong volcanic-geothermal area in Yunnan. This area shows signs of active intraplate tectonics, geothermal activity, and mantle material upwelling, providing excellent conditions for hydrogen generation and migration. Regions within the central Precambrian cratonic areas, such as the western margin of the Ordos Basin and basement uplift zones in the Sichuan Basin. Here, identifying favorable plays combining Precambrian iron-rich formations and deep faults, analogous to those in the Bourakebougou area of the Mali Basin, is a key target.

Author contributions

YL: Conceptualization, Investigation, Methodology, Writing – original draft. QM: Writing – review & editing, Formal Analysis, Supervision, Visualization. XH: Writing – review & editing, Conceptualization, Funding acquisition, Methodology, Project administration. WL: Formal Analysis, Supervision, Visualization, Writing – original draft. YW: Investigation, Supervision, Visualization, Writing – review & editing. JL: Investigation,

Writing – review & editing. YZ: Data curation, Resources, Writing – review & editing. LH: Formal Analysis, Writing – review & editing. QL: Formal Analysis, Writing – review & editing. JC: Data curation, Resources, Writing – review & editing. DZ: Data curation, Resources, Writing – review & editing.

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Conflict of interest

Author QM was employed by the company SINOPEC.

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