

# The Origin and Occurrence of Natural Hydrogen

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**Abstract:** Hydrogen is an attractive, clean, sustainable energy source primarily produced via industry. At present, most reviews on hydrogen mainly focus on the preparation and storage of hydrogen, while the development and utilization of natural hydrogen will greatly reduce its cost. Natural hydrogen has been discovered in many geological environments. Therefore, based on extensive literature research, in this study, the distribution and sources of natural hydrogen were systematically sorted, and the identification method and occurrence state of natural hydrogen were examined and summarized. The results of this research show that hydrogen has been discovered in oceanic spreading centers, transform faults, passive margins, convergent margins, and intraplate settings. The primary sources of the hydrogen include alterations in Fe(II)-containing rocks, the radiolysis of water, degassed magma, and the reaction of water- and silica-containing rocks during the mechanical fracturing. Hydrogen can appear in free gas, it can be adsorbed and trapped in inclusions. Currently, natural hydrogen exploration is in its infancy. This systematic review helps to understand the origin, distribution, and occurrence pattern of natural hydrogen. In addition, it facilitates the exploration and development of natural hydrogen deposits, thus enabling the production of low-cost hydrogen.

**Keywords:** natural hydrogen; carbon neutral; serpentinization; hydrogen distribution; exploration of hydrogen reservoirs



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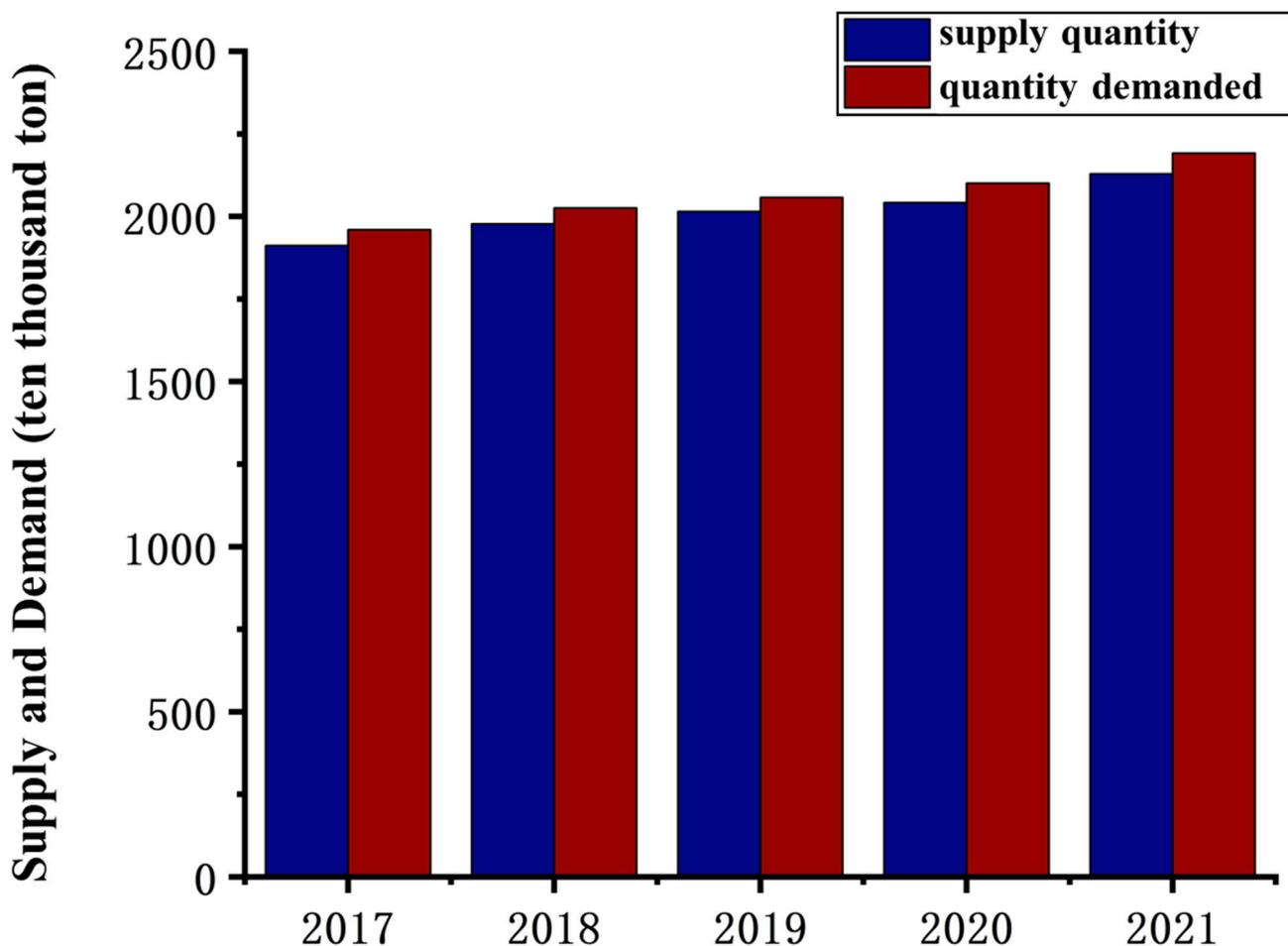
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## 1. Introduction

The growing global consumption of fossil fuel energy associated with climate change and environmental concerns has prompted extensive research into developing renewable energy sources to replace the current dependence on limited fossil fuel resources. Promising renewable energy sources, such as solar, wind, tidal, geothermal, biomass, and hydrogen energies, have been developed [1]. Hydrogen is a high-quality fuel. The product of its combustion is water, it can achieve zero-carbon emissions, and it is renewable. Therefore, it is considered a clean and sustainable energy source [2]. Furthermore, hydrogen can be converted into electric energy via fuel cells. As a chemical raw material, it plays a vital role in the industry (production of synthetic ammonia, methanol, and petroleum refining process of hydrogenation reaction). Clear H<sub>2</sub> offers large quantity and long-duration green energy storage, and its green derivatives (methanol, and ammonia) avoid expensive long-distance electric grid networks [3]. H<sub>2</sub> can also supply stable power demand for aquaculture systems and be used as feedstock for the refinery processes. H<sub>2</sub> also has applications in the propulsion systems of ships, submarines, and other vessels [4,5]. Figure 1 shows supply and demand balance in China's hydrogen industry for the period of 2017–2021; the demand for hydrogen in China has increased annually in this period.

Clean hydrogen has attracted wide attention, and electrolytic water is one of the most promising methods for hydrogen production. At present, there are four technologies in total. The first is alkaline water electrolytic cell technology (AWE), which has high technological maturity and long service life [6]. The second technology is proton exchange membrane (PEM), which has high current density, high operating pressure, more environmental

protection, small cell size and wide power regulation range, but the precious metals, platinum and iridium, used for PEM electrolysis result in PEM costing 3–5 times the cost of AWE [7]. Solid oxide electrolytic cell (SOEC) operates at high temperature (500–900 °C), and uses steam instead of liquid water. Current development focuses on commercialization, upgrading, life extension and cost reduction [8]. At present, it is mostly used in areas rich in heat energy. AEM is a relatively cutting-edge technology with faster response and higher current density, but membrane materials and device assembly are mostly in the laboratory research stage [9].



**Figure 1.** Hydrogen supply and demand balance in China's hydrogen industry for the period of 2017–2021.

Hydrogen storage has always been a key issue in the development of hydrogen energy, so there are a lot of research reports on hydrogen storage [10,11]. Hydrogen storage is divided into gaseous hydrogen storage, liquid hydrogen storage, and solid hydrogen storage, according to the phase state of hydrogen. Gaseous hydrogen storage is hydrogen compressed and stored in a high-pressure vessel [12]. It is suitable for large-scale and long-distance situations. Its advantages include fast hydrogen speed, relatively mature technology, and normal temperature operation and low cost; however, hydrogen is easy to leak [13]. There are also many studies of underground hydrogen storage, suitable for large-scale gaseous hydrogen storage, such as using abandoned oil fields [14]. Liquid hydrogen storage is a process in which hydrogen is compressed, cooled to 21 K and then stored in a special adiabatic vacuum container [15]. Its advantage is that the volume energy density of liquid hydrogen is several times higher than that of compressed storage, but its liquefaction process has high energy consumption, high cost and leakage risk [15,16]. Solid

hydrogen storage is the storage of hydrogen through physical or chemical adsorption. It has high storage capacity, safe transportation and good economy [17]. However, at ambient conditions, physical hydrogen storage material has low hydrogen storage capacity [18]. In addition, metal hydrides cannot release hydrogen at low temperatures because of their slow kinetics [17,18]. Therefore, the development of hydrogen storage materials with high hydrogen storage capacity and low constraints has been a challenge for the growth of hydrogen energy industry.

Future energy structures must develop more economical and feasible low-carbon or zero-carbon hydrogen production methods. Ubiquitous natural underground hydrogen may become the primary pillar of any coming energy revolution [19–22]. At present, the review of hydrogen mainly focuses on the preparation, storage and transportation of hydrogen, and the content of natural hydrogen is relatively little. However, exploration and development of natural hydrogen reserves will greatly reduce the cost of hydrogen. Therefore, we need to understand the characteristics of natural hydrogen including its distribution, origin, occurrence state, etc.

In the past, the importance of underground hydrogen was overlooked [19]. Indeed, underground hydrogen reserves were widely believed to be nonexistent because hydrogen diffuses rapidly in the air. Consequently, hydrogen quickly leaves its point of origin and cannot remain in geological traps for extended periods [23]. Hydrogen is also reactive and usually reacts with oxygen, which makes it difficult for hydrogen to appear as a free gas. Furthermore, hydrogen, hydrogen sulfide, and methane are consumed at hydrothermal vents to provide food for microbes. However, hydrogen might have been neglected in the past because there was no well-developed equipment analysis. It was reported that even in the 1990s, the equipment required to analyze hydrogen was not employed in many surveys [24]. So far, only a small part of modern portable natural gas analyzers has included hydrogen sensors in their designs. Estimating the frequency at which hydrogen is missed or misidentified in hydrogen-rich samples is challenging due to the lack of appropriate detection techniques for measuring hydrogen concentrations [24]. Therefore, the significance of natural hydrogen has not been appreciated. Another plausible reason for this is that most drilling worldwide occurs in sedimentary basins, which constitute half of the Earth's surface. However, these locations are unlikely to contain abundant hydrogen [25].

In recent years, natural hydrogen has been discovered in many geological environments, and geologists from many countries have shown great interest [26–28]. To date, there has been limited exploration of potentially hydrogen-rich geological reservoirs and no rigorous quantitative assessment of resources. The geological environments of Precambrian ultramafic bedrock or hyperalkaline igneous intrusive rocks may be sweet spots for hydrogen exploration [29]. The discovery of natural hydrogen wells in the Taoudeni Basin in Mali [20] could become a turning point in this nascent effort. Consequently, studying the distribution, generation mechanism, and occurrence of hydrogen is necessary to assess its productive potential. Moreover, the existence and abundance of hydrogen on Earth have long been a mystery. Fuller comprehension of these measures may be vital to understanding the deep evolution of the Earth's interior, dynamic state, thermal structure, crust, and hydrosphere.

Recent reviews on natural hydrogen mainly focus on the genetic methods of natural hydrogen [30] and the occurrence of natural hydrogen is almost not covered. Therefore, based on an extensive study of the literature, issues such as natural hydrogen distribution, origin, and occurrence are expounded from a geological perspective in this paper. It summarizes the progress of natural hydrogen exploration and development to guide the exploration of natural hydrogen.

## 2. Methodology

Based on keywords, we selected and downloaded articles including those covering the topics of natural hydrogen distribution, the origin of natural hydrogen, the identification

of hydrogen, and the occurrence of natural hydrogen. The desk research method was used in this study, which is usually used in scientific research to analyze the available data. Google Scholar, Elsevier, Science-Direct, and library were used to obtain books, academic dissertation, research papers and review papers (Figure 2). For the data cited in the articles, we referred to the earliest citation to ensure the reliability of primary data. The timeliness, professionalism and completeness of the downloaded paper are evaluated.

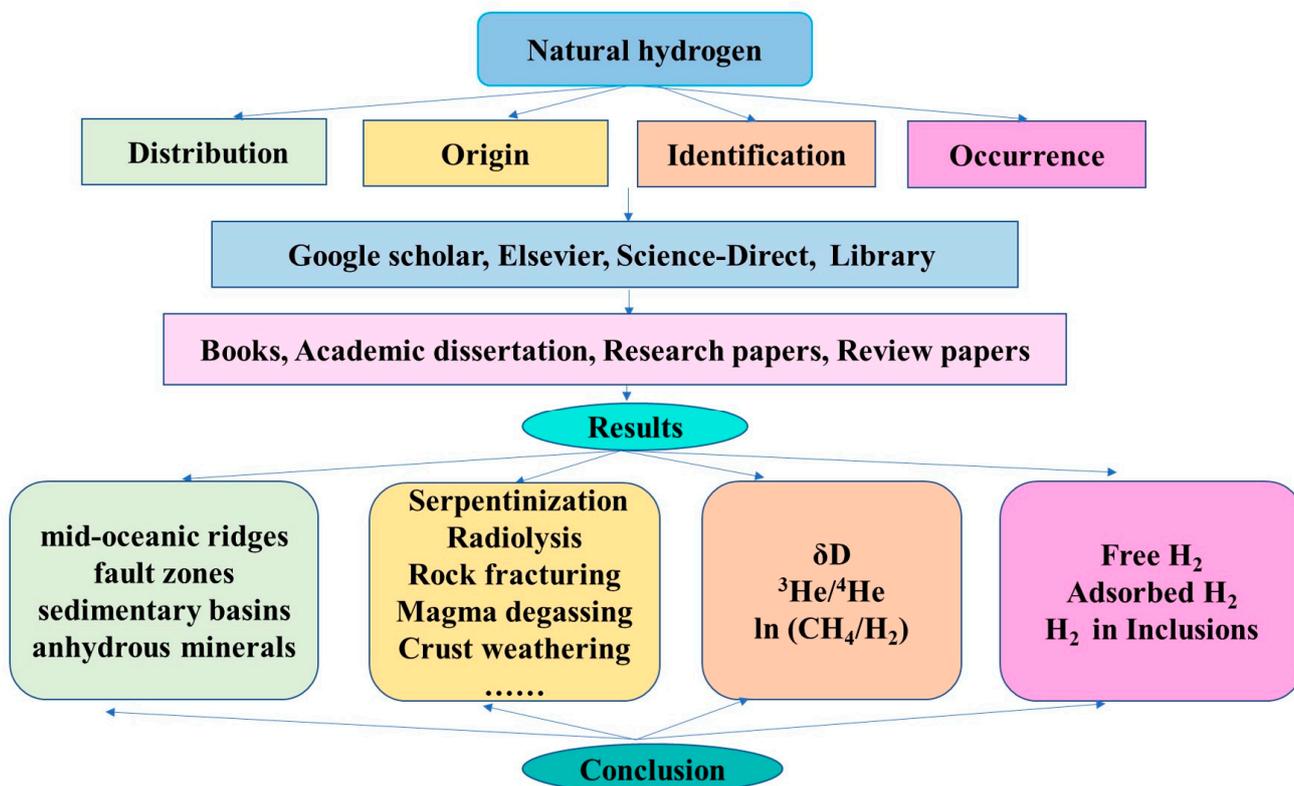


Figure 2. Scheme of the research method.

### 3. Hydrogen Distribution

Abiotic hydrogen (natural hydrogen gas that is not produced by biological activity) has been detected in many subaerial and submarine environments, including oceanic spreading centers, transform faults, passive margins, convergent margins, and intraplate settings. The first reliable evidence of natural hydrogen occurred in the 1970s [31]. The probes used for these discoveries were refined in 1997 by the French Institute for Marine Development, whose undersea robots explored black chimneys 2300 m below the surface on the Atlantic Ridge, south of the Azores. The robots discovered hydrogen-rich hydrothermal fluids while tracing a methane source to locate hydrothermal vents on the ocean floor. Over the years, the French team located seven natural hydrogen escape points along the Atlantic Ridge. American, Russian, and Japanese scientists have made similar discoveries elsewhere [32]. It was determined that hydrogen was generated because of the interactions of water with ultrabasic oceanic rocks. These hydrothermal fluids could be potential triggers for the development of early life. Much of the oceanic lithosphere comprises rocks rich in iron minerals, easily oxidized by seawater. This oxidation process is surprisingly complex because the distribution of iron during hydrothermal alteration involves several Mg–Fe minerals (with solid solutions) whose compositions vary with temperature, protolithogenic composition, and water–rock ratio. Serpentinization peridotite is likely the most abundant hydrothermal cycling rock type in slowly and ultraslowly expanding midocean ridges where magma supply is limited. Hundreds of natural hydrogen seepages associated with circulating hydrothermal fluids through serpentinization, such as the Rainbow hydrother-

mal vent (mid-Atlantic Ridge), have been detected in ultramafic rocks on the seafloor and in ophiolites on continents [32–35].

Abnormal hydrogen concentrations are frequently detected in fault zones. Fault zones are favorable routes for fluid migration in the Earth's crust because many connected and open fractures are located along the fracture plane. Thus, faults may connect deep hydrogen sources to the surface. Some studies have focused on monitoring hydrogen in the soil near crucial geological faults to assess earthquake precursors, such as in Japan [36] and near the San Andreas fault in California [37]. Wakita et al. reported finding hydrogen (up to 3 vol%) in soil gases near the Yamankasi fault (Japan) [38]. This discovery led to subsequent studies confirming that unusually high hydrogen concentrations were discovered in soils covering active faults, especially before earthquakes [38,39]. Data from hundreds of soil gas measurements of hydrogen in Kansas, USA, indicate that fractures are the preferred transit route for hydrogen [23]. McCarthy et al. also determined a positive correlation between fracture and hydrogen content in soil gas research in Kansas [40]. The study of hydrogen in Ukraine and Belarus revealed that the North Pripyat fault zone had the highest hydrogen concentrations [41]. Another study analyzed the results of hydrogen tests in groundwater. The authors reported that the hydrogen concentration of groundwater associated with deep faults was two orders of magnitude higher than that of groundwater in surrounding areas [42].

Researchers have detected hydrogen trapped in shale and coal beds in sedimentary basins. The authors performed pyrolysis experiments on shales and coals to prove the relationship between hydrogen and organic matter [43]. Sedimentary organic matter may be a vital hydrogen source. However, there are few reports on dissociating C–H bonds in sedimentary organic matter to produce native hydrogen. Suzuki et al. investigated the changes in the concentrations such as CO<sub>2</sub>, H<sub>2</sub>, and CH<sub>4</sub> in the gas released during shale and super detritus crushing under different thermal maturation and metamorphism degrees [44]. The isotopic compositions of CH<sub>4</sub> and H<sub>2</sub> in shales and super detritus were tested to understand the interrelationships between gas components. The primary ingredient of the residual gas in shales and metapelites are CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>, which are consistent with the release sequence of sedimentary organic matter [44,45]. The much lower  $\delta^2 H_{H_2}$  values can be interpreted as isotopic fractionation associated with the hydrogen dissociation from carbon–hydrogen bonds. These results indicate that a large amount of hydrogen originates from sedimentary organic matter [44].

Water reacts with fresh mineral surfaces and ferrous oxide to produce hydrogen [46–48], but this reaction is unreliable because it depends on the intermittent opening of cracks to expose the fresh rock surface. More reliable and more extensive hydrogen sources exist in anhydrous minerals of nominally igneous and metamorphic rocks. Standard crustal igneous rocks, such as granite, andesite, and labradorite, were used to conduct crushing experiments used to demonstrate hydrogen diffusion [49]. At least 70 nmol of H<sub>2</sub>/g diffused from coarsely crushed andesite, which is equivalent to 5000 cm<sup>3</sup> of H<sub>2</sub>/m<sup>3</sup> rock at standard pressure and temperature. Single crystal fracture experiments showed that the hydroxyl pair is converted into an H<sub>2</sub> molecule + peroxygenic bond O<sub>3</sub>Si/<sup>OO</sup>SiO<sub>3</sub> using in situ oxidation–reduction (redox) reactions. When the peroxy chain becomes part of the mineral structure, hydrogen molecules diffuse out of the newly fractured mineral surface. The experimental results showed that hydrogen molecules can be obtained from a small amount of water dissolved in the mineral as hydroxyl (OH) or O<sub>3</sub>Si–OH if the mineral crystallizes in an aqueous environment. If this mechanism occurred in a natural environment, the entire column would be a volumetric hydrogen source. Therefore, 4.20 km-deep rock columns could represent a volumetric hydrogen source inside the mineral. Suppose that hydrogen molecules are formed at approximately 400 °C during cooling. Further cooling will reduce their solubility in the solid matrix, establishing a thermodynamic driving force to expel hydrogen molecules from mineral particles. This process should result in long-term hydrogen exhausts. In rock columns, hydrogen diffusion from mineral particles is controlled by the hydrogen partial pressure in intergranular space.

The hydrogen concentration in mineral particles is noticeably higher. The practical effect is that most of hydrogen will be retained within the mineral particles in the presence of an intercrystalline water film. If microorganisms live in intergranular water films [50], hydrogen diffuses out of the mineral particles in response to the partial pressure difference generated when microorganisms consume hydrogen. If the equilibrium is greatly disturbed, e.g., in areas of tectonic activity and intermittent opening of cracks and fissures along faults [46], hydrogen diffuses out more easily [51]. Therefore, rock columns contain large amounts of hydrogen, formed by the redox transformation of hydroxyl pairs in nominally anhydrous minerals. This hydrogen may be used to maintain deep microbial communities.

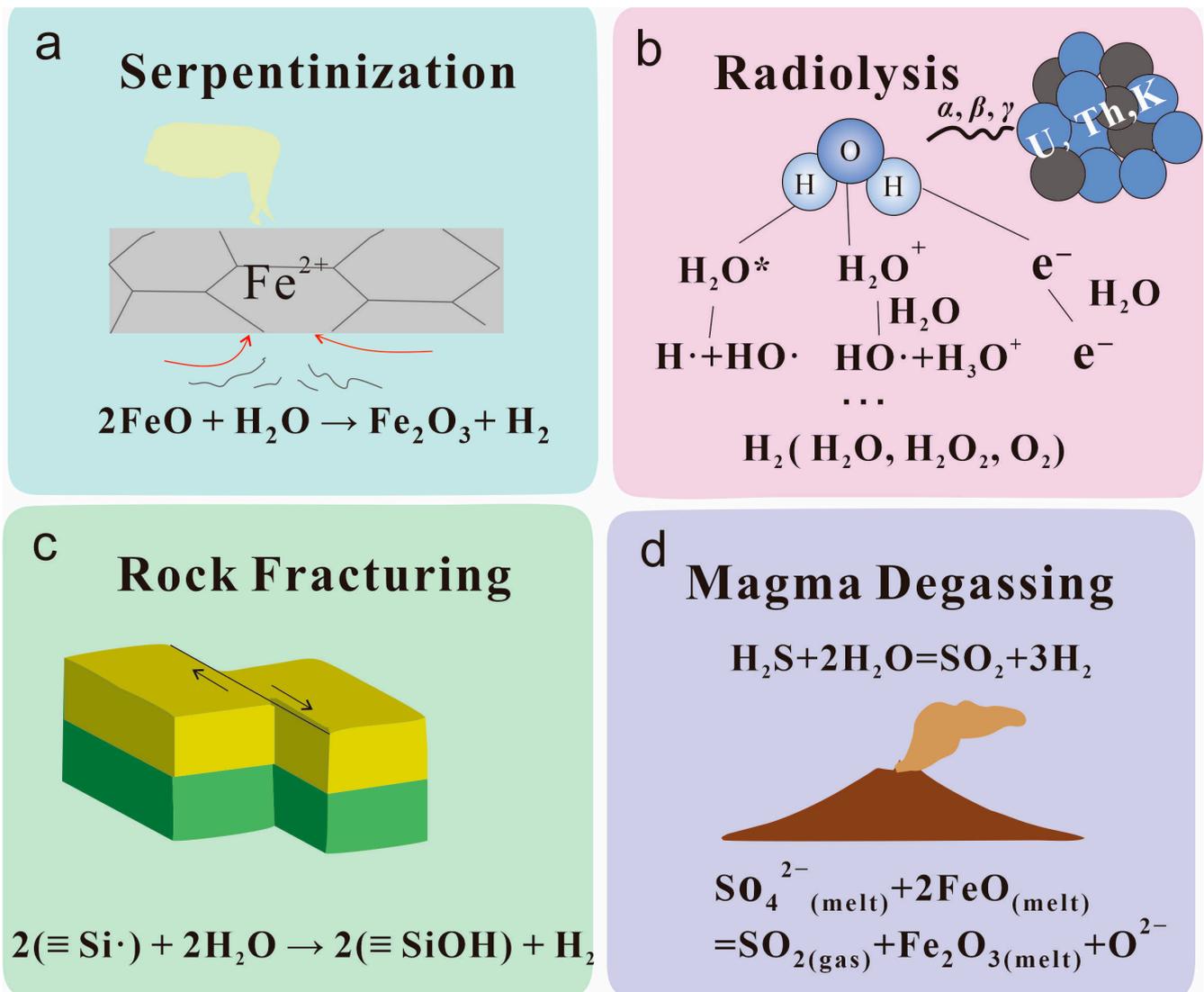
## 4. Origin and Identification of Natural Hydrogen

### 4.1. Origin

Natural hydrogen has been extensively studied in the recent decades, notably after the discovery of hydrogen-rich fluids at midocean ridges. The primary hydrogen sources of these locations include the alteration in Fe(II)-containing rocks [52,53]; the radiolysis of water due to the radioactive decay of uranium, thorium, and potassium; degassed magma; and the reaction of water and surface-free radicals during mechanical fracturing of silica-containing rocks [54].

#### 4.1.1. Serpentinization

Peridotite is the most abundant rock type to accommodate hydrothermal cycling in slowly and ultraslowly expanding midocean ridges where magma supply is limited. Hydrothermal alteration of peridotite (serpentinization) leads to interrelated solution–precipitation, redox reactions, and hydrogen formation (Figure 3a). Olivine and plagioclase are the most abundant peridotite minerals that are unstable under hydrothermal conditions. The general description of this complex process is  $2(\text{FeO})_{\text{rock}} + \text{H}_2\text{O} \rightarrow (\text{Fe}_2\text{O}_3)_{\text{rock}} + \text{H}_2$ , where  $(\text{FeO})_{\text{rock}}$  represents the ferrous iron ( $\text{Fe}^{2+}$ ) component of pyrosilicates.  $(\text{Fe}_2\text{O}_3)_{\text{rock}}$  represents iron ( $\text{Fe}^{3+}$ )-bearing altered minerals [55]. Other iron-bearing secondary minerals contained in serpentine (e.g., chlorite, ferrosilite) play a minor role in hydrogen formation but might become crucial under specific geochemical conditions. Serpentine in midocean ridge environments are typically rich in magnetite, indicating high-temperature serpentinization, extreme reducing conditions [56], and a continuous heat supply of cooled igneous rocks near the ridge axis. When peridotite serpentinizes at temperatures below  $\sim 200$  °C, magnetite is present only in small amounts, as reflected in the lower susceptibility of the altered rocks. However, serpentine without magnetite may be oxidized similarly to its magnetite-rich counterpart because iron can be precipitated as a component of serpentine minerals instead of magnetite. Thus, serpentine is essential for hydrogen formation at low temperatures. Because serpentine action at midocean ridges has been occurring for most of the Earth's history, the mass of hydrogen produced is enormous. Away from the ridge axis, hydrothermal alteration of peridotite can occur at lower temperatures and may happen at slower rates. As serpentine moves further from the axis by seafloor expansion, the remaining ferrous iron undergoes complete oxidation, resulting in additional hydrogen production if the oxygen in the leachate is depleted. Temperate serpentinization systems also exist in other geological settings where peridotite and percolate fluids are in contact, such as magmatic-poor passive margins, pre-arc environments of subduction zones, and ophiolites. The forearc of a subduction zone represents the primary geological environment for the large-scale interaction between water fluid and mantle peridotite. The hydrogen flux in the pre-arc mantle directly depends on the water flux in the subducted plate. Suppose that only 10% of the water discharged from the plate at the pre-arc depth is used for serpentinized peridotites. In that case, the Mariana forearc alone could constitute up to 25% of the global hydrogen production at the midocean ridge. After subduction, serpentinite is widely detected in greenstone belts, ophiolites, and metamorphic rocks.



**Figure 3.** Diagram showing the main sources of hydrogen (modified from [56]). (a) Serpentinization of rocks generates hydrogen if water is reduced during the oxidation of ferrous to ferric iron. (b) Radiolysis produces hydrogen during splitting of water through radioactive decay. (c) Rock fracturing generates hydrogen on the wet surfaces of active faults. (d) Volcanoes emit hydrogen when  $\text{SO}_2$  is degassed at low pressure.

#### 4.1.2. Radiolysis

The radiation released by decaying radioactive elements in marine rocks, such as uranium ( $^{238}\text{U}$  and  $^{235}\text{U}$ ), thorium ( $^{232}\text{Th}$ ), and potassium ( $^{40}\text{K}$ ), can produce  $\alpha$ ,  $\beta$ , and  $\gamma$  radiation, excite and ionize water, producing free radicals leading to hydrogen (Figure 3b). Thus, the H–O bond in water is decomposed, and hydrogen and hydroxyl radicals are produced. Then, two hydrogen radicals react to form hydrogen  $2\text{H}\cdot \rightarrow \text{H}_2$  [57,58]. The production of hydrogen by radiolysis requires simple geochemical components (water and radionuclides) common on Earth and elsewhere in the solar system. Furthermore, radiolysis occurs under all temperature and pressure conditions where water is stable, even if water takes the form of ice, steam, or hydrated salts.  $\text{H}_2\text{O}$  radiolysis differs from other forms of abiotic hydrogen production because the decomposition of neutrally charged  $\text{H}_2\text{O}$  molecules yields complementary soluble oxidants (e.g.,  $\text{H}_2\text{O}_2$ ,  $\text{O}_2$ , and  $\text{O}^-$ ) and reducing agents ( $\text{H}_2$ ). This is in contrast to serpentine, where the oxidation products precipitate to minerals such as magnetite, iron olivine, and radiolite. Radioactive hydrogen generation

also occurs in the oceanic basalt crust and seafloor sediments. Therefore, the process of hydrogen generation is common in the crust. However, the radiation decomposition of hydrogen depends on the number of radioactive nuclide concentrations, the fracture pore space availability of H<sub>2</sub>O, and the fluid in the dissolved concentrations of anions and cations such as salt. The concentration of radionuclides in the continental crust is higher than that in the basaltic oceanic crust. Therefore, hydrogen production will be higher in the continental crust relative to the oceanic crust for the same porosity. When H<sub>2</sub>O radiolysis occurs in sediments or crystalline rocks, water is primarily confined to pore and fracture spaces. Thus, rock permeability and porosity are crucial for estimating hydrogen production from crustal regions with characteristic radionuclide concentrations [59,60]. The radiolysis of hydrated salts also produces hydrogen. Specific minerals (such as zeolites) also increase hydrogen produced by radiolysis.

#### 4.1.3. Rock Fracturing

Rock rupture breaks chemical bonds and generates free radicals that react with water to form hydrogen:  $2(\equiv \text{Si}\cdot) + 2\text{H}_2\text{O} \rightarrow 2(\equiv \text{SiOH}) + \text{H}_2$  (Figure 3c) [47,61]. The unusually high concentrations of hydrogen in soil gases associated with tectonic faults are attributed to fault movement during rock crushing and its associated free radical formation [39]. Mechanical forces dissociate covalent Si–O bonds in silicate minerals to produce surface-free radicals  $\equiv \text{Si}\cdot$  and  $\equiv \text{SiO}\cdot$  (homolytic) and charged surface radicals  $\equiv \text{Si}^+$  and  $-\text{O} - \text{Si} \equiv$  (hetero). Once these surfaces are speciated, they either recombine to form siloxane bonds (Si–O–Si) or react with water via  $\text{Si}\cdot + \text{H}_2\text{O} \rightarrow \text{SiOH} + \text{H}\cdot$ , which releases hydrogen as a by-product as follows:  $\text{H}\cdot + \text{H}\cdot \rightarrow \text{H}_2$ . This process, known as mechanical or medical hydrogen generation, may be widespread in fault zones. Faults are standard geological features in orogenic belts, subduction zones, continental rifts, passive margins, spreading centers, transition faults, and fault zones. Hydrogen is generated when these faults are active. In creeping faults, hydrogen generation may continue, whereas in locked faults, hydrogen generation might be episodic and limited to slip events. Mechanical and medical hydrogen generation is not limited to tectonic faults. It can occur anywhere silicate rocks are crushed. A good example is subglacial bedrock crushing, where hydrogen generation can support microbial ecosystems near the freezing point of water, a process that may even have sustained life during global glaciation [62]. Other processes that cause rock fragmentation include freezing wedges (freeze–thaw), salt wedges, thermal shrinkage during cooling or expansion during heating, rock wear (sandblasting and erosion in rivers and surf zones), gravity impacts (landslides or rock falls), meteorite impacts, and reaction-driven fractures. However, the effectiveness of these processes in generating hydrogen is unclear.

#### 4.1.4. Magma Degassing

Hydrogen also exists in carbon–oxygen–hydrogen (COH) magma systems:  $2\text{H}_2\text{O} + \text{CH}_4 = 4\text{H}_2 + \text{CO}_2$  (Figure 3d). At magmatic temperatures (~1200 °C), this equilibrium shifts strongly to the right, indicating that hydrogen may be a component of the magma [63]. Burst rocks are midocean ridge basalts (MORBs) with unusually high gas contents and are regarded as lava without any history of degassing before an eruption [64,65]. Early Mid-Atlantic Ridge (MAR) samples had fragments that popped on the deck of the ship after their extraction by dredging, before any analysis could be performed. The fragments contained 0.881 mL/g of dissolved gas, of which 26.7% was hydrogen [64].

#### 4.1.5. Crust Weathering

As seawater cools and ages, the oceanic crust changes, and the following reactions occur at cooler temperatures (<250 °C):  $2(\text{FeO})_{\text{rock}} + 4\text{H}_2\text{O} \rightarrow 2\text{Fe}(\text{OH})_3 + \text{H}_2$ ,  $2(\text{FeO})_{\text{rock}} + 2\text{H}_2\text{O} \rightarrow 2\text{FeOOH} + \text{H}_2$ , and  $2(\text{FeO})_{\text{rock}} + \text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2$  [66]. Samples from deep-sea and offshore drilling projects indicate that crustal weathering occurs within the ejecta and continues until the age of crust reaches ~10 to 20 Ma [66]. Alteration is typically limited to fractures and fracture margins, and the middle and lower oceanic crust is less exposed

to weathering. For example, the gabbros samples recovered from active tectonic scarps of rapidly expanding ridges are young and typically have oxidation rates of less than 10%. Dredge samples from the more slowly expanding ridges and outcrops of the middle and lower ocean crust are older and more oxidized (50%) [67,68].

#### 4.1.6. High-Temperature Basalt Alteration

The alteration of oceanic crust by seawater during high temperatures (350–400 °C) changes most ferrous silicates to ferrous minerals. However, a small fraction is converted into iron-bearing minerals to form hydrogen via  $3(\text{Fe}_2\text{SiO}_4)_{\text{rock}} + 2\text{H}_2\text{O} \rightarrow 3\text{SiO}_2 + 2\text{Fe}_3\text{O}_4 + 2\text{H}_2$  [69]. Although the depth at which hydrothermal fluids penetrate the oceanic crust is unknown, limited sampling indicates that the upper crust changes while the lower crust remains unchanged [68]. Pasquet et al. detected natural hydrogen gas in the Rift Valley of Djibouti, East Africa [70]. They performed linear sampling and collected altered/fresh basalt and gas from the area in situ. In their study locale, only small amounts of hydrogen exist at the surface. Their data suggest that natural hydrogen is transported through iron minerals in basalt and deep fluids at high temperatures (approximately 270 °C) in the Earth's crust in the Rift region.

#### 4.1.7. Lava–Seawater Interaction

The interaction of seawater and extruded lava produces hydrogen via  $2(\text{FeO})_{\text{magma}} + (\text{H}_2\text{O})_{\text{seawater}} \rightarrow (\text{Fe}_2\text{O}_3)_{\text{rock}} + \text{H}_2$  [71,72]. Determining the extent of the lava–seawater interaction is challenging, but seawater interacts extensively with the jet surface, as evidenced by the fragmented and hardened crust.

#### 4.1.8. Crystallization

In the late crystallization process, hydrogen will be generated when the dissolved water in the magma oxidizes ferrous iron,  $3(\text{FeO})_{\text{magma}} + (\text{H}_2\text{O})_{\text{magma}} \rightarrow (\text{FeO} \cdot \text{Fe}_2\text{O}_3)_{\text{rock}} + \text{H}_2$ .

#### 4.1.9. Pyrite Formation

During the inorganic formation of pyrite and  $\text{H}_2$ , the stoichiometric yield of  $\text{H}_2$  has been quantified [73,74]. This reaction could occur in the characteristic high-temperature black smoke mouth of MOR. The pyrite contained in seafloor and chimney deposits primarily precipitate from hydrothermal fluids, with chemical reactions  $\text{Fe}^{2+} + 2\text{H}_2\text{S} \rightarrow \text{FeS}_2 + \text{H}_2 + 2\text{H}^+$  and  $\text{Cu}^+ + \text{Fe}^{2+} + 2\text{H}_2\text{S} \rightarrow \text{CuFeS}_2 + 0.5\text{H}_2 + 3\text{H}^+$  [75].

### 4.2. Identification

In studies on hydrogen genesis, the component content and isotopic composition characteristics of other gases coproduced with  $\text{H}_2$  (such as  $\text{CH}_4$  and He) have been primarily used for comprehensive studies [76–78]. Since the early 1980s, hydrogen gas has been located in Kansas wells near the Midcontinent Rift System [79,80]. Two wells (CFA Oil Scott #1 and CFA Oil Heins #1) yielded 29–37 mole% hydrogen during the period of 1982–1985. A new well drilled in 2008 (CFA Oil Sue Duroche #2) sampled gas and brine from a Pennsylvanian aquifer. The well was tested by Donald C. Clark and Guélard in 2017. The latter analyzed the molecular and isotopic compositions of the major gases and noble gases, providing new insight into the origins of hydrogen [81].

Newell et al. reported gas found in the WTW Operating Wilson #1 well in Forest City Basin, northeastern Kansas [80]. The chemical composition of the gas was similar to the Scott #1 and Heins #1 wells. The chemical composition is 17.2%  $\text{H}_2$ , 34.6%  $\text{N}_2$ , 45.1%  $\text{CH}_4$  and a small amount of helium and argon. The Damien distinction of hydrogen (mean  $-789\text{‰}$ ) was comparable to the low  $\delta\text{D}$  values at the CET #1 and Scott #1 wells. The  $\text{CH}_4$  characteristics (mean  $\delta^{13}\text{C} -57\text{‰}$ ,  $\delta\text{D} 362\text{‰}$ ) were biogenic. The R/Ra ( $^3\text{He}/^4\text{He}_{\text{sample}}/^3\text{He}/^4\text{He}_{\text{atmosphere}}$ ) of 0.035 shows that hydrogen originated predominantly from continental crust rocks [80]. These results are insufficient to draw definitive conclusions on the sources of Kansas hydrogen, although possible origins have been dis-

cussed [52,81,82]. These authors concluded that the basic composition of these gases is similar to that discovered in ophiolitic environments, that the presence of a base of ultramafic rock complexes suggests that hydrogen may have been produced by oxidation of Fe(II) over a long period of time. This environment may be similar to other areas where continental serpentinization may occur. Kimberlite contains serpentine structure and rich magnetite deposits that may also provide Fe(II) [83,84].

The  $\delta D$  of  $H_2$  is modern in the Sue Duroche #2 well, ranging from  $-717\text{‰}$  to  $-799\text{‰}$ , with an average value of  $-760\text{‰}$ . The average values for Scott #1 and Heins #1 are  $-793\text{‰}$  and  $-781\text{‰}$ , respectively. The  $\delta D$  values of  $H_2$  in the Heins #1 and Scott #1, measured in 2008 [33,34], are similar to those measured in 1987 [52]. Based on the  $^3\text{He}/^4\text{He}$  ratio, the  $^3\text{He}$  enrichment compared to classical crustal values suggested that mantle input may contribute significantly to the accumulation of hydrogen bearing in Kansas [77].

However, because the He content in some hydrogen-containing natural gas is very low, it is challenging to determine its content and isotopic composition, making it challenging to determine hydrogen genesis. The methane, hydrogen, and hydrogen isotope contents of natural gas in geological bodies can be accurately measured. Thus, the isotopic composition of hydrogen in different geological bodies has also been systematically analyzed [33,76,83–86].

Meng et al. proposed a method to identify hydrogen genesis using the relationship between  $H_2$ – $CH_4$  and hydrogen isotopic compositions [87]. If hydrogen is primarily of the crust origin, the rocks and water involved in the water–rock reaction are all originating from the crust, which might be caused by the water’s energy decomposition by radioactive substances in sedimentary rocks. The primary geochemical characteristics of the crustal hydrogen are that the hydrogen isotopic composition is greater than  $-700\text{‰}$ , and the value of  $\ln(CH_4/H_2)$  is less than  $-8$ . The mantle-derived hydrogen, e.g., the minerals involved in the reaction with water and rock, primarily originates from deep-source minerals containing  $Fe^{2+}$ , and water originates from deep geological conditions. The primary geochemical characteristics of the mantle-derived hydrogen are that the hydrogen isotopic composition is less than  $-700\text{‰}$  and the value of  $\ln(CH_4/H_2)$  is greater than  $-4$ . The residual hydrogen gas after  $CO_2$ -rich fluid oxidation on the surface has less content, but the difference in methane content before and after oxidation is insignificant. However, surface factors can influence the hydrogen gas, and the primary geochemical characteristics are that the  $\delta D$  value of the hydrogen isotopic composition is greater than  $-700\text{‰}$  and  $\ln(CH_4/H_2)$  is greater than  $-8$ . After the deep-source hydrogen-rich fluid is oxidized on the surface, hydrogen retains the characteristics of the deep source. However, after some hydrogen is oxidized, the methane content decreases and the  $\ln(CH_4/H_2)$  value decreases. The  $\delta D$  value of the remaining hydrogen is less than  $-700\text{‰}$ , and  $\ln(CH_4/H_2)$  is less than  $-4$  [87].

## 5. Hydrogen Occurrence

### 5.1. Free Hydrogen

“Free hydrogen” refers to hydrogen that migrates freely through the pores or fissures of rocks (or strata). It is one of the primary occurrences of natural hydrogen. Hyperalkaline springs in ophiolite in Voltri Massif (Italy) outgas free hydrogen. Persistent burning-gas seeps were first identified near Antalya, Turkey, and studies have shown that these active vents have been present for at least 2500 years [29]. The vent gas contains 7.5–11.3% hydrogen. The ancient city of Olympos near Antalya, southwest Turkey, is named after Mount Olympos and dates to the 2nd century BC, during the Hellenistic period. The Chimaera gas seeping near Antalya has been active for thousands of years and is the source of the first Olympic fire in the Hellenistic period [34,88]. Deep and pressurized gas accumulations are necessary to sustain the Chimaera gas flow for millennia, and they could have been charged by an active inorganic source [88]. One study showed that wells in northeastern Kansas had yielded hydrogen-rich gas for several years, determining that a high proportion of hydrogen existed in free gas soon after the drilling of the Sue Duroche #2 well [89].

A leak similar to that in Antalya was discovered in the Philippines approximately two centuries ago. The gas combustion produced a flame continuing to this day, and the hydrogen content remains stable, with a measured content of 41.4–44.5% [34]. Researchers have also detected natural hydrogen in nearly 30 countries and across different geological environments, including in ophiolite, Precambrian rocks, igneous rocks, volcanic gases, geysers, hot springs, tubular kimberlite rock masses, ore bodies, oil and gas fields, coal basins, sedimentary rocks, and salt deposits (Table 1). The measured free hydrogen content varies for the same geological environments but different generation areas and detection depths. The lowest discovered hydrogen content was only a single-digit value, but the highest hydrogen content can exceed 90% [88–94]

**Table 1.** The occurrence of different types of hydrogen.

Free gas	Oil and gas fields Ore bodies Kimberlite pipes Volcanic gas Hot springs Faults
Adsorbed	Sedimentary basins
In inclusions	In ultrabasic rocks In precambrian rocks In igneous rocks In volcanic rocks
Dissolve in water	Hydrocarbon fields Ground water In waters from fractured Precambrian Shield rocks

Circular and elliptical depressions (fairy circles) caused by natural hydrogen escaping to the surface (Figure 4) have been located in North Pass Basin, St. Francis Basin, Western Australia, North Carolina, Central Russia, Southern Gironde, US, Brazil, France, and Mali [95–100].

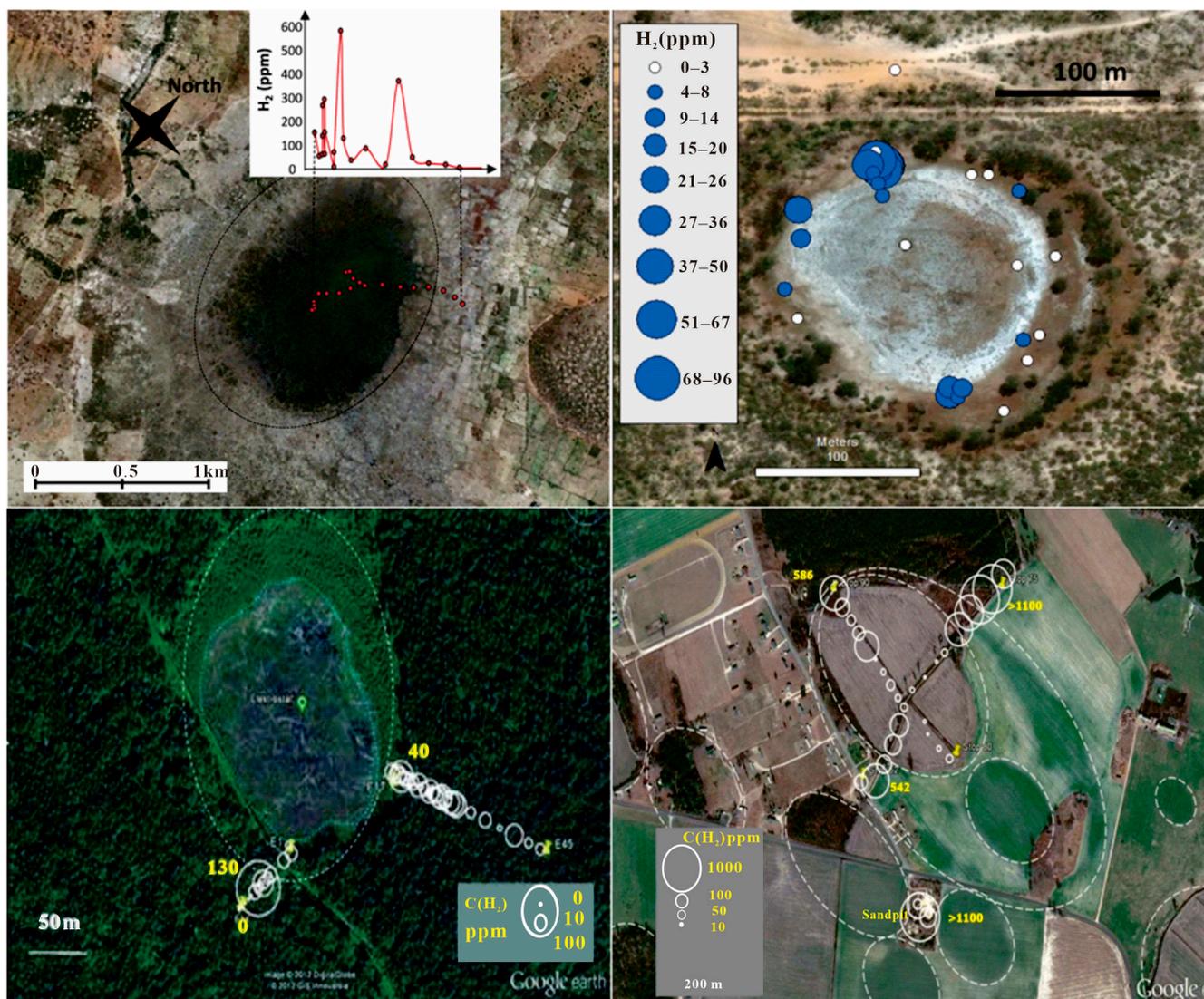
Free hydrogen accumulates and forms natural hydrogen reservoirs. A well that was drilled north of Bamako revealed 98% pure hydrogen in the Tambaoura Basin, southwest of the Taoudenni Great Basin. Volcanoes, geothermal springs, and deep faults are typical hydrogen sources. Shallow seismic surveys show flower-like structures in dolomite caused by strike–slip tectonic deformation. Hydrogen gas is thought to be produced in these flower-like structures [20].

### 5.2. Adsorbed Hydrogen

Natural hydrogen can be trapped inside various rock types as inclusions or adsorption product. Truche et al. determined that the clay rocks of the Cigar Lake uranium deposit in northern Saskatchewan, Canada, were dominated by illite, chlorite, and kaolinite and contained 500 ppm hydrogen. During the 1.4 Ga lifetime of the Cigar Lake uranium deposit, 4–17% of the hydrogen produced by water radiolysis was sequestered in the surrounding clay alteration halo, with chlorite being the primary mineral adsorbing hydrogen [101].

A recent study reported mapping hydrogen and other gases at multiple (165) sites in Ukraine, primarily in oil and gas fields, coal mines, celestial bodies, and offshore shelf areas [29,102]. The flow of hydrogen through aqueous porous media was reduced by a factor of 10 compared to that through pure water. The obstruction of hydrogen diffusion by saturated water sediments could be related to the van der Waals radius (the distance at which van der Waals forces are effective). The study’s authors note that molecular hydrogen and hexadecane inert gases have similar radii. Therefore, the migration characteristics of these gases in porous media are similar. Traps and aquifers might impede hydrogen

migration [34]. However, the van der Waals radius of hydrogen molecules varies with pressure, the presence of other molecules, and other factors [103].



**Figure 4.** Fairy circles from Mali, Australia, Russia and the United States. (**Upper Left**) A large accumulation of natural hydrogen in Bourakebouougou (Mali); (**Upper Right**) natural hydrogen seeps identified in the North Perth Basin, Western Australia; (**Lower Left**) natural molecular hydrogen seepage associated with Surficial, rounded depressions on the European Craton in Russia; (**Lower Right**) evidence for natural molecular hydrogen seepage associated with Carolina bays (surficial, ovoid depressions on the Atlantic Coastal Plain, in the USA).

### 5.3. Hydrogen in Inclusions

Natural fluid inclusions in minerals (commonly in quartz) provide unique data on drainage systems. Fluid inclusions containing hydrogen have been recognized in numerous geological environments. Hydrogen has been found in inclusions of samples from ultrabasic, Precambrian, igneous, and volcanic rocks tubular kimberlite, ore bodies, coal basins, sedimentary or metamorphic rocks, and rock salt deposits [96,104,105]. Analysis of samples has shown that the hydrogen concentrations in the inclusions are not always uniform, ranging from 0.2% to 100%. Smith et al. probed mineral inclusions from large diamonds and detected abundant slivers of iron metal surrounded by reducing gases [19]. This indicates that the large diamonds grew from liquid metal in the Earth's mantle. These inclusions provide direct evidence of a long-suspected metal precipitation reaction requiring a more

reductive mantle. In 13 samples, hydrogen was also detected, accompanying intense CH<sub>4</sub> signals. Furthermore, the study of Raman maps showed CH<sub>4</sub> and H<sub>2</sub> concentrated at the inclusion nucleus [19]. A study by Klein detected CH<sub>4</sub> and H<sub>2</sub> fluid inclusions trapped in a calcite crystal from ophicarbonates in the Lanzo peridotite massif (Italian Alps) [106].

Minerals in the rift zone contain gas inclusions with a high hydrogen content. In the oceanic rift, the average hydrogen concentration found in inclusions was 21.4%, and more hydrogen detections were reported for inclusions in rocks of Precambrian age [107].

## 6. Conclusions

Natural hydrogen exploration is in its infancy, similar to oil and gas exploration in the late 19th century [19]. Unlike natural gases, geological hydrogen is a carbon-free, sustainable resource continuously generated underground. Natural hydrogen can be classified as a renewable energy source and has been referred to as the clean energy of the future [25,93]. Its inexhaustible and environmentally friendly characteristics dictate that it should garner more attention in the coming years.

Hydrogen also has an established role in maintaining long-term biogeochemical reactions [59,62]. As the primary chemical energy source for microbial and animal symbiosis, it may, alongside hydrogen sulfide and methane, strongly influence the distribution, abundance, and diversity of subsurface life because it occurs among compounds that fuel organisms at hydrothermal vents [50,108–110]. At these locations, chemicals such as hydrogen, methane, and hydrogen sulfide are released. Hydrogen is more abundant than methane or hydrogen sulfide. It stores more energy and can be used for microbial metabolism. Hydrogen is also central to many hypotheses regarding the origin and evolution of life. Therefore, better understanding of hydrogen in the lithosphere could help in advancing the search for extraterrestrial life. At present, most reviews on hydrogen focus on the preparation and storage of hydrogen, while there are relatively few reviews on natural hydrogen, and the limited articles mainly focus on the generation and distribution of natural hydrogen. Here, we have offered a preliminary study on the genesis of natural hydrogen. Natural hydrogen has been discovered in many geological environments including oceanic spreading centers, transform faults, passive margins, convergent margins, and intraplate settings. The primary sources of natural hydrogen include the radiolysis of water, serpentinization, degassed magma, and the reaction of water and surface-free radicals during the mechanical fracturing of silica-containing rocks. In our paper, a relatively complete review of natural hydrogen is formed from the distribution of natural hydrogen, the generation and identification of chemical indexes of natural hydrogen, and then the occurrence of natural hydrogen. Natural hydrogen occurs in free gas; it is adsorbed or trapped in inclusions, and dissolved in groundwater.

In the future, the research of natural hydrogen should focus more on the occurrence state of natural hydrogen (natural hydrogen exists in different states under different temperature and pressure conditions), the underground migration mode (direction, force and resistance of migration), and the accumulation mode of hydrogen. Solving these problems will help in guiding the subsequent exploration of hydrogen reservoirs.

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### Nomenclature

CO	Carbon monoxide
CO <sub>2</sub>	Carbon dioxide
H <sub>2</sub>	Hydrogen
H <sub>2</sub> S	Hydrogen sulfide
CH <sub>4</sub>	Methane
FeO	Ferrous oxide
Fe <sub>2</sub> O <sub>3</sub>	Ferric oxide
FeOOH	Hydroxyl oxidize iron
Fe <sub>3</sub> O <sub>4</sub>	Ferroferric oxide
FeS <sub>2</sub>	Ferrous disulfide
N <sub>2</sub>	Nitrogen
COH	Carbon–oxygen–hydrogen
MORBs	Midocean ridge basalts
MAR	Mid-Atlantic Ridge
H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide
O <sub>2</sub>	Oxygen
SiO <sub>2</sub>	Silicon dioxide

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