Contents lists available at ScienceDirect



Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser



# Natural hydrogen in the energy transition: Fundamentals, promise, and enigmas

Rubén Blay-Roger<sup>a</sup>, Wolfgang Bach<sup>b,c</sup>, Luis F. Bobadilla<sup>a</sup>, Tomas Ramirez Reina<sup>a,d</sup>, José A. Odriozola<sup>a,d</sup>, Ricardo Amils<sup>e,f</sup>, Vincent Blay<sup>g,\*</sup>

<sup>a</sup> Department of Inorganic Chemistry & Materials Science Institute of Seville, Mixed Center CSIC-University of Seville, Av. Américo Vespucio 49, 41092, Seville, Spain

<sup>b</sup> MARUM Center for Marine Environmental Sciences, University of Bremen, Bremen, Germany

<sup>c</sup> Faculty of Geoscience, University of Bremen, Bremen, Germany

<sup>d</sup> Department of Chemical and Process Engineering, University of Surrey, Guildford, GU2 7XH, United Kingdom

e Departamento de Biología Molecular, Facultad de Ciencias, Universidad Autónoma de Madrid, UAM, Cantoblanco, 28049, Madrid, Spain

<sup>f</sup> Centro de Biología Molecular Severo Ochoa, CSIC-UAM, 28049, Madrid, Spain

<sup>g</sup> Department of Microbiology and Environmental Toxicology, University of California Santa Cruz, Santa Cruz, CA, 95064, United States

ARTICLE INFO

Keywords:

Hvdrogen

Gold hydrogen

Orange hydrogen

Serpentinization

Geoengineering

Microorganisms

Hvdrothermal

## ABSTRACT

Beyond its role as an energy vector, a growing number of natural hydrogen sources and reservoirs are being discovered all over the globe, which could represent a clean energy source. Although the hydrogen amounts in reservoirs are uncertain, they could be vast, and they could help decarbonize energy-intensive economic sectors and facilitate the energy transition. Natural hydrogen is mainly produced through a geochemical process known as serpentinization, which involves the reaction of water with low-silica, ferrous minerals. In favorable locations, the hydrogen produced can become trapped by impermeable rocks on its way to the atmosphere, forming a reservoir. The safe exploitation of numerous natural hydrogen reservoirs seems feasible with current technology, and several demonstration plants are being commissioned. Natural hydrogen may show variable composition and require custom separation, purification, storage, and distribution facilities, depending on the location and intended use. By investing in research, in the mid-term, more hydrogen sources could become exploitable and geochemical processes could be artificially stimulated in new locations. In the long term, it may be possible to leverage or engineer the interplay between microorganisms and geological substrates to obtain hydrogen and other chemicals in a sustainable manner.

## 1. Hydrogen in the energy transition

As the world transitions beyond fossil fuels towards a more sustainable and low-carbon future, hydrogen is becoming a key player in the energy mix. Hydrogen is highly versatile, able to power transportation, industry, and buildings, and can help reduce greenhouse gas emissions. While hydrogen has been utilized in industrial processes and fuel cells for decades, as shown in Fig. 1A, recent technological advances and the growing menace of climate change have heightened the interest in hydrogen for decarbonizing the energy system [1,2].

Fig. 1B depicts the demand for hydrogen since 1985. The demand in 2021 stood at 94 Mt (million metric tons), and it is projected to double by 2030, reaching 180 Mt [3,4]. Currently, around 75 Mtpy (million metric tons per year) of pure hydrogen and 45 Mtpy of hydrogen blends,

such as syngas, are produced to meet the demand [2,3]. Fig. 1A depicts the various sources of hydrogen production in 2021, highlighting that most hydrogen production comes from fossil fuel reforming, with only a small portion derived from alternative sources like electrolysis. At present, the cost difference between these processes is represented in Fig. 1D, with hydrogen produced from fossil fuels (grey hydrogen) costing \$1.2 per kilogram compared to \$4 per kilogram through electrolysis (green hydrogen) [10,11]. Over time, however, it is expected that the costs associated with electrolyzers will decrease, that solar electricity will become cheaper, and that raw material costs in fossil fuel reforming will increase (Fig. 1E), favoring electrolysis. Apart from cost, the carbon footprint associated with fossil fuel reforming, even with carbon capture and utilization technologies (CCUs), is considerably higher than that of electrolysis, which makes electrolysis a more

https://doi.org/10.1016/j.rser.2023.113888

Received 18 August 2023; Received in revised form 2 October 2023; Accepted 10 October 2023 Available online 21 October 2023 1364-0321/@ 2023 The Authors Published by Elsevier Ltd. This is an open access article under the CC B3

1364-0321/© 2023 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

<sup>\*</sup> Corresponding author. *E-mail address:* vroger@ucsc.edu (V. Blay).

Recently, a third approach has emerged in the field: natural hydrogen. This refers to naturally occurring molecular hydrogen that forms and accumulates on Earth. For decades it went unnoticed, as it was assumed it would be formed in too small amounts or diffuse away too quickly. Moreover, analytical methods used in field studies were often not suited to detect this gas. Today, however, it is gaining popularity among scientists, entrepreneurs, and ecologists. Current estimations suggest that approximately 20 Mtpy of natural hydrogen are escaping from the surface into the atmosphere [12]. Most of this hydrogen travels up to the ionosphere and ends up escaping into space [13-15]. The genesis of natural hydrogen is primarily attributed to a geochemical process known as serpentinization (see section 2). It was long believed that natural hydrogen deposits could not be formed, and, to date, no large-scale exploitation of geological hydrogen has been carried out. However, this view has changed with studies conducted in geological formations where hydrogen release occurs continuously [12, 16-19]. These studies have confirmed the presence of vast geological formations where hydrogen accumulated over time. Moreover, the pioneering exploitation carried out by Hydroma in Mali (West Africa) has demonstrated the potential for industrial-scale exploitation of this resource. Consequently, it is reasonable to think that substantial amounts of already-produced hydrogen could be trapped throughout the globe.

Besides natural hydrogen, another hydrogen source produced from geological substrates is being considered: orange hydrogen. Natural hydrogen (also referred to as gold, white, or native hydrogen) is hydrogen produced deep within the Earth that becomes trapped by impermeable barriers on its way to the atmosphere, similar to the way petroleum was stored over time. On the other hand, orange hydrogen results from the anthropogenic stimulation of the same geochemical processes that produce natural hydrogen. From an economic standpoint, the supply of raw material (water) occurs through water infiltrating or being redirected from the surface or from bodies of water. The required energy is naturally provided by the environment as geothermal energy. These factors are particularly important, since the main economic



**Fig. 1. A)** Hydrogen demand and production in 2021 and 2030 [2,3]. **B)** Evolution of hydrogen demand from 1990 to 2030 [4]. Grey, green, and red colors represent past, current, and future estimates, respectively. **C)** Carbon footprint for H<sub>2</sub> production processes (2021) [5–7,8]. **D)** Global projected hydrogen production cost (2060) [9]. Note that the data originates from a company with interests in the sector. **E)** Evolution of key cost drivers of electrolysis and fossil fuel reforming [5–7].

challenges for current hydrogen production processes are the supply of raw materials (in fossil fuel reforming) and the energy costs (in electrolysis). Although more studies assessing the carbon footprint of natural and orange hydrogen are needed, their carbon footprint can be lower than that of current approaches (Fig. 1C) [8].

This document aims to introduce natural hydrogen and orange hydrogen in an accessible manner to a broad audience. Section 2 presents the topic of hydrogen formation deep within the Earth, with a specific focus on one of the primary abiotic reactions, known as serpentinization. Additionally, biological processes and their potential contributions to hydrogen production are mentioned. Section 3 takes a practical stance by considering various known deposits, methods of detection, and profiling industrial players in the field. In Section 4, the extraction, storage, and distribution process for natural hydrogen is surveyed, including specific considerations on orange hydrogen. Lastly, we share some perspectives on the future of this field.

### 2. Formation of hydrogen in nature

The formation of natural hydrogen is showed in Fig. 2 and can involve multiple processes, including biological processes (e.g., decomposition of organic matter, fermentative processes) and abiotic processes (e.g., radiolysis, direct H<sub>2</sub>O reduction), with serpentinization being the most significant abiotic process [20]. Serpentinization occurs when water interacts with ultramafic rocks [21], which are low-silica rocks rich in reduced metals. They primarily consist of iron and magnesium minerals, with olivine being the main constituent. Olivine is a solid solution of fayalite (Fe<sub>2</sub>SiO<sub>4</sub>) and forsterite (MgSiO<sub>4</sub>). Other components may also be present, such as pyroxene.

Ultramafic rocks make up the Earth's upper mantle, the top section of which is part of the lithosphere. It underlies the more silica-rich crust, and it fractures when mechanically stressed. Serpentinization reactions take place when water infiltrates the Earth's lithospheric mantle along these fractures. These processes are common along plate boundaries, such as mid-ocean ridges, transform faults, and subduction zones. Ultramafic rocks are also common in ophiolite complexes and in fold belts that represent sutures between collided tectonic plates. When waterexposed ultramafic rocks undergo serpentinization, hydrogen is produced as a byproduct [21].

The serpentinization of olivine, shown in Fig. 3, involves two main reactions: hydration and oxidation. The hydration of olivine produces new minerals, such as serpentine  $(Mg_3Si_2O_5(OH)_4)$  and brucite  $(Mg(OH)_2)$ . Serpentine can incorporate only small amounts of ferrous iron and most of it is oxidized by water to form magnetite  $(Fe_3O_4)$ , producing H<sub>2</sub> in the process. Ferrous brucite may be an intermediate phase in the process [22–24]. Depending on the bedrock composition, the serpentinization process can be much more complex, as the presence of heteroatoms (e.g., Ni and C) introduces additional phases and reactions (e.g., formation of Ni<sub>3</sub>Fe and Fe<sub>5</sub>C<sub>2</sub>) [25].

A critical property of ultramafic rocks that enables substantial H<sub>2</sub> production is their low silica content, which results in the formation of alteration minerals that largely exclude Fe<sup>2+</sup> from their structure, like serpentine and brucite. This enables oxidation by water and the formation of H<sub>2</sub> (Schikorr reaction). In contrast, silica-rich rocks like basalts tend to sequester a greater proportion of Fe<sup>2+</sup> in silicate alteration minerals such as chlorite and amphibole, which readily incorporate Fe<sup>2+</sup> into their structure instead of converting it to Fe<sup>3+</sup>. As a result, the hydrothermal alteration of basalt generates much lower amounts of H<sub>2</sub> compared to the serpentinization of ultramafic rocks, despite basalt having a higher Fe<sup>2+</sup> content [26].

The rate of serpentinization of the parent rock is mainly controlled by three variables: temperature, pressure, and the water-to-rock mass ratio. The optimal temperature range for the process is between 200 and 300 °C [27]. Experimental studies at low pressure ( $\leq$ 500 bar) show that



Fig. 2. Different hypotheses about the origin of natural hydrogen deposits [12]. Although the formation of natural hydrogen seems to have a primarily abiotic origin, other theories about its genesis are being considered. Investigating the sources and mechanisms of its formation is key to the long-term exploitation of this resource in a sustainable manner.



**Fig. 3.** Diagram of natural and orange hydrogen formation and exploitation, along with the key reactions involved in the serpentinization process (bottom left) and the phase diagram of quartz (bottom right. Temperature is represented along the x-axis and quartz activity along the y-axis) [21]. As water infiltrates through the crust, it can reach depths and rock compositions that are suitable for the process of serpentinization [1]. The rock bed undergoes hydration and oxidation during serpentinization, resulting in the production of natural hydrogen [2]. The hydrogen generated migrates towards the surface through fissures and cracks in the crust. It can then escape into the atmosphere [3] or become trapped by impermeable barriers, where it accumulates and forms deposits [4]. Some of these natural hydrogen deposits could be industrially exploited [10].

below this temperature range, the process occurs at very low rates, while at temperatures higher than 320-350 °C, olivine remains stable [23,28, 29]. At higher pressure (3-20 kbar), the optimal temperature increased and the serpentinization rate increased up to 4 times [30]. The access of water to the rock, and therefore the water-to-rock mass ratio, also critically affects the serpentinization rate [21]. Water significantly affects the mobility of different metallic compounds and provides a suitable medium for these chemical processes. Additional parameters, such as the rock composition and impurities present in the reacting water, also play an important role in the reaction. For instance, the presence of aluminum has been shown to increase the serpentinization rate of olivine at 340 °C and 2 kbar [31]. Recently, Song and co-workers indicated that small amounts (<1 %) of nickel in the parent rock greatly enhance the rate of serpentinization reactions at low temperatures (<100  $^{\circ}$ C) [32]. Ultramafic rocks containing pyroxene in addition to olivine may serpentinize faster than monomineralic olivine: recent experiments with olivine-orthopyroxene powder (230 °C, 350 bar, water-to-rock mass ratio of 2) achieved a 53 % serpentinization in just 1 vear of reaction [22].

Besides serpentinization, hydrogen can also be produced in the subsurface by other abiotic processes and by microbial metabolism [33]. Many microorganisms produce  $H_2$  through fermentation and nitrogen fixation reactions in their metabolism (Fig. 2), which are leveraged for the design of hydrogen-producing bioreactors [34,35]. This type of microbial activities are also found in the subsurface [33,36]. Many identified microorganisms can only obtain energy through fermentation

and they play an important role on the biogeochemical cycles in the deep subsurface [33,37]. Unfortunately, the importance of biological activity in the natural production of  $H_2$  in the subsurface is not well understood. Recently, it has been shown that an important proportion of the  $H_2$  detected in the subsurface of the Iberian Pyrite Belt is produced biologically [38]. Importantly, hydrogen may also be utilized as a source of energy by other microorganisms in the subsurface ecosystem. Studies of other mineral substrates and locations is needed to assess the extent of the biological contribution to natural  $H_2$  formation.

## 3. Natural hydrogen hotspots

Estimating the amount of naturally occurring hydrogen that can be extracted or stimulated based on current data is challenging, although upper and lower bounds can be drawn. As an upper bound estimate, we can consider that, on average, peridotite can provide approximately 2–4 kg of H<sub>2</sub> per cubic meter upon oxidation. With an estimated  $10^{12}$  Mt of peridotites in Earth's upper crust (top 7 km), there is a total of  $10^8$  Mt of hydrogen that could be theoretically generated from the subsurface [39]. To put this in perspective, such an amount would provide a supply of 1000 Mtpy of H<sub>2</sub> for 100,000 years [40]. As a lower bound estimate, Smith and colleagues estimated the potential hydrogen production from the Samail Ophiolite in Oman [41]. With a total volume of ultramafic rock around 125,000 km<sup>3</sup>, of which only 50 % is serpentinized, it could provide approximately 260 Mt of hydrogen, exceeding the current world demand for one year [4]. Of course, these estimates relating the amount

of rock to hydrogen production are very crude. However, they illustrate the latent potential that natural hydrogen could have. From another angle, combining data from various studies [2,12,42-45] it has been estimated that the natural hydrogen being formed on Earth could account for approximately 85 % of the current human-made production [12]. This estimate also has much uncertainty and it does not consider the hydrogen already formed and stored underground or the potential of stimulated H<sub>2</sub> production. It is also important to note that tectonic activity continuously refreshes rocks, with approximately 1000 Mt of peridotites being produced each year [39]. Therefore, these values might also underestimate the actual potential of natural hydrogen resources.

Although the exploitation of natural hydrogen is in its infancy, the numbers of boreholes, potential deposits discovered, and companies involved are increasing rapidly as observed in Fig. 4, where a detail of locations and some emergent companies is presented [12]. While numerous research projects worldwide are investigating natural hydrogen resources, detailed information about quantities, costs, and specific locations is often kept secret. Although many specific locations of interest are kept secret, several general areas with increased probability of hydrogen formation are known. In particular, underwater subduction zones, where water supply is constant and iron exposure is frequent due to plate movements, are coupled with natural hydrogen production [46]. Fossil oceanic spreading centers (ophiolites) and suture zones, representing complete subduction of an ocean basin where continents collided, are also promising targets for hydrogen prospecting [47,48]. On land, hydrogen seeps can often be identified by the creation

of circular structures known as "fairy circles," which can serve as points of interest for natural hydrogen exploration (Fig. 4) [16,49].

One of the investigated fairy circles first is in Bourakébougou (Mali) and it has enabled uninterrupted hydrogen energy supply to the town since 2011. This natural reservoir has a diameter of more than 8 km. Prinzhofer and co-workers investigated this reservoir confirming the presence of up to five stacked layers of high-purity hydrogen on an old cratonic basement mainly composed of pyroxene, and proposed that its industrial exploitation could be cheaper than the cost of synthetic hydrogen [19]. In another fairy circle of 500 m diameter in Brazil, gas flows of up to 178,000 m<sup>3</sup> per day were estimated [17]. Differences in the release of H<sub>2</sub> during day and night were also detected, leading to the conclusion that there is a saturation mechanism of H<sub>2</sub> in the fairy circle that reaches its maximum desorption rate during the day [17]. Confirming the presence of deposits responsible for the release of this gas using seismic techniques could increase the interest in exploiting this location. In Chimaera (Turkey), uninterrupted hydrogen flows have been detected for over 2000 years [51]. In Aragón (Spain), the presence of a significant deposit of natural hydrogen beneath the Pyrenees mountain range has been confirmed [52]. Lefeuvre and colleagues studied a 10  $\times$  10 km grid, taking and analyzing over 1000 in situ samples to identify different hydrogen hotspots in the region. Furthermore, they identified a saline formation that would have enabled the accumulation of this natural hydrogen. A company called Helios Aragon has been established to exploit this deposit, aiming for an annual extraction of  $5.5 \cdot 10^4$  to  $7 \cdot 10^4$  metric tons per year of pure hydrogen,



Fig. 4. Detail of known natural hydrogen deposits and fairy circles. Fairy circles can be found in regions around the world with diverse diameters, locations, and densities. Although the precise mechanism behind their formation remains enigmatic, they are often good indicators in the search for natural hydrogen [16]. Photos reproduced with permission from Refs. [17,50].

comparable to the production from a current steam methane reforming plant [11,53]. The company also anticipates a lower production cost for natural  $H_2$  compared to other technologies. In Australia, over 40 licenses for exploring natural hydrogen deposits have been issued since 2021 [54]. One of these companies, Gold Hydrogen, has confirmed a deposit in southern Australia with an estimated extractable hydrogen quantity ranging from 1.3 to 8.8 Mt [55].

The initial localization of natural hydrogen deposits can be challenging. A major technique utilized to this end is seismic prospecting, which applies seismic waves to the ground and measures their reflection [56]. The time elapsed between the emission of the seismic wave and its reception at the detector, including reflections, provides an internal view of a few cubic kilometers underground. The generation of these waves is typically done with electric vibrators, which offer greater safety than traditional explosives. Nonetheless, seismic techniques frequently suffer from intrinsic noise produced by the measurement apparatus, leading to extended analysis periods aimed at extracting dependable information through noise reduction [57]. Furthermore, the interpretation and processing of these methods are intricate, demanding a profound mastery of the technique to extract meaningful insights. Companies like Xcalibur Multiphysics also deploy search techniques in airplanes capable of flying over hard-to-reach locations.

While seismic techniques can provide information on the dimensions of a gas reservoir, its exact composition must be confirmed through prospecting and chromatographic analysis [58]. Chromatographic analysis should be carried out using a carrier gas that allows the detection of hydrogen, such as He. Historically, however, chromatographic analysis of underground gases was often performed using H<sub>2</sub> as the carrier gas, which may have contributed to natural hydrogen deposits going undetected [12].

Estimating the amount of hydrogen contained in a reservoir requires combining seismic data with prospecting at different distances and depths from the initial analysis point. This allows triangulating the deposit's position and depth. Additional factors to consider in the exploitation of a natural hydrogen reservoir include its location, size, technical practicality, safety, composition, pressure, and the rate at which the reservoir may be naturally replenished. Monitoring the pressure evolution as gas is extracted also provides key information about the size and durability of the reservoir.

## 4. Exploitation of geological hydrogen

The extraction of natural hydrogen can be carried out by adapting technology currently employed for natural gas extraction [59]. Briefly, once the potential reservoir is confirmed by seismic techniques, a drilling rig is used to penetrate rock layers, while pipes are employed to facilitate the drilling. The continuous circulation of mud helps control the temperature and pressure throughout the drilling process. During this process, various issues can occur such as the loss of recirculated mud through infiltration into the rock, mud contamination, or pipe blockages. These problems can be minimized by selecting an appropriate drilling path and periodically checking the quality of the recirculated mud during drilling. Once the gas reservoir is reached, the pipes are lined with dense concrete to minimize gas migration and ensure structural integrity [55]. It is especially important to ensure the structural integrity of the installation by respecting the concrete drying times and operating with caution due to the reactive and diffusive nature of H<sub>2</sub>. A H<sub>2</sub> leak at low depths can be dangerous due to the potential to form flammable and explosive mixtures with O2. High-pressure valves are employed to control the extraction and maintain pressure within the reservoir. Once the pipes are in place, extracting hydrogen becomes relatively straightforward [59]. Extraction occurs through pipelines installed in the perforated rock, using the pressure of the pressurized hydrogen (usually >500 bar) to fill tanks for small-scale distribution.

Besides natural hydrogen, the production of orange hydrogen also has potential. However, there are currently no companies dedicated to

this enhanced or stimulated extraction of hydrogen, making it difficult to provide details. To produce orange hydrogen, a suitable rock formation at an optimal reaction temperature would be required, which could be accessible to existing mining technology. Considering a geothermal gradient of approximately 30 °C/km, a formation with the right temperature for the process of 200-300 °C could potentially be found at depths between 5 and 10 km [60,61]. In this depth range, the lithostatic pressure would be around 2000 bar (assuming a typical formation density of  $2750 \text{ kg/m}^3$ ). Drilling has reached depths up to 12 km, so a suitable formation could be accessible to current technology [62]. In addition to finding a suitable formation, it would be necessary to encounter an impermeable rock layer (e.g., halite) at shallower depths [63]. This layer would prevent hydrogen diffusion towards the surface. Once the rock formation were reached, water to stimulate the process would have to pumped at very high pressure. Although pumping water at great depth and pressure is not without challenges, much experience has been gained with the widespread of fracking technology in recent years, which could prove very useful for the stimulation of H<sub>2</sub>. Once orange hydrogen were produced and accumulated, it may be possible to use extraction technology similar to that for natural hydrogen. An approach to the production of orange hydrogen can be observed in Fig. 3. The main difference with natural hydrogen lies in the pumping of water from a reservoir to the reactive bedrock.

Hydrogen possesses high molecular diffusivity, which makes largescale storage of synthetic hydrogen a major challenge [64]. Cryogenic tanks and pipelines are used for small-scale distribution and immediate consumption. Alternatively, underground geological structures like salt caverns are being investigated as large-scale hydrogen storage facilities [65]. These are cavities formed by the dissolution of salt deposits in thick salt beds or domes deep underground [66]. They can provide secure and isolated storage environments, as the salt walls act as natural barriers against leakage [67]. Moreover, the plasticity of salt enables the caverns to withstand high pressures without collapsing, creating an ideal environment for hydrogen storage [63]. Efforts are underway to find suitable natural salt deposits, and countries like Poland are starting to develop an industry around this concept [68]. Overall, large-scale hydrogen storage is a subject of significant industrial interest. Since natural hydrogen is naturally stored in geological traps, the discovery of natural hydrogen deposits could not only provide the value of the hydrogen within it, but also the value of the reservoir itself.

One drawback of natural hydrogen can be its purity. Although deposits with very high purity have been found, impurities are frequently present [17,69], including gases such as nitrogen, methane, or unreacted CO<sub>2</sub>, as well as moisture. The purity of natural hydrogen largely depends on the quality of the water that reached the reactive rock. Water often contains particles, carbonates, and CO<sub>2</sub> that can produce organic impurities through Fischer-Tropsch mechanisms, as the pressure, temperature, and composition of the rock favor such reactions [27,70–72]. Therefore, processing this gas may requires the use of desiccants (already used in all hydrogen stored in caverns due to similar impurities) and separation of light gases using membranes, cryogenic distillation, or pressure swing adsorption [73-75]. While separation costs could rapidly increase the production cost of natural hydrogen from some locations, certain impurities (e.g., CH<sub>4</sub>) could also have market value. In the case of orange hydrogen, purity could be controlled by injecting water with controlled composition (as in electrolysis) to minimize potential contaminants and subsequent purification. However, purity requirements depend on the application. For example, if the goal is combustion for energy production, organic impurities along with moisture would pose a lesser problem [76].

Natural hydrogen can be transported in various forms, and the most cost-effective transportation option will depend on factors such as distance, scale, and intended use [77]. For long-distance transport of large quantities, pipelines become most cost-effective [78]. Small quantities, like those needed for refueling stations, are typically more efficiently transported by trucks. Liquefaction of hydrogen provides higher energy

density compared to compressed hydrogen, but it comes with a higher production cost. Metal hydrides are another option for local storage of smaller quantities like those required in light vehicles. However, their main drawback is the production cost of suitable metal alloys and their increased weight [79,80]. Ammonia storage offers an even higher energy density than liquid hydrogen and can be stored at low pressure (1 bar) [81,82]. However, the drawback is that releasing hydrogen from ammonia by dehydrogenation requires significant energy. Hydrogenation and dehydrogenation of LOHCs (liquid organic hydrogen carriers) are less energy-intensive compared to ammonia, but the amount of hydrogen that can be extracted is lower [83,84]. These considerations highlight that the most cost-effective strategy depends on the specific application and context.

Overall, natural hydrogen offers significant potential to help decarbonize multiple sectors, including industries such as refineries, methanol production plants, and ammonia manufacturing facilities. Additionally, the transportation sector is poised for expansion through the development of new e-fuels and the adoption of ammonia as alternative fuels. Localized energy production using hydrogen presents an attractive option, and ongoing investigations into blending natural gas and hydrogen for heat supply demonstrate their compatibility with existing infrastructure [85]. Indeed, countries like UK already embrace some kind of hydrogen/natural gas blending strategy in their domestic gas heating system [86]. For industrial applications requiring high temperatures, such as steam crackers and cement kilns, hydrogen also emerges as a promising substitute for fossil fuels [87]. The integration of natural hydrogen into various sectors can thus accelerate the transition to a more sustainable and low-carbon economy.

#### 5. Next steps for geological hydrogen

The industrial exploitation of natural hydrogen is still in its earliest stages, but it has the potential to become a significant source of hydrogen. Pioneering companies in the field of natural hydrogen exploitation offer a proof of principle. With its comparatively low production cost and carbon footprint, natural hydrogen holds great promise in supporting society throughout the energy transition. However, it is necessary to increase research efforts to evaluate the potential of this resource.

At this point, the authors envision two parallel lines of work for natural hydrogen and orange hydrogen. On the natural hydrogen side, continuing to search for more deposits and conducting in-depth evaluations of already discovered reservoirs, including techno-economic and life cycle assessment studies, will provide a more comprehensive understanding of this resource. To this end, bureaucratic and political support will be crucial in facilitating both the search and research. Otherwise, progress can be very slow and cumbersome past the laboratory scale. Countries like Australia, where legislation supports exploration and extraction, are experiencing the emergence of a novel economic sector around natural hydrogen.

Besides abiotic production, the significance of natural microbial  $H_2$  production in the deep subsurface is currently unknown [38]. Active  $H_2$  producing microorganisms isolated from the subsurface are currently under study to evaluate their biotechnological potential [88,37]. It would be of interest to evaluate their natural *in situ* subsurface activity as well, or the possibility of introducing them in underground locations with suitable geological substrates or pre-existing identified organic matter. An adequate phenotypic and genotypic characterization can teach us about their optimal operating conditions, and if the addition of required nutrients could stimulate their natural  $H_2$  subsurface activity. The identification of subsurface  $H_2$  production by microorganisms seems feasible in the mid-term, but the quantitative evaluation of their performance will need an important investment and should be considered a longer-term endeavor.

Studies on the natural and stimulated regeneration of the reactive bed should also be conducted to ensure sustainable, long-term exploitation of geological hydrogen. For instance, leveraging microorganisms that utilize Fe<sup>3+</sup> as their final electron acceptor in metabolism could be an interesting research direction to accelerate rock regeneration by replenishing Fe<sup>2+</sup> (e.g., adapting the Feammox process) where other nutrients are available [89–93]. Additionally, the incorporation of different molecules into the pumped water to couple different reactions with serpentinization could be interesting. For example, the incorporation of dissolved CO<sub>2</sub> in the water to form solid carbonates during the serpentinization process, could enable the capture of CO<sub>2</sub> while producing H<sub>2</sub>. On the orange hydrogen side, there are even more challenges and unknowns to investigate before it can be exploited at the industrial scale. Here, the study of serpentinization reactions in laboratories could provide essential knowledge. In Section 2, the challenge of controlling this reaction, which has seen limited laboratory research, has been emphasized.

In our opinion, the data available to date offers compelling evidence for the availability of a much-needed alternative energy source as society transitions beyond fossil resources. However, in-depth research is necessary to ascertain the durability of natural hydrogen reserves. As learned from the exploitation of fossil fuels, all deposits are finite. Therefore, as we start to exploit natural hydrogen resources safely, efficiently, and equitably, we should also invest research efforts in stimulation and in biotechnological solutions that could further improve the accessibility and sustainability of geological resources.

#### Declaration of competing interest

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

## Data availability

No data was used for the research described in the article.

#### References

- Seck GS, Hache E, Sabathier J, Guedes F, Reigstad GA, Straus J, et al. Hydrogen and the decarbonization of the energy system in europe in 2050: a detailed modelbased analysis. Renew Sustain Energy Rev 2022 Oct;167:112779.
- [2] Hydrogen: Overview [Internet]. International Renewable Energy Agency (IRENA). Available from: https://www.irena.org/Energy-Transition/Technology/Hydrogen.
- [3] International Energy Agency. Hydrogen analysis. Internet]. [cited May 29] Available from: https://www.iea.org/reports/hydrogen; 2023.
- [4] International Energy Agency. Global energy review [Internet]. 2021. Available from: https://www.iea.org/reports/global-energy-review-2021; 2021.
- [5] Yadav D, Banerjee R. Net energy and carbon footprint analysis of solar hydrogen production from the high-temperature electrolysis process. Appl Energy 2020 Mar; 262:114503.
- [6] Navas-Anguita Z, García-Gusano D, Dufour J, Iribarren D. Revisiting the role of steam methane reforming with CO2 capture and storage for long-term hydrogen production. Sci Total Environ 2021 Jun;771:145432.
- [7] Bajpai S, Shreyash N, Singh S, Memon AR, Sonker M, Tiwary SK, et al. Opportunities, challenges and the way ahead for carbon capture, utilization and sequestration (CCUS) by the hydrocarbon industry: towards a sustainable future. Energy Rep 2022 Nov;8:15595–616.
- [8] [Internet]. [cited Activities natural hydrogen hydroma. 2023 May 29. Available from: https://hydroma.ca/activities-natural-hydrogen/.
- [9] Helios Aragon | Solutions to the green hydrogen deficit. Internet]. [cited May 31]. Available from: https://helios-aragon.com/; 2023.
- [10] Romagnoli F, Blumberga D, Pilicka I. Life cycle assessment of biohydrogen production in photosynthetic processes. Int J Hydrogen Energy 2011 Jul;36(13): 7866–71.
- [11] Nazir H, Louis C, Jose S, Prakash J, Muthuswamy N, Buan MEM, et al. Is the H2 economy realizable in the foreseeable future? Part I: H2 production methods. Int J Hydrogen Energy 2020 May;45(27):13777–88.
- [12] Zgonnik V. The occurrence and geoscience of natural hydrogen: a comprehensive review. Earth Sci Rev 2020 Apr;203:103140.
- [13] Catling DC, Zahnle KJ, McKay CP. Biogenic methane, hydrogen escape, and the irreversible oxidation of early Earth. Science 2001 Aug 3;293(5531):839–43.
- [14] Owen JE. Atmospheric escape and the evolution of close-in exoplanets. Annu Rev Earth Planet Sci 2019 May 30;47(1):67–90.
- [15] Blay V, Barrios Rivas JL, Xiao Z. Separation of air components and pollutants by the Earth's gravitational field. Chemosphere 2019 Oct;232:453–61.

#### R. Blay-Roger et al.

- [16] Frery E, Langhi L, Maison M, Moretti I. Natural hydrogen seeps identified in the North Perth basin, western Australia. Int J Hydrogen Energy 2021 Sep;46(61): 31158–73.
- [17] Prinzhofer A, Moretti I, Françolin J, Pacheco C, D'Agostino A, Werly J, et al. Natural hydrogen continuous emission from sedimentary basins: the example of a Brazilian H2-emitting structure. Int J Hydrogen Energy 2019 Mar;44(12):5676–85.
- [18] Etiope G. Massive release of natural hydrogen from a geological seep (Chimaera, Turkey): gas advection as a proxy of subsurface gas migration and pressurised accumulations. Int J Hydrogen Energy 2023 Mar;48(25):9172–84.
- [19] Prinzhofer A, Tahara Cissé CS, Diallo AB. Discovery of a large accumulation of natural hydrogen in Bourakebougou (Mali). Int J Hydrogen Energy 2018 Oct;43 (42):19315–26.
- [20] Milkov AV. Molecular hydrogen in surface and subsurface natural gases: abundance, origins and ideas for deliberate exploration. Earth Sci Rev 2022 Jul; 230:104063.
- [21] Frost BR, Beard JS. On silica activity and serpentinization. J Petrol 2007 Apr 3;48 (7):1351–68.
- [22] McCollom TM, Klein F, Moskowitz B, Berquó TS, Bach W, Templeton AS. Hydrogen generation and iron partitioning during experimental serpentinization of an olivine–pyroxene mixture. Geochem Cosmochim Acta 2020 Aug;282:55–75.
- [23] McCollom TM, Bach W. Thermodynamic constraints on hydrogen generation during serpentinization of ultramafic rocks. Geochem Cosmochim Acta 2009 Feb; 73(3):856–75.
- [24] Templeton AS, Ellison ET. Formation and loss of metastable brucite: does Fe(II)bearing brucite support microbial activity in serpentinizing ecosystems? Phil Trans 2020 Feb 21;378(2165):20180423.
- [25] Steinthorsdottir K, Dipple GM, Cutts JA, Turvey CC, Milidragovic D, Peacock SM. Formation and Preservation of brucite and awaruite in serpentinized and Tectonized mantle in central British columbia: implications for carbon mineralization and nickel mining. J Petrol 2022 Nov 1;63(11):egac100.
- [26] Wetzel LR, Shock EL. Distinguishing ultramafic-from basalt-hosted submarine hydrothermal systems by comparing calculated vent fluid compositions. J Geophys Res 2000 Apr 10;105(B4):8319–40.
- [27] Berndt ME, Allen DE, Seyfried Jr WE. Reduction of CO2 during serpentinization of olivine at 300 °C and 500 bar. Geology 1996 Apr 1;24(4):351–4.
- [28] Malvoisin B, Brunet F, Carlut J, Rouméjon S, Cannat M. Serpentinization of oceanic peridotites: 2. Kinetics and processes of San Carlos olivine hydrothermal alteration: kinetics of Serpentinization. J Geophys Res 2012 Apr;117(B4). n/a-n/a.
- [29] McCollom TM, Klein F, Robbins M, Moskowitz B, Berquó TS, Jöns N, et al. Temperature trends for reaction rates, hydrogen generation, and partitioning of iron during experimental serpentinization of olivine. Geochem Cosmochim Acta 2016 May;181:175–200.
- [30] Huang R, Sun W, Ding X, Zhao Y, Song M. Effect of pressure on the kinetics of peridotite serpentinization. Phys Chem Miner 2020 Jul;47(7):33.
- [31] Andreani M, Daniel I, Pollet-Villard M. Aluminum speeds up the hydrothermal alteration of olivine. Am Mineral 2013 Oct 1;98(10):1738–44.
- [32] Song H, Ou X, Han B, Deng H, Zhang W, Tian C, et al. An overlooked natural hydrogen evolution Pathway: Ni <sup>2+</sup> Boosting H<sub>2</sub> O reduction by Fe(OH) <sub>2</sub> oxidation during low-temperature serpentinization. Angew Chem Int Ed 2021 Nov 2;60(45): 24054–8.
- [33] Gregory S, Barnett M, Field L, Milodowski A. Subsurface microbial hydrogen cycling: natural occurrence and implications for industry. Microorganisms 2019 Feb 15;7(2):53.
- [34] Chang J. Biohydrogen production with fixed-bed bioreactors. Int J Hydrogen Energy 2002 Nov;27(11–12):1167–74.
- [35] Nandi R, Sengupta S. Microbial production of hydrogen: an overview. Crit Rev Microbiol 1998 Jan;24(1):61–84.
- [36] Escudero C, Oggerin M, Amils R. The deep continental subsurface: the dark biosphere. Int Microbiol 2018 Jun;21(1–2):3–14.
- [37] Amils R, Escudero C, Oggerin M, Puente Sánchez F, Arce Rodríguez A, Fernández Remolar D, et al. Coupled C, H, N, S and Fe biogeochemical cycles operating in the continental deep subsurface of the Iberian Pyrite Belt. Environ Microbiol 2023 Feb; 25(2):428–53.
- [38] Sanz JL, Rodriguez N, Escudero C, Carrizo D, Amils R. Biological production of H<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub> in the deep subsurface of the iberian pyrite belt. Environ Microbiol 2021 Jul;23(7):3913–22.
- [39] Kelemen PB, Matter J, Streit EE, Rudge JF, Curry WB, Blusztajn J. Rates and mechanisms of mineral carbonation in peridotite: natural processes and recipes for enhanced, in situ CO <sub>2</sub> capture and storage. Annu Rev Earth Planet Sci 2011 May 30;39(1):545–76.
- [40] Osselin F, Soulaine C, Fauguerolles C, Gaucher EC, Scaillet B, Pichavant M. Orange hydrogen is the new green. Nat Geosci 2022 Oct;15(10):765–9.
- [41] Smith NJP, Shepherd TJ, Styles MT, Williams GM. Hydrogen exploration: a review of global hydrogen accumulations and implications for prospective areas in NW Europe. Geological Society, London, Petroleum Geology Conference Series 2005 Jan;6(1):349–58.
- [42] Holloway JR, O'Day PA. Production of CO<sub>2</sub> and H<sub>2</sub> by Diking-eruptive events at mid-ocean ridges: implications for abiotic organic synthesis and global geochemical cycling. Int Geol Rev 2000 Aug;42(8):673–83.
- [43] Holland HD. Volcanic gases, black smokers, and the great oxidation event. Geochem Cosmochim Acta 2002 Nov;66(21):3811–26.
- [44] Ehhalt DH, Rohrer F. The tropospheric cycle of H<sub>2</sub>: a critical review. Tellus B 2009 Jan 1;61(3):500.
- [45] Novelli PC, Lang PM, Masarie KA, Hurst DF, Myers R, Elkins JW. Molecular hydrogen in the troposphere: global distribution and budget. J Geophys Res 1999 Dec 20;104(D23):30427–44.

#### Renewable and Sustainable Energy Reviews 189 (2024) 113888

- [46] Moretti I, Baby P, Alvarez Zapata P, Mendoza RV. Subduction and hydrogen release: the case of Bolivian altiplano. Geosciences 2023 Apr 4;13(4):109.
- [47] Merdith AS, Real PG, Daniel I, Andreani M, Wright NM, Coltice N. Pulsated global hydrogen and methane flux at mid-ocean ridges driven by Pangea Breakup. cited 2023 Jul 7 Geochemistry, Geophysics, Geosystems [Internet] 2020 Apr;21(4). Available from: https://onlinelibrary.wiley.com/doi/abs/10.1029/201 9GC008869.
- [48] Liu Z, Perez-Gussinye M, García-Pintado J, Mezri L, Bach W. Mantle serpentinization and associated hydrogen flux at North Atlantic magma-poor rifted margins. Geology 2023 Mar 1;51(3):284–9.
- [49] Myagkiy A, Moretti I, Brunet F. Space and time distribution of subsurface H<sub>2</sub> concentration in so-called "fairy circles": insight from a conceptual 2-D transport model. BSGF Earth Sciences Bulletin. 2020;191:13.
- [50] Getzin S, Yizhaq H, Tschinkel WR. Definition of "fairy circles" and how they differ from other common vegetation gaps and plant rings [cited 2023 Jun 14]. In: Bello F, editor. J Vegetation science [Internet], vol. 32; 2021 Nov. 6). Available from: https://onlinelibrary.wiley.com/doi/10.1111/jvs.13092.
- [51] Hosgormez H, Etiope G, Yalçin MN. New evidence for a mixed inorganic and organic origin of the Olympic Chimaera fire (Turkey): a large onshore seepage of abiogenic gas. Geofluids 2008 Nov;8(4):263–73.
- [52] Lefeuvre N, Truche L, Donze FV, Ducoux M, Barré G, Fakoury RA, et al. Native H2 exploration in the western Pyrenean foothills [Internet]. Geochemistry 2021 May; 22(6) [cited 2023 May 6]. Available from: https://essopenarchive.org/doi/full/10 .1002/essoar.10507102.1.
- [53] Collodi G, Azzaro G, Ferrari N, Santos S. Techno-economic evaluation of deploying CCS in SMR based merchant H2 production with NG as feedstock and fuel. Energy Proc 2017 Jul;114:2690–712.
- [54] Natural hydrogen | energy & mining. Internet]. [cited]. Available from: https ://www.energymining.sa.gov.au/industry/energy-resources/geology-and-prosp ectivity/natural-hydrogen; 2023.
- [55] Gold Hydrogen. Natural hydrogen exploration drilling and well testing [Internet]. Australia; Report No.: RAM-HSE-REP-004. Available from: https://www.goldhy drogen.com.au/ramsay-project/; 2023.
- [56] Selley RC, Sonnenberg SA. Methods of exploration [cited 2023 Oct 2]. In: Elements of petroleum geology [Internet]. Elsevier; 2023. p. 43–166. Available from: https: //linkinghub.elsevier.com/retrieve/pii/B9780128223161000033.
- [57] Ringler AT, Steim J, Wilson DC, Widmer-Schnidrig R, Anthony RE. Improvements in seismic resolution and current limitations in the Global Seismographic Network. Geophys J Int 2020 Jan 1;220(1):508–21.
- [58] Mainson M, Heath C, Pejcic B, Frery E. Sensing hydrogen seeps in the subsurface for natural hydrogen exploration. Appl Sci 2022 Jun 23;12(13):6383.
- [59] ENGIE Innovation [Internet]. H2 in the underground: are salt caverns the future of hydrogen storage?. cited May 29]Available from: http://innovation.engie.com/en /news/news/did-you-know-/hydrogen-underground-storage-salt-caverns/25906; 2023.
- [60] Macenić M, Kurevija T, Medved I. Novel geothermal gradient map of the Croatian part of the Pannonian Basin System based on data interpretation from 154 deep exploration wells. Renew Sustain Energy Rev 2020 Oct;132:110069.
- [61] Barbier E. Geothermal energy technology and current status: an overview. Renew Sustain Energy Rev 2002 Jan;6(1–2):3–65.
- [62] Clarke J, McDowell R, Matzko J, Hearn P, Milton D, Percious D, et al. The Kola superdeep drill hole: a detailed summary. Academy's Continental Scientific Drilling Committee; 1986.
- [63] Watkins J, Kaldi J, Watson M. Geological storage of gas: evaluation of seal properties for containment of Carbon Dioxide, Methane and Hydrogen [Internet] SSRN Journal 2022 [cited 2023 Jun 6]; Available from: https://www.ssrn. com/abstract=4297078.
- [64] Tarhan C, Çil MA. A study on hydrogen, the clean energy of the future: hydrogen storage methods. J Energy Storage 2021 Aug;40:102676.
- [65] Zivar D, Kumar S, Foroozesh J. Underground hydrogen storage: a comprehensive review. Int J Hydrogen Energy 2021 Jul;46(45):23436–62.
- [66] Aftab A, Hassanpouryouzband A, Xie Q, Machuca LL, Sarmadivaleh M. Toward a fundamental understanding of geological hydrogen storage. Ind Eng Chem Res 2022 Mar 9;61(9):3233–53.
- [67] Lankof L, Urbańczyk K, Tarkowski R. Assessment of the potential for underground hydrogen storage in salt domes. Renew Sustain Energy Rev 2022 May;160:112309.
- [68] Tarkowski R. Perspectives of using the geological subsurface for hydrogen storage in Poland. Int J Hydrogen Energy 2017 Jan;42(1):347–55.
- [69] Neal C, Stanger G. Hydrogen generation from mantle source rocks in Oman. Earth Planet Sci Lett 1983 Dec;66:315–20.
- [70] Peter Szatmari (2). Petroleum Formation by fischer-Tropsch synthesis in plate tectonics [cited 2023 Jun 6] Bulletin [Internet] 1989;73. Available from: htt p://search.datapages.com/data/doi/10.1306/44B4A2CB-170A-11 D7-8645000102C1865D.
- [71] Zhao Z, Liu X, Lu H, Peng P. Abiotic Hydrocarbons generation simulated by fischer-Tropsch synthesis under hydrothermal conditions in ultra-deep basins. Acta Geol Sin 2022 Aug;96(4):1331–41.
- [72] Lur'e MA. Is the Fischer-Tropsch process possible in a geologic medium? Geochem Int 2014 Dec;52(12):1084–6.
- [73] Adhikari S, Fernando S. Hydrogen membrane separation techniques. Ind Eng Chem Res 2006 Feb 1;45(3):875–81.
- [74] Luberti M, Ahn H. Review of Polybed pressure swing adsorption for hydrogen purification. Int J Hydrogen Energy 2022 Mar;47(20):10911–33.
- [75] Bernardo G, Araújo T, Da Silva Lopes T, Sousa J, Mendes A. Recent advances in membrane technologies for hydrogen purification. Int J Hydrogen Energy 2020 Mar;45(12):7313–38.

#### R. Blay-Roger et al.

Renewable and Sustainable Energy Reviews 189 (2024) 113888

- [76] Boudghene Stambouli A, Traversa E. Fuel cells, an alternative to standard sources of energy. Renew Sustain Energy Rev 2002 Sep;6(3):295–304.
- [77] Moradi R, Groth KM. Hydrogen storage and delivery: review of the state of the art technologies and risk and reliability analysis. Int J Hydrogen Energy 2019 May;44 (23):12254–69.
- [78] Stiller C, Svensson AM, Møller-Holst S, Bünger U, Espegren KA, Holm ØB, et al. Options for CO2-lean hydrogen export from Norway to Germany. Energy 2008 Nov;33(11):1623–33.
- [79] Lototskyy M, Tolj I, Davids MW, Bujlo P, Smith F, Pollet BG. "Distributed hybrid" MH–CGH2 system for hydrogen storage and its supply to LT PEMFC power modules. J Alloys Compd 2015 Oct;645:S329–33.
- [80] Lototskyy MV, Tolj I, Pickering L, Sita C, Barbir F, Yartys V. The use of metal hydrides in fuel cell applications. Prog Nat Sci: Mater Int 2017 Feb;27(1):3–20.
- [81] Lamb KE, Dolan MD, Kennedy DF. Ammonia for hydrogen storage; A review of catalytic ammonia decomposition and hydrogen separation and purification. Int J Hydrogen Energy 2019 Feb;44(7):3580–93.
- [82] Wijayanta AT, Oda T, Purnomo CW, Kashiwagi T, Aziz M. Liquid hydrogen, methylcyclohexane, and ammonia as potential hydrogen storage: comparison review. Int J Hydrogen Energy 2019 Jun;44(29):15026–44.
- [83] Eypasch M, Schimpe M, Kanwar A, Hartmann T, Herzog S, Frank T, et al. Modelbased techno-economic evaluation of an electricity storage system based on Liquid Organic Hydrogen Carriers. Appl Energy 2017 Jan;185:320–30.

- [84] Niermann M, Timmerberg S, Drünert S, Kaltschmitt M. Liquid Organic Hydrogen Carriers and alternatives for international transport of renewable hydrogen. Renew Sustain Energy Rev 2021 Jan;135:110171.
- [85] Castek R, Harkin S. Evidence review for hydrogen for heat in buildings. 2021. Sep [cited 2023 Jun 7]; Available from: https://era.ed.ac.uk/handle/1842/37964.
- [86] UK hydrogen strategy. Available from: https://www.gov.uk/government/publ ications/uk-hydrogen-strategy; 2021.
- [87] Liu W, Zuo H, Wang J, Xue Q, Ren B, Yang F. The production and application of hydrogen in steel industry. Int J Hydrogen Energy 2021 Mar;46(17):10548–69.
  [88] Hallenbeck PC. Fundamentals of the fermentative production of hydrogen. Water
- Sci Technol 2005 Jul 1;52(1-2):21-9.
   [89] Luu YS. Microbial mechanisms of accessing insoluble Fe(III) as an energy source.
- World J Microbiol Biotechnol 2003;19(2):215–25.
   [90] Malik L, Hedrich S. Ferric iron reduction in extreme acidophiles. Front Microbiol
- 2022 Jan 12;12:818414.
- [91] Quatrini R, Jedlicki E, Holmes DS. Genomic insights into the iron uptake mechanisms of the biomining microorganism Acidithiobacillus ferrooxidans. J Ind Microbiol Biotechnol 2005 Dec;32(11–12):606–14.
- [92] Zhu T, ting, xia Lai W, Zhang YB, Liu Y, wen. Feammox process driven anaerobic ammonium removal of wastewater treatment under supplementing Fe(III) compounds. Sci Total Environ 2022 Jan;804:149965.
- [93] Wang W, Ding B, Hu Y, Zhang H, He Y, She Y, et al. Evidence for the occurrence of Feanmox coupled with nitrate-dependent Fe(II) oxidation in natural enrichment cultures. Chemosphere 2022 Sep;303:134903.