

Natural Hydrogen: Promising opportunities for Exploration & Production

INTRODUCTION

The global energy sector is transforming and hydrogen (the most energy-rich gas) is likely to play an increasingly prominent role as a clean energy carrier. Many countries have identified hydrogen as a key pathway to decarbonise their transport, industry processes, heating and energy storage sectors.

Hydrogen is almost exclusively manufactured for industrial use, with around 840 Bm³ per year being produced worldwide (Wood Mackenzie 2021).

It can be produced artificially via a variety of different pathways and the primary methods for production of hydrogen *with low carbon emissions* being

- water electrolysis using renewable energy (green hydrogen)
- steam reformation of natural gas paired with carbon capture and storage (CCS; blue hydrogen)
- coal gasification combined with CCS (also blue hydrogen).

Note:

- the majority of produced hydrogen originates from hydrocarbon-based feedstock without CCS (grey hydrogen) since the economics for the electrolytic production of green hydrogen (0.1% of total H₂ production) requires improvement (Wood Mackenzie 2021).
- For a large-scale hydrogen industry to develop, hydrogen storage is key and hydrogen storage in salt caverns is considered the most promising approach for large-scale seasonal storage (HyUnder 2013; Caglayan et al. 2020).

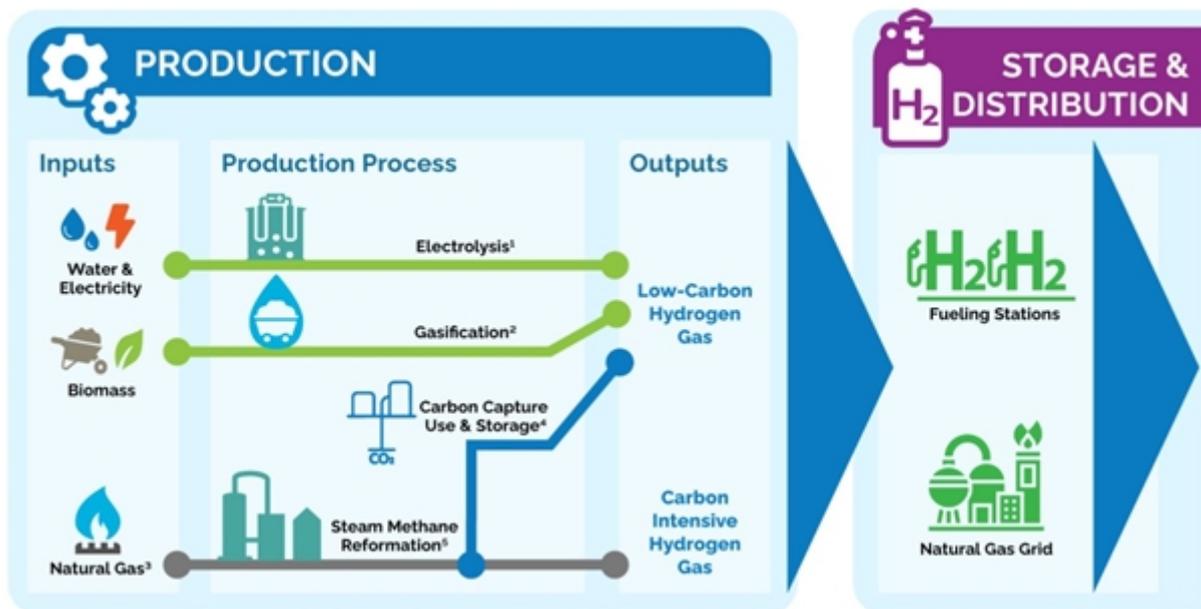
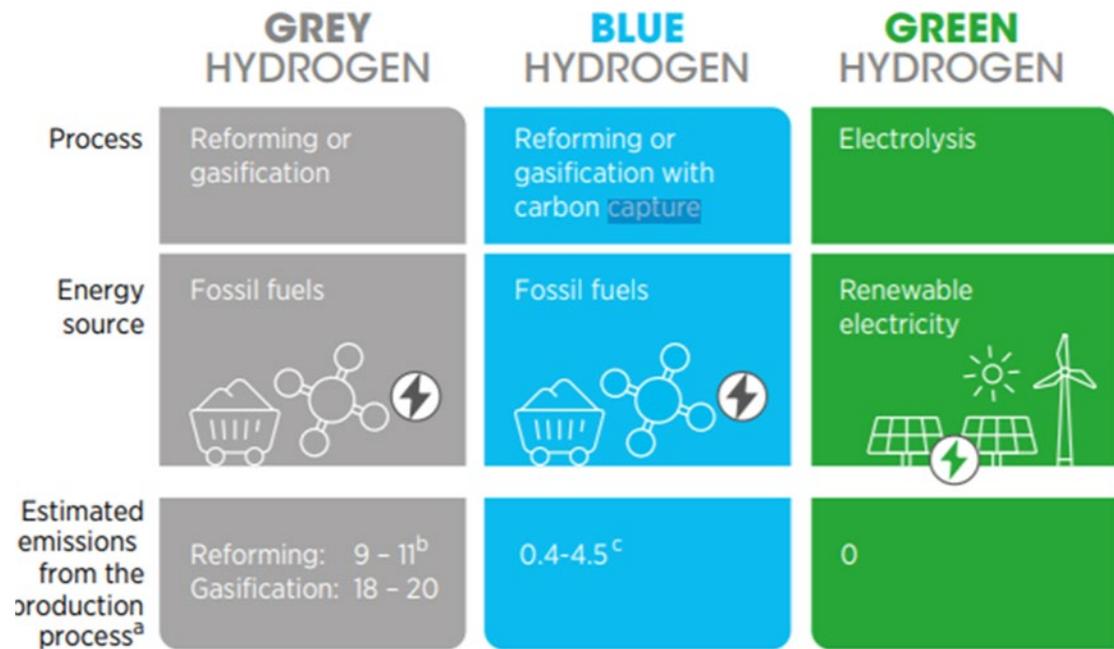


Fig # 1 - Primary methods for hydrogen production



Note: a) CO_{2-eq}/kg = carbon dioxide equivalent per kilogramme; b) For grey hydrogen, 2 kg CO_{2-eq}/kg assumed for methane leakage from the steam methane reforming process. c) Emissions for blue hydrogen assume a range of 98% and 68% carbon capture rate and 0.2% and 1.5% of methane leakage.

Fig # 2 –Selected colours code typology of hydrogen production

Hydrogen is seemingly ubiquitous in the subsurface, being classified as *natural or native or geological*.

Geological hydrogen could revolutionise the low-carbon future as it can be exploited economically

- removing the need for clean water - used during green hydrogen electrolysis
- eliminating the need for expensive Carbon Capture and Storage (CCS) associated with blue hydrogen.

The processes that create natural hydrogen are not fully understood and the discovery of this potentially renewable resource raises several questions related to:

- *Commercial accumulations*
- *Method of exploitation*
- *Legal implications of exploring for hydrogen*
- *Costs of production*
- *Can it decarbonise and compete with existing (grey and blue) hydrogen feedstock, or even green hydrogen?*
- *Hydrogen storage in the subsurface?*

It is found in a large range of geological settings

- oceanic and continental crust
- volcanic gases
- hydrothermal systems

The present known sources of natural hydrogen seem to be abiotic, however, discussions highlighted that natural hydrogen can be considered as both biogenic or abiotic, because source interpretations can be subjective, and there is still much to learn about hydrogen and microorganisms.

GEOLOGICAL OCCURRENCES, SOURCES AND SINKS OF NATURAL HYDROGEN

More specifically, natural hydrogen is present in a range of geological environments such as crystalline basement, volcanic, ultramafic and peralkaline igneous complexes, geothermal and mineral systems, graphite, evaporite deposits and anoxic sediments, as well as in conventional and unconventional gas and oil fields, and coal seam gas (Gregory et al. 2019).

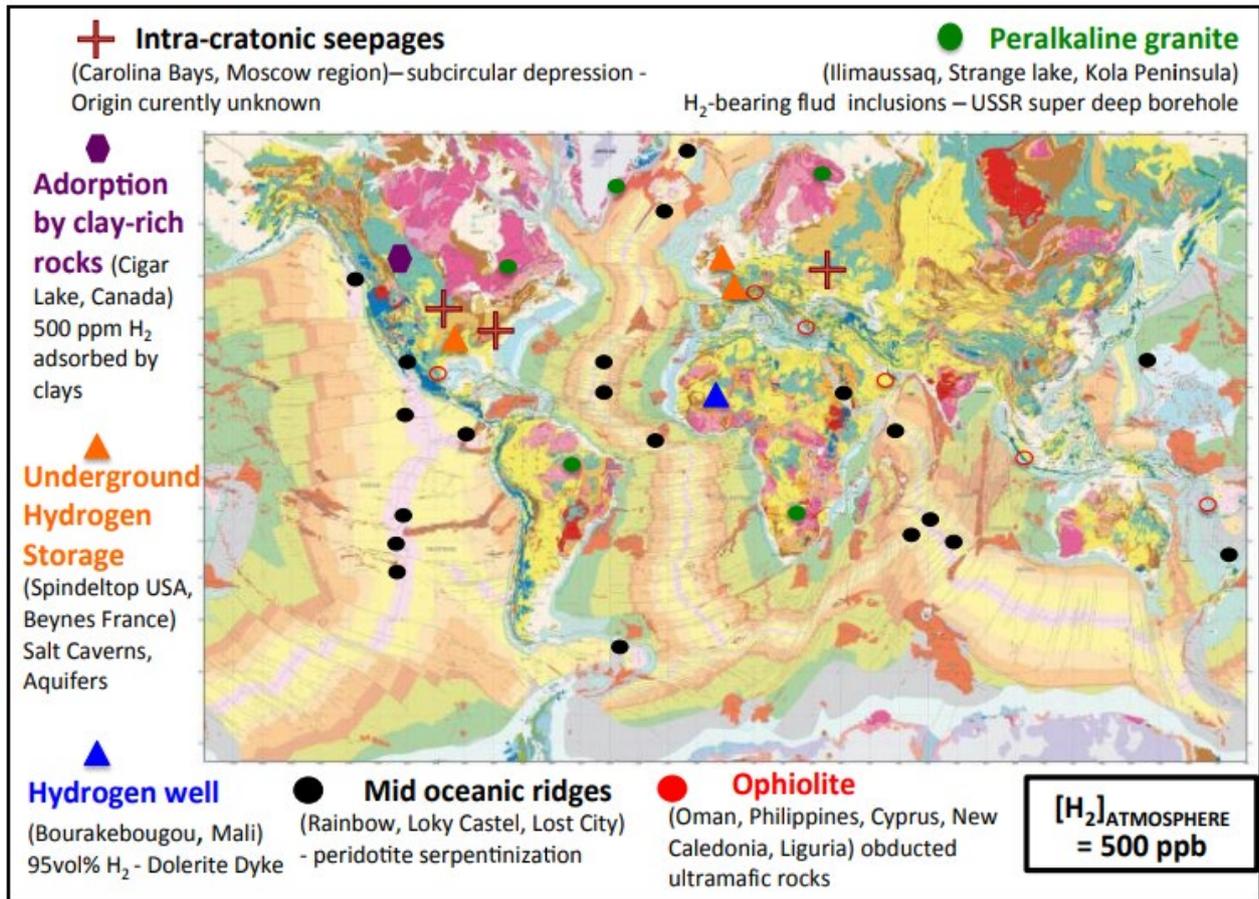


Fig # 4 - Global distribution of natural hydrogen sources. Deep H₂ geological storages is also shown

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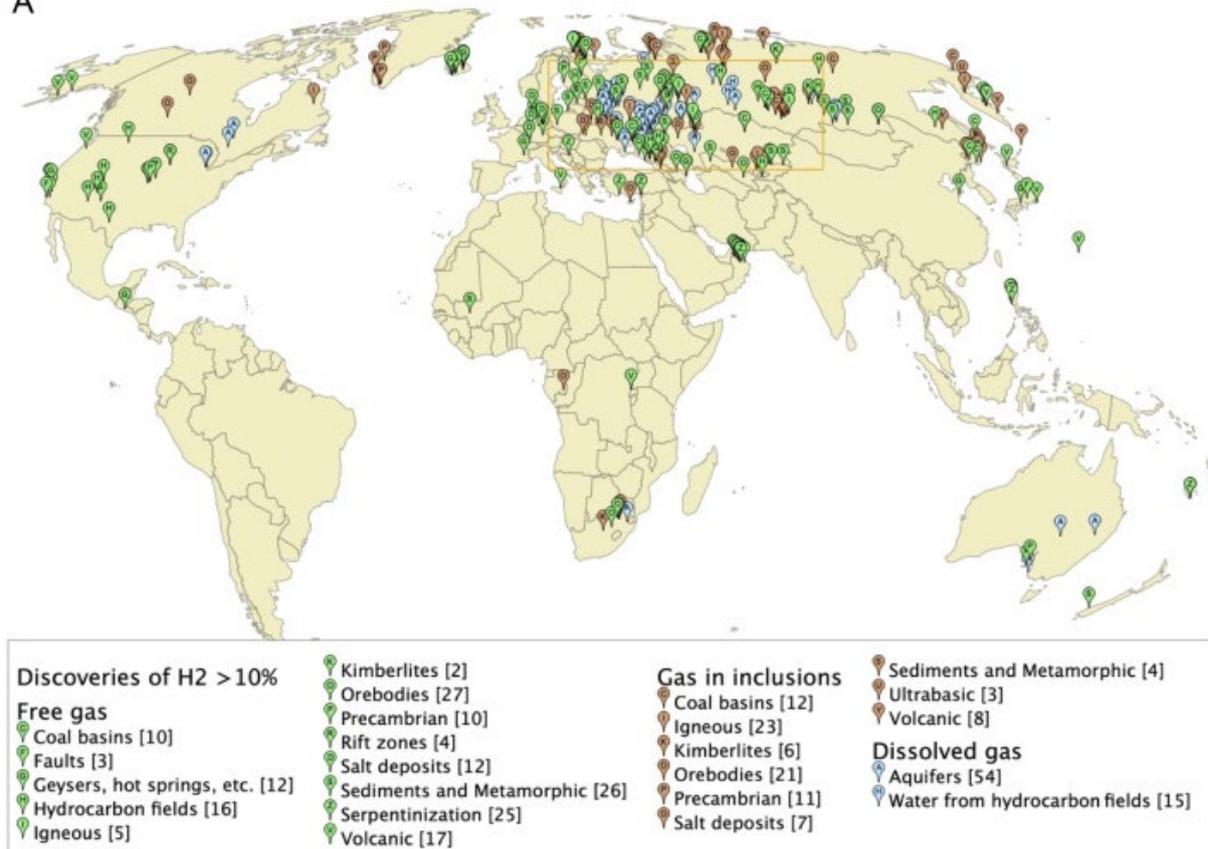


Fig # 5 – Hydrogen discoveries and geological environments

Since H₂ is mobile and chemically active, gases stored for millennia in reservoir rocks may require a continuous replenishment of H₂ from disparate source(s) (Dubessy et al. 1989; Zgonnik 2020).

H₂ contents within gas and oil fields, in general, are commonly lower than surrounding rocks suggesting a chemical reaction between H₂ and the emplaced organic matter (Zgonnik 2020).

Natural H₂ sources can be classified natural into two groups (Zgonnik, 2020):

1. primary hydrogen stored within the earth's hydridic core and mantle (Larin 1993; Walshe et al. 2005; Walshe 2006)
2. secondary hydrogen generated from chemical reactions within the mantle and crust.

Natural H₂ can be regarded as having either an abiogenic (Reeves and Fiebig 2020) or a biogenic source, of which the latter includes both thermogenic (Tissot and Welte 1984; Hunt 1996) and microbial (Nandi and Sengupta 1998; Hallenbeck and Benemann 2002) processes.

The isotopic signature of H₂ can be used to help determine its origin.

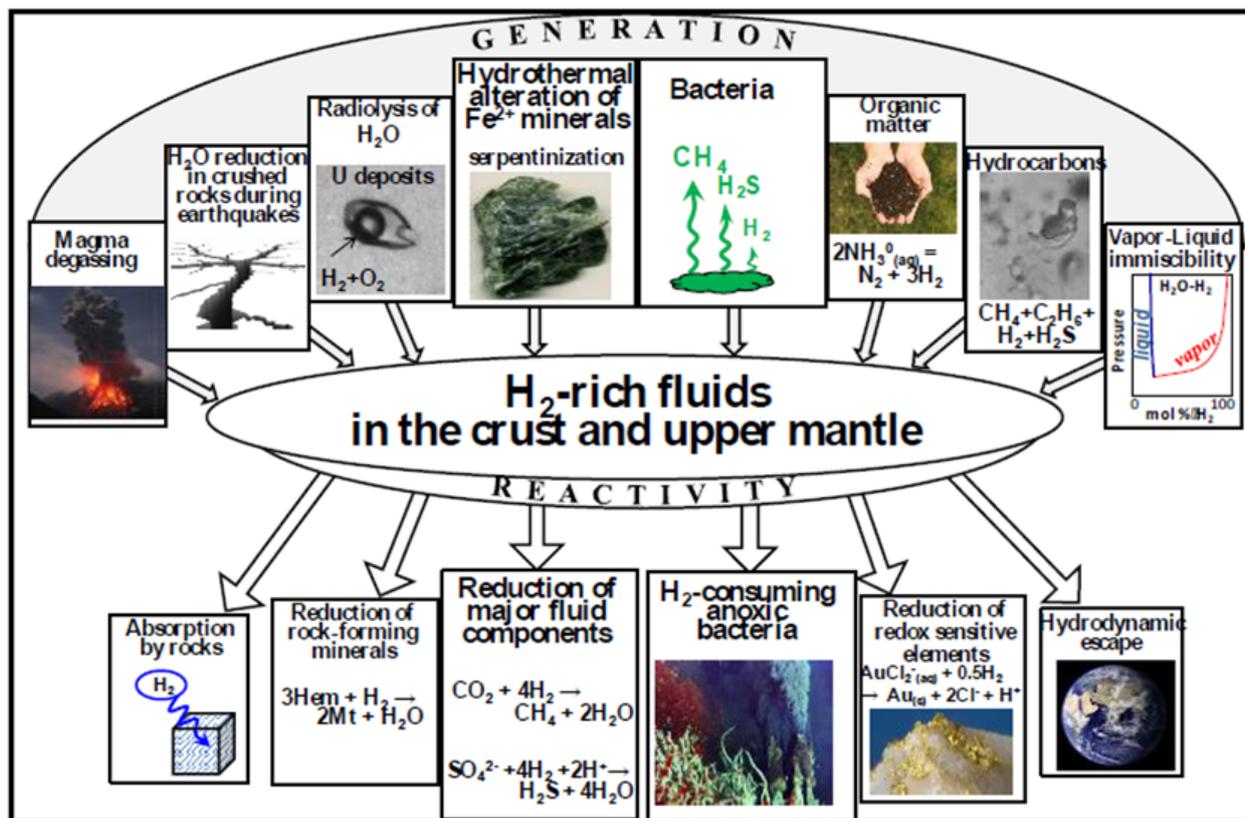


Fig # 6 - Main H₂ sources and sinks in the crust

SOURCES OF NATURAL HYDROGEN

Primary source of natural hydrogen

Hydrogen and helium (He) on earth have their roots in the formation of the universe and the solar system.

Primordial H₂ was initially captured then dissociated to form a hydritic core and lower mantle during the formation of the earth (Rumyantsev 2016), estimated to be some 4.54 billion years ago 50 million years (National Geographic 2021). Some consider primary H₂ resources infinite for human usage, if only accessible (Larin 1993; Zgonnik 2020; Moretti et al. 2021b).

Ultramafic rocks dominate the mantle and fluids in the lower mantle are likely to contain methane (CH₄), H₂ and water (H₂O), whereas in the upper mantle they comprise carbon dioxide (CO₂) and water. This primordial source of hydrogen is in the form of stored primary metal hydride and is considered the dominant form of hydrogen on earth (Zgonnik 2020).

These metal hydrides release H₂ through processes resulting in the continuous and intermittently violent injections into the upper mantle and crust. Such large-scale fluid migration can have major impacts on all earth processes within the upper lithosphere, biosphere, hydrosphere and atmosphere (Walshe et al. 2005; Walshe 2006).

Secondary sources of natural hydrogen

Secondary (abiogenic) sources of natural hydrogen are potentially the largest yet-to-find resources, although exploration for petroleum and the recovery of biogenic natural gas (with non-commercial H₂) is the largest currently exploited resource.

Abiogenic H₂ might influence crustal redox chemistry that control deposition of ore mineralisation (Walshe et al. 2005; Zgonnik 2020), and hence the analysis of gases from mines would be beneficial (Boreham et al. 2021).

Numerous abiogenic sources of natural H₂ are summarised in Table 1, with serpentinisation, radiolysis and volcanic and hydrothermal vents being considered some of the most important geological processes

Water–rock interactions involving iron	References
Serpentinisation of mafic–ultramafic rocks.	Truche <i>et al.</i> 2020; Worman <i>et al.</i> 2020; Zgonnik 2020
Late stage crystallisation of basic magma where dissolved water oxidises Fe ^{2b} to Fe ^{3b} .	Schrenk <i>et al.</i> 2013; Sherwood Lollar <i>et al.</i> 2014; Etiope and Whitticar 2019
Hydration of biotite in felsic rocks (e.g. granite).	Briere <i>et al.</i> 2017; Murray <i>et al.</i> 2020
Water hydrolysis accompanying Fe and Fe ^{2b} oxidation (anaerobic corrosion) most likely catalysed by metal hydroxides at low temperature, crustal weathering and by Ca produced from the radioactive decay of ⁴⁰ K.	Neal and Stranger 1983; Guélard <i>et al.</i> 2017; Worman <i>et al.</i> 2020
Hydrothermal hydration of siderite in sedimentary basins and metasedimentary rocks: 3FeCO ₃ + H ₂ O(aqueous) = Fe ₃ O ₄ + 3CO ₂ (aqueous) + H ₂ (aqueous).	Seewald 2001; Milesi <i>et al.</i> 2015

Radiolysis	References
Radiolysis of water by alpha, beta and gamma radiation released in the radioactive decay of U-, Th- and K-bearing minerals.	Boyd <i>et al.</i> 1973; Vovk 1987; Dubessy <i>et al.</i> 1989; Smith <i>et al.</i> 2005; Dzaugis <i>et al.</i> 2016; Bouquet <i>et al.</i> 2017; Parnell and Blamey 2017; Truche <i>et al.</i> 2018; Zgonnik 2020
Radiation-induced polymerisation of methane and destruction of organic matter.	Boreham and Davies 2020, and references therein

Other mechanisms in the geosphere	References
Volcanic activity and hydrothermal vents where equilibrium reactions favour H ₂ ; i.e. $\text{CO} \rightleftharpoons \text{H}_2\text{O} + 2 \text{CO}_2 \rightleftharpoons \text{H}_2$, $\text{H}_2\text{S} \rightleftharpoons 2\text{H}_2\text{O} + 2 \text{SO}_2 \rightleftharpoons \text{H}_2$, and $\text{SO}_2 \rightleftharpoons 2\text{H}_2\text{O} + 2 \text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_2$.	Holland 2002
Cataclastics (cohesive granular faulted rock) of silicates in the presence of water and in igneous rocks and associated with upper crustal processes (e.g. earthquakes).	Kita <i>et al.</i> 1982; Sugisaki <i>et al.</i> 1983; Apps and van de Kamp 1993; Freund <i>et al.</i> 2002; Hirose <i>et al.</i> 2011, 2012; Klein <i>et al.</i> 2020
Mechanochemical reaction of phosphate to produce phosphine (PH ₃) and its subsequent hydrolysis to H ₂ .	Hoeman 1944; Glindermann <i>et al.</i> 2005
H ₂ released from fluid inclusions is widespread in Precambrian basement rocks, particularly granites, and their eroded remnants deposited in sedimentary basins are likely to be a significant H ₂ resource.	Parnell and Blamey 2017
Decomposition of methane to form graphite and H ₂ at high (> 600°C) temperature.	Apps and van de Kamp 1993; Holland 2002; Smith <i>et al.</i> 2005; Dzaugis <i>et al.</i> 2016; Bouquet <i>et al.</i> 2017; Parnell and Blamey 2017; Truche <i>et al.</i> 2018; Boreham and Davies 2020, and references therein; Zgonnik 2020
Oxidative coupling of methane catalysed by alkali metal and lanthanide oxides has been demonstrated in the laboratory at high (> 650°C) temperature. Potentially, similar reactions could occur in the subsurface with the involvement of O ₂ from water radiolysis.	Lunsford 1990; Lehmann and Baerns 1992
Metasomatism of upper mantle and crustal rocks with the infiltration of metal hydrides from the deeper mantle.	Walshe <i>et al.</i> 2006
Mixing of waters with differing ionisation potentials, i.e. fresh and saline waters.	Goebel <i>et al.</i> 1984
Formation of pyrite by the reaction of hydrogen sulfide (H ₂ S) with Fe ²⁺ and/or siderite and with pyrrhotite, which may also be mediated by microorganisms.	Drobner <i>et al.</i> 1990; Hofstra and Cline 2000; Thiel <i>et al.</i> 2019
Oxidation of sulfate and associated with ammonia (NH ₃) released from ammonium-bearing minerals at high temperature.	Dubessy <i>et al.</i> 1989; Li <i>et al.</i> 2009
Cooling and decompression in a hydrothermal CO ₂ -CH ₄ -C fluid system.	Tsunogae and Dubessy 2009

Anthropogenic	References
Artefacts of drilling and metal corrosion.	Goebel <i>et al.</i> 1984; Bjornstad <i>et al.</i> 1994; Erzinger <i>et al.</i> 2006; Mørkved <i>et al.</i> 2009; Thiessen <i>et al.</i> 2009; Wenger <i>et al.</i> 2009; Feldbusch <i>et al.</i> 2018; Truche <i>et al.</i> 2020; Halas <i>et al.</i> 2021

Serpentinisation is the most studied reaction pathway to H₂ in the subsurface and it occurs with the circulation of hydrothermal fluids through mafic–ultramafic rocks on the seafloor at deep-sea hydrothermal vents and in continental ophiolites.

Serpentinisation can occur at temperatures from just above ambient to 330–400 C, depending on pressure (Evans et al. 2013; Mayhew et al. 2013; McCollom and Seewald 2013).

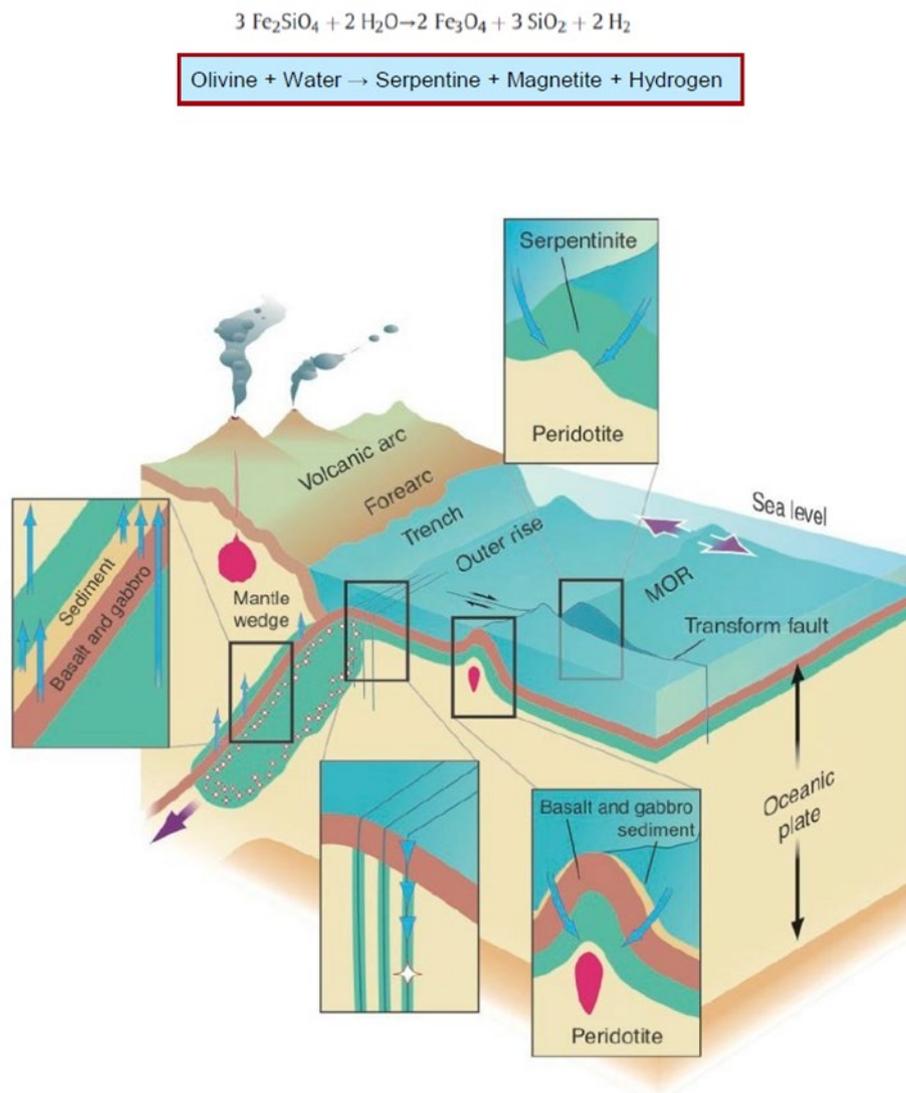


Figure # 7 - Schematic representation of the main serpentine formation areas (from Kerrick, 2002; Ulrich, 2010). The pink arrows represent the movement of the plates, the magmatic areas are represented in red, the blue arrows show the infiltration and extraction areas of fluid. (1) Circulation of hydrothermal fluids in the ridge axis. (2) Serpentinization of the abyssal peridotite triggered by transforming faults. (3) Serpentinization induced by the play of normal faults formed by the subduction plunging of the plate forming a local extensive regime. (4) Serpentinization of the mantle corner by fluids resulting from the dehydration of the plunging plate

The mantle lithosphere could also support serpentinisation (Brovarone et al. 2017). Low temperature (100 C) H₂ production is associated with a spinel reactant and a cubic crystal structure. The spinel can either be as impurities in the initial reactant or the serpentinisation product (Mayhew et al. 2013).

Hydrogen yield from serpentinisation is directly linked with the fraction of reduced iron in the reactant mineral (e.g. olivine or pyroxene with variable Fe/Mg ratios) and the proportion converted to Fe³⁺ (McCollom and Seewald 2013; Murray et al. 2020).

In felsic rocks (e.g. granites), biotite can also hydrate to generate H₂ (Table 1). Nevertheless, high redox potentials, low temperatures and the addition of CO₂ can increase H₂ yield from granites (Murray et al. 2020).

Radiolysis of water in the geosphere is another significant mechanism of generating natural H₂ that is amenable to modelling and resource estimation (Sherwood Lollar et al. 2014; Warr et al. 2019; Boreham et al. 2021. Zgonnik (2020) considers volcanic and hydrothermal vents to be the most dominant H₂ source, having the highest estimated natural H₂ production rates.

A hydridic source from the lower mantle and core are theorised to be the ultimate largest 'H' reservoir (Zgonnik 2020, where H₂ can either continually migrate upwards or be released with episodic injection into the upper mantle/crust where the metal hydrides can undergo metasomatism and water hydrolysis.

Biogenic sources

Biogenic sources of natural hydrogen include both thermo-genic and microbial origins.

In the former, H₂ is a by-product of diagenesis and thermal maturation, while in the latter, H₂ producers and H₂ consumers generally work in consortia (Boone et al. 1989; Noar et al. 2015; Gregory et al. 2019) and provide an important H₂ sink.

During diagenesis, the polymerisation of hydrocarbon C–C bonds results in the formation of kerogen and minimal release of H₂.

Thermogenic liberation of H₂ occurs during subsequent catagenic scission of hydrocarbon C–C bonds during the generation of gas and oil, coal seam gas (Gregory et al. 2019, and references therein) and petroleum cracking (Briere et al. 2017). During metagenesis, the progressive aromatisation of the residual kerogen also leads to production predominantly of CH₄ but also some H₂ (Tissot and Welte 1984; Hunt 1996).

Thermolysis of alkanes and CH₄ at 200 C and 500 C, respectively (Tissot and Welte 1984) also result in the release of H₂

NATURAL HYDROGEN MIGRATION AND REACTIVITY

Once produced, H₂ can react with oxidized elements - mineralized or dissolved in geological fluids - or diffuse toward the surface and escape into the oceans or the atmosphere. This hydrogen can then be either a source of energy for bacterial developments, or as a reagent for abiotic hydrocarbons synthesis, but rarely, if ever, as a carbon-free energy resource. Its high mobility and reactivity at high T, as well as at low T in the presence of bacteria, are considered to prevent its accumulation in the geological media.

This view was recently challenged by two major discoveries of geological environments where H₂ is trapped in deep sedimentary formations overlying intra-cratonic crystalline basements.

- Widespread H₂ enrichment in water-saturated clay-rich rocks at 20°C surrounding the Cigar-Lake uranium deposits, Athabasca, Canada.
 - Thermal desorption measurements reveal that H₂ is enriched up to 500 ppm (i.e. 0.25 mol.kg⁻¹ of rock) in these water-saturated rocks having a very low total organic content (<0.5 wt%). Such H₂ uptake is comparable and even exceeds adsorbed methane capacities reported elsewhere for pure clay minerals or shales. Up to 17% of H₂ produced by water radiolysis over the 1.4 Ga- lifetime of the Cigar Lake uranium ore deposit, accounting for about 500 tones, have been trapped in the surrounding clay alteration haloes. As a result, sorption

processes on layered silicates must not be overlooked as they may exert an important control on the fate and mobility of H₂ in the crust.

- Large accumulation of H₂ in the Taoudeni Basin, Bourakebougou field, Mali.
 - Recent exploratory wells in Mali, close to the village of Bourakebougou, confirm the presence of an extensive H₂ field featuring at least five stacked reservoir intervals containing significant H₂ content (up to 98 vol.% of gas) and covering an estimated area higher than 8 km in diameter. The relatively pure H₂ reservoirs are associated with traces of methane, nitrogen and helium. The geological stratigraphic accumulation of H₂ is linked to the presence of multi overlaid doleritic sills and aquifers that seem to prevent upward gas migration and leakage.

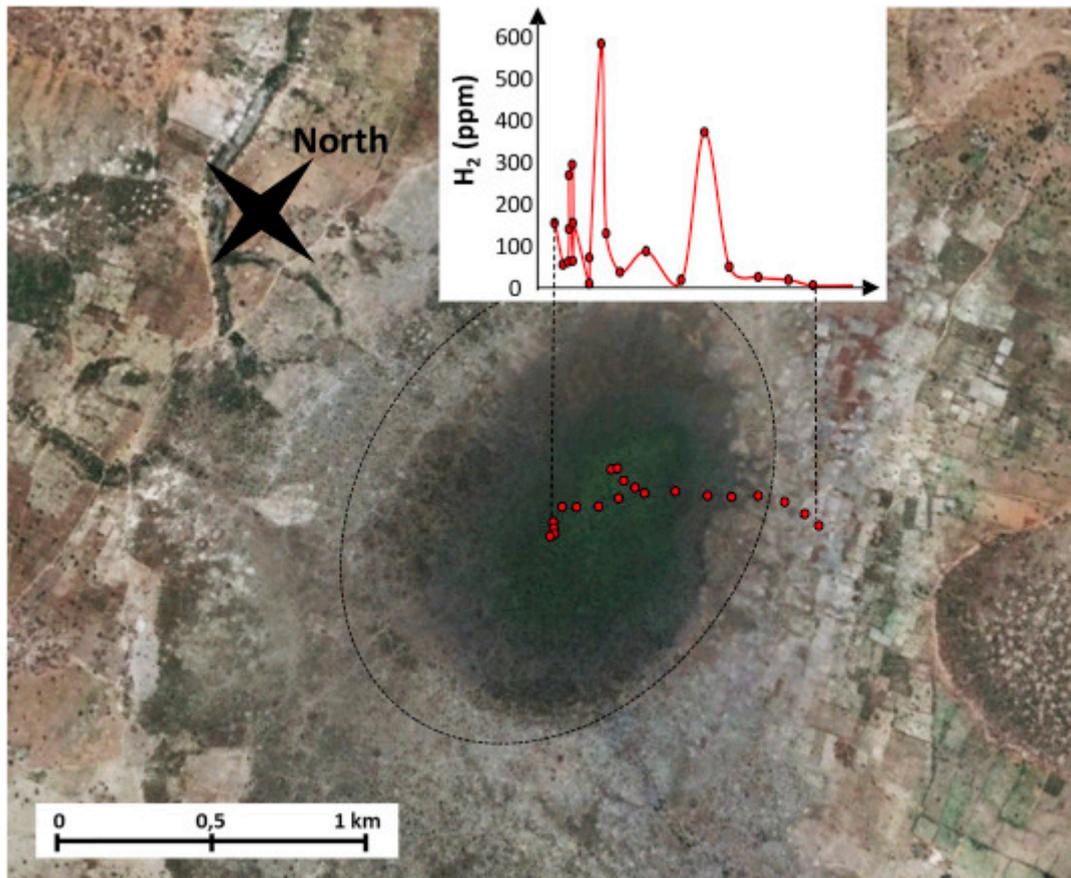


Fig # 8 -Discovery of a large accumulation of natural hydrogen in Bourakebougou (Mali)

New experimental data and reactive transport models are needed to investigate H₂ transport and storage in deep geological environments. Fundamental data such as H₂ solubility, vapor-liquid partitioning, or mineral adsorption under geologically relevant conditions are still lacking. The mechanism for H₂ trapping may rely on a combination of both H₂ adsorption properties and low solubility acting in concert as an impermeable barrier. Any attempt at modeling H₂ behavior in deep geological media will remain misleading in the absence of quantitative data on these two key processes.

EXPLORING FOR NATURAL HYDROGEN

Following the discoveries of oil and gas seeps, the “tipping point” for the petroleum industry was the well drilled by Colonel Drake. The current state of exploration for native hydrogen resembles the beginnings of oil exploration.

Geologists should now adopt the tripartite concept of “source rock, reservoir, and trap” in the exploration for native hydrogen and abiotic gases. Some important parts of the native hydrogen system are already known.

Following a discovery pathway analogous to that of the petroleum industry, the first method of exploration may be to find H₂ seeps in areas where source rocks are known. Seeps of native hydrogen and abiotic gases have already been localized in numerous places in subaerial settings.

Three main types of source rocks have already been identified:

1. ultrabasic rocks;
2. iron-rich cratons;
3. uranium-rich rocks.

For the first two sources, the production of H₂ is linked to the oxidation of Fe(II) by H₂O. For the third source, the production of H₂ is attributable to the radiolysis of H₂O by natural radioactivity. The transformation of H₂ into abiotic CH₄ can occur under some circumstances through the Sabatier or Fischer–Tropsch reactions (Reeves and Fiebig 2020 this issue). This means that detection of abiotic methane may be a useful indicator for the presence of native hydrogen.

A practical application of the understanding of H₂ behavior in the continental crust would be to develop a specifically design exploration guide. Currently, apart from targeting ophiolitic massifs or circular structures in flat sedimentary terrain overlaying cratonic basements, there is no extended exploration guide, nor any dedicated exploration well (apart the recently drilled exploratory wells in Mali).

Knowledge of hydrogen migration and accumulation in the crust is too limited to seriously consider an extensive exploration campaign. This is not surprising since 99% of the deep drilling programs are dedicated to oil and gas exploration/production in geological contexts that are not particularly relevant for hydrogen targeting. Here, we describe what could be a preliminary exploration guide based on a global ‘source-transport-accumulation’ understanding of H₂-concentrating process and combining methods used for ore targeting (so-called strategic, tactic and punctual targeting).

1. one of the key points related to potential source areas is the presence of gravity and magnetic anomalies that are typically characteristic of iron-rich rocks. These rock formations with strong anomalies, such as ultramafic rocks, or peralkaline granites, can be found at the outcrops but also are observed a few thousand meters below the continental surface. These formations often correspond to ophiolitic sutures or to peridotite massifs sandwiched during orogenic phases. The presence of Archean greenstone belts (e.g. Canadian and Fennoscandian Shields) containing ultramafic rocks may also represent excellent H₂-producing zones either via serpentinization, or water radiolysis. There are also intra-cratonic zones (e.g. Russia, North Carolina in the USA, or Mali) that may display significant H₂ fluxes, with no clear link with ultramafic rocks. Hydrothermal alteration of other Fe(II)-bearing minerals such as those listed above (amphibole, mica, chlorite) may be envisaged in these latter cases.
2. the structural/tectonic context and the presence of faults deeply rooted in the basements capable of draining a potential deep and scattered source will certainly play a very important role. A structural, gravimetric and seismic survey will be relevant to target potentially active deep faults able to drain hydrogen produced at depth where the P-T conditions are optimal.
3. if there are storage areas (i.e. a reservoir) of H₂ at depth, it will also be necessary to consider the nature of the different lithologies (e.g. mineralogy, porosity, total organic content) and develop prospection methods similar to those implemented for ore targeting. Surface seepages may be either in connection with the source rock or with an intermediate leaking reservoir. Thus, mapping H₂ concentration anomaly in soils and outcropping rock formations at different scales will be extremely instructive when superimposed to geological, seismic, and gravimetric data. Many unknown seepages are waiting for explorers to reveal their potential.

Considering the possibility to explore/detect deep reservoir of natural hydrogen in soils or aquifers close to Earth's surface appear to be severely limited for three reasons:

- a) the extremely small size of the H₂ molecule allows it to diffuse very rapidly through near-surface environments into the atmosphere
- b) the high reactivity of H₂ with many oxidants (such as Fe-oxides, Mn-oxides, and nitrates) can rapidly destroy H₂ in oxidized near-surface environments
- c) numerous microorganisms are avid consumers of H₂ as a source of energy to support their metabolisms (Ménez 2020 this issue), and these organisms may deplete H₂ in shallow environments. On this latter point, a rich literature exists that shows the link between the development of life and the availability of H₂ at Earth's surface (Martin et al. 2008; Russell et al. 2010). All these adverse factors suggest that the most successful exploration efforts are likely to involve drilling to a depth where these near-surface processes will be excluded

HYDROGEN SYSTEM VS. PETROLEUM SYSTEM

The petroleum system concepts as well as all the tools that allow us to quantify the fluid circulation within the subsurface have been shaped after years of researches and data acquisition. For the hydrogen system, the set of parameters that must be met for a deposit to exist, will have similarities but also differences.

Source, migration pathway, reservoirs, and seals remain mandatory. The various sources of H₂ are becoming better known and the rate of the generation appears to be fast. If, as it is subscript in Mali, and as it is clearly the case in all the smokers and volcanic areas, H₂ is continuously generated by the water/rock interaction it will be present in the gas, or dissolved gas as long as water is available.

The size of the reservoirs is not an issue, as one may consider a replenishment of the reservoir through human times as for geothermal reservoirs. This represents a main difference with the petroleum systems.

The migration pathways, hence the potential distance between the source rock and the accumulation, remain the least well-known part of the system.