Natural hydrogen the fuel of the 21st century

Laurent Truche[1,*], and *Elena F.* Bazarkina[2,3]

[1]Université Grenoble Alpes, CNRS, ISTerre, F-38000 Grenoble, France
[2]Institut Néel, UPR 2940 CNRS – Université Grenoble Alpes, F-38000 Grenoble, France
[3]IGEM RAS, 119017 Moscow, Russia

Abstract. Much has been learned about natural hydrogen (H_2) seepages and accumulation, but present knowledge of hydrogen behavior in the crust is so limited that it is not yet possible to consider exploitation of this resources. Hydrogen targeting requires a shift in the long-standing paradigms that drive oil and gas exploration. This paper describes the foundation of an integrated source-to-sink view of the hydrogen cycle, and propose preliminary practical guidelines for hydrogen exploration.

1 Let's go targeting natural hydrogen

The quest for sustainable energy supply at low environmental and economical cost is a major driver in the current context of the energy transition toward a low carbon society. Hydrogen (H_2) is a carbon-free fuel *par excellence* because its oxidation (i.e. combustion, fuel cells) emits only water. However, to this point, H_2 has only been regarded as an energy vector and not as a credible large-scale alternative to hydrocarbons since most production methods (e.g. methane steam reforming) currently in use only postpone CO_2 emissions. Its massive production through water hydrolysis using renewable energy is also very challenging, as it requires both pure water resources and local storage infrastructures.

The discoveries of hundreds of natural H_2 seepages, generally connected with circulation of hydrothermal fluids through ultramafic rocks [1-3], both under the seafloors and on the continents, remove these obstacles but raise important questions regarding the energy potential that these sources can represent [4] (Fig. 1). In addition, recent observations of intra-cratonic seepages and accumulations with no obvious genetic link to ultramafic formations challenges current understanding of H_2 production and fate in the crust [5-7]. The natural production of hydrogen is a recent area of scientific research, but little is known about H_2 generation, migration, consumption and potential accumulation. To date, there is neither exploration strategy nor any resource assessment, as practical guidelines for hydrogen targeting are lacking. It now appears necessary to study how H_2 migrates and becomes trapped in the Earth's crust in order to reasonably assess the recovery potential of this primary natural production.

* Corresponding author: laurent.truche@univ-grenoble-alpes.fr
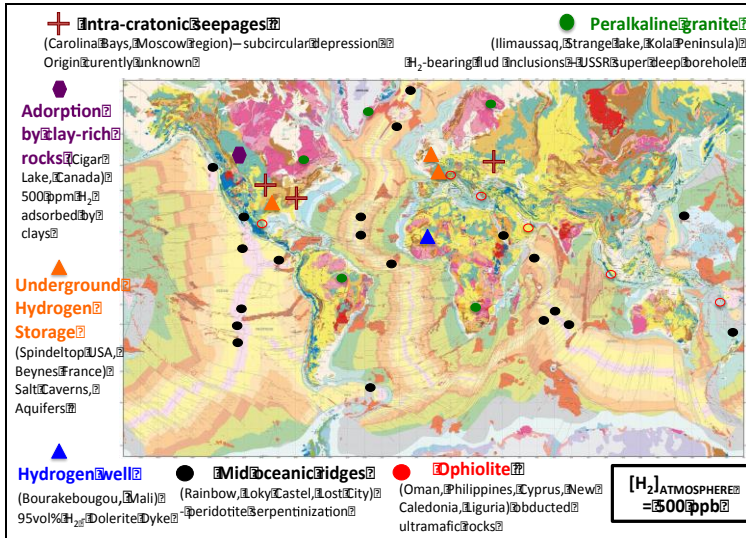
Fig. 1. Global distribution of natural hydrogen sources. Deep H_2 geological storages is also shown.

2 Hydrogen generation: challenging the "olivine monopoly"

Hydrogen is naturally produced by different reaction processes occurring in the Earth's crust (Fig. 2). The bests known are (i) the hydrothermal alteration of ultramafic rocks [8], (ii) the radiolysis of water due to U, Th, and K radioactive decay [9], (iii) the activity of certain fermentative anaerobic bacteria and cyanobacteria [10], (iv) the formation of FeS_2 from FeS [11], (v) the decomposition of methane into C-graphite and H_2 under upper mantle conditions [12], or even (vi) mechano-radical processes triggered by friction of fresh silicate mineral surfaces exposed in active faults [13]. Among these potential H_2 sources, serpentinization of ultramafic rocks remains by far the most studied. Oxidation of Fe(II)-bearing minerals (e.g. olivine, pyroxene) mainly into magnetite (Fe(II)/Fe(III) mixed oxide) leads to the concomitant reduction of water into H_2 [1, 8], according to:

$$6[(Mg_{1,5}Fe_{0,5})SiO_4] + 7H_2O_{(aq)} = 3[Mg_3Si_2O_5(OH)_4] + Fe_3O_4 + H_{2(gas)} \tag{1}$$
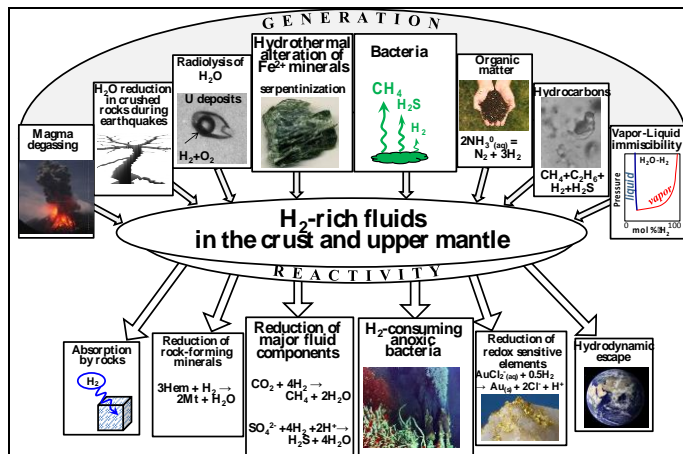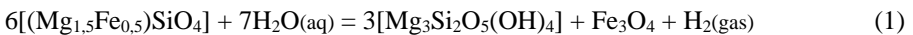
Fig. 2. Main H_2 sources and sinks in the crust.

The first observations of natural gas emissions containing H_2 date back almost a century [1, 14], but these occurrences were considered as anecdotal until about twenty years ago. It was only with the discovery of H_2-rich submarine hydrothermal vents in the late 1970s that systematic studies on the origin of natural H_2 were undertaken [2, 3]. New field studies were then conducted onshore, using the occurrence of obducted ultramafic rocks (e.g. Oman, Philippines, Turkey, Liguria-Italia, New Caledonia) as a prospecting guide [15], by analogy with the geological context of the mid-oceanic ridges (Fig. 2).

This brief history of both the first discoveries of natural H_2 sources and their associated generation mechanisms led to the paradigm that "only hydrothermal alteration of olivine-rich ultramafic rocks can produce significant amount of hydrogen". However, several geological observations suggest alternative processes to the olivine serpentinization for H_2 generation.

(1) Hydrogen is a major gas component (up to 30%) trapped in evaporite formations, and in particular in salt deposit containing significant amount of carnallite and other hydrated potassic salts [16]. This hydrogen may have several origins: (i) production during early biodegradation of organic matter, (ii) water radiolysis due to elevated concentration of ^{40}K and ^{87}Rb, and (iii) exogenic sources and subsequent migration into evaporite formations.

(2) Hydrogen may be particularly enriched in coals. Levshounova [17] reports hydrogen content ranging from 2.9 to 40% in former Soviet Union coal derived gases. Hydrogen, produced at the early stage of organic matter maturation may remains trapped or adsorbed within the micropores of coals, as it is the case for methane.

(3) Hydrogen is particularly enriched in peralkaline intrusive rocks such as Lovozero, Khibiny (Kola Peninsula, Russia), Ilimaussaq (Greenland), and Strange Lake (Canada) plutons [18]. Fluid inclusions may contain up to 40 mol% H_2, and the Kola super-deep borehole [19] is known for its surprisingly high H_2 production. It is proposed that hydrothermal alteration of Fe(II)-bearing amphibole (arfvedsonite) may generate H_2 in these contexts, according to:

$$3Na_3Fe^{II}_4Fe^{III}Si_8O_{22}(OH)_2 + 2H_2O_{(aq)} = 9NaFe^{III}Si_2O_6 + 2Fe_3O_4 + 6SiO_2 + 5H_{2(gas)} \quad (2)$$

(4) Hydrogen seepages have been recently discovered in subcircular depressions located in intra-cratonic basins with no clear association with ultramafic complexes, such as the East European craton in Russia [5], the Atlantic coastal plain in North Carolina, USA [6], or the Taoudeni basin, Mali [7]). The nature of the source is currently highly debated.

Clearly, olivine serpentinization is not the only process able to trigger H_2 production. Bacterial fermentation, water radiolysis, and hydrothermal alteration of other Fe(II)-bearing minerals such as amphibole, mica, chlorite or siderite are likely to play this role.

3 Hydrogen migration and reactivity: the known unknown

Once produced, H_2 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 [9, 20], or as a reagent for abiotic hydrocarbons synthesis [8], but rarely, if ever, as a carbon-free energy resource [4]. 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 H_2 is trapped in deep sedimentary formations overlying intra-cratonic crystalline basements.

   i. *Widespread H_2 enrichment in water-saturated clay-rich rocks at 20°C surrounding*

the Cigar-Lake uranium deposits, Athabasca, Canada [21]. Thermal desorption measurements reveal that H_2 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 H_2 uptake is comparable and even exceeds adsorbed methane capacities reported elsewhere for pure clay minerals or shales. Up to 17% of H_2 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 H_2 in the crust.

ii.   *Large accumulation of H_2 in the Taoudeni Basin, Bourakebougou field, Mali* [7]**.** Recent exploratory wells in Mali, close to the village of Bourakebougou, confirm the presence of an extensive H_2 field featuring at least five stacked reservoir intervals containing significant H_2 content (up to 98 vol.% of gas) and covering an estimated area higher than 8 km in diameter. The relatively pure H_2 reservoirs are associated with traces of methane, nitrogen and helium. The geological stratigraphic accumulation of H_2 is linked to the presence of multi overlaid doleritic sills and aquifers that seem to prevent upward gas migration and leakage.

New experimental data and reactive transport models are needed to investigate H_2 transport and storage in deep geological environments. Fundamental data such as H_2 solubility, vapor-liquid partitioning, or mineral adsorption under geologically relevant conditions are still lacking. The mechanism for H_2 trapping may rely on a combination of both H_2 adsorption properties and low solubility acting in concert as an impermeable barrier. Any attempt at modeling H_2 behavior in deep geological media will remain misleading in the absence of quantitative data on these two key processes.

4 Hydrogen targeting: providing practical exploration guidelines

Finally, a practical application of the understanding of H_2 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 very recently drilled exploratory wells, that have been completed close to a fortuitous discovery made in the late 1980's near Bourakebougou, Mali [7]. 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 H_2-concentrating process and combining methods used for ore targeting (so-called strategic, tactic and punctual targeting).

First, 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 H_2-producing zones either via serpentinization, or water radiolysis [21]. There are also intra-cratonic zones (e.g. Russia, North Carolina in the USA, or Mali) that may display significant H_2 fluxes [5-7], 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.

Second, 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.

Third, if there are storage areas (i.e. a reservoir) of H_2 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 H_2 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 awaiting for explorers to reveal their potential.

References

1. C. Neal, and G. Stanger, *Earth Planet Sci Lett* **66**, 315-320 (1983)
2. J.L. Charlou et al., *J Geophys Res* **101**, 899-919 (1996)
3. D.S. Kelley et al., *Science* **307**, 1428-1434 (2005)
4. N.J.P. Smith et al., In Doré, A.G. & Vining, B.A. (eds) *Petroleum Geology : North-West Europe and Global perspectives-Proc 6th Petrol Geol Conf*, 349-358 (2005)
5. N. Larin et al., *Nat Resour Res* **24**, 369-383 (2015)
6. V. Zgonnik et al., Prog Earth Planet Sci **2**, 31 (2015)
7. A. Prinzhofer et al., *Int J Hyd Ener* **43**, 19315-19326 (2018)
8. M. McCollom, and J.S. Seewald, *Elements* **9**, 129-134 (2013)
9. L.-H. Lin et al., *Gcubed* **6**, Q07003 (2005)
10. R. Nandi, and S. Sengupta, *Crit Rev Microbio* **24**, 61-84 (1998)
11. E. Drobner et al., *Nature* **346**, 742-744 (1990)
12. A. Kolesnikov et al., *Nat Geosci* **2**, 566-570 (2009)
13. T. Hirose et al., *Geophys Res Lett*, **38**, (2011)
14. C. Bohdanowicz., *AAPG Bulletin* **18**, 746-759 (1934)
15. E. Deville E, and A. Prinzhofer, *Chem Geol*, **440**, 139-147 (2016)
16. A.F. Smetannikov, *Geochem Int* **49**, 916-924 (2011)
17. S.P. Levshounova, *Doklady Acad. Sci*., USSR Earth Sci Sect **272**, 73-75 (1983)
18. J. Potter et al., *Lithos* **183**, 114-124 (2013)
19. S.V. Ikorsky et al., *Geol J* **107**, 145-52 (1993)
20. B. Sherwood Lollar et al., *Nature* **516**, 379-382 (2014)
21. L. Truche et al., *Earth Planet Sci Lett* **493**, 186-197 (2018)