Natural H\(_2\) exploration: tools and workflows to characterize a play

Dan Lévy\(^1,\,*\), Vincent Roche\(^2,3\), Gabriel Pasquet\(^2\), Valentine Combaudon\(^2,4\), Ugo Geymond\(^1,4\), Keanu Loiseau\(^2,5\), and Isabelle Moretti\(^2,3\)

\(^1\) Institut de physique du globe de Paris (IPGP), CNRS, Université Paris Cité, 1 rue jussieu, 75005, Paris, France
\(^2\) Laboratoire des Fluides Complexes et leurs Réservoirs (LFCR), E2S UPPA, Université de Pau et des Pays de l’Adour, Avenue de l’université, 64000 Pau, France
\(^3\) Institut des Sciences de la Terre de Paris (ISTeP), Université Pierre et Marie Curie, 4 place Jussieu, 75005 Paris, France
\(^4\) IFP Energies Nouvelles (IFPEN), 1-4 Av. du Bois Préau, 92852 Rueil-Malmaison, France
\(^5\) CVA-Engineering, 2 Rue Johannes Kepler, 64000 Pau, France

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Abstract. Natural dihydrogen (H\(_2\)) exploration is now active in various countries, but tools and workflows that help to characterize prospective zones are still poorly defined. This review paper is dedicated to share our experience in characterizing H\(_2\) plays based on exploration efforts carried out in many countries in Europe, North and South America, Africa, and Oceania between 2017 and 2023. We decided to focus on onshore exploration where three main reactions are generating H\(_2\): (i) redox reactions between Fe\(^{2+}\) and H\(_2\)O, (ii) radiolysis of water and, (iii) organic late maturation where H\(_2\) comes from hydrocarbons. This leads to classify the H\(_2\) generating rocks (H\(_2\)-GR) into four types that seem us the more likely to be of economic interest: basic and ultrabasic rocks of oceanic/mantellic affinity (H\(_2\)-GR1), iron-rich bearing sedimentary and intrusive rocks (H\(_2\)-GR2), radioactive continental rocks (H\(_2\)-GR3) and organic matter-rich rocks (H\(_2\)-GR4). For the pre-fieldwork, the workflow aims to target new promising areas for H\(_2\) exploration. Cross-referencing the presence of H\(_2\)-GR in the basement, classical geological-hydrodynamic features (fault, water source), and already-known H\(_2\) occurrences at the surface remain essential but should be accompanied by remote sensing analyses to detect possible H\(_2\) occurrences. For the fieldwork, the focus is made on gas and rocks. A discussion is led concerning the importance of punctual measurements and long-term monitoring of gas seepages, that allow to conclude on dynamics of H\(_2\) leakage from depth through space and time. For the post-fieldwork, we present the most useful analytical tools to characterize H\(_2\) gas seepages and the suspected H\(_2\)-GR. The critical parameters to estimate the H\(_2\) potential of a rock are the content in Fe\(^{2+}\)/Fe\(_{tot}\) (H\(_2\)-GR1 and H\(_2\)-GR2), the content of radioactive elements U, Th, K (H\(_2\)-GR3), and the total organic content (H\(_2\)-GR4). The hydrogen exploration is in its infancy and all the profession is attempting to define an automated and fast workflow. We are still far away from it due to a lack of data, yet this review presents a practical guide based on the current knowledge.

Keywords: Natural H\(_2\), Exploration, H\(_2\) generating rocks, H\(_2\) play.

1 Introduction

Dihydrogen (H\(_2\)) is an important molecule used in the chemical industry as well as in the mobility sector. But, the main processes of producing H\(_2\) are based on the use of hydrocarbons and coals which emit CO\(_2\). The green hydrogen formed by electrolysis from green electricity is also considered as an important player in the future H\(_2\) market because of its lower carbon impact. However, since the discovery in 2007 (Diallo et al., 2022) of an almost pure H\(_2\) accumulation in a well in Mali, the idea that natural hydrogen could be considered as a primary energy without greenhouse gases emission is emerging. Yet, the discovery of this well has been fortuitous, and at that time, the natural H\(_2\) exploration was at its early stage (Smith et al., 2005).

Since then, a lot of new studies were launched based on the multiple works on serpentinization, a process known to produce H\(_2\) in the mid-oceanic ridges (MOR; Klein et al., 2017; Mével, 2003; Proskurowski et al., 2006) and new evidence of H\(_2\) presence in other geological contexts (Boreham et al., 2021; Larin et al., 2015; Lefèvre et al., 2021; Prinzhofer et al., 2018, 2019; Zgonnik et al., 2015). It has been 10 years since H\(_2\) was actively explored and the acquired data and experience have only been rising (Truché et al., 2020). Whereas several reviews appear on defining the different sources of H\(_2\) (Worman et al., 2020; Zgonnik, 2021), this study aims to present a practical guide to share our experience in characterizing H\(_2\) plays based on exploration efforts carried out in many countries in Europe, North and South America, Africa, and Oceania between 2017 and 2023.
2020), it is not always relevant in terms of risks taken to produce natural H$_2$ (Gaucher et al., 2023). Here, we discuss exploring H$_2$ onshore which is consistent with H$_2$ production. Moreover, we decided to focus on the first steps of the exploration and we do not take into consideration the seals and reservoirs allowing the accumulation of H$_2$.

Based on our experience of H$_2$ exploration in many regions of the world (France, Italy, Iceland, Brazil, Republic of Djibouti, Ethiopia, South Africa, Namibia, Bolivia, and Australia), we propose tools to efficiently explore this new resource divided into four steps: (i) pre-fieldwork consisting on spotting the H$_2$ hot spots thanks to existing literature and remote sensing techniques, (ii) fieldwork during which we acquire in situ gas data and samples of potential rocks of interest, (iii) post-fieldwork during which we perform laboratory analyses on gas and rocks, and (iv) discussion of results to better characterize a play.

2 Pre-fieldwork

Pre-fieldwork consists in reviewing all available data that may provide information indicating the presence of H$_2$ (i.e., seepage or measurement of H$_2$ in water sources or wells generally done for another purpose) and/or the presence of H$_2$-generating rocks (H$_2$-GR) at various scales (e.g., country, basin) to select and define a prospective area. We first present a review of the lithologies as well as minerals favorable to the H$_2$ generation to locate the main areas of interest. Then we present the different tracers indicating the presence of H$_2$ and we propose a new approach based on remote sensing to investigate H$_2$ occurrences in Sub-Circular Depressions (SCDs). Finally, we present a workflow combining all these tools.

2.1 Lithologies of interest for H$_2$ generation

To target the locations where H$_2$ can be present in abundance, it is important to first define the processes that generate H$_2$. However, as previously mentioned, we will not emphasize the processes occurring offshore or in geothermal areas. Indeed, offshore will not be immediately profitable to produce natural H$_2$ (Gaucher et al., 2020), it is not always relevant in terms of risks taken to produce H$_2$. Moreover, no company is targeting volcanic H$_2$, which may come from the decomposition of H$_2$S (Zgonnik, 2020), and it will not be addressed here.

Other processes like degassing of deep H$_2$ (Zgonnik, 2020), and mechanoradical (Hirose et al., 2011), could also contribute to the generation of H$_2$ but we would not mention it because it is currently difficult to trace it in the context of H$_2$ exploration. Moreover, no company is targeting volcanic H$_2$, which may come from the decomposition of H$_2$S (Zgonnik, 2020), and it will not be addressed here.

These three aforementioned processes lead us to divide the main H$_2$-GR into four main groups presented in Figure 1:

- **H$_2$-GR1**: Basic and ultrabasic rocks from mantelic/ oceanic affinity (e.g., peridotite, gabbro, basalt); their hydrothermal alteration generates H$_2$ through different reactions like the serpentinization process.
- **H$_2$-GR2**: Iron-bearing rocks (sedimentary rocks such as banded iron formations (BIFs), intrusive rocks such as biotite-rich granites . . . ) that generate H$_2$ through oxidation-reduction processes during aqueous alteration.
- **H$_2$-GR3**: Radioactive rocks that may generate H$_2$ through radiolysis, in the presence of H$_2$O.
- **H$_2$-GR4**: Organic-rich rocks such as coal, shale, and coaly shale that generate H$_2$ at high temperatures. It is the only group generating H$_2$ independent of H$_2$O.

(ii) Radiolysis involves the natural radioactive decay of the elements such as uranium, potassium, and thorium. In this case, radiolysis leads to the dissociation of water molecules, if present, into H and OH. This mechanism is usually invoked in the Archean and Proterozoic domains where rocks contain uranium-, potassium- and thorium-rich minerals.

(iii) It was recently shown that the late pyrolysis of organic matter (especially coal and shaly coal) also generates H$_2$ that may remain as a free gas (Horsfield et al., 2022; Mahlstedt et al., 2022; Suzuki et al., 2017).

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(i) For many years, hydrogen was considered to be mainly generated by the reaction of serpentinization which is the process of aqueous alteration of peridotite into serpentine, where the olivine is altered into serpentine and magnetite produces H$_2$. This process takes place mainly in the MOR at temperatures between 150 °C and 350 °C (Klein et al., 2013) and also onshore on the ophiolites at lower temperatures (Etioppe et al., 2011; Neal and Stanger, 1983; Vacquand et al., 2018). If we simplify the reaction of alteration, the serpentinization process can be considered a redox reaction where Fe$^{2+}$ in olivine is oxidized into Fe$^{3+}$ in magnetite while reducing water into H$_2$:

$$2\text{Fe}^{2+} + \text{H}_2\text{O} = \text{Fe}^{3+}_2\text{O}_3 + \text{H}_2.$$ (1)

Redox reactions are present in many alteration processes that are now considered favorable for the production of H$_2$, like the alteration of Banded Iron Formations (BIFs; see e.g. Geymond et al., 2022), containing magnetite that can be altered into maghemite and/or hematite. These rocks are mainly present in cratonic areas and recent experimental alteration studies showed that such a process could occur at low temperatures (Geymond et al., 2023).

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associated minerals forming the rock can catalyze or inhibit these reactions. Thus, it is important to characterize the mineralogical assemblage. The minerals are presented in Table 1 and the reaction paths for redox reactions are given in Appendix A.

Figure 2 shows four maps that we synthesized based on the worldwide distribution of H2 GR introduced previously. The first map indicates the spatial surface distribution of H2_GR1 consisting of slices of oceanic lithosphere onto the continent (named ophiolites) that could undergo serpentinization. H2 measurements (green dots) potentially related to this process are located in several places related to ophiolites/peridotitic massifs such as in Spain (Ronda, Etiopie et al., 2016), Oman (Chavagnac et al., 2013; Neal and Stanger, 1983), Turkey (Chimaera, Etiopie et al., 2011), Philippines (Zambales, Abrajano et al., 1988), New Zealand (Etiope et al., 2006), India (Srivastava et al., 2006), and Iceland (Harris et al., 2003). In Figure 2, the H2 GR2, H2 GR3, and H2 GR4 are also presented in the maps. H2 GR2 and H2 GR3 are related to iron-bearing rocks consisting of magnetite, pyrrhotite, and other minerals such as garnet, siderite, and Mg-rich minerals. H2 GR4 is related to organic-rich rocks such as kerogens.

Table 1. H2 generating rocks (H2 GR) and their related minerals of interest for H2 generation.

<table>
<thead>
<tr>
<th>Geological context</th>
<th>Oceanic rocks</th>
<th>Continental rocks</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2 GR type</td>
<td>H2 GR1: Oceanic lithosphere, Ophiolites</td>
<td>H2 GR2: Iron-bearing rocks (BIF, greenstone belts)</td>
</tr>
<tr>
<td>Process</td>
<td>Redox reactions</td>
<td>Redox reactions</td>
</tr>
<tr>
<td>Minerals of interest</td>
<td>Olivine, Pyroxene, Amphibole, Chlorite, Serpentine, Magnetite, Pyrrhotite</td>
<td>Olivine, Pyroxene, Amphibole, Chlorite, Serpentine, Magnetite, Garnet, Siderite, Pyrrhotite</td>
</tr>
<tr>
<td>H2 GR3: Granitic and sedimentary rocks</td>
<td>H2 GR4: Organic-rich rocks (shale, coal)</td>
<td></td>
</tr>
<tr>
<td>Minerals of interest</td>
<td>Radiolysis</td>
<td>U-minerals, Micas, K-feldspars, Organic matter (kerogens)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Clay minerals</td>
</tr>
</tbody>
</table>
Fig. 2. Global presence of $\text{H}_2$ GR indicated on a topographic map (ESRI National Geographic USA Topo Maps). (a) The spatial distribution of ophiolites from Vaughan and Scarrow (2003). (b) Cratonic and proterozoic zones (Furnes et al., 2015) combined with fairy circles location (Larin et al., 2015; Zgonnik et al., 2015) and BIFs (Aftabi et al., 2021). (c). Distribution of uranium provinces differentiated by lithologies from the International Atomic Energy Agency (2021). (d) Spatial distribution of coal deposits. Note that dots from the study of Zgonnik (2020) correspond to $\text{H}_2$ detections in various environments at concentrations $\geq 10$ vol.%.
Caledonia (Deville and Prinzhofer, 2016), and in the Balkans (Lévy et al., 2023). Even if the ophiolites represent small areas on the land scale compared to MORs, they represent a huge potential for serpentinization and therefore $\text{H}_2$ generation.

Figure 2b shows the location of $\text{H}_2$ GR2 that corresponds mainly to BIFs (red dots) occurrences associated with cratonic areas, including also Proterozoic rocks. At first glance, there is a correlation between these old rocks, $\text{H}_2$ detections, and SCDs, some of which are proven to be related to $\text{H}_2$ emanations (Geymond et al., 2022; Moretti et al., 2021). Indeed, all these indicators are often localized close to BIFs (Brazil, Australia, the United States, Namibia, and Russia). But, other lithologies (igneous rocks, Precambrian rocks, or associated with ore bodies) present mainly in Archean and Proterozoic rocks are also associated with $\text{H}_2$. For example, hydrothermal alteration of peralkaline intrusions (e.g., Strange Lake in Canada, Lovozero, and Khibiny in Russia) may lead to $\text{H}_2$ generation (Truche et al., 2021). In such a context, the Fe$^{2+}$-bearing amphibole is considered as a reducer, and water is an oxidant (1). Other mine areas look also promising as evidenced by Boreham et al. (2021) and Malvoisin and Brunet (2023).

Figure 2c combines the uranium provinces and the Archean and Proterozoic rocks. The $\text{H}_2$ GR3 corresponds therefore to the rocks that can generate $\text{H}_2$ from the radiolysis of water. Such a process may be present everywhere but with different intensities. At large scale, there are some overlaps with the Archean and Proterozoic domains because these rocks contain various uranium- and thorium-rich minerals. Further, the best way to identify the radiolysis mechanism is probably related to the presence of He, because crustal He could only be generated by radioactivity. They are sometimes found together such as in Australia (Leila et al., 2022), South Africa (Karolyté et al., 2022), and the USA (Halford et al., 2022).

Finally, Figure 2d indicates the spatial distribution of the coal resources. There is no clear correlation between the $\text{H}_2$ measurements (HC fields, water from HC fields, and coal basins following the classification of Zgonnik (2020) and coal deposits yet. This implies that $\text{H}_2$ potential is probably underestimated in the coal deposit areas. In general, it is better to have more than one $\text{H}_2$ GR in the selected country to increase the probability of success, and/or a large zone with a potential $\text{H}_2$ GR. For example, Australia, the USA, Brazil, and Russia have at least three types of $\text{H}_2$ GR.

2.2 Indicators of the $\text{H}_2$ presence

After locating the potential zones of interest for $\text{H}_2$ generation, different methods can be used to focus on zones that are targets for $\text{H}_2$ production. First, work on finding data in the available literature has to be done. Indeed, some interesting information can indicate the direct presence of $\text{H}_2$ in wells or gas seeps. If no data on the $\text{H}_2$ presence is available, it is possible to map the different gas emissions (dissolved or not) in boreholes, free gas vents, or as bubbles whatever the flux.

2.2.1 Boreholes and seismic data

Many discoveries of $\text{H}_2$ occurrences were made after drilling campaigns for Oil and Gas (O&G), mining, or hydrogeological purposes (Fig 3a). In the Yorke Peninsula (Australia), $\text{H}_2$ was noted for the first time in the early 20th century after the drilling of an oil exploration well, the Minlaton Oil Bore (Ward, 1933) which reached 548 m in depth. Similarly, in Kansas (USA), eight oil exploration wells were drilled in the 1980s. Scott#1 (677 m) and Heins#1 (770 m) wells gave unusual free gas compositions with an average $\text{H}_2$ of 29 and 37 vol.%, respectively (Coveney et al., 1987; Guéard et al., 2017). In more recent exploration wells, $\text{H}_2$ is often not mentioned but it makes sense to revise all the available literature. For example, Zgonnik (2020) compiled hundreds of sites where $\text{H}_2$ has already been measured based on archive data (Fig. 2). In Australia (around Adelaide), in the USA (Kansas), and in Spain, the first natural $\text{H}_2$ exploration licenses have been taken around historic wells with $\text{H}_2$-rich gases. Thus, well reports and associated survey reports must be examined carefully to derisk large areas. Here, $\text{H}_2$ can be directly mentioned, or in certain cases, hidden in “undefined inflow gases”. It is important to mention that $\text{H}_2$ may also be generated by causing oxidation.

The gas chimneys and pockmarks (Fig. 3b) are also proof of gas dismigration. Well-imaged on high-resolution 3D offshore seismic data, they could be also visible onshore, even on 2D seismic lines. Gas chimneys are rooted in the basement and have been, for instance, described in Australia (Leila et al., 2022). Such features make it possible to be confident of the existence of a gas flow at depth, even if the gas chemistry cannot be extrapolated.

Geophysical data can be acquired to detect the presence of dense and/or magnetic $\text{H}_2$ GR like mantellic rocks and BIF, from gravity (Leeduivre et al., 2021) and magnetic susceptibility measurements respectively.

2.2.2 Free gas vents

There are a few surface markers that allow us to recognize $\text{H}_2$ emanations. If the concentration is large enough, self-ignition of $\text{H}_2$ can occur, with an invisible flame. When blended with CH$_4$, the flame can be observed. Such a permanent fire is a curiosity often reported as in Chimaera in Turkey. This “flaming rock” has been known since at least 2000 AD, and recent analyses revealed $\text{H}_2$ concentrations up to 11 vol.% in the free gas mixture whereas CH$_4$ concentrations reach ~87 vol.% (Etiope et al., 2011). In areas of geothermal activity, fumaroles have also to be targeted (Fig 3c, South Lópe, Bolivia; Moretti et al., 2023). For example, $\text{H}_2$ contents ranging from 0.2 to 4.6 vol.% and around 0.7 vol.% were measured in H$_2$O-rich free gases rising to the surface at around 95 °C in the Larderello geothermal zone (Leila et al., 2021) and in the Asal rift (Pasquet et al., 2021) respectively.

2.2.3 Dissolved gases and bubbling water:

Dissolved gases and bubbling water reflect the pathway of fluids within the crust and therefore testify and offer
potential proxies of water-rock interaction processes (Fig. 3d). The H₂ may first be dissolved in the aqueous phase since high pressure increases the solubility of H₂ (Lopez-Lazaro et al., 2019). A decrease in pressure near the surface triggers H₂ exsolution, favoring the bubbling in spring waters. This is observed for instance in the ophiolitic contexts that currently get serpentinized. H₂-rich bubbling is reported in New Caledonia (up to 36 vol.%), Oman (up to 87 vol.%), the Philippines (up to 59 vol.%), and the Balkans (up to 84%) (Lévy et al., 2023; Randazzo et al., 2021; Vacquand et al., 2018). In this kind of spring, the water is usually hyperalkaline, with a pH higher than 9 often related to the serpentinization process. So, the presence of bubbles in water could be a good candidate to find natural hydrogen when H₂ GRs have been identified in the area. Before going to the field, therefore it is recommended to identify these thermal manifestations (e.g., fumaroles, springs).

2.2.4 The special case of SCDs

SCDs are an important marker of H₂ flow in the soils (Figs. 3e–3h). They have been first described and linked to H₂ presence in Russia (Larin et al., 2015) and then targeted all over the world (in the USA, Zgornik et al., 2015; Mali, Prinzhofer et al., 2018; Brazil, Prinzhofer et al., 2019; Moretti et al., 2021b; and Australia, Frery et al., 2021; Moretti et al., 2021a). However, all the SCDs are not related to H₂ emanations. The first publications were only based on the geometric parameters of the SCDs.
(size, depth, density). Here, we present the recent improvements in the detection of H₂-related SCDs.

2.2.4.1 Morphological characteristics

Size, slope, and depth. The SCDs have a circular and/or ovoid feature shape in the landscapes (Figs. 3e and 3g) and may be easily identified from satellite images such as Google Earth images (Figs. 3f and 3h). In rare cases, the shape is a dome-like structure (SCDo) and may reach also a few meters in height. When present in an area, the SCDs are numerous often exceeding one hundred. Depending on the location, the size of the circle generally varies from 25 m to 1 km in diameter and a few meters in depth. Moretti et al. (2021a) used a statistical approach to the size of the circle in terms of equivalent diameter which corresponds to a perfect circle diameter having the same area as the SCD. They showed also a relationship between this equivalent diameter and the depth that is around 1% and that the slope at the border of the depression is usually less than 3%. Thus, slope mapping may be used to identify rapidly the SCDs. For example, Figure 4 indicates the differences between these natural structures (central part), the anthropic ones (perfect circles NW), and the rivers in the Minas Gerais region in Brazil. In this area, 86 SCDs have been reported with an average depth/diameter of 0.013 (Moretti et al., 2021a). These three characteristics (depth, depth/diameter, and slope) allow us to differentiate the karst-related dolines from the SCDs even if the size could be similar.

In parallel, other SCDs could be observed from satellite images although they happen to be not related to any H₂ emanations when we go further on the field (Fig. 5). Additional criteria might help when the differences from the satellite images are not straightforward with the H₂-related SDCs. In the case of Namibia and South Africa, some depressions are characterized by both ovoid and circular shapes, exhibiting a gap of vegetation and are only a few meters deep but are probably related to wind activity in these desert areas and/or to termite activity (Tinley, 1971), even though other processes are not totally excluded (e.g., plants with poisonous Euphorbia plants, Theron (1979) or rodent activity, Cox (1987)). Some of them are located in the northern part of South Africa, in the low and high topographic zones, and measure only a few meters in diameter (Fig. 5a). They are also numerous in Namibia, and are easily differentiated by their small sizes and their regular hexagonal patterns with a clear degree of spatial ordering. Others are located in the desert in the southeastern part of Namibia and related to dunes activity favored by wind flow blowing (Fig. 5b). The size of the depressions here is a few hundred meters in diameter and tens of meters in depth. Thus, the systematic anisotropy of the depth and slope with regard to the wind direction is a criterion that has to be checked.

2.2.4.2 Multispectral anomalies

To better characterize the H₂-related SCDs, Moretti et al. (2022) have recently proposed a proxy based on Landsat Multispectral Images through their Normalized Difference Vegetation Index (NDVI) and Soil Adjusted Vegetation
Index (SAVI) combined with the coastal aerosol band. They observed that, in the case of H₂ seepage, the vegetation evolves within the circular structure ranging from scarce in the center to healthy toward the edge. Such a particular evolution allows them to discriminate H₂-emitting structures from other depressions. Figure 6 shows indexes that highlight the SDCs from satellite data on the Brazilian structure studied by Prinzhofer et al. (2019) and (Moretti et al., 2021b).

Further, other indexes may be used to differentiate the SDCs from the rest like the gamma-ray anomalies described in Brazil around the SCDs (Rigollet and Prinzhofer, 2022) or the ferrous mineral ratio that can also be estimated from the Landsat image. This latter ratio can be used to detect iron-bearing rocks outcropping at a regional scale.

2.2.4.3 Evolution of SCDs with time
Other data could be also interesting to evaluate the change of SCDs over time. Google Earth satellite images may be watched through time and the onset of SCDs has been already observed in Russia (Larin et al., 2015) as well as in the USA (Zgonnik et al., 2015). In areas where agricultural activity is intense, it can be noted that the efforts of farmers to cultivate the SCDs areas failed. A few years later, the vegetation anomaly related to the SCDs comes back. Further, in the same way, the Landsat images may be used to characterize SCDs evolution. In some specific regions, the timing of the vegetation indexes acquisition above the SDCs could influence the interpretation. Indeed, both NDVI and SAVI depend on rainfalls or snow precipitations. If those precipitations are important, the indexes can change drastically. This is particularly the case for cold areas such as Russia (Fig. 7). Here, snow is present and covers the SCDs a part of the year. It is therefore important to show the related RVB image before interpreting the results. But, in our experience, the SCDs related to gas emanations are always visible. Finally, the study of the soil vertical displacement using high-resolution DEM and/or interferometry would be also interesting to ensure that

Fig. 5. Sub-circular structures without H₂ emanations and without vegetation observed (a, c) on the field and (b, d) on Google Earth. See Appendix B for coordinates.
Fig. 6. SCDs in Brazil (see location Fig. 4). (a) Satellite Google Earth image. (b, c) Vegetation Indexes deduced from the Landsat infrared images showing healthy vegetation in red around SCDs. Note that they highlight three major H₂-emitting structures as well as a larger one that encompasses them. (d) Aerosol index showing low concentrations in light blue around SCDs.

Fig. 7. (a) Comparison of the expression of SCDs in Russia in summer and winter and (b, c) zoom in the black square on SAVI and aerosol data. See Appendix B for coordinates.
the structure is still active, however, there is no publication on such a technique.

2.3 Workflow for the pre-fieldwork

Two points are important to get a probability map of H₂ and to define a pre-field workflow: (1) selecting the favorable geological areas for H₂ generation combining potential H₂ GR and subsurface data and (2) reporting known and suspected H₂ occurrences (Fig. 8). In addition, if the area of interest is located on an ophiolite, hyper alkaline fluids, direct proxy of current serpentinization (Abrajano et al., 1988; Barnes et al., 1967; Deville and Prinzhofer, 2016; Neal and Stanger, 1983), have to be mapped. Conversely, in intracratonic contexts, a relation between the presence of SCDs and the presence of H₂ has been made and the study of SCDs is very useful in such contexts, although obviously, the presence of SCD is neither necessary nor sufficient, to confirm, or invalidate, an H₂ accumulation.

3 Fieldwork: sampling and measurements

3.1 Gas

For all the aforementioned source types of H₂ emissions, different sampling protocols have been used in the past years based on the experience of other gas emanations. Before collecting the gas, the first step is to channel the flux in an adapted way to prevent any additional air contamination. Then two main ways of sampling exist depending on the analyses of interest and the gas content.

3.1.1 Sampling

3.1.1.1 Channelizing the gas flux

Based on literature and field trip experiences, Figure 9 presents various ways to efficiently channel fluxes depending on their source types.

For the free gas vents (Fig. 9a) or bubbling water (Fig. 9b), the protocol detailed in Pasquet et al. (2021) can be used. It consists in placing a funnel upside down just above the gas flow. Our funnel is connected to a silicon tube that is resistive regarding elevated temperatures around 100 °C. By putting the extremity of the tube in a water container and observing the formation of bubbles, we ensure that the gas flux circulates in the whole tube and that no contamination of atmospheric air comes by the exit of the tube. We recommend waiting several minutes for gas bubbling in the container to expel any ambient air remaining in the tube and to flush the line with the gas of interest. In the case of bubbling water sources, the protocol is the same, except that the funnel should be placed below the water surface to prevent air contamination.

For boreholes (Fig. 9c), the channelizing is already done by the casing itself. As described in Guélard et al. (2017), a plugged drill hole header prevents any air contamination and allows the accumulation of the free gas phase or the water pressure depending on the artesian pressure inside the drill hole. In the case of an artesian well, connecting the borehole plug valve to a semi-closed container is necessary to favor the gas exsolving.

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Contrary to other source types, soil gas (Fig. 9d) is much more difficult to channelize since the involved fluxes are discontinuous and much weaker. We can note that no consensus yet exists on the right way to sample...
A one-meter-deep hole can be drilled in the soil at first. To limit H₂ generation artifacts related to the drilling, percussion rather than rotation should be privileged (Lefeuvre et al., 2021) but from our experience, the results are often the same. Afterward, a tube equipped with several holes at the bottom is pulled down in the drilling hole, channelizing the gas to the top of the tube. By closing the valve at the top of the tube, the soil gas moving upward starts to accumulate and can be sampled after various times of accumulation depending on the flux involved (hours to days).

3.1.1.2 Sampling: vials vs. aliquots
The first method presented in Figure 9e shows gas sampling into vials usually applied for major gas analyses. The technique consists of connecting a three-way valve on the tubing to channel the gas flux. One of the three ways is equipped with a butyl septum and allows gas to accumulate after the flushing. Stinging the septum of the vial already under vacuum with a syringe, the pressurized gas is then collected. Although the container septum should be completely gas-tight, we suggest slightly overpressurizing the glass container to ensure that the gas leak is oriented outward in case of minor septum breakdown during transportation and thus preserves the quality of the sample. Usually, we roughly overpressurize by a factor of 1/3. To go further, varnish should also be added to cover septums where they have been stung in the case of prolonged sample storage. The use of vials is fast and economical and thus appears very appropriate when a lot of samples are collected. However, as described earlier, the method involves several sources of possible contamination during sampling,
transportation, and storage: among others, the use of a syringe with a needle that is in contact with atmospheric air and/or the uncertainty concerning the air tightness of the septum are major sources of possible additional sample contamination.

For higher-quality sampling, another standard technique detailed in Figure 9f is used. This method consists of connecting the gas container, called an aliquot, directly to the tubing to drive the gas flux. The aliquot is equipped with close/open valves at each extremity, allowing the sampling system to be separated from the channelizing tubing. While the flux is high enough, we recommend collecting the gas by closing the valves after several minutes of flushing, to ensure the sampling purity. Such a technique is very efficient for sampling but implies at least extras in terms of logistics and therefore only a few samples were collected. However, this method is recognized as very efficient while working on very low-concentrated gas, in the noble gas field, for example.

3.1.2 Gas measurements

3.1.2.1 Punctual acquisitions

Measurements. First in situ measurements of H$_2$ were related to safety issue and earthquake prediction. It has been done for instance in the USA along the San Andreas Fault (Sato et al., 1986) or in Russia in the early 2000s (Firstov and Shirokov, 2005). At this time, a geophysical H$_2$ detector was designed, based on a change in the capacitance of the metal–insulator–semiconductor electronic transition under the influence of hydrogen in the soil. The instrument was used during several field campaigns in the following years for punctual acquisitions (Larin et al., 2015; Zgonnik et al., 2015), before being progressively abandoned in aid of geochemical detectors.

Over the last years, the portable instruments GA2000 and then GA5000 or BIOGAS5000 from Geotech$^®$ became the norm (Fig. 10a) (Frery et al., 2021; Lefeuvre et al., 2021; Leila et al., 2021; Lévy et al., 2023; Moretti et al., 2022; Pasquet et al., 2021; Prinzhofer et al., 2019). However, sampling the gas within the first meters of soil could be challenging and frustrating due to the very large air content in the close-to-surface soil, usually more than 95 vol.% with, depending on the cases, few vol.% of CH$_4$ or CO$_2$. These instruments are equipped with H$_2$-sensitive electrochemical cells able to quantify H$_2$ from 0 to 1000 ppmv with a precision down to the ppmv and thus revealed as very efficient tools. In addition, they also detect O$_2$, CO$_2$, CH$_4$, and optionally CO and H$_2$S. The analyzer does not measure directly the N$_2$ but gives a balance value usually interpreted as the N$_2$. The number of detected gases could be customized when purchasing the sensors. One limitation of the GA instruments resides in the H$_2$ detection threshold of 1000 ppmv that prevents an H$_2$ quantification while seeps are H$_2$-rich. To get through this limitation, the use of the Variotec 460 Tracergas is starting. This instrument, originally designed to detect leaks of H$_2$ in industrial infrastructures and construction sites, is now used for H$_2$...
Representativeness. Concerning the representativeness of one measurement on an H2 seeping system, studies demonstrated a strong variability in space and time of H2 fluxes, particularly in the case of soil gas (Moretti et al., 2021b; Prinzhofer et al., 2018; Zgonnik et al., 2015). As such, getting a “zero value” should not be considered proof of a non-emitting H2 system, as well as getting one high H2 value should not be considered evidence of an active H2 system. The efficiency of such portable instruments lies in the ease to multiplicate the number of analyses in a short lapse of time and thus get free from the aforementioned bias. Statistical work based on several hundreds of measurements allows us to draw global trends (Moretti et al., 2022), so we suggest doing at least a few tens of measurements in each studied SCD. On the other hand, in the areas where systematic soil gas measurements have been done in various SCDs, it seems that their behavior is very similar (Brazil, Moretti et al., 2021a; Prinzhofer et al., 2019; Namibia, Moretti et al., 2022; Australia, Frery et al., 2021). The strategy could be to select one of them after a few random measurements and then do a hundred measurements in a given one at different times of the day. We suggest also extending the measurements out of the area without vegetation. In case of a fault leaking, the H2 content in the soil are depending on the distance to the fault and so cross-sections perpendicular to the fault scarce (even if it is not visible) should be done (Lefeuvre et al., 2022).

3.1.2.2 Long-term monitoring

Long-term monitoring, essentially implemented for the study of soil gas H2, allows us to better define the space and time variability described above. The principle is similar to in situ soil gas measurements. An H2 probe is buried at a shallow depth of about 1 m. Automatic measurement is performed regularly over long periods. So far, the main example of such monitoring is the study conducted on H2-emitting SCDs in Brazil (Fig. 10b) (Moretti et al., 2021a; Prinzhofer et al., 2019). There, two structures were monitored for 6–8 months by the means of 44 and 51 PARHyS detectors developed by Engie programmed to get one measurement per hour (Rosanne, 2020). Cyclic pulses were observed in H2 levels, with a maximum during the days and a minimum during the nights. The origin of this periodic signal remains a matter of debate but it could come from atmospheric pressure variations (Cathles and Prinzhofer, 2020) or cyclic pulses in-depth (Myagkiy et al., 2020a,b). The earth’s tide, on the opposite, happened to be neglectable and unable to explain the single daily maximum (Simon et al., 2020).

In addition to this soil breathing with a 24 h period, the long-term monitoring showed large pulses, that usually saturated the regular sensors for 2 days and are unpredictable on our current knowledge. They are rare, when 10 sensors were installed for 2 months, only one large peak has been recorded (Prinzhofer et al., 2019). Among the hundred sensors, which were at a distance of about 80 m, one recorded almost one large pulse per week (Moretti et al., 2021a). The pump power of the PARHyS has been adjusted to that of the GA5000 for comparisons and therefore the volume of soil, which is analyzed during the 2 min long measure, is small and corresponds to a distance of drainage of about 2 cm. The lack of correlation between the signals measured from the various sensors seems to indicate that the H2 pulses measured with this monitoring correspond to independent events that affect only a small zone. It is therefore more representative to use tens of sensors. The previous authors concluded that there is no way to deduce an average behavior of a structure from just a couple of measurements.

Concerning the tools available for these permanent measurements one may note that various laboratories are
currently working on new ones. The companies 45-8 Energy and Solexperts launched SurfMoG H2 in February 2023 for undergoing H2 monitoring. But, on-site comparisons are not yet available. With these techniques, we can measure repetitive concentrations to try to compute a recharge flow within the soils.

### 3.1.2.3 Gas fluxes estimates

Once the concentrations are measured, evaluating the fluxes may help to quantify the emitted H2 volumes, since 100 vol.% of H2 in a very low flux seep could be less interesting than 1 vol.% of H2 in a very high flux seep. In the case of H2 emissions from free gas vents, bubbling water, or boreholes, estimating the fluxes should be easy as they are high enough to be channelized and measured with a flowmeter without air contamination. On the contrary, H2 fluxes from soil gas are low, and quantifying them cannot be done using a simple flowmeter tool.

Over the years, efficient tools have been developed to study soil gas fluxes such as closed chambers (Figs. 11a and 11b), which progressively adapted to the study of H2. The principle consists in measuring the evolution through time of a gas of interest in a closed chamber settled onto the soil ground. Since the exact volume and the footprint

![Fig. 11. Flux sampling. (a) Closed chamber apparatus scheme designed for measuring CO2 in soil gas (Rochette et al., 1997). (b) Evolution of H2O concentration in a closed chamber through time, fitted with a non-linear equation (Wagner et al., 1997). (c, d) Gas fluxes map acquired on the Chimaera seep with the associated satellite image (Etiope, 2023). See Appendix B for coordinates.](image)
Fig. 12. Images showing different outcrops, samples, and various in situ analyses. (a, b) Mn-Fe bearing rocks in Namibia. (c) BIF core from Australia. (d) Portable XRF instrument for in situ major element analysis. (e, f) Kappameters KM7 and G-857 for magnetic susceptibility measurements. See Appendix B for coordinates.
of the chamber are known, a correlation between the time and the gas concentration in the chamber can be established following linear or exponential laws, giving access to gas fluxes, for instance in mol.m$^{-2}$.d$^{-1}$ (Wagner et al., 1997). Recently, the first study dedicated to evaluating H$_2$ flux thanks to closed chambers was on Chimaera-free gas vents (Etiope, 2023). Within the closed chamber, 30 cm in diameter, a concentration measurement was realized every minute. A flux map of the area was built, providing results with natural H$_2$ fluxes up to 5000 kg.km$^{-2}$.d$^{-1}$ (Fig. 11c). One may note that the chamber is not always the right choice because it can affect the flow or even stop it when it is mainly diffusive, which can result in artificial low values.

Nevertheless, we must keep in mind that what we measure with the closed chamber or permanent sensors is just some leakage. They are reassuring about the existence of an active H$_2$ system but say nothing about the subsurface reserves and even about the deep flow. Spending too much time to perfectly measure these H$_2$ soil gas contents will not, in our opinion, decrease the uncertainties inherent to the exploration phase.

3.2 Rocks

Sampling rock is essential for understanding the various processes that can generate H$_2$. This implies that sampling needs to be done in accordance with standard practice in the mining industry. In that sense, cross-sections combined with structural measurements must be performed, for example, to understand the global geological framework of the rocks sampled and/or to estimate the volume of an interesting lithology. The pressure-temperature evolution changes also the characteristic of the rock and may influence the content of Fe$^{2+}$. This is the case in Namibia where magnetite-bearing rocks are mainly found in highly metamorphic units in the Damara Belt (Figs. 12a and 12b). Further, in the case of H$_2$ from water/rock interactions, many studies showed a very large heterogeneity of e.g. iron content in rocks at all scales ranging from a few millimeters to several kilometers. It is, therefore, necessary to take several samples at different places to reflect heterogeneities. In addition to the outcrops, some countries (e.g., Australia and the USA) provide free access to their core libraries for both researchers and operators, particularly for the cores from previous drilling programs. When well data are available, cores or cuttings are ideal for obtaining a complete description of the generating interval, like the description of the cuttings in the Asal Rift and the identification of an H$_2$ system (Pasquet et al., 2023). They also avoid the effects of near-surface weathering, which can affect the Fe$^{2+}$/Fe$^{3+}$ ratio (Fig. 12c).

Depending on the H$_2$-GR studied, several methods and approaches may be used in the field for rock examinations. X-Ray Fluorescence (XRF) is one of them (Fig. 12d). This method is fast, reliable, and non-destructive and provides access to major element concentrations in the rock. Further, magnetic susceptibility could also be a fast field proxy to determine the state of alteration/serpentinization.

The magnetic susceptibility of a rock is controlled by the type and amount of magnetic minerals in its paragenesis (Martín-Hernández et al., 2004), and the main carrier of this signal is the magnetite due to its ferromagnetic behavior. Field measurements are quite simple and fast when the H$_2$ GR is outcropping. Kappameters allow to acquire the magnetic susceptibility, such as the portable KM7 that only requires a small plane interface to perform the measurement (Fig. 12e). To avoid the impact of the weathering, these measurements have to be performed on fresh outcrops. In addition, measurements of the magnetic field could be done in the same type of rocks. This can be performed using a G-857 Memory-Mag Proton Precession Magnetometer (Fig. 12f). The magnetic field measured on the surface corresponds to the interaction between the external core’s magnetic field and the magnetic behavior of the minerals.

3.3 Workflow for the fieldwork

The workflow developed for in situ gas measurements is given Figure 13. After punctual analyses, the locations of H$_2$-rich locations can allow us to perform long-term monitoring and gas flux assessment. In addition, the rocks associated with the gas can be analyzed in situ by different techniques (e.g., XRF, magnetism). The sampling of H$_2$-rich gas and rocks is finally done to make laboratory analyses.

4 Post-fieldwork: laboratory analyses

The rocks and gas samples collected during fieldwork must be analyzed in the laboratory to conduct further chemical and petrological measurements since they both hold complementary clues to understanding the “whole” H$_2$ system. Rocks carry evidence of the mechanisms leading to H$_2$ generation at depth, while gases provide insights into physicochemical parameters and the source. Numerous analytical tools are available for the full characterization of rock and gas samples. This section aims to present those analytical techniques that appear essential for the study of H$_2$-related seepages and H$_2$-generating rocks.

4.1 Gas characterization

4.1.1 Bulk gas chemical quantification

Following the semi-quantitative and limited measurements during the fieldwork, the precise characterization of the gas samples in the laboratory should begin with the study of the bulk gas chemical composition. Here, quantifying H$_2$ levels is of prime interest because (i) it validates or invalidates the discovery of H$_2$ seepages and (ii) provides information about the total amount of H$_2$ emitted, which could be used to estimate the leakage coming from the depth. Several gaseous species are commonly found in association with H$_2$-related seepages such as O$_2$, N$_2$, He, Ar, light HC, or CO$_2$. Their respective abundances in the
gas mixture hold clues to understanding the dynamic of the H₂ system at depth, which are discussed. For instance, high levels of crustal He in the bulk gas could be seen as a marker of radiolysis because the radioactive decay produces He.

Among the variety of tools available to determine the bulk gas composition, Gas Chromatography (GC) is the most used for H₂ exploration. GC devices are often equipped with a Thermal Conductivity Detector (TCD) that provides a good compromise between a wide range of species detection and quantification accuracy, especially for inorganic compounds (Guélard et al., 2017; Lefeuvre et al., 2021; Zgonnik et al., 2015). For the specific purpose of organic gases quantification associated with H₂, such as light hydrocarbons, an additional Flame Ionization Detector (FID) is used offering a higher degree of precision than a TCD (Prinzhofer et al., 2018; Sherwood Lollar et al., 2006).

4.1.2 Isotopic composition

In nature, the atoms of the same element can have different masses, named isotopes. The isotopic composition of a gas is usually measured by Isotopic Ratio Mass Spectrometer (IRMS), and in some cases directly connected to a GC. After passing through the GC, the gas is ionized. Ions are then separated depending on their mass/charge ratio which allows us to measure the isotopic ratios.

The isotopic composition reflects the fractionation mechanisms occurring during geological processes. Two types of isotope fractionation exist: (i) equilibrium fractionation and (ii) kinetic fractionation. In the first case, the isotopes fractionate following the thermodynamic law that depends mainly on temperature evolution. For example, while two chemical species carry the same element, like H₂ and H₂O, the H isotopic abundance of both species is known to isotopically equilibrate through the reaction (2) as a function of a thermodynamical law dependent on temperature (Horibe and Craig, 1995). In the second case, the isotopes fractionate depending on their masses. The higher the relative difference of mass between isotopes, the higher will be the fractionation.

$$\text{H}_2\text{O} + \text{HD} = \text{HDO} + \text{H}_2.$$  \hspace{1cm} (2)

For H₂-related seepages, the isotopic composition of H₂, CH₄, CO₂, N₂, and He are usually measured (if present), since the isotopic signatures of these gases give access to physicochemical parameters related to H₂ origin, trapping, and migration. For instance, as previously mentioned, He enriched in ⁴He is known to originate from radiolysis (Ballentine and Burnard, 2002). Thus, a ⁴He-rich seepage infers crustal H₂ formed via radiolysis.

In the discussion, the δ, ε, and R/Ra notations are used. They are presented with the example of H isotopes:

Fig. 13. Fieldwork proposed workflow. In situ measurements and sampling strategy for gases and rocks.
\[ \delta D = \left( \frac{(D/H)_{\text{sample}}}{(D/H)_{\text{standard}}} - 1 \right) \times 1000. \]  

\[ \varepsilon = 1000 \times \ln \left( \frac{(D/H)_{\text{sample}}}{(D/H)_{\text{standard}}} \right). \]  

\[ R/Ra = \frac{(^{3}\text{He}^{4}\text{He})_{\text{sample}}}{(^{3}\text{He}^{4}\text{He})_{\text{atmospheric}}} . \]

4.2 Petrographic characterization

The analytical tools for petrography can be broadly divided into two categories: (i) tools that provide quantitative information on samples (e.g., amount of Fe, size of minerals) and (ii) tools dedicated to observe samples at various scales. In the specific context of H\(_2\) exploration and considering that the content of specific elements (Fe, U, Th, or Organic matter) is key to assess the H\(_2\)-generating potential of rocks, we believe that the quantitative tools are more important. From a fundamental point of view, however, observing the paragenesis is important to improve the knowledge about H\(_2\) dynamics (e.g., which mineral is highly reactive or not, at which temperature). All the tools and their characteristics are listed in Appendix C.

4.2.1 Bulk quantification tools

When investigating the H\(_2\) potential of lithologies related to water-rock interactions, ICP (Inductively Coupled Plasma – Mass Spectrometry or Optical Emission Spectroscopy) and XRF (X-Ray Fluorescence spectrometry) are the techniques to get access to Fe, U, Th, and K as well as other major and trace element concentrations in the bulk sample. Their operating principle does not allow us to know the redox state of the elements. In the case of Fe-oxidation-related H\(_2\) generation, the redox state of the element is meaningful information because it determines whether a rock is still able to produce H\(_2\) currently. Although other techniques exist for this purpose, such as titration in solution associated with ICPs, \(^{57}\text{Fe}\) Mössbauer spectroscopy should be privileged to obtain Fe-speciation in the bulk rock sample. Using this method, the redox state is obtained in each mineral family constitutive of the bulk rock sample. It must be said that all information provided at the bulk rock sample scale can also be collected at a mineral scale, using other techniques that are not described here.

X-Ray Diffraction (XRD) is commonly used to evaluate the mineralogy of the bulk rock sample and thus to determine which phase carries the element of interest (i.e., Fe, U, Th, or K). Thanks to quantification algorithms such as the Rietveld method, the proportion of each phase in the mineral assemblage can be assessed.

When investigating the H\(_2\) potential of organic matter-rich rocks, evaluating the Total Organic Content (TOC) and the paleo-maturation is essential. The Rock-Eval pyrolyzer, used for decades by O&G companies (Behar et al., 2001; Espitalie et al., 1980), gives this information.
Additional paleotemperature markers could be used to cross-check the pyrolyzer’s results, such as the Vitrinite Reflection or Raman data. For the coal, the rank may be also quantified, affecting the kinetics of pyrolysis and the H₂ generation potential (Yan et al., 2020; Zhang et al., 2020).

4.2.2 Observation tools

While trying to understand the generation of H₂, observing the samples to complete bulk rock chemistry and mineralogical quantitative analyses becomes mandatory (Fig. 14). For instance, if we consider a Fe-rich rock that is known to source H₂, and that carries two different Fe-rich minerals, the only way to determine which mineral sources H₂ is to observe them at the microscopic scale, and thus collect information about their respective stabilities in the mineralogical assemblage. Two different types of observation tools exist: (i) optical and (ii) electron microscopy. They essentially differ by the nature of the particle (photon or electron) interacting with the sample and the size of the feature they are able to image. Optical microscopy allows us to work at a resolution reaching down to a few microns. At such resolution, alteration rings surrounding Fe²⁺-minerals being altered, H₂-bearing fluid inclusions, as well as radioactive decay halo within biotite, are interesting features to observe (Fig. 2). Electron microscopies such as Scanning Electron Microscopy (SEM) or Transmission Electron Microscopy (TEM) should be used to reach a higher resolution, down to the nanometer. Combining electron microscopy with in situ quantitative techniques such as Electro Probe Micro-Analyzer (EPMA) enables us to know precisely the chemistry of minerals of interest and draw conclusions about the processes sustaining H₂ generation.

4.2.3 Representativeness of data

The representativeness of the previously described analyses and observations could be challenged while trying to conclude, especially when the study aims to characterize the potential of a geological formation as H₂ GR.

At the sample scale first, it must be kept in mind that imaging techniques provide 2D information, such as the mineral abundances in the thin section, that are not always representative of the 3D equivalent volume. Only X-Ray Microtomography (XCT) can tackle this limitation since this technique allows us to image and quantify minerals distribution in cm³–m³ rock plugs. Otherwise, bulk rock analyses should be privileged to favor the representativeness of the results.

At the geological formation scale then, it is reasonable to imagine that natural rocks can present heterogeneities in composition, or different degrees of alteration in the case of water-rock interactions, along the stratigraphic column. Thus, it appears fundamental to study multiple samples and cross-reference the acquired information to obtain a realistic characterization of the H₂ GRs.

4.2.4 Workflow for H₂-generating rocks

The workflow developed for laboratory-based gas and rock analysis is given in Figure 15. We have selected what we believe are the most efficient and complementary tools to
quickly characterize the H2 potential of an H2 GR whether it is related to iron oxidation reactions (H2 GR1 and H2 GR2), radiolysis (H2 GR3) or late organic matter maturation (H2 GR4). To ensure the representativeness of the H2 potential assessment of the generating rock, one should consider performing this workflow on multiple samples coming from different depths within the studied rock formation.

- First, an ICP analysis should be done to determine the total bulk concentrations of elements of interest such as Fe, U, Th, or K. Rocks without one of these compounds in significant amounts should be disregarded as a potential H2 GR.
- In case of suspected overmature TOC-rich source rock, a Rock-Eval analysis should allow to distinguish organic-rich rocks H2 GR4, the maturation should also be quantified. It could be done directly from the pyrolyzer data if the characteristics of the immature source rock are known but additional values such as vitrinite reflectance or other paleothermometers allow additional quantification.
- Second, 57Fe Mössbauer spectroscopy should be performed on iron-rich rocks to determine the speciation of Fe. Fe2+-rich rocks should be considered as high H2 potential generating rocks regarding redox processes while Fe3+-rich rocks should not be considered as potential generating rocks for future H2 production, although they could have produced H2 in the past.
- Third, identification of the minerals that carry Fe2+, U, Th, or K should be performed on thin sections using optical and electron microscopy. The identification of Fe-bearing minerals should help to assess the H2 potential of the rock, depending on the proper reactivity of each mineral during water-rock interaction.
- Finally, XCT should be done on core samples to extrapolate at a larger scale the quantifications and observations made at low scale, and thus estimate the true potential to source H2 normalized to its volume. It must be noted that XCT is essential to efficiently evaluate the true potential of the H2 GRs as it allows to consider of mineralogical heterogeneities at a micrometric scale. It is mandatory to know the mineral assemblage of the studied rock to correctly identify the Fe or U, Th, K-bearing phase in the studied XCT volume.

5 Discussion

5.1 Significance of measuring gas composition

5.1.1 Bulk data

The major gases commonly associated with H2 are CH4 and N2. The H2-CH4-N2 ternary diagram presented in Figure 16 is therefore usually used to plot the gas data. Attempts to classify the different ophiolitic sources have been made (Vacquand et al., 2018). Regarding the gas data that contain H2, CH4, and N2 as major gases, we observe the N2-CH4 trend and the H2-CH4 trend. However, it remains difficult to differentiate a source type based on the H2-CH4-N2 ternary diagram. The most H2-rich gas is from the well of Bourakebougou in Mali (Prinzhofer et al., 2018).

This diagram does not include other gases and one has to check if H2, CH4, and N2 are indeed the major gases to best interpret it. For example, CO2-rich sample data usually plot in the N2-CH4 trend.

The data on hydrocarbons C2-C6+ are important because their presence can give indications about a source related to a petroleum system for example. But if we want more insights into the physicochemical parameters related to the gas, we need to use the isotopes as done in the next section.

5.1.2 Isotopic data

The isotopic data can be used as geothermometers when possible and as tracers of the different geological sources. A compilation of available isotopic data in the literature from ophiolites (~H2 GR1), and intracontinental areas (~H2 GR3) is given in Figure 17.

When compiling the H isotopic data (Fig. 17a), we observe that the δD (3) of H2 measured on ophiolites is lower than −585‰. Most of the data of the H2 continental measurements have also a δD lower than −600‰. However, some data from Sherwood Lollar et al. (1988) are up to −138‰ and desorption data from Truche et al. (2018) also show high δD. The δD of H2 alone is not an efficient tool to discriminate one source from another. However, it can be combined with the assumed/measured δD of H2O, often used as a geothermometer to evaluate the last temperature of equilibration of H isotopes. However, the δD of H2O is not always measured and its evaluation can be difficult.

The isotopic signature of CH4 can be useful to trace its origin. Using the abacus of Etiope et al. (2017), we observe that continental data are consistent with the different
isotopic “boxes”. We can note that a gas emanating from a thermogenic source, like H$_2$ GR4 would plot in the thermogenic area and that some continental data would be consistent with such an origin. Data from the ophiolites does not only show a signature from serpentinization as usually supposed and should be explained by other processes. Xia and Gao (2022) recently showed that mainly all signatures of CH$_4$ in nature could be obtained by microbial fractionation. The use of this isotopic tool is then to be used with caution to differentiate at first a source.

H$_2$-H$_2$O and CH$_4$-H$_2$O are two geothermometers usually used to trace the last temperature at which the system isotopically equilibrated (and not a temperature of H$_2$ generation for example). However, we can only determine a temperature of equilibration when the system is at equilibrium. This can be observed in Figure 17c by the represented isotopic equilibrium curve in a graph combining the isotopic data of H$_2$, H$_2$O, and CH$_4$ using the $\varepsilon$ notation (4). If the data do not align with this curve, the system is not at equilibrium. It is mentioned that CH$_4$-H$_2$O re-equilibrates slower than the H$_2$-H$_2$O system. Therefore, a point out of this trend could reflect the reequilibration of the H$_2$-H$_2$O system but not the CH$_4$-H$_2$O system which might reflect a higher and more pristine temperature. Some low values of $\varepsilon$(H$_2$-H$_2$O) could be associated with microbial activity (Suda et al., 2014).

We globally observe that for most of the compiled data, the temperatures of equilibration are low and mainly out of isotopic equilibrium. This could reflect that the system did not have the necessary time to reequilibrate. This could also be associated with microbial activity.

Finally, the He isotopic composition expressed as R/Ra (5) is presented in Figure 17d. We can distinguish three trends:

- $R/Ra = 1$: the main contribution of He is atmospheric.
- $R/Ra << 1$: the main contribution of He is crustal.
- $R/Ra >> 1$: the main contribution of He is mantellic.

Continental data show a major crustal contribution. The gas from the ophiolites has a variety of isotopic compositions with a contribution from the crust, the mantle, and the atmosphere.

The isotopic data may give important information like the temperature and/or the source. However, especially for H$_2$, the data have to be interpreted by combining several isotopic systems to be conclusive.

5.2. H$_2$ generating potential across the different types of H$_2$ GRs

5.2.1 Case studies of H$_2$-GR potential characterization

The assessment of the H$_2$ potential of H$_2$-GR is of prime interest because it might decide which geographic
areas are worth targeting for H₂ exploration. Primarily, the potential of a natural sample is a function of the content of Fe or U, Th, K, or TOC in the rock, which can easily be assessed through laboratory analyses as described previously in Section 4.2. But, the processes involved in H₂ generation are different for each type of H₂_GR.

In the case of water-rock interactions related to H₂ generation, assessing the potential of natural samples is not straightforward because no efficient tool exists yet to rapidly determine the generation potential of a rock by Fe-oxidation (H₂_GR1 and H₂ GR2) or radiolysis (H₂_GR3) from one single analysis. Concerning H₂_GR1 and H₂_GR2 (Fe-oxidation), the potential of rocks often comes from experimental studies, laboriously trying to mimic natural environments by reacting mineral powders and anoxic water. Starting parameters are fully controlled and their evolutions are monitored through time, allowing conclusions to be drawn on H₂ production rates as well as kinetics, which enables extrapolation for geological relevant timeframes. Although all the experimental studies display variability in the approaches and starting parameters, H₂ generations versus temperature are reported in Figure 18. The data plotted are not exhaustive but highlight some important points discussed below:

1. Ultrabasic rocks and associated minerals (i.e., peridotite and olivine) are the most tested reactants (Barbier et al., 2020) because the generation of H₂ was first evidenced during the serpentinization process. However, the few new starting materials tested (pyroxene, amphibole, Fe-carbonates, Fe-oxides) show a comparable H₂ productiveness, which is encouraging in the search for new H₂_GRs around the world.

2. The major part of experimental works has been conducted at elevated temperatures, above 150 °C, probably to reach the optimum temperature for serpentinization, estimated at around 300 °C (Klein et al., 2013; McCollom and Bach, 2009). Various ranges of pressure have been tested, especially in the case of serpentinization. See Barbier et al. (2020) for discussion.

3. Subsequently, a limited number of studies have been dedicated to low-temperature alteration but according to the data available in the literature, serpentinization is a low H₂ generator (Neubeck et al., 2011). Observation directly infers that a high-potential material at a high temperature can be a low-potential material at a low temperature and vice versa. Thus, every mineral and rock of interest should probably be tested in both domains of temperature as well as in the presence and absence of catalysts.

4. Finally, although these results must be interpreted cautiously since they result from the alteration of mineral powder rather than cohesive rocks with much lower reactive surface and permeability, redox reactions leading to H₂ generation seem to be a fast process at geological scales. Several mmol.kg⁻¹rock are indeed generated within weeks from these experiments (Fig. 18).
Concerning H$_2$ GR3 (radiolysis), the generation potential of a rock is mainly evaluated through modeling, using the radioactive element content, the related radioactive decay, and the amount of radiation available (i.e., not removed as heat), as well as the volume of water that may be in contact with the rock. A study aiming to assess the generation rate from this type of H$_2$ GR3 proposed a value of 0.3–3 nmol.L$^{-1}$.y$^{-1}$ in Precambrian intracratonic basins such as Witwatersrand in South Africa (Lin et al., 2005), which corresponds to 0.12–1.2 µmol.kg$_{rock}^{-1}$.My$^{-1}$ is based on the chosen porosity.

Concerning H$_2$ GR4 (late maturation of organic matter), the assessment of the H$_2$ potential is easier as it is performed by one single analysis conducted on Rock-Eval. In the Songliao and Cooper basins, the maximum H$_2$-generating potential is similar for organic-rich lacustrine shales and coals, respectively, and was estimated up to 136 mmol.kg$_{rock}^{-1}$ (Horsfield et al., 2022; Mahlstedt et al., 2022). The maximum generation rate was estimated using an Arrhenius law at 6.8 mmol.kg$_{rock}^{-1}$.My$^{-1}$ at around 250 °C. Early generated H$_2$ is most likely further reacted with pyrolysis intermediates in nature. Basin modeling is now clearly needed to model the H$_2$ generation against time and depth (Boreham et al., 2023) and to include the other elements of the H$_2$ system (i.e., migration, trapping, and preservation).

5.2.2 Questioning the possibility of a common framework to compare all H$_2$ GR

The methodologies used to quantify the potential of H$_2$ generation differ from one H$_2$ GR to another. Maybe the industry will gradually realize that only one of the H$_2$ GR types generates the majority of accumulations and that the contribution of the others can be neglected. This ranking remains hard to achieve, notably because the geodynamic parameters controlling each type of H$_2$ generation are different. The role of the temperature, time, and water availability is different and the fact that the retention time in the reservoirs is mainly unknown in many cases makes the problem more complex. As seen in the previous section, Fe-oxidation is dependent on temperature and water circulation. Radiolysis is exclusively dependent on water circulation and remaining TOC is dependent on the initial TOC but also on temperature history. Draw comparisons from the aforementioned case studies remain very qualitative, but two points should be discussed:

1. Concerning the temperature dependency, it is interesting to point out that H$_2$ can be generated over a wide range of temperatures from both Fe-oxidation and radiolysis, although the degree of Fe-oxidation in minerals will differ depending on the temperature and water availability.

2. Concerning the time scales involved in H$_2$ generation, intracratonic radiolysis is very slow and the maturation of shales under regular burial rate requires million years to generate µmol to mmol per kg$_{rock}$. Long-term accumulation under a good seal seems mandatory to constitute economic resources. In parallel, the kinetics of H$_2$ generation from Fe-oxidation in natural environments is still a matter of debate but seems to be much faster, inferring H$_2$ could be continuously produced nowadays in favorable environments.

5.3 Model of H$_2$ accumulation?

The number of case studies is too small to know which type of accumulations will be mainly found. By analogy to other fluids systems in the subsurface, the community mainly thinks in terms of accumulation created by a trap, a reservoir rock, and a seal. In the O&G world, the accumulation may be old with a charge which is considered fossil since there is no recharge at the time scale of the field production. On the opposite, within the geothermal world, the explorations are also looking for a reservoir below a seal but the recharge in hot steam could be fast enough to be adjusted to the production. We believe that H$_2$ accumulations could be explained using two settings: (i) H$_2$ dynamic system and (ii) H$_2$ long-term accumulation. These two models are extremes, and it is likely that reality will often be somewhere in between.

H$_2$ dynamic system

If the H$_2$ is generated at a high generation rate (like from H$_2$ GR1 and H$_2$ GR2), one may consider the system as a dynamic one. There is no need for a trap but a recent seal would slow down the flow and allows accumulations (Prinzhofer and Cacas-Stentz, 2023). We can take the example of ophiolites, which can produce H$_2$ at the basis of the sequence where peridotites are fractured and where the formed H$_2$ is more or less sealed by the impermeable non-fractured peridotite above. It is an optimistic model since the charge of the reservoir could be forever, at a human time scale, but pessimistic in the sense of what has been produced previously is lost.

To constrain the model, more parameters have to be taken into account, like the water migration altering the rocks, through the porosity and the permeability (Karolyte et al., 2022). Moreover, when the water is associated with the gas, its analysis can be relevant, giving information about its age. Based on the geochemical tool used, we can have access to a residence time varying from several months to several million years. This can be very helpful when an H$_2$ production model has to be built based on the alteration of rocks by the measured water. Moreover, the impact of microbiology on the consumption-production of H$_2$ has also to be taken into account in the model. For example, the modeling done by (Myagkiy et al., 2020a,b) shows that microbial activity may strongly reduce the H$_2$ flow at low temperatures. Therefore, the flux is expected to be stronger at depth.

Long-term accumulations

Like in petroleum systems, this model includes an H$_2$ GR, a trap, a reservoir rock, and a seal. Salt is proven to be a good seal, in the subsurface storage facilities but also at geological time scale. In the Amadeus Basin in central Australia, a Neoproterozoic salt layer seals the CH$_4$, H$_2$,
5.4 Are the natural H₂ resources promising?

If three H₂ GR are present in the same area, which one ranks first? In our opinion, it is still very difficult to propose a classification of the H₂ GR as well as of the surface indices that will allow us to be more or less optimistic about the H₂ resources in an area. Regarding reserves and proven reserves, it is more uncertain since the number of wells dedicated to H₂ exploration is very low.

Up to now, all the discoveries have been fortuitous looking for water or oil and gas. Finding H₂ without looking for can be seen as very positive, as it infers we should find even more H₂ while looking for it. The case of Mali is interesting, in the sense that around twenty wells drilled since the discovery well also found H₂-rich gas (Diallo et al. 2022; Maiga et al. 2023).

It is similarly difficult to propose a classification of the critical factors to explore a region. From our experience, each field trip campaign in a selected area resting on pre-field work that targeted the presence of H₂_GR and vegetation index anomalies appeared successful and H₂ was found. It suggests that in many places when a H₂_GR is present at depth together with H₂ surface or subsurface indices, there is an active H₂ release today.

In Mali, there are existing wells with H₂ presence, SCDs, and a Neoproterozoic cratonic area. In the USA, where the exploration is active, H₂_GR, H₂-related SCDs, and old wells with H₂ are all present. Australia is a similar case. In South Australia for instance, old subsurface data already confirmed the presence of H₂, SCDs are numerous, and the craton is iron-rich. Alternatively, when only one single criterion was found during pre-field work, either the presence of an H₂_GR or some SCDs with ambiguous characteristics, field trip results often turned out disappointing.

At the current level of knowledge, or lack thereof, we must certainly remain modest and optimistic and just acquire new data. Soil gas sampling and further gas and rock analyses are globally cheap to acquire and may help to lower the risk in an area. Basin modeling could be done to quantify the water and gas circulation. However, surface indices say nothing about the potential of the area for economic production compared to fully calibrated models.

Various evaluations of the H₂ resources have been published during the last years and this is a recurring question, especially from those who doubt that this resource can change the game. Some authors (Larin et al. 2015; Smith et al. 2005) considered since the beginning that this resource could be major but the first estimates concerning the natural H₂ generation that have been published were globally rather low. They increase recently with the increasing knowledge about natural H₂ generation.

Two global evaluations published in 2020 converged close to 23 Mt/yr (Worman et al. 2020; Zgonnik 2020), corresponding to a quarter of the current H₂ world consumption.

Worman et al. (2020) and co-authors only considered the oceanic domain and estimated that 12 Mt/yr may come from the magma crystallization, about 10 Mt/yr from the serpentinization, and 1 Mt/yr from the radiolysis. Zgonnik (2020) considered that 23 Mt/yr are produced by the MOR and ophiolites and that the radiolysis is almost negligible (0.38 Mt/yr). This author did not estimate the deep H₂ flow, the primordial H₂ coming from the mantle, and the core degassing, nor the potential generation from the iron-rich sedimentary facies. Both studies considered that the 23 Mt/yr is a lower-bound estimate and, as a fact, only 2 of the 4 H₂_GR described in the present paper were considered. These different authors converge on the fact that processes such as the alteration of basalts, the degassing of magma, the alteration of the oceanic crust at low temperatures, or the pyrritization generate lower quantities compared to serpentinization. Again, these estimates were done independently but they were based on the knowledge at that time, or at least a model of H₂ generation admitted as mostly due to serpentinization. H₂_GR2 and H₂_GR4 have now to be taken into account in the global H₂ production models.

For H₂_GR4, the late maturation of coal and organic-rich source rocks, we have to consider resources and reserves as in the O&G industry. For the Songlia Basin (China), the H₂ resources are estimated at 4631 Gt which means about 46,000 yr of the current world consumption (0.1 Gt/yr) (Horsfield et al. 2022). For the Copper Basin in Australia, the resources are estimated at 0.16 Gt (from the coal) and 0.06 Gt (from the shale and coaly shale), so 0.22 Gt (Mahlstedt et al. 2022). These last authors extrapolated these results considering the size and depth of the basin where organic-rich shale has a maturity over VR 3.5% and proposed 3.5 10¹² t. The transition from resources to reserves and then to prove reserves will definitively result in a decrease of one or two orders of magnitude, especially if in many cases the H₂ reservoir seal is not perfect (Prinzhofer and Cacas-Stentz 2023) but these numbers highlight the fact that the natural H₂ resource is there. The community no longer has to argue about whether this resource is available, but rather where H₂ is currently accumulated and/or where the flow is large enough to allow production.

Supplementary material

Supplementary materials are available at https://doi.org/10.2516/stet/2023021/olm

- Database of the soil gas analyses done in the various case studies.
- Major gas data plotted Figure 16.
- Isotopic data plotted Figure 17.

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References


Appendix A

Minerals at the origin of the generation of H₂ from H₂_GR

Olivine

Olivine (Mg,Fe)₂SiO₄ is by far the most studied mineral for the assessment of natural H₂ potential since the discovery of H₂ flows at Mid Oceanic Ridges and later in ophiolitic context. Olivine consists in a solid solution between its ferrous and magnesium endmembers: fayalite (Fe₂SiO₄) and forsterite (Mg₂SiO₄), respectively. Olivine is highly present in ultrabasic and basic rocks. Peridotites are generally enriched in forsterite. Concerning the H₂ potential of olivine, fayalite is the endmember of interest, as it carries the Fe²⁺ susceptible to be oxidized. Its alteration during hydrothermal alteration, called serpentinitization, leads to the oxidation of Fe and reduction of H₂O to form H₂. A wide range of temperature is favorable for H₂-forming serpentinitization, up to >400 °C and down to <100 °C, with an optimum determined around 300 °C (Klein et al., 2013). Secondary minerals formed during serpentinitization differ along with the temperature, from magnetite and Mg-serpentine at T > 200 °C to Fe-serpentine at T < 200 °C.

6(Mg,Fe²⁺)₂SiO₄ + 7H₂O → 3(Mg,Fe²⁺,³⁺)₃Si₂O₅(OH)₄ + + Fe²⁺Fe³⁺₂O₄ + H₂. \( (A.1) \)

Pyroxene

Pyroxenes, such as olivine, are silicates present in the mafic and ultramafic rocks. They are divided in two different subgroups: the orthopyroxenes which are solid solution with the general formula (X, Y)₂Si₂O₆ with X and Y cations being Fe²⁺ and Mg²⁺ and the clinopyroxenes which are solid solution of the general formula X₂YZ₂O₆ where X have 

Pyroxenes are defined by two pure endmembers: ferrosilite (Fe₂Si₂O₆) and enstatite (Mg₂Si₂O₆). Clinopyroxenes are defined by several endmembers: two sodic with jadeite (NaAlSi₂O₆) and aegirine (NaFe³⁺Si₂O₆) and a calcic one with wollastonite (Ca₂Si₂O₆) being the pure calcic pole. As for olivines, solid solutions between these poles are often observed with diopside (Fe < 50 mol%) and Ca < 50 mol%), hedenbergite (Fe > 50 mol% and 45 < Mg < 50 mol%), augite (20 < Ca < 45 mol% i.e., high-Ca pyroxene) or pigeonite (5 < Ca < 20 mol% i.e., low-Ca pyroxene). If we consider, the redox potential of these pyroxenes, orthopyroxenes and especially ferrosilite appear to have the highest iron content and thus the highest H₂ potential.

Associated with other phases such as plagioclase in basalts, rich in calcium and aluminum, pyroxenes, instead of serpentinitization, will undergo a chloritization and amphibolitization reactions depending on the temperature. Secondary minerals will be tremolite, chlorite, talc, hornblende and epidote (Plumlee, 1999). In contrary to serpentinization, these reactions will not produce, directly, high H₂ content.

Amphiboles

Amphiboles are very usual minerals of plutonic and metamorphic rocks. They are double-chain (SiO₄ tetrahedra) silicates. The general formula is AB₄C₂T₅O₉(OH)₂ where site A (octahedral) can be K or Na; site B (octahedral) can be Na, Ca, Mg, Fe²⁺, Mn²⁺, Li, Zn, Ni, and Co; site C (octahedral) can be Al, Fe³⁺, Mn³⁺, Cr, Ti, Zn, Ni, and Co; and site T (tetrahedral) can be Si, Al, and Ti (Leake et al., 1997). Amphiboles can be categorized in different groups: calcic, sodic, calc-sodic or ferro-magnesio-amphiboles. Substitution between Mg and Fe are very common in amphiboles (Deer et al., 2013) and therefore can be of primary interest in the study of H₂. As the groups of amphiboles are too large, we will focus mainly on the main observed Fe²⁺-rich amphiboles. It is the case for grunerite (Fe²⁺, Mg,Mn)₇(Si₈O₂₂)(OH)₂ when Fe²⁺ > Mg, which is a common mineral from metamorphosed banded ironstones and in silicic volcanic rocks and can be rich up to 45% of Fe²⁺ (ox%) (Klein, 1964). There is also anthophyllite (Mg,Fe³⁺)₂(Al₂Si₈O₂₂)(OH)₂; ferrohornblende (Ca₉Fe₄Al(Si₉AlO₂₂)(OH)₂; actinolite Ca₂(Mg,Fe³⁺)₅Si₈O₂₂(OH)₂ with an unusual ferroactinolite; clinoxyphane Na₂(Mg,Fe²⁺)₃Al₂(Si₈O₂₂)(OH)₂ to riebeckite Na₂(Fe³⁺,Mg)₃Fe²⁺₂(Si₈O₂₂)(OH)₂ (Deer et al., 2013).

These amphiboles carry Fe²⁺ and can therefore be altered into a Fe³⁺-rich phase. This is the case of the sodic amphibole arvedsonite that can be altered into aegirine in peralkaline granites, which is one hypothesis for the presence of H₂ associated to peralkaline granites (Truche et al., 2021):

3Na₃Fe²⁺₄Fe³⁺₄Si₈O₂₂(OH)₂ + 2H₂O = 9NaFe³⁺Si₂O₆ + + 2Fe²⁺Fe³⁺₂O₄ + 6SiO₂ + 5H₂. \( (A.2) \)

Phyllosilicates

Phyllosilicates are composed of tetrahedral and octahedral sheets. Each tetrahedra are made of one cation T (Si⁴⁺, Al³⁺, and Fe³⁺), linked to four oxygen atoms. Three of them are shared with adjacent tetrahedra and form a hexagonal mesh pattern. Each octahedra are made of a cation O (Fe²⁺, Mg²⁺, Al³⁺, and Fe³⁺) linked to 6 oxygen atoms. Octahedron are linked to others by sharing edges. Tetrahedra and octahedra are linked together by sharing a common plane. These characteristics are used to differentiate three categories of phyllosilicates: 1:0 layer or TO clay minerals such as kaolinite and serpenite, 2:1 layer or TOT clay minerals such as micas, smectite or talc, 2:1:1 layer or TOTO clay minerals such as chlorite (Bergaya and Lagaly, 2013). Serpentines of ideal composition (Mg,Fe)₂Si₂O₅(OH)₄ are 1:1 trioctohedral layer minerals (Bergaya and Lagaly, 2013). Mg-rich serpentine such as lizardite, antigorite, and chrysotile have been highly studied during the past...
decades as they are produced by serpentinization. When coupled to water reduction, it produces $\text{H}_2$ and ferric iron is then incorporated to magnetite and serpentine in variable proportions (A.1) depending on the initial iron content of the primary phase (Shervais et al., 2005). Greenalite and cronstedtite are the iron-rich serpentines with the formula being respectively $\left(\text{Fe}^{2+},\text{Fe}^{3+}\right)_{2.5}\text{Si}_3\text{O}_8(\text{OH})_4$ and $\left(\text{Si},\text{Fe}^{3+}\right)_{2}\text{O}_5(\text{OH})_4$. In that sense, serpentine is a marker of hydrogen past and/or present production. The optimum for serpentinization, and thus to $\text{H}_2$ production, occurs at 320 °C.

\[
\text{Smeectites} \text{ are } 2:1 \text{ dioctahedral } M^{\text{II}}(R^2_+)(R^2_+R^3_+)(R^2_+R^3_+)\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O or triomclanadr} M^{\text{II}}(R^2_+R^3_+)\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O layer minerals (x, y being the layer charge resulting from tetrahedral and octaedral sites, R}\text{2}^+ \text{and R}\text{3}^+ \text{being the divalent and trivalent octahedral cations, and } M^{\text{II}} \text{being the monovalent interlayer cation). Interlayer cation are commonly Na}^+, K^+, Ca^2+, \text{and Mg}^{2+} \text{ions. Fe}^{2+}, \text{Mg}^{2+}, \text{Al}^{3+}, \text{and Fe}^{3+} \text{ions commonly occupy octahedral sites. The iron-rich smectite is the dioctahedral nontronite with the following structural formula (Fe}^{2+}\text{Fe}^{3+})\text{Si}_2\text{O}_5(\text{OH})_2 \cdot n\text{H}_2\text{O. Smeectites are known to form under a wide range of conditions from subsurface weathering to hydrothermal conditions.}
\]

\[
\text{Micas are } 2:1 \text{ dioctahedral } (R^2_+R^3_+\text{Si})\text{Si}_4\text{O}_{10}(\text{OH})_2 \text{ or triomclanadr } (R^2_+R^3_+)\text{Si}_4\text{O}_{10}(\text{OH})_2 \text{ layer minerals. Biotite, with the following structural formula K(Mg,Fe)}^{2+}\text{Si}_3\text{O}_10(\text{OH})_2, \text{is the most common mica and is commonly found in acid and intermediate rocks, such as granites. They are formed under magmatic conditions. During the alteration of these granites, it is the biotite that allows the release of } \text{Fe}^{3+} \text{into the solution following the equation (A.1), to form H}_2 \text{ and magnetite in variable proportions. Oxo-carbonates are Fe-carbonate rich, de-}
\]

\[
\text{Carbonates}
\]

Although few studies demonstrated in the past that the alteration of siderite (FeCO$_3$) can lead to the formation of $\text{H}_2$ and CH$_4$ through a possible reaction presented in equation (A.2) (Milesi et al., 2016). Interest of the scientific community concerning Fe-carbonates remained limited until recently. However, late identification of SCDs close to Banded Iron Formations as well as gold mineralization that are Fe-carbonate rich, definitely launched the debate on the true generation potential of this class of minerals (Boreham et al., 2021; Geymond et al., 2022). Preliminary thermodynamic calculations suggested that siderite is a good $\text{H}_2$ generator at $T < 200 \text{ °C}$, validating that it is worth to study further this kind of minerals (Malvoisin and Brunet, 2023).

\[
3\text{Fe}^{2+}\text{CO}_3 + \text{H}_2\text{O} \rightarrow 2\text{Fe}^{3+}\text{Fe}^{3+}\text{O}_4 + 3\text{CO}_2 + \text{H}_2. \quad \text{(A.3)}
\]

\[
\text{Oxides}
\]

Fe-oxide are known for years to play a key-role in $\text{H}_2$ generation since magnetite ($\alpha$-Fe$_2$O$_3$) incorporates $\text{Fe}^{3+}$ during serpentinization of basic rocks at $T > 200 \text{ °C}$ (Tutolo et al., 2020). As such, the presence of magnetite in basic rocks, even if they can be of primary origin, is often used as a proxy to evaluate the rate of serpentinization and thus the $\text{H}_2$ generation (Malvoisin et al., 2012). Magnetite, like other spinel type minerals such as chromite (FeCr$_2$O$_4$), are also thought to catalyze $\text{H}_2$ generation during water-rock reactions, for instance during the serpentinization, or conversion of $\text{H}_2$ into CH$_4$ through the Sabatier’s reaction (Mayhew et al., 2013).

In parallel, the fact that a remnant of $\text{Fe}^{2+}$ is present in magnetite (1/3 of total Fe theoretically) recently raised questions about its potential to generate $\text{H}_2$ related to further grade of Fe oxidation. A recent experimental study demonstrated that magnetite gets destabilized in anoxic water, following the equation (A.3), to form $\text{H}_2$ and maghemite ($\gamma$-Fe$_2$O$_3$), another Fe-oxide only bearing $\text{Fe}^{3+}$ (Geymond et al., 2023), especially below 100 °C. Magnetite is present as a major component in many rocks, and these results widen the potential source rock that could generate $\text{H}_2$ (Geymond et al., 2022). Banded Iron Formations, very rich in magnetite, are now considered as a possible $\text{H}_2$ generating rock.

\[
2(\alpha - \text{Fe}^{2+}\text{Fe}^{3+}\text{O}_4) + \text{H}_2\text{O} \rightarrow 3(\gamma - \text{Fe}^{3+}\text{O}_3) + \text{H}_2. \quad \text{(A.5)}
\]
Sulphides

Ferrous iron sulphide, like pyrrhotite, is widely present in the hydrothermal systems of basic rocks and pegmatites. It is often found in association with other sulphides such as pyrite and chalcopyrite. It is of interest in the production of H₂, which this time does not involve the reduction of water but the oxidation of H₂S gas. This reaction often occurs in volcanic hydrothermal settings. Thus, pyrite is a potential marker mineral for H₂ production, if the geological context is suitable. Here is the example of the alteration of trolleyite into pyrite associated to the formation of H₂:

\[
\text{FeS} + \text{H}_2\text{S} \rightarrow \text{FeS}_2 + \text{H}_2. \quad (A.6)
\]

References of Appendix A


Appendix B

Coordinates of the sites discussed in the paper and of the pictures from the fieldworks.

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## Appendix C

Analytical tools to study a rock H₂ potential with their characteristics.

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<th>Limitations</th>
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<th>Limit of detection</th>
<th>Sample type</th>
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<td>Characterization of the Total Organic Content (TOC)</td>
<td></td>
<td></td>
<td></td>
<td>Powder</td>
<td>min/min/min</td>
</tr>
<tr>
<td></td>
<td>Access to mineral and organic contents but also thermal analysis of C and S</td>
<td></td>
<td></td>
<td></td>
<td>(~10 mg)</td>
<td></td>
</tr>
<tr>
<td>X-ray fluorescence</td>
<td>Major elements concentrations (Fe, S, U, Th, K)</td>
<td>Does not detect trace elements</td>
<td></td>
<td>Depends on the element</td>
<td>Soli, powder, liquid</td>
<td>–/min/min</td>
</tr>
<tr>
<td>Inductively Coupled Plasma – Mass</td>
<td>Majors, minors, traces, and ultratrace elements concentrations (Fe, S, U, Th, K)</td>
<td></td>
<td></td>
<td>ppb</td>
<td>Powder</td>
<td>hours/hours/days</td>
</tr>
<tr>
<td>Spectrometry/Optical Emission Spectroscopy (ICP-MS/OES)</td>
<td>Identification and quantification of iron-bearing phases and iron specification in each phase</td>
<td></td>
<td></td>
<td></td>
<td>(~100 mg)</td>
<td></td>
</tr>
<tr>
<td>⁵⁷Fe Mössbauer spectroscopy</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Powder</td>
<td>hours/days/days</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(~400 mg)</td>
<td></td>
</tr>
<tr>
<td>X-Ray Diffraction</td>
<td>Phase identification, quantitative composition</td>
<td>Do not differentiate polymorphs or minor phase</td>
<td></td>
<td>–</td>
<td>Powder</td>
<td>hours/hours/hours</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(~500 mg)</td>
<td></td>
</tr>
<tr>
<td><strong>Observation tool</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Optical microscopy</td>
<td>Paragenesis, texture, alteration features</td>
<td>Low resolution</td>
<td>μm</td>
<td>–</td>
<td>Thin section</td>
<td></td>
</tr>
<tr>
<td>Electro Probe Micro-Analyzer (EPMA)</td>
<td>Quantitative measurements of concentration of the element heavier than Li (Fe, S, U, Th, K) punctual or map</td>
<td>μm</td>
<td>ppm</td>
<td></td>
<td>Thin section</td>
<td>hours/day(s)/days</td>
</tr>
</tbody>
</table>

(Continued on next page)
<table>
<thead>
<tr>
<th>Analyses</th>
<th>Objectives</th>
<th>Limitations</th>
<th>Spatial resolution</th>
<th>Limit of detection</th>
<th>Sample type</th>
<th>Duration of preparation/analysis/processing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scanning Electron Microscopy (SEM)</td>
<td>High-resolution imaging semi-quantitative measurements of concentration of the element heavier than Li (Fe, S, U, Th, K) punctual or map analysis.</td>
<td>Semi-quantitative</td>
<td>nm</td>
<td>–</td>
<td>Thin section</td>
<td>hours/hours/hours</td>
</tr>
<tr>
<td>Raman Microspectroscopy</td>
<td>Phase identification</td>
<td>µm</td>
<td>Thin section</td>
<td>hours/days/days</td>
<td>Thin section</td>
<td>hours/days/days</td>
</tr>
<tr>
<td>X-Rays Microtomography (XCT)</td>
<td>Volume and propagation of elements of interest-bearing phase in the whole rock.</td>
<td>µm</td>
<td>cm³–m³ core</td>
<td>hours/hours/days</td>
<td>cm³–m³ core</td>
<td>hours/hours/days</td>
</tr>
</tbody>
</table>