



**HAL**  
open science

## Orange hydrogen is the new green

Florian Osselin, Cyprien Soulaine, C. Fauguerolles, E. C. Gaucher, Bruno Scaillet,  
Michel Pichavant

### ► To cite this version:

Florian Osselin, Cyprien Soulaine, C. Fauguerolles, E. C. Gaucher, Bruno Scaillet, et al.. Orange hydrogen is the new green. *Nature Geoscience*, 2022, 15, pp.765-769. <10.1038/s41561-022-01043-9>. <insu-03858117>

**HAL Id: insu-03858117**

**<https://insu.hal.science/insu-03858117v1>**

Submitted on 18 Nov 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

# Orange hydrogen is the new Green

F. Osselin<sup>1\*</sup>, C. Soullaine<sup>1</sup>, C. Fauguerolles<sup>1</sup>, E. C. Gaucher<sup>2</sup>, B. Scaillet<sup>1</sup> and M. Pichavant<sup>1</sup>

<sup>1\*</sup>Institut des Sciences de la Terre d'Orléans, Université d'Orléans, CNRS, BRGM UMR7327, 1A Rue de la Ferrollerie, 45100 Orléans, France.

<sup>2</sup>Institute of Geological Science, Bern University..

## 1 Abstract

Maintaining the global warming well below 2°C, as stipulated in the Paris Agreement, will require a complete overhaul of the world energy system. Hydrogen is considered to be a key component of the decarbonization strategy for large parts of the transport system, as well as some heavy industries. Today, about 96% of current hydrogen production comes from the steam reforming of coal or natural gas (labeled Black and Grey hydrogen, respectively). If hydrogen is to become a solution, then Black and Grey hydrogen need to be replaced by a low-carbon option. One method that has received much attention is to produce so-called Green hydrogen by coupling water electrolysis with renewable energies. However, green hydrogen is expensive and energy intensive to produce. In this communication, we explore an alternative option and highlight the benefits of rock-based hydrogen (White and Orange) compared with classic electrolysis-based technologies. We show that the exploitation of native

001  
002  
003  
004  
005  
006  
007  
008  
009  
010  
011  
012  
013  
014  
015  
016  
017  
018  
019  
020  
021  
022  
023  
024  
025  
026  
027  
028  
029  
030  
031  
032  
033  
034  
035  
036  
037  
038  
039  
040  
041  
042  
043  
044  
045  
046

047 hydrogen and its combination with carbon sequestration has the potential to  
048 fuel a large part of the energy transition without the substantial energy and  
049 raw material cost of Green hydrogen.  
050

051

052

053

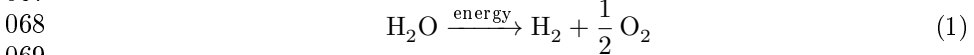
## 054 **2 Main**

055

056 To meet the Net Zero Emission Scenario (NZE) of the International Energy  
057 Agency [1], about 17,000 TWh of hydrogen-based energy will be consumed  
058 in the world in 2050. This hydrogen is usually seen as being provided by  
059 large facilities using renewable electricity to convert water to hydrogen through  
060 electrolysis (Green hydrogen). The energy cost for hydrogen production is  
061 related to the splitting of the water molecule into hydrogen and oxygen:  
062

063

064



066

067 and is directly calculated from the Gibbs energy of formation of water (120  
071 MJ/kg<sub>H<sub>2</sub></sub> at 25°C – THERMOPDEM database [2]). Considering an 80% effi-  
072 cient electrolyser, this corresponds to about 400 Mt of hydrogen, or about five  
073 times the amount consumed in 2020 [1]. These 17,000 TWh represent more  
074 than the electricity produced by both China and the USA in 2020, about 63%  
075 of the world’s electricity production, and more than twice the current world-  
076 wide production of electricity from renewable energies. Meeting this figure will  
077 then require an unprecedented upscaling of both electrolysis and renewable  
078 energies.  
079

080 Blue hydrogen does not fare better due to the extra cost related to CCS  
081 and is probably only a temporary solution [3]. Some authors are even more  
082 critical, arguing that the imperfect capture of CO<sub>2</sub> associated with methane  
083 losses along the whole chain leads to increased greenhouse gas emissions with  
084 only little benefits from pure Grey hydrogen [4]. Another critical shortcoming

085

086

087

088

089

090

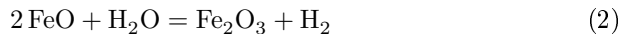
091

092

of Blue hydrogen is the continued reliance on fossil fuel. This last issue also impacts an emerging production technique, sometimes referred to as Turquoise, and which consists in producing H<sub>2</sub> from methane but with graphite-C and not CO<sub>2</sub> as a resulting product. This technology is still in development but could also play a key role in the coming years.

### 3 A greener hydrogen

The Earth's subsurface is a giant and undervalued hydrogen factory. Long considered anecdotic, the current estimations give a rough estimate of 20 Mt of native hydrogen escaping from the surface towards the atmosphere each year [5]. Estimates vary widely but everything suggests that the subsurface is actually producing significantly more, and that this value is just the tip of the iceberg. Natural hydrogen is most commonly produced by the reduction of water to hydrogen following the anoxic and abiotic oxidation of ferrous iron to the orange-coloured ferric iron [6]:



This oxidation occurs, for example, under the ocean floor [7, 8], where peridotites – magnesium silicate rocks which contain up to 10%wt of ferrous iron – become hydrated at temperatures between 200 and 400°C by the percolation of seawater. This process, known as serpentinization, also occurs at lower temperatures and pressures on land-based ophiolite-peridotite massifs [9]. Serpentinization is estimated to produce around 1-2 Mt of hydrogen per year [10] at oceanic ridges where it is the most active. However, serpentinization is not the only process producing hydrogen and anywhere water meets reduced iron, there is a possibility to produce hydrogen if the right conditions of temperature, fluid composition and pressure are met (e.g. archaean

4 *Orange hydrogen is the new Green*

139 Banded-Iron Formations [11], peralkaline and biotite-rich granites [12, 13]).  
140 On land, numerous native hydrogen seeps (usually mixed with methane [14])  
141 have been localized (e.g. Oman, Japan, New Caledonia, Greece, Spain, Italy,  
142 California) [15], France [16], Australia, Brazil [17], Kansas [18]). Some are even  
143 known since the antiquity such as the Mount Chimaera (Yanartaş, Turkey)  
144 which continuously produces a mixture of 87%*vol.* CH<sub>4</sub> and 10%*vol.* H<sub>2</sub> [14].  
145 Exploitation of this hydrogen offers then an interesting alternative to Green  
146 and Blue hydrogen by completely skipping the electrolysis and simply col-  
147 lecting the hydrogen emitted by natural underground processes. This White  
148 hydrogen is already under production in Mali where a well drilled for water  
149 turned out to produce a 98%*vol* hydrogen stream currently used power the  
150 entire village of Bourakebougou for the last 10 years [19]. The actual source  
151 of the hydrogen remains unknown but chances are that the reduction of iron  
152 is involved deep underground.  
153  
154  
155  
156  
157  
158  
159  
160  
161  
162  
163

## 164 4 Orange Hydrogen

165 It is possible to go even further and go Orange. This color, which refers to  
166 the color of oxidized iron, follows the same principles of White hydrogen and  
167 looks to make the Earth provide most of the work for hydrogen production.  
168 Yet, instead of using a passive approach of exploration/exploitation, Orange  
169 hydrogen follows a proactive way and searches to stimulate the reaction. This  
170 is done by injecting water *in situ* in identified reactive formations and collect  
171 the hydrogen-saturated water from recovery wells surrounding the injection  
172 point (Fig. 1). This approach can also be adopted for Fe-rich mine wastes and  
173 steel slags [20] in an *ex situ* surface reactor which has the advantage of being  
174 easier to control and set-up. Additionally, the magnetite particles (Fe<sub>3</sub>O<sub>4</sub>)  
175 resulting from the oxidation process have a commercial value, especially in  
176  
177  
178  
179  
180  
181  
182  
183  
184

the pharmaceutical industry. However, the significantly lower volumes of raw materials available for *ex situ* Orange Hydrogen and the prohibitive financial and environmental cost of extracting and grinding new feedstock makes the *ex situ* solution less attractive than the *in situ* one.

*In situ* Orange hydrogen requires more energy than White hydrogen production, but the outputs will be significantly higher, while production costs will likely remain under Blue/Green ones. An average peridotite can provide around 2-4 kg<sub>H<sub>2</sub></sub>/m<sup>3</sup> upon complete oxidation. With 10<sup>20</sup> kg of peridotites in the upper crust (top 7km) [21], there are 100 trillions tons of hydrogen to be extracted from the subsurface, sufficient for 250,000 years at a rate of 400 Mt/year. This is not even considering that over these timescales, tectonic activity will refresh the peridotites at a rate of 10<sup>12</sup> kg/year [21]. The exploitation of the whole volume is obviously unrealistic due to technical, economic and regulatory reasons, but even a small percentage would make Orange hydrogen a key player in the achievement of the NZE scenario.

The real game-changing impact of Orange hydrogen, is that the very same formations which naturally produce hydrogen are also the perfect location for carbon sequestration [22]. These formations are part of the deep carbon cycle, balancing the concentration of atmospheric carbon dioxide through its reaction with silicate rocks. This natural weathering has allowed the capture of 99.9% of the total carbon on Earth as solid, stable carbonates [23], but is now getting rapidly outpaced by the increase in anthropic emissions since the industrial era. Matter *et al.* [24] calculated for example that 30 trillions tons of CO<sub>2</sub> can be stored in the Oman Ophiolite (the largest on-land peridotite massif), and 100 trillions tons globally. For comparison, the CO<sub>2</sub> anthropic emissions in 2020 are estimated at 33 billions tons.

185  
186  
187  
188  
189  
190  
191  
192  
193  
194  
195  
196  
197  
198  
199  
200  
201  
202  
203  
204  
205  
206  
207  
208  
209  
210  
211  
212  
213  
214  
215  
216  
217  
218  
219  
220  
221  
222  
223  
224  
225  
226  
227  
228  
229  
230

231 In Iceland, Carbfix, a company built on the results of several European  
232 Union's research projects, has been injecting 72,000 tons of carbon dioxide  
233 in the island basaltic formation for about 10 years with great success [25,  
234 235 26]. A similar pilot injected 1000 tons of pure liquid CO<sub>2</sub> in the Columbia  
236 River Basalts near Wallula (USA). Cores retrieved 2 years after the injection  
237 presented unequivocal evidence of the mineralization of the injected CO<sub>2</sub> [27].  
238 However, neither of these large-scale pilots considered the hydrogen production  
239 associated with the CO<sub>2</sub> mineralization process despite the iron-rich nature of  
240 the targeted basalts and thus the possibility of coupled production [28].  
241

242 The list of Orange hydrogen advantages does not end here. In contrast to  
243 electrolysis, where only specifically tuned water compositions can be used, nat-  
244 245 ural oxidation of iron as well as carbon mineralization works very well with  
246 seawater [29] or even wastewater, alleviating significantly the water cost of  
247 248 249 250 hydrogen production. Target formations can also contain elements of economic  
251 interest such as Li, Ni, Co... as is usually the case in serpentinite formations  
252 [30]. The dissolution of the primary minerals following the injection will release  
253 254 255 these elements in the percolating fluids, which can be extracted in parallel to  
256 257 258 hydrogen by fractionated precipitation. Similar processes are currently in use  
259 in Uranium recovery [31] and extraction of Li in parallel to heat is being con-  
260 sidered in geothermal applications [32]. Orange hydrogen differs significantly  
261 from the alternatives as it does not rely on critical raw materials as electrolysis  
262 263 264 processes, and can even produce them as by-products of the main operation.  
265 266

267 Laboratory experiments on the reactivity of magnesium silicates with car-  
268 bon dioxide have shown that a mixture of NaHCO<sub>3</sub> and dissolved CO<sub>2</sub> can  
269 270 achieve complete carbonation over the course of a few hours to a few days [33].  
271 Carbonation rate is a direct function of the CO<sub>2</sub> partial pressure but the rate  
272 of serpentinization seems either unaffected [34] or slightly accelerated [35] by  
273 274 275 276

the presence of CO<sub>2</sub>. Both carbonation and serpentinization reaction rates are also strongly temperature-dependent, and follow a bell-shaped curve with an maximum respectively at 185°C and between 250 and 280°C for serpentinization [36, 37]. Maintaining a high rate of H<sub>2</sub> production and CO<sub>2</sub> mineralization requires thus a careful control of the downhole temperature. Luckily, serpentinization and carbonation are very exothermic (respectively  $\Delta H = 250$  kJ/kg and  $\Delta H = 760$  kJ/kg). Once the process is initiated, the desired temperature can be obtained through self-heating with a heat production from the chemical reactions balancing the heat losses through convection and conduction, as well as the cooling induced by the injection of colder fluids [24, 38]. This self-heating behavior allows reducing production costs as no surface heating of the injected fluids is necessary, but requires a careful control of the injection rate. Interestingly, some of this heat can be extracted from the recovered fluids in a geothermal-like process and be reused to power the facility with recovered fluid temperatures up to 200-300°C (considering the combined action of exothermic reaction and formation temperatures e.g. 250°C for Carbfix2 [39]).

Kelemen *et al.* [38] calculate a carbonation rate of  $4.10^9$  tCO<sub>2</sub>/year for the stimulation of 1 km<sup>3</sup> of peridotite at 185°C ( $5.10^6$  kg/s of carbonation, CO<sub>2</sub> partial pressure between 75 and 300 bars). Extrapolating their calculation with 10%wt FeO, this leads to a rate of 5 Mt<sub>H<sub>2</sub></sub>/year for 1 km<sup>3</sup> of peridotite ( $5.10^4$  kg/s for serpentinization in the same conditions). In Figure 2 are represented hydrogen production rates from batch [40–42] and reactive percolation [43] experiments. In all cases, measured hydrogen production is significant and approaches the maximum production which can be expected from these rocks. A linear fit of the data gives rates from 0.1 to 3 Mt<sub>H<sub>2</sub></sub>/km<sup>3</sup>/year, similar to the extrapolation from Kelemen *et al.* [38]. As a result, experimental

277  
278  
279  
280  
281  
282  
283  
284  
285  
286  
287  
288  
289  
290  
291  
292  
293  
294  
295  
296  
297  
298  
299  
300  
301  
302  
303  
304  
305  
306  
307  
308  
309  
310  
311  
312  
313  
314  
315  
316  
317  
318  
319  
320  
321  
322

323 data from laboratory experiments support directly the preliminary estima-  
324 tions. Extra research is however necessary to assess the potential of other types  
325 of formations for hydrogen production combined with carbon sequestration.  
326

327 This means that, while it is not expected that Orange hydrogen will solely  
328 meet the 400 Mt for the NZE scenario, it has the potential to provide a sig-  
329 nificant part of it, at a fraction of the energy and raw/critical mineral cost of  
330 electrolyzers. In other words, Orange hydrogen promises to provide abundant,  
331 clean, rock-based, carbon-negative, and price-competitive energy to fuel the  
332 energy transition towards the NZE scenario.  
333  
334  
335  
336  
337  
338  
339  
340

## 341 5 Challenges for Orange hydrogen

342  
343 Developing Orange hydrogen faces numerous scientific challenges, which can  
344 be sorted in 3 different categories:  
345

- 346  
347 1. Accurate description, quantification and mapping of the resource, taking  
348 into account the iron grade of the targeted rock formation and its technical  
349 and societal accessibility.  
350  
351  
352
- 353 2. Identification of the ideal pressure, temperature, flow rate, fluid composi-  
354 tion for the optimized production of hydrogen and carbon mineralization.  
355  
356 These settings need to account for the precipitation of parasitic minerals  
357 competing with carbonate precipitation, the incorporation of Fe into pre-  
358 cipitating minerals preventing its oxidation and H<sub>2</sub> production, as well as  
359 the careful control of porosity to prevent any clogging by the precipitat-  
360 ing minerals. Parasitic reactions are for example at work in the experiment  
361 from Grozeva *et al.* [41] represented on Figure 2. The injection of a CO<sub>2</sub>-rich  
362 fluid mid-experiment lead to a decrease in H<sub>2</sub> in the reactor. The process  
363 consuming the hydrogen was however, not clearly identified.  
364  
365  
366  
367  
368

3. Field-scale optimization of the injection and recovery of the fluids to maximize the impacted zone and minimize hydrogen losses. This includes research on reservoir stimulation (hydraulic fracturing and chemical stimulation) and potential induced (micro)-seismicity, as well as the microbiology of low-temperature reservoirs which, if left unchecked, can consume the produced H<sub>2</sub> and impact significantly the yield.

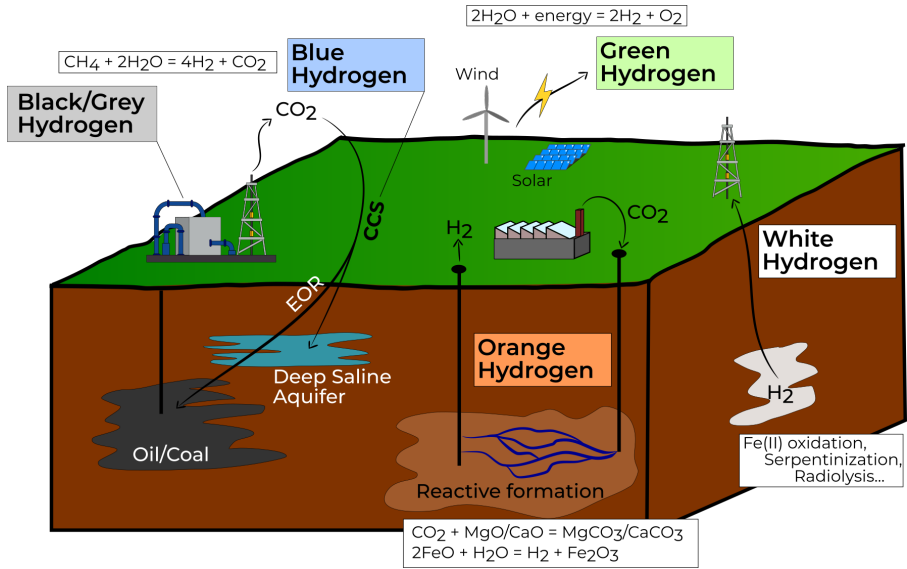
These challenges cover a wide range of scales and disciplines and require a combined effort to offer a satisfactory solution. The first challenge falls within the scope of geologists and economists, the second is related to thermodynamics and geochemistry as well as the physics of coupled processes in porous media. The third one concerns reservoir engineering and simulations, geotechnics and microbiology. Given the scale of the projects, social acceptance will also be a key point in the development of the technology, in particular in the case of induced-seismicity.

One example of these multidisciplinary and multiscale challenges is the proper modeling of the porosity/permeability relationship during the process. Carbonation of target rocks leads to the precipitation of carbonate minerals within the porosity as well as the precipitation of serpentine, which is less dense than the minerals it replaces. As such, the porosity and thus the permeability of the rock will be a function of the dynamic balance between dissolution of the primary minerals and the precipitation of the secondary minerals. If the latter occurs faster, it is likely that some clogging will occur with dramatic effects on the long-term viability of the process. Yet, the only two large-scale pilots for geological mineralization of CO<sub>2</sub> have not evidenced any clogging or permeability decrease, even several years after the beginning of the injection in the case of Carbfix [26]. Moreover, natural settings are proofs that carbonation can be going on for tens to hundreds of thousands of years without any clogging [44].

415 Reaction-induced fracturing, which is often invoked to explain the maintained  
416 permeability during some natural processes despite adverse molar volume evo-  
417 lution is the process during which a growing mineral in a confined space is able  
418 to generate large stresses on the surrounding matrix, enough to fracture it and  
419 open new percolation paths for the fluid [45–47]. However, up to date, not only  
420 does the modeling of such fracturing still fail to reproduce the experimental  
421 observations but experiments of reactive percolation where such phenomenon  
422 is expected, usually do not present any evidence that reactive-induced fractur-  
423 ing occurred [43, 48, 49]. The control of reaction-induced fracturing and the  
424 overall control of the reactivity and injectivity during the production of Orange  
425 hydrogen (potentially through targeted hydraulic fracturing) is of paramount  
426 importance for the viability of the process and requires a deeper understand-  
427 ing of the microscopic behavior of dissolution/precipitation as well as a proper  
428 upscaling of these processes to reservoir and field scale.  
429  
430  
431  
432  
433  
434  
435  
436  
437  
438  
439  
440  
441  
442  
443

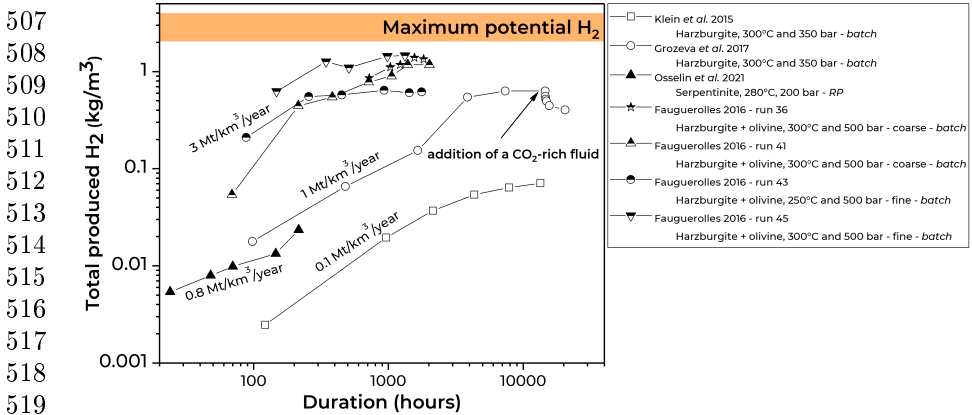
## 444 **6 Conclusion**

445  
446 We are at a tipping point for the climate, and the exploitation of Orange  
447 hydrogen is an additional technology which could prevent a dramatic evolu-  
448 tion. Hydrogen is nowadays a controversial energy carrier as it is considered  
449 by some as an easy way to transport energy and decarbonize the transporta-  
450 tion sector, while others see it as an unnecessary intermediate and advocate a  
451 full electric switch. This controversy becomes irrelevant if White and Orange  
452 hydrogen are included in the debate. Their production does not require as  
453 much electricity or raw materials as Green hydrogen and Orange hydrogen  
454 offers also the possibility to store enough CO<sub>2</sub> to curb global warming.  
455  
456  
457  
458  
459  
460



**Fig. 1** The different colors of Hydrogen. Black/Grey H<sub>2</sub> is from steam reforming. It turns Blue through the addition of CCS, either through permanent storage (e.g. in deep saline aquifers) or through Enhanced Oil Recovery (EOR). On the other end of the spectrum, Green hydrogen is produced by electrolysis using renewable energies. White hydrogen corresponds to the exploitation of subsurface-sourced natural hydrogen. Orange hydrogen is a proactive take on White hydrogen and consists in injecting in a reactive formation a carbon-enriched solution. Geochemical reactions lead to the precipitation of solid carbonates while hydrogen is formed and recovered from the fluid.

In addition to energy considerations, the decarbonization of the world's energy mix will require an unprecedented upscaling in the production of renewable energies and the associated batteries and thus in ore mining, especially for Nickel-Cobalt ( $\times 20 - 25$ ) and Lithium ( $\times 40$ ) [50]. Every million tons of White and Orange hydrogen means at least 120 TJ (or 33GWh) of electricity saved. This saved electricity as well as the saved critical metals can be used for more batteries, electric car or wind turbines in order to accelerate the energy transition. If we add the carbon storage ability of Orange hydrogen, we might just have the solution for some of the energy problems of the coming decades.



**Fig. 2** Measured hydrogen in both batch and reactive percolation experiments. In controlled conditions, the production of  $H_2$  is significant and reaches values close to the theoretical maximum. RP = Reactive Percolation

## 7 Corresponding Author

524  
525  
526  
527 All correspondence should be addressed to F. Osselin (florian.osselin@cnr-  
528 orleans.fr).

## 8 Acknowledgment

530  
531  
532  
533 This research was supported by the LABEX Voltaire (ANR-10-LABX-100-01)  
534  
535  
536 and EQUIPEX PLANEX (ANR-11-EQPX-0036).  
537  
538

## 9 Author contribution

539  
540  
541  
542  
543 FO - design of the study, drafting the article and data acquisition. CF - data  
544 acquisition. CS, EG and BS revisions. MP - design of the study.  
545  
546  
547  
548

## 10 Competing interests

549  
550  
551  
552 The authors declare no competing interests.

## References

- [1] International Energy Agency. World Energy Outlook 2021 - revised version October 2021 (2021). URL [www.iea.org/weo](http://www.iea.org/weo) .
- [2] Blanc, P. *et al.* Thermoddem: A geochemical database focused on low temperature water/rock interactions and waste materials. *Applied Geochemistry* **27** (10), 2107–2116 (2012). URL <http://dx.doi.org/10.1016/j.apgeochem.2012.06.002>. <https://doi.org/10.1016/j.apgeochem.2012.06.002> .
- [3] International Energy Agency. The Future of Hydrogen. Tech. Rep., International Energy Agency (2019). URL <https://linkinghub.elsevier.com/retrieve/pii/S1464285912700275>.
- [4] Howarth, R. W. & Jacobson, M. Z. How green is blue hydrogen? *Energy Science and Engineering* **9** (10), 1676–1687 (2021). <https://doi.org/10.1002/ese3.956> .
- [5] Zgonnik, V. The occurrence and geoscience of natural hydrogen: A comprehensive review. *Earth-Science Reviews* **203** (July 2019), 103140 (2020). URL <https://doi.org/10.1016/j.earscirev.2020.103140>. <https://doi.org/10.1016/j.earscirev.2020.103140> .
- [6] Klein, F. *et al.* Iron partitioning and hydrogen generation during serpentinization of abyssal peridotites from 15°N on the Mid-Atlantic Ridge. *Geochimica et Cosmochimica Acta* **73** (22), 6868–6893 (2009). <https://doi.org/10.1016/j.gca.2009.08.021> .
- [7] Kelley, D. S. *et al.* A Serpentinite-Hosted Ecosystem: The Lost City Hydrothermal Field. *Science* **307** (5714), 1428–1434 (2005). URL <http://>

- 599 [www.sciencemag.org/cgi/doi/10.1126/science.1102556](http://www.sciencemag.org/cgi/doi/10.1126/science.1102556). [https://doi.org/](https://doi.org/10.1126/science.1102556)  
600 [10.1126/science.1102556](https://doi.org/10.1126/science.1102556) .  
601  
602
- 603 [8] Cannat, M., Fontaine, F. & Escartín, J. in *Serpentinization and*  
604 *associated hydrogen and methane fluxes at slow spreading ridges* 241–  
605 264 (2010). URL [http://www.agu.org/books/gm/v188/2008GM000760/](http://www.agu.org/books/gm/v188/2008GM000760/2008GM000760.shtml)  
606 [2008GM000760.shtml](http://www.agu.org/books/gm/v188/2008GM000760/2008GM000760.shtml).  
607  
608
- 609 [9] Neal, C. & Stanger, G. Hydrogen generation from mantle source rocks in  
610 Oman. *Earth and Planetary Science Letters* **66**, 315–320 (1983). URL  
611 <http://linkinghub.elsevier.com/retrieve/pii/0012821X83901449>. [https://](https://doi.org/10.1016/0012-821X(83)90144-9)  
612 [doi.org/10.1016/0012-821X\(83\)90144-9](https://doi.org/10.1016/0012-821X(83)90144-9) .  
613  
614
- 615 [10] Worman, S. L., Pratson, L. F., Karson, J. A. & Klein, E. M. Global rate  
616 and distribution of H<sub>2</sub> gas produced by serpentinization within oceanic  
617 lithosphere. *Geophysical Research Letters* **43** (12), 6435–6443 (2016).  
618 URL <http://doi.wiley.com/10.1002/2016GL069066>. [https://doi.org/10.](https://doi.org/10.1002/2016GL069066)  
619 [1002/2016GL069066](https://doi.org/10.1002/2016GL069066) .  
620  
621
- 622 [11] Geymond, U., Ramanaidou, E., Lévy, D., Ouaya, A. & Moretti, I. Can  
623 Weathering of Banded Iron Formations Generate Natural Hydrogen? Evi-  
624 dence from Australia, Brazil and South Africa. *Minerals* **12** (2) (2022).  
625 <https://doi.org/10.3390/min12020163> .  
626  
627
- 628 [12] Truche, L. *et al.* Hydrogen generation during hydrothermal alteration of  
629 peralkaline granite. *Geochimica et Cosmochimica Acta* (2021). URL [https://](https://doi.org/10.1016/j.gca.2021.05.048)  
630 [doi.org/10.1016/j.gca.2021.05.048](https://doi.org/10.1016/j.gca.2021.05.048). [https://doi.org/10.1016/j.gca.2021.](https://doi.org/10.1016/j.gca.2021.05.048)  
631 [05.048](https://doi.org/10.1016/j.gca.2021.05.048) .  
632  
633  
634  
635  
636  
637  
638  
639  
640  
641  
642  
643  
644

- [13] Murray, J. *et al.* Abiotic hydrogen generation from biotite-rich granite: A case study of the Soultz-sous-Forêts geothermal site, France. *Applied Geochemistry* **119** (May 2019) (2020). <https://doi.org/10.1016/j.apgeochem.2020.104631> .
- [14] Etiope, G., Schoell, M. & Hosgörmez, H. Abiotic methane flux from the Chimaera seep and Tekirova ophiolites (Turkey): Understanding gas exhalation from low temperature serpentinization and implications for Mars. *Earth and Planetary Science Letters* **310** (1-2), 96–104 (2011). URL <http://dx.doi.org/10.1016/j.epsl.2011.08.001>. <https://doi.org/10.1016/j.epsl.2011.08.001> .
- [15] Gaucher, E. C. New perspectives in the industrial exploration for native hydrogen. *Elements* **16** (1), 8–9 (2020). <https://doi.org/10.2138/gselements.16.1.8> .
- [16] Lefeuvre, N. *et al.* Native H<sub>2</sub> Exploration in the Western Pyrenean Foothills . *Geochemistry, Geophysics, Geosystems* **22** (8), 1–20 (2021). <https://doi.org/10.1029/2021gc009917> .
- [17] Moretti, I., Brouilly, E., Loiseau, K., Prinzhofer, A. & Deville, E. Hydrogen emanations in intracratonic areas: New guide lines for early exploration basin screening. *Geosciences (Switzerland)* **11** (3) (2021). <https://doi.org/10.3390/geosciences11030145> .
- [18] Guélard, J. *et al.* Natural H<sub>2</sub> in Kansas: Deep or shallow origin? *Geochemistry, Geophysics, Geosystems* **18** (5), 1841–1865 (2017). URL <http://doi.wiley.com/10.1002/2016GC006544>. <https://doi.org/10.1002/2016GC006544> .

- 691 [19] Prinzhofer, A., Tahara Cissé, C. S. & Diallo, A. B. Discovery of a large  
692 accumulation of natural hydrogen in Bourakebougou (Mali). *International*  
693 *Journal of Hydrogen Energy* **43** (42), 19315–19326 (2018). <https://doi.org/10.1016/j.ijhydene.2018.08.193> .
- 697  
698 [20] Kularatne, K. *et al.* Simultaneous ex-situ CO<sub>2</sub> mineral sequestration  
699 and hydrogen production from olivine-bearing mine tailings. *Applied*  
700 *Geochemistry* **95** (May), 195–205 (2018). URL [https://doi.org/10.1016/](https://doi.org/10.1016/j.apgeochem.2018.05.020)  
701 [j.apgeochem.2018.05.020](https://doi.org/10.1016/j.apgeochem.2018.05.020). [https://doi.org/10.1016/](https://doi.org/10.1016/j.apgeochem.2018.05.020)  
702 [j.apgeochem.2018.05.](https://doi.org/10.1016/j.apgeochem.2018.05.020)  
703 [020](https://doi.org/10.1016/j.apgeochem.2018.05.020) .
- 704  
705  
706 [21] Kelemen, P. B. *et al.* Rates and Mechanisms of Mineral Carbon-  
707 ation in Peridotite: Natural Processes and Recipes for Enhanced, in  
708 situ CO<sub>2</sub> Capture and Storage. *Annual Review of Earth and Plane-*  
709 *tary Sciences* **39** (1), 545–576 (2011). URL [http://www.annualreviews.](http://www.annualreviews.org/doi/10.1146/annurev-earth-092010-152509)  
710 [org/doi/10.1146/annurev-earth-092010-152509](http://www.annualreviews.org/doi/10.1146/annurev-earth-092010-152509). [https://doi.org/10.1146/](https://doi.org/10.1146/annurev-earth-092010-152509)  
711 [annurev-earth-092010-152509](https://doi.org/10.1146/annurev-earth-092010-152509) .
- 712  
713  
714  
715  
716  
717 [22] Kelemen, P. *et al.* In situ carbon mineralization in ultramafic rocks:  
718 Natural processes and possible engineered methods. *Energy Procedia*  
719 **146** (August), 92–102 (2018). URL [https://linkinghub.elsevier.com/](https://linkinghub.elsevier.com/retrieve/pii/S1876610218301450)  
720 [retrieve/pii/S1876610218301450](https://linkinghub.elsevier.com/retrieve/pii/S1876610218301450). [https://doi.org/10.1016/j.egypro.2018.](https://doi.org/10.1016/j.egypro.2018.07.013)  
721 [07.013](https://doi.org/10.1016/j.egypro.2018.07.013) .
- 722  
723  
724  
725  
726 [23] Gaillardet, J., Dupré, B., Louvat, P. & Allègre, C. J. Global silicate  
727 weathering and CO<sub>2</sub> consumption rates deduced from the chemistry of  
728 large rivers. *Chemical Geology* **159** (1-4), 3–30 (1999). [https://doi.org/](https://doi.org/10.1016/S0009-2541(99)00031-5)  
729 [10.1016/S0009-2541\(99\)00031-5](https://doi.org/10.1016/S0009-2541(99)00031-5) .
- 730  
731  
732  
733  
734  
735  
736

- [24] Matter, J. M. & Kelemen, P. B. Permanent storage of carbon dioxide in geological reservoirs by mineral carbonation. *Nature Geoscience* **2** (12), 837–841 (2009). URL <http://www.nature.com/articles/ngeo683>. <https://doi.org/10.1038/ngeo683> .
- [25] Gíslason, S. R., Sigurdardóttir, H., Aradóttir, E. S. & Oelkers, E. H. *A brief history of CarbFix: Challenges and victories of the project's pilot phase*, Vol. 146 (2018).
- [26] Snæbjörnsdóttir, S. *et al.* Carbon dioxide storage through mineral carbonation. *Nature Reviews Earth and Environment* **1** (2), 90–102 (2020). <https://doi.org/10.1038/s43017-019-0011-8> .
- [27] McGrail, B. P. *et al.* Wallula Basalt Pilot Demonstration Project: Post-injection Results and Conclusions. *Energy Procedia* **114** (November 2016), 5783–5790 (2017). URL <http://dx.doi.org/10.1016/j.egypro.2017.03.1716>. <https://doi.org/10.1016/j.egypro.2017.03.1716> .
- [28] Combaudon, V. & Moretti, I. Generation of Hydrogen along the Mid-Atlantic Ridge: Onshore and Offshore. *Geology, Earth & Marine Sciences* **3** (4), 1–14 (2021). <https://doi.org/10.31038/gems.2021343> .
- [29] Voigt, M. *et al.* An experimental study of basalt–seawater–CO<sub>2</sub> interaction at 130 °C. *Geochimica et Cosmochimica Acta* **308**, 21–41 (2021). <https://doi.org/10.1016/j.gca.2021.05.056> .
- [30] Lawley, C. J. *et al.* Precious metal mobility during serpentinization and breakdown of base metal sulphide. *Lithos* **354–355** (2020). <https://doi.org/10.1016/j.lithos.2019.105278> .

- 783 [31] Lagneau, V., Regnault, O. & Descostes, M. Industrial Deployment of  
 784 Reactive Transport Simulation: An Application to Uranium In situ Recov-  
 785 ery. *Reviews in Mineralogy and Geochemistry* **85** (1), 499–528 (2019).  
 786 <https://doi.org/10.2138/rmg.2019.85.16> .  
 787  
 788  
 789
- 790 [32] Stringfellow, W. T. & Dobson, P. F. Technology for Lithium Extrac-  
 791 tion in the Context of Hybrid Geothermal Power. *PROCEEDINGS, 46th*  
 792 *Workshop on Geothermal Reservoir Engineering* (2021) .  
 793  
 794  
 795
- 796 [33] O'Connor, W. *et al.* Aqueous Mineral Carbonation: Mineral Availability,  
 797 Pretreatment, Reaction Parametrics, and Process Studies. *Doe/Arc-*  
 798 *Tr-04-002* (April), 1–19 (2005). URL [https://www.netl.doe.gov/](https://www.netl.doe.gov/FileLibrary/Research/Coal/NETLAlbanyAqueousMineralCarbonation.pdf)  
 799 [FileLibrary/Research/Coal/NETLAlbanyAqueousMineralCarbonation.](https://www.netl.doe.gov/FileLibrary/Research/Coal/NETLAlbanyAqueousMineralCarbonation.pdf)  
 800 [pdf.](https://www.netl.doe.gov/FileLibrary/Research/Coal/NETLAlbanyAqueousMineralCarbonation.pdf) <https://doi.org/10.13140/RG.2.2.23658.31684> .  
 801  
 802  
 803  
 804
- 805 [34] Oelkers, E. H., Declercq, J., Saldi, G. D., Gislason, S. R. & Schott, J.  
 806 Olivine dissolution rates: A critical review. *Chemical Geology* **500** (Octo-  
 807 ber), 1–19 (2018). <https://doi.org/10.1016/j.chemgeo.2018.10.008> .  
 808  
 809  
 810
- 811 [35] Wang, J., Watanabe, N., Okamoto, A., Nakamura, K. & Komai,  
 812 T. Pyroxene control of H<sub>2</sub> production and carbon storage  
 813 during water-peridotite-CO<sub>2</sub> hydrothermal reactions. *Inter-*  
 814 *national Journal of Hydrogen Energy* **44** (49), 26835–26847  
 815 (2019). URL <https://doi.org/10.1016/j.ijhydene.2019.08.161><https://linkinghub.elsevier.com/retrieve/pii/S0360319919331799>. <https://doi.org/10.1016/j.ijhydene.2019.08.161> .  
 816  
 817  
 818  
 819  
 820  
 821  
 822  
 823
- 824 [36] Chizmeshya, A. V. G., McKelvy, M. J., Squires, K., Carpenter, R. W.  
 825 & Bearat, H. A Novel Approach to Mineral Carbonation: Enhancing  
 826 Carbonation While Avoiding Mineral Pretreatment Process Cost. *Tech.*  
 827  
 828

- Rep., Arizon State University (2007). URL <http://www.osti.gov/servlets/purl/924162-e8RuYF/>. arXiv:1011.1669v3. 829  
830  
831  
832
- [37] Lamadrid, H. M., Zajacz, Z., Klein, F. & Bodnar, R. J. Synthetic 833  
Fluid Inclusions XXIII . Effect of temperature and fluid composition on 834  
rates of serpentinization of olivine. *Geochimica et Cosmochimica Acta* 835  
(2020). URL <https://doi.org/10.1016/j.gca.2020.08.009>. [https://doi.org/](https://doi.org/10.1016/j.gca.2020.08.009) 836  
[10.1016/j.gca.2020.08.009](https://doi.org/10.1016/j.gca.2020.08.009) . 837  
838  
839  
840  
841
- [38] Kelemen, P. B. & Matter, J. M. In situ carbonation of peridotite for 842  
CO<sub>2</sub> storage. *Proceedings of the National Academy of Sciences* **105** (45), 843  
17295–17300 (2008). <https://doi.org/10.1073/pnas.0805794105> . 844  
845  
846  
847
- [39] Gunnarsson, I. *et al.* The rapid and cost-effective capture and sub- 848  
surface mineral storage of carbon and sulfur at the CarbFix2 site. 849  
*International Journal of Greenhouse Gas Control* **79** (August), 117–126 850  
(2018). URL <https://doi.org/10.1016/j.ijggc.2018.08.014>. [https://doi.](https://doi.org/10.1016/j.ijggc.2018.08.014) 851  
[org/10.1016/j.ijggc.2018.08.014](https://doi.org/10.1016/j.ijggc.2018.08.014) . 852  
853  
854  
855  
856
- [40] Klein, F. *et al.* Fluids in the Crust. Experimental constraints on fluid- 857  
rock reactions during incipient serpentinization of harzburgite. *American* 858  
*Mineralogist* **100** (4) (2015). <https://doi.org/10.2138/am-2015-5112> . 859  
860  
861  
862
- [41] Grozeva, N. G., Klein, F., Seewald, J. S. & Sylva, S. P. Experimental study 863  
of carbonate formation in oceanic peridotite. *Geochimica et Cosmochim-* 864  
*ica Acta* **199**, 264–286 (2017). URL [http://dx.doi.org/10.1016/j.gca.2016.](http://dx.doi.org/10.1016/j.gca.2016.10.052) 865  
[10.052](http://dx.doi.org/10.1016/j.gca.2016.10.052)<https://linkinghub.elsevier.com/retrieve/pii/S001670371630655X>. 866  
<https://doi.org/10.1016/j.gca.2016.10.052> . 867  
868  
869  
870  
871  
872  
873  
874

- 875 [42] Fauguerolles, C. *Etude Expérimentale de la production d'H<sub>2</sub> associée à la*  
876 *serpentinisation des péridotites au niveau des dorsales océaniques lentes.*  
877  
878 Ph.D. thesis, Université d'Orléans (2016).  
879  
880
- 881 [43] Osselin, F., Pichavant, M., Champallier, R., Ulrich, M. & Raimbourg,  
882 H. Reactive transport experiments of coupled carbonation and serpen-  
883 tinization in a natural serpentinite. Implication for hydrogen produc-  
884 tion and carbon geological storage. *Geochimica et Cosmochimica Acta*  
885 **318**, 165–189 (2022). URL [https://linkinghub.elsevier.com/retrieve/pii/](https://linkinghub.elsevier.com/retrieve/pii/S0016703721006943)  
886 [S0016703721006943](https://linkinghub.elsevier.com/retrieve/pii/S0016703721006943). <https://doi.org/10.1016/j.gca.2021.11.039> .  
887  
888  
889
- 890
- 891 [44] Menzel, M. D. *et al.* Carbonation of mantle peridotite by CO<sub>2</sub>-rich fluids:  
892 the formation of listvenites in the Advocate ophiolite complex (Newfound-  
893 land, Canada). *Lithos* **323** (2018). [https://doi.org/10.1016/j.lithos.2018.](https://doi.org/10.1016/j.lithos.2018.06.001)  
894 [06.001](https://doi.org/10.1016/j.lithos.2018.06.001) .  
895  
896  
897  
898
- 899 [45] Jamtveit, B., Austrheim, H. & Malthes-Sorensen, A. Accelerated hydra-  
900 tion of the Earth's deep crust induced by stress perturbations. *Nature*  
901 **408** (6808), 75–78 (2000). <https://doi.org/10.1038/35040537> .  
902  
903  
904
- 905 [46] Osselin, F. *et al.* Stress from NaCl crystallisation by carbon dioxide injec-  
906 tion in aquifers. *Environmental Geotechnics* **2** (5), 280–291 (2015). URL  
907 <http://www.icevirtuallibrary.com/doi/10.1680/envgeo.13.00057>. [https://](https://doi.org/10.1680/envgeo.13.00057)  
908 [doi.org/10.1680/envgeo.13.00057](https://doi.org/10.1680/envgeo.13.00057). [https://](https://doi.org/10.1680/envgeo.13.00057)  
909 [doi.org/10.1680/envgeo.13.00057](https://doi.org/10.1680/envgeo.13.00057) .  
910  
911
- 912 [47] Zhu, W. *et al.* Experimental evidence of reaction-induced fracturing dur-  
913 ing olivine carbonation. *Geophysical Research Letters* **43** (18), 9535–9543  
914 (2016). <https://doi.org/10.1002/2016GL070834> .  
915  
916  
917  
918  
919  
920

- [48] van Noort, R., Wolterbeek, T., Drury, M., Kandianis, M. & Spiers, C. 921  
 The Force of Crystallization and Fracture Propagation during In-Situ 922  
 Carbonation of Peridotite. *Minerals* **7** (10), 190 (2017). URL <http://www.mdpi.com/2075-163X/7/10/190>. <https://doi.org/10.3390/min7100190> . 923  
 924  
 925  
 926  
 927
- [49] Luhmann, A. J. *et al.* Chemical and physical changes during seawater 928  
 flow through intact dunite cores: An experimental study at 150–200 929  
 °C. *Geochimica et Cosmochimica Acta* **214**, 86–114 (2017). URL 930  
<http://dx.doi.org/10.1016/j.gca.2017.07.020>. <https://doi.org/10.1016/j.gca.2017.07.020> . 931  
 932  
 933  
 934  
 935  
 936
- [50] International Energy Agency. The Role of Critical 937  
 Minerals in Clean Energy Transitions – Analysis – 938  
 IEA. Tech. Rep. (2021). URL [https://www.iea.org/reports/the-role-of-critical-minerals-in-clean-energy-transitions/](https://www.iea.org/reports/the-role-of-critical-minerals-in-clean-energy-transitions/executive-summary) 939  
[executive-summary](https://www.iea.org/reports/the-role-of-critical-minerals-in-clean-energy-transitions/executive-summary). 940  
 941  
 942  
 943  
 944  
 945  
 946  
 947  
 948  
 949  
 950  
 951  
 952  
 953  
 954  
 955  
 956  
 957  
 958  
 959  
 960  
 961  
 962  
 963  
 964  
 965  
 966