Hydrogène Orange: expériences et perspectives

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Natural Hydrogen

- **Abiotic oxidation of iron:** \(2\text{FeO} + \text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + \text{H}_2\)
- Radiolysis
- Magmatic degassing

- 20Mt escaping every year from the subsurface to the atmosphere (Zgonnik 2020)
- \(10^{20}\) kg of peridotite on the first 7km of Earth (Kelemen 2008)
  - 1 kg\(_{\text{H}_2}/\text{m}^3\), potential \(10^8\) Mt
Natural Carbonation

**Peridotite**

\[(\text{CaO, MgO}) + \text{CO}_2 \rightarrow (\text{Ca,Mg})\text{CO}_3\]

**Listwanite**: geological formation resulting from the extensive carbonation of peridotites

99.9% of total C stored as carbonates

Kelemen & Matter 2011

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Orange Hydrogen: Stimulated Natural H₂

- **Stimulated production**
  - ✓ 100 000 years of H₂
  - ✓ Controlled production rate
  - ✓ Simplified exploration
  - ✓ No excavation/mining
  - ✓ No stress on freshwater resources

- **Combination of CO₂ and H₂**
  - ✓ Economically more robust

× More complicated process
× Requires injection & fracking
× Not « renewable »
Orange Hydrogen in the lab

Reactive percolation experiments
Cores 5.6mm dia. – few cm long
P < 500 bar – < 400°C

Osselin et al. GCA, 2022
Orange Hydrogen in the lab

Natural Serpentinite:
50% Serpentine
20% Opx
11% Cpx
13% Olivine
5% Aragonite
1% Spinel

Injection at 280°C
2 experiments with pure NaCl
1 experiment with NaCl+NaHCO$_3$
Results

General decrease of carbonates

General increase of carbonates
Results – Carbonate precipitation

Initially opened fractures get filled with calcite

\[ \text{CO}_2 \]

Before experiment

After experiment
Results – Carbonate precipitation

Initially opened fractures get filled with calcite

Secondary percolation paths also appear clogged with calcite (SEM)

Multiscale precipitation
**Results** – Carbonate precipitation

**CO₂**
Initially opened fractures get filled with calcite

Secondary percolation paths also appear clogged with calcite (SEM)

**Multiscale precipitation**

**noCO₂**
Aragonite veins get emptied on all scales
Results – Carbonate precipitation

**Much denser and brighter network of carbonates** - MnO pollution from inox corrosion.
**Results** – Silicate alteration

**CO$_2$**

Complete replacement of olivines by serpentine mesh in main and secondary percolations paths

Absence of olivine alteration in low flow zones
Results – Silicate alteration

**CO₂**

Complete replacement of olivines by serpentine mesh in main and secondary percolations paths

Absence of olivine alteration in low flow zones

**noCO₂**

Similar replacement pattern but chrysotile instead of lizardite
Hydrogen production

Maximum potential $\text{H}_2$

- Osselin et al. 2021
  - Serpentine, 280°C, 200 bar - RP
- noCO2-1
  - Serpentine, 280°C, 200 bar - RP
- noCO2-2
  - Serpentine, 280°C, 200 bar - RP
- Faugerolles 2016 - run 36
  - Harzburgite + olivine, 300°C and 500 bar - coarse - batch
- Faugerolles 2016 - run 41
  - Harzburgite + olivine, 300°C and 500 bar - coarse - batch
- Faugerolles 2016 - run 43
  - Harzburgite + olivine, 250°C and 500 bar - fine - batch
- Faugerolles 2016 - run 45
  - Harzburgite + olivine, 300°C and 500 bar - fine - batch
- Hochscheid 2020
  - Harzburgite, 300°C and 500 bar - batch
- Hochscheid 2020
  - Harzburgite, 225°C and 500 bar - batch

Osselin et al. Nature Geoscience 2022
CO$_2$/H$_2$ interaction

Carbonaceous matter likely generated by CO$_2$ reduction with H$_2$

nCO$_2$ + xH$_2$ → C$_n$H$_m$ + H$_2$O
Permeability evolution

![Graph showing permeability evolution over elapsed time (days) with normalized permeability on the y-axis and elapsed time in days on the x-axis. The graph compares two conditions: 280°C and 280°C + CO₂. At 280°C + CO₂, the permeability decreases to a value of $k_0 \sim 10^{-15}$ m².]
Hydrochemical Coupling – Permeability evolution

Normalized permeability (-)

Elapsed time (days)

Calcite clogging

$280^\circ C$

$280^\circ C + CO_2$

$k_0 \sim 10^{-15} m^2$
Hydrochemical Coupling – Permeability evolution

- **No clogging**

- **Calcite clogging**

Normalized permeability

- **280°C**
- **280°C + CO₂**
- **k₀ ~ 10⁻¹⁵ m²**

Elapsed time (days)
Hydrochemical Coupling

Porosity of the serpentine matrix
-Microporosity
-Smaller fractures
-Large fractures
-Secondary percolation paths
-Almost no flow

Main percolation paths
-Focus most of the flow

Graph showing pore volume (ml/g) vs. pore diameter (μm).
Hydrochemical Coupling

Porosity of the serpentine matrix

Main percolation paths
Focus most of the flow

Secondary percolation paths

Need to precipitate here for actual permeability decrease

Almost no flow

Porosity of the serpentine matrix

Almost no flow

Microporosity

Large fractures

Smaller fractures

Pore volume (ml/g)

Pore diameter (µm)
Hydrochemical Coupling – Permeability evolution

Calcite is the only mineral precipitating fast enough to clog the main percolation paths.
Hydrochemical Coupling – Permeability evolution

Calcite is the only mineral precipitating fast enough to clog the main percolation paths.

No mineral is fast enough to precipitate in the main percolation paths.

Calcite clogging

No clogging
Scientific Conclusion

✧ **Importance of THMC coupling in Earth Science processes.**
  - Complicated chemistry
  - Local equilibria
  - Variable flow rates
  - Importance of pressure and mechanics

✧ **Despite a large molar volume variation, silicates are not responsible for permeability drop.**
  - It’s not the variation of molar volume, it’s the location of the precipitation that matters.

✧ **Despite clogging, reasonable carbonation of 5.6% of total injected CO₂ at 280° as well as a 3% to 8% H₂ yield in the CO₂-free case.**
Perspectives

◊ Potential to be a game-changer for the energy transition
  ◊ Market of $1000B.

◊ The current state of research shows it is possible, but:
  ◊ What are the best P, T, Q, x conditions of injection?
  ◊ How does the permeability/porosity evolve during the process?
  ◊ How does the surface area evolve – passivation?
  ◊ What is the influence of microbiology on the yield?

Lots of science to do, collaborations are very much welcomed!