

# Experimental study of the co-valorization of carbon dioxide storage through hydrogen production in ultramafic formations

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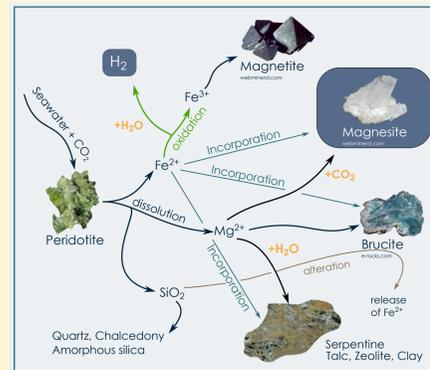
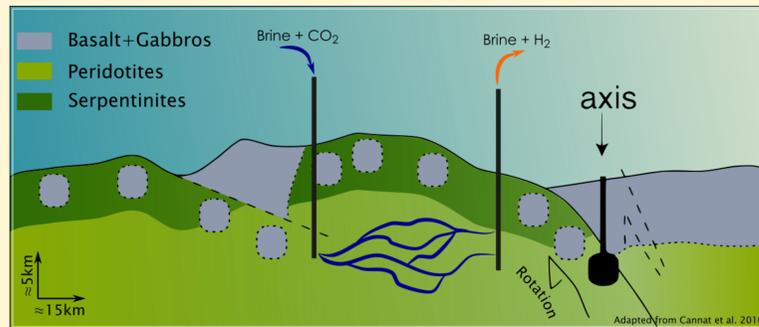
## Abstract

With the recent GIEC report about global warming urging humanity to limit the global temperature increase to 2°C maximum, research on the geological storage of carbon dioxide appears more important than ever. However, the injection in geological formations (such as deep saline aquifers and depleted gas/oil fields) of supercritical CO<sub>2</sub>, stores it in the porosity of the host rock raising legitimate concern about the safety and long-term behavior of such dynamic multiphase hydrosystems. Additionally, the economic and energetic weight of such storage complicates its development at the world scale without strong political incentives. The storage of CO<sub>2</sub> in ultramafic formations in some specific contexts appears, on the contrary, as a very appealing technology since it involves the safe mineralization of the carbon by precipitation of carbonates with the major alkaline earth metals (i.e. Mg, Ca...) leached from the formation itself. Moreover, as these rocks contain high amounts of ferrous iron, its oxidation by the water co-injected with CO<sub>2</sub> produces dihydrogen, which can be economically valuable rendering the whole process more viable. Large ophiolite formations (Oman, Papua New Guinea, east coast of Adriatic Sea...) are expected to have a storage capacity of several billion tons of CO<sub>2</sub> and could produce similar amounts of clean dihydrogen. We present experimental results on the mineral carbonation of natural cores of serpentinites by the continuous percolation of carbon-saturated water. We show that the dimensionless Péclet (relative importance of diffusion and convection processes), and Damköhler (relative importance of convection and chemical processes) numbers as well as the initial geometry of the porosity and permeability control the localization of the silicate dissolution and the carbonate precipitation in the porous medium. We also show that the chemical behavior is principally controlled by the reactivity of calcium-bearing silicates (wollastonite, diopside) and the precipitation of calcite as well as the initial iron content of the different phases. Such results are particularly interesting for the design and the optimization of pilot sites and the development of this technology at industrial scale.

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The development of Negative Emission Technologies appears as one of the most appealing solution for the global reduction of anthropic carbon dioxide emissions. In this study, we are leveraging the reactivity of silicate minerals in order to **develop an in situ green hydrogen production coupled with CO<sub>2</sub> mineralization**. The objectives of the project are to (1) optimize the conditions (P, T, protolith, redox) for both processes (2) characterize the hydrochemical coupling during the reactive percolation of the carbonated brine in a partially serpentinized peridotite and (3) integrate the coupling with mechanics and in particular reaction-induced fracturing and crystallization pressure

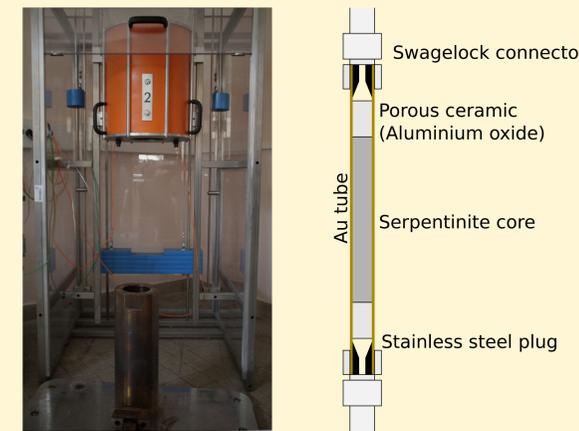


The protolith used for the experiments is a **serpentinite** from the SW Indian Ridge

- Several successive generations of serpentine
- Relics of olivine, ortho and clinopyroxenes
- Traces of magnetite and Cr-spinel

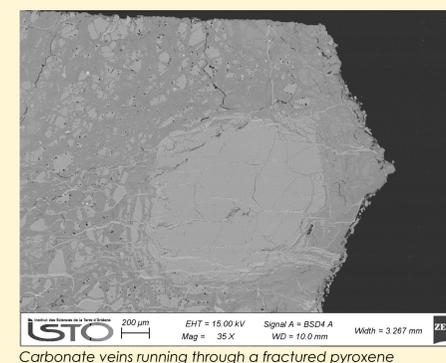
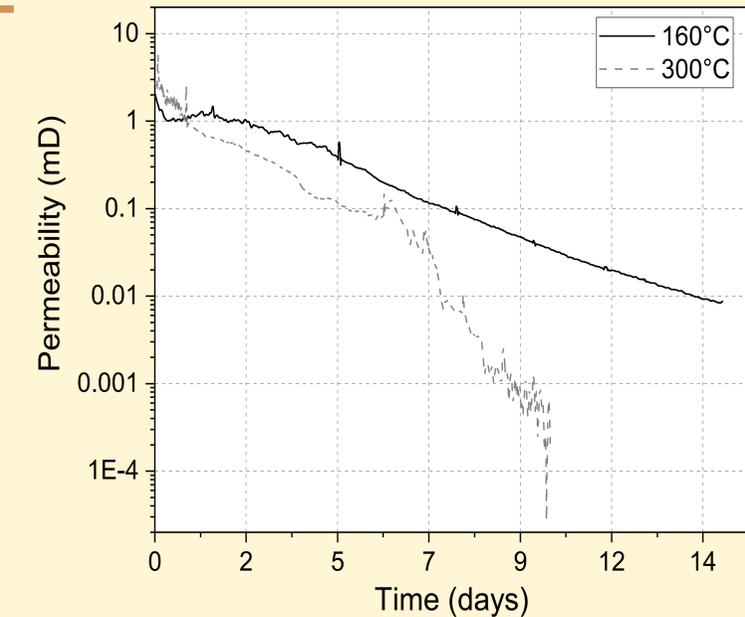
10% porosity. Permeability controlled by fractures ( $\approx 100\mu\text{m}$ )

## Reactive percolation experiments



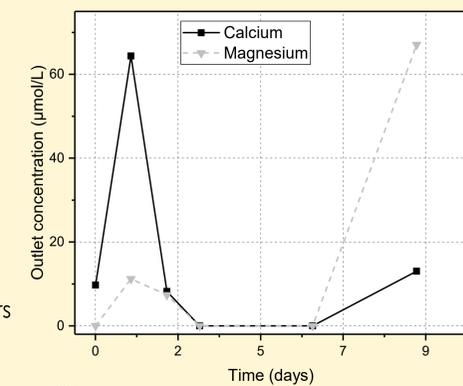
**Reactive percolation apparatus** for the study of hydrothermal reactions

- Drilled cores  $\phi 5.6\text{mm}$  - few cm long
- Up to 500 bars and 300°C
- Inlet solution identical to batch reactions



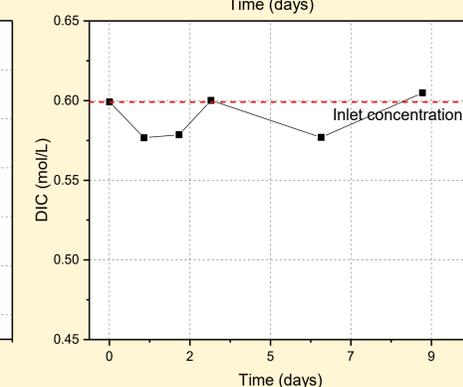
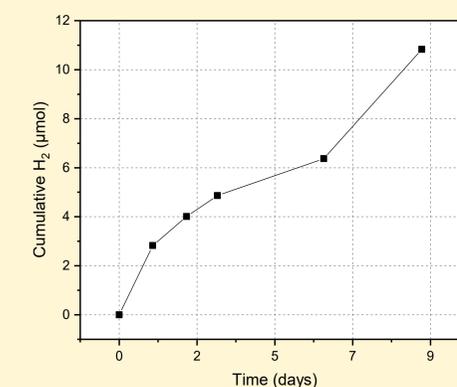
**Experiment @160°C**

- Injection during 15 days
- Pressure drop from 2 to 30 bars
- Flow rate  $\approx 0.01 - 0.02 \text{ ml/min}$
- 2500 pore volumes injected



**Experiment @300°C**

- Injection during 5 days
- Pressure drop from 2 to 80 bars
- Flow rate  $\approx 0.01 - 0.02 \text{ ml/min}$
- 1600 pore volumes injected



**In 9 days, we obtained 1.6% of the H<sub>2</sub> yield and 13% of the carbonation yield**

## Conclusion

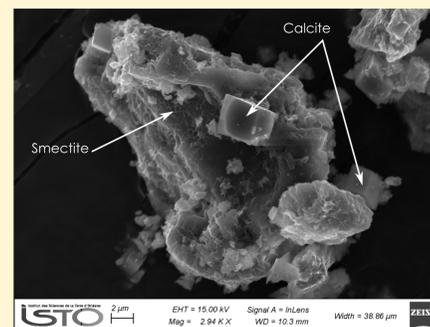
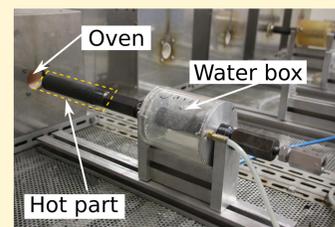
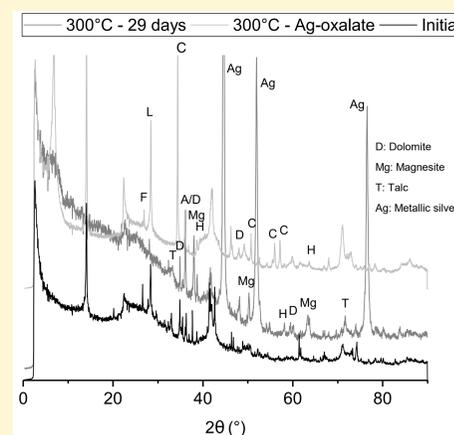
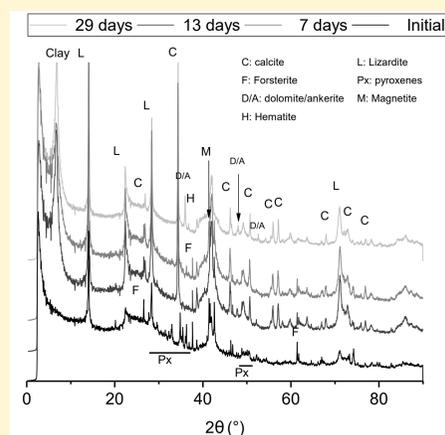
Experiments show clearly **the potential for carbonation and hydrogen production** of a peridotite, even partially serpentinized. However, the clogging of the core limits dramatically the yield. Controlled Reaction-Induced Fracturing can potentially enable a sustained injection.

- Continue characterizing the chemistry of the system with batch experiments
- Pursue reactive percolation experiments at different temperatures and with varying fluid chemistries
- Develop a coupled modeling of the THMC behavior, in particular including mechanical feedbacks

## Batch Experiments

Reactions @300°C and 165°C - 500 bar

- 50 mg serpentinite (<50  $\mu\text{m}$ )
- 100 mg Solution 5% NaHCO<sub>3</sub> 2% NaCl
- 100 mg silver oxalate for the second series ( $X_{\text{CO}_2}=0.5$ )



In each case, **carbon dioxide is the limiting reactant**

- Disappearance of pyroxenes and the majority of forsterite
- Formation of carbonates (magnesite, calcite and solid solutions)
- Only a little magnetite but presence of hematite (oxidation)
- Reaction of serpentine in the case of oxalate
- Reduction of Ag<sup>+</sup> to Ag(s)
- No reactivity with CO<sub>2</sub> in the absence of water