

# *“Towards zero emission geothermal plants in the framework of the H2020 GECO project: Insights on gas re-injection in geothermal reservoir and serpentinite carbonation from batch reactor experiments”*

*Gabriele Biccocchi<sup>1,2\*</sup>, Andrea Orlando<sup>1</sup>, Giovanni Ruggieri<sup>1</sup>, Daniele Borrini<sup>2</sup>, Andrea Rielli<sup>3</sup>, and Chiara Boschi<sup>3</sup>*

*\*corresponding author, [gabriele.biccocchi@unifi.it](mailto:gabriele.biccocchi@unifi.it)*

*<sup>1</sup>CNR - National Research Council of Italy, Institute of Geosciences and Earth Resources, Via La Pira 4, 50121 Florence, Italy*

*<sup>2</sup>Department of Earth Sciences, University of Florence, Via La Pira 4, 50121 Florence, Italy*

*<sup>3</sup>CNR - National Research Council of Italy, Institute of Geosciences and Earth Resources, Via Giuseppe Moruzzi 1, 56124 Pisa, Italy*

CNR-



UNIVERSITÀ  
DEGLI STUDI  
FIRENZE

**DST**  
Dipartimento di  
Scienze della Terra



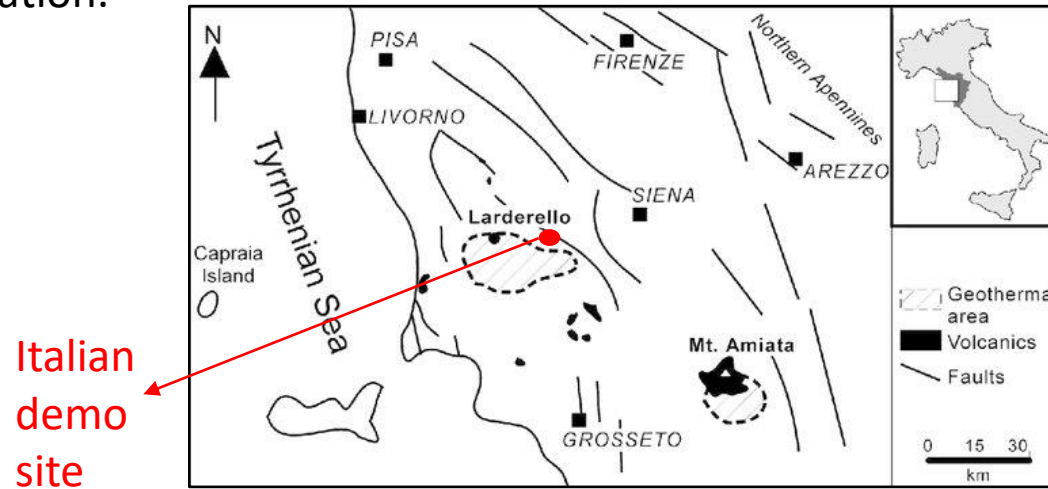
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement N° 818169.



This presentation is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

# GECO PROJECT AND AIMS

- The EU H2020 GECO (Geothermal Emission Gas Control) project is aimed to produce new technologies to limit emissions from geothermal power generation by either gas re-injection or its use to produce commercial material through serpentinite carbonation.



[from Manzella, 2009 Ann. Geophys](#)

- The realization of a closed loop geothermal power plant has been planned in the Italian demo site, N-E of Larderello geothermal area (Tuscany, central Italy), where gas will be re-injected in a reservoir constituted by phyllites and micaschists.

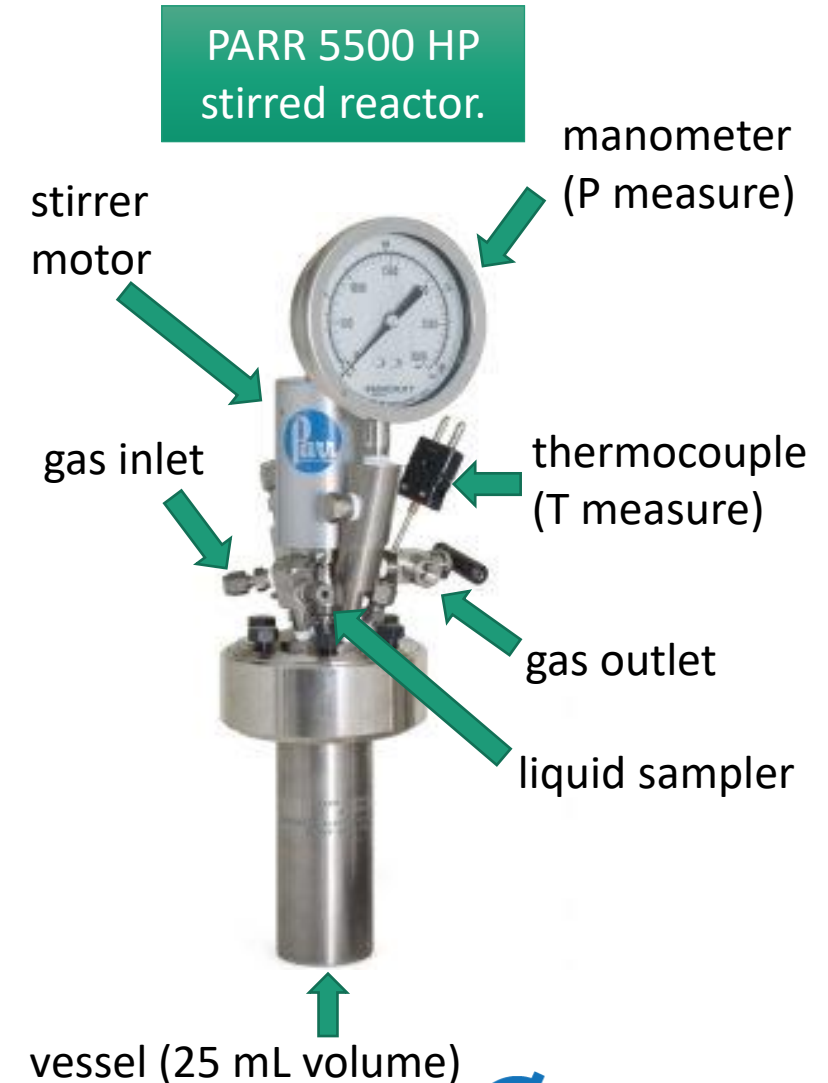
- To this aim a set of water-gas-rock interaction experiments was performed in order to:
  - investigate the interaction between  $\text{CO}_2\text{-H}_2\text{S}$  gas mixture to be reinjected, representative of the geothermal fluids exploited at Larderello, and phyllites and micaschists of the reservoir;
  - optimize the conditions for  $\text{CO}_2$  mineral sequestration by reacting  $\text{CO}_2\text{-H}_2\text{S}$  gas mixture with different serpentinitised ultramafic rocks outcropping and buried in the nearby area.

# EXPERIMENTAL RUNS: GENERAL SET-UP

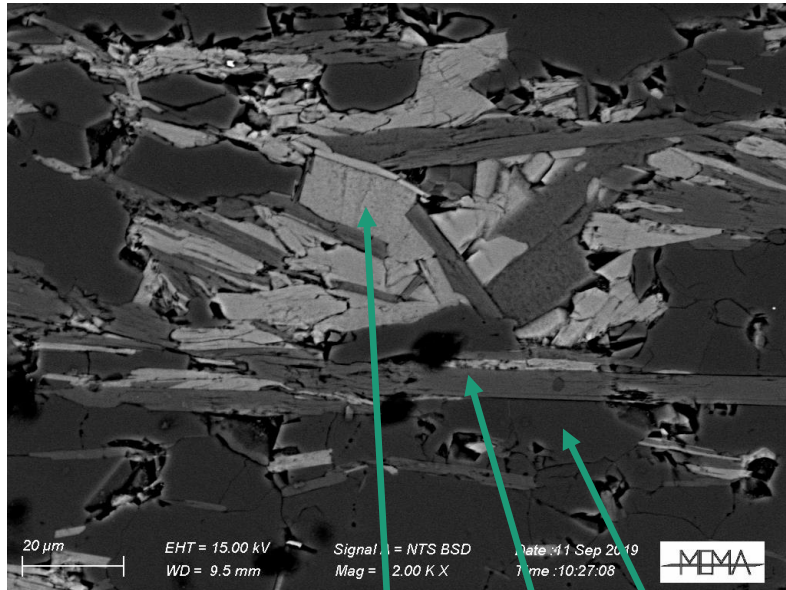
- Reactants are contained in a vessel of **25 ml** of volume, where a  $\text{CO}_2\text{-H}_2\text{S}$  (**98-2%**) gas phase is injected (pressure 22-25 bar).

this mixture is representative of geothermal fluids of southern Tuscany

- Rock powders (size 63-125  $\mu\text{m}$ ) with a liquid phase (ultrapure ion free Milli-Q<sup>®</sup> water) are put into the vessel and continuously mixed by a stirrer.
- Liquid is degassed by  $\text{N}_2$  bubbling (to remove  $\text{O}_2$  and avoid to influence the Eh) prior to inject the gas mixture and start the run.
- Solid-to-liquid ratio was set to **1:5** (2.5-3.6 g of powder and 12.5-18 ml of Milli-Q<sup>®</sup>) in order to achieve during the experiments a liquid-to-gas ratio representative of that of fluid to be reinjected.
- Liquid composition is obtained via IC, ICP-OES and acidimetric titration.
- Solid retrieved after the experiments analysed via XRPD (LoD= 5%) and SEM-EDS.



# MINERAL ALTERATION PATHS IN PHYLLITES AND MICASCHISTS



FB2 sample

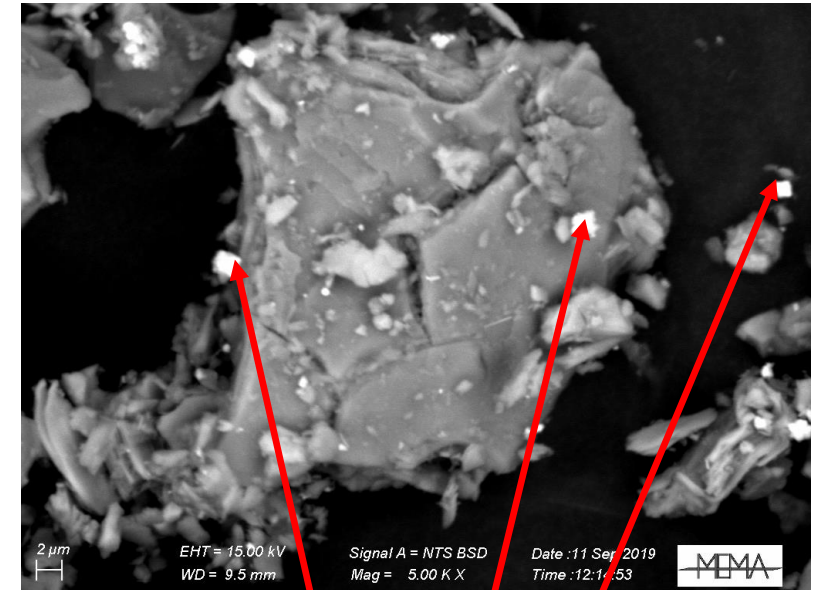
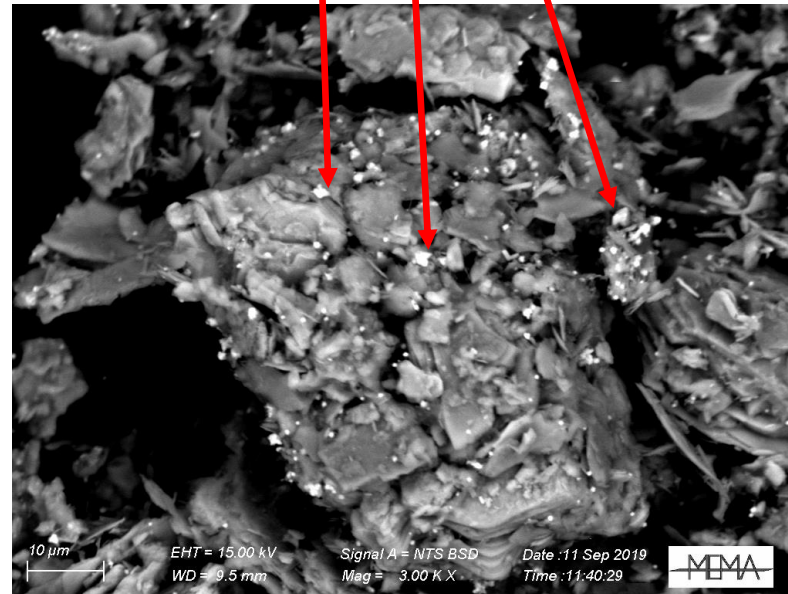
Fe-chlorite

Quartz

Phengite



Formation of tiny **pyrite** crystals on the surface of **phyllite** (FB2 sample, powder) after 5 days of reaction with  $\text{CO}_2 + \text{H}_2\text{S}$  at  $90^\circ\text{C}$



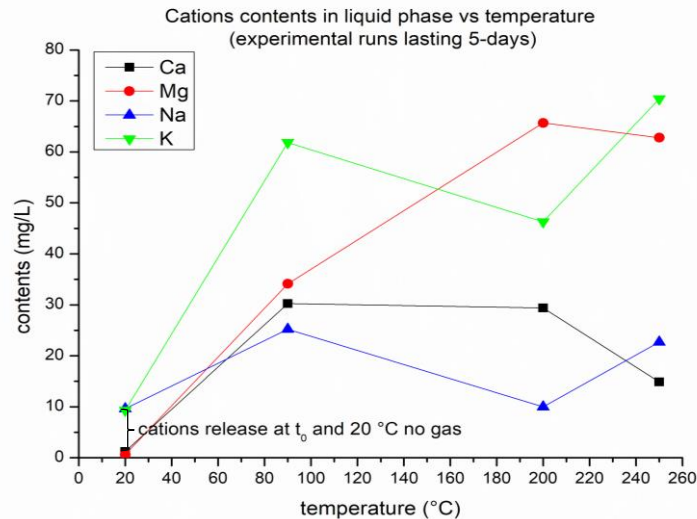
Formation of tiny **pyrite** crystals on the surface of **micaschist** (MIC5 sample, powder) after 5 days of reaction with  $\text{CO}_2 + \text{H}_2\text{S}$  at  $90^\circ\text{C}$

# MINERAL ALTERATION PATHS IN PHYLLITES AND MICASCHISTS

- no authigenic carbonates mineral detected as a result of the experiments
- small amounts (<3% by weight) of pyrite detected in almost all the experimental conditions via SEM-EDS

## Phyllite (FB2 sample):

- phengite (P) and chlorite (C) are leaked and represents the major the ions source in solutions; quartz amount passively increase at higher temperatures (>200 °C);
- with respect to the exp at 90 °C Na<sup>+</sup> and K<sup>+</sup> amounts in solutions drop at 200 °C and increase at 250°C.

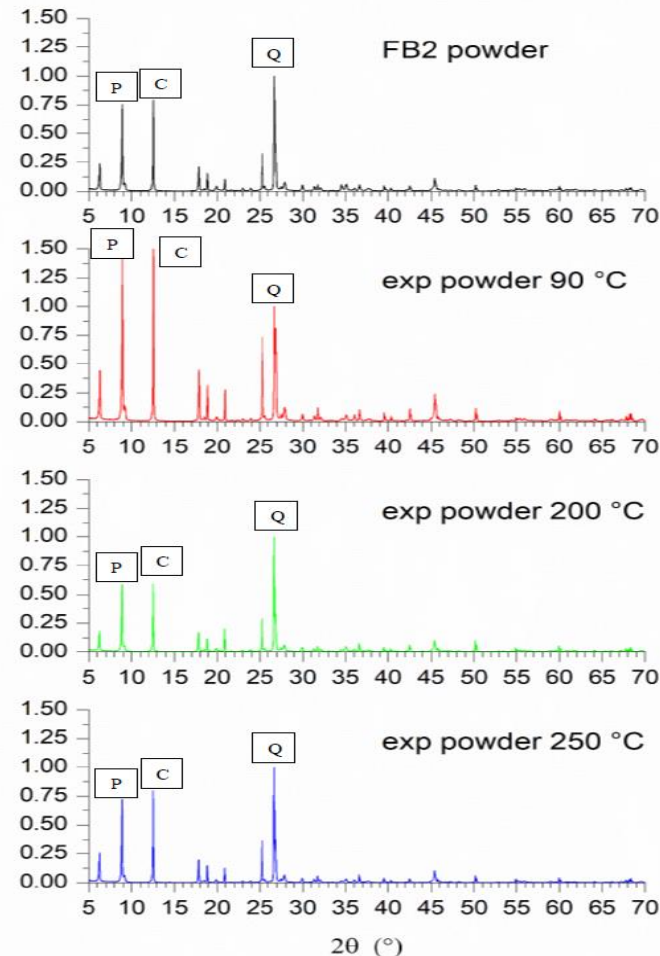


## Micaschist (MIC5 sample):

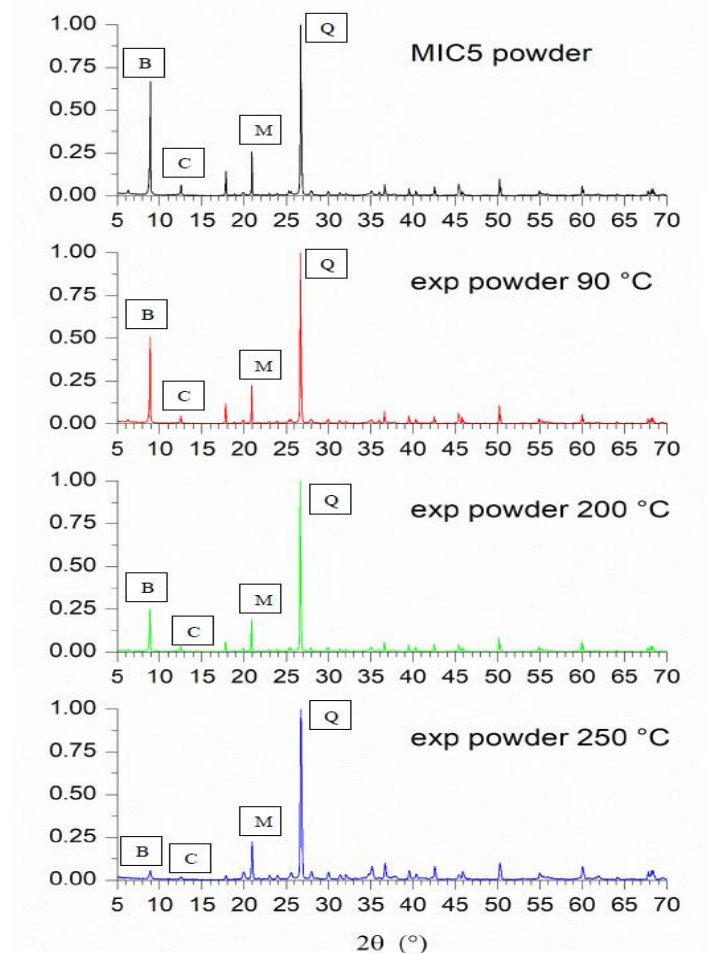
- chlorite (C) and, especially, biotite (B) are consumed to form authigenic muscovite (M) and quartz (Q) amount passively increase.

Experiments performed with 5-day of duration, P=22-25 bar CO<sub>2</sub>+H<sub>2</sub>S (98-2 %), T=90-200-250 °C

XRPD of pristine and reacted powder (phyllites)



XRPD of pristine and reacted powder (mica schists)



pH=5.0-5.4 Ca<sup>2+</sup>=15-34 mg/L Mg<sup>2+</sup>=7-66 mg/L HCO<sub>3</sub><sup>-</sup> = 160-450 mg/L

# CO<sub>2</sub> MINERAL SEQUESTRATION SCENARIOS FROM NATURAL ANALOGUES IN THE OPHIOLITES OF SOUTHERN TUSCANY

Jurassic ophiolites of Southern Tuscany host localized massive precipitation of Mg-carbonates in two different scenarios:

- after water-rock interaction with deep CO<sub>2</sub>-rich fluids uprising through tectonics lineages (1) or
- in response to surficial circulation of meteoric water at equilibrium with atmospheric CO<sub>2</sub> (2).

## 1. Magnesite **high T** – *serpentinised harzburgite*



*Magnesite vein from the Castiglioncello deposit*

## 2. Hydromagnesite **low T** – *serpentinised dunite*

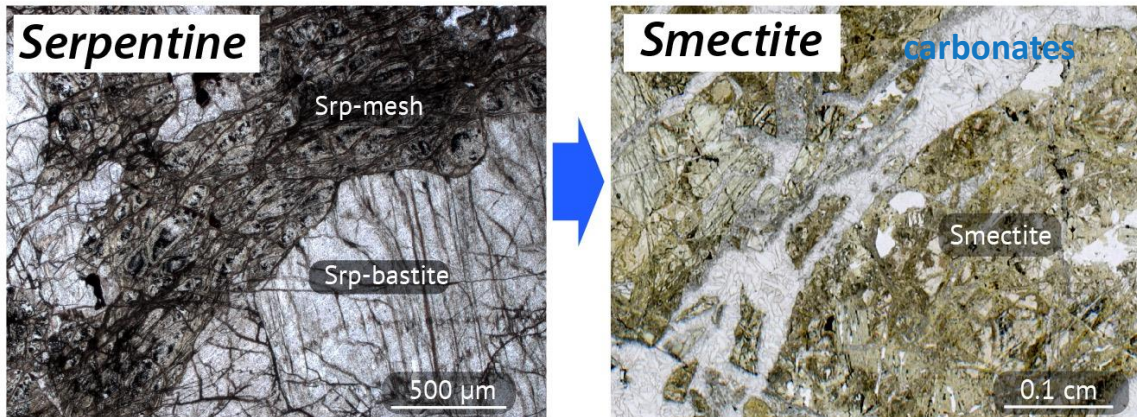


*Hydromagnesite from the Montecastelli ophiolite complex*

# CARBONATES FORMATION PROCESSES

## 1. Magnesite-dolomite – **serpentinised harzburgite**

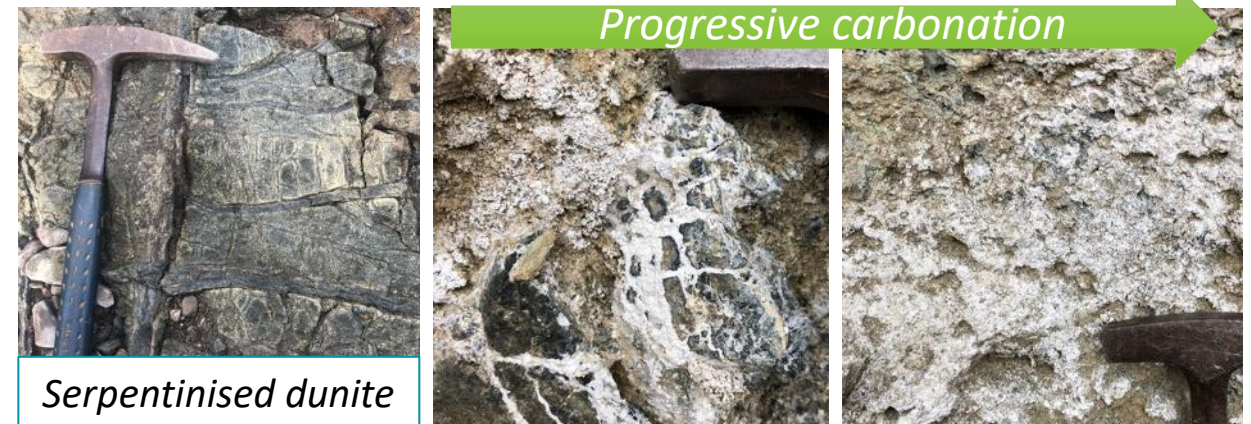
- CO<sub>2</sub>-rich fluids interacted with serpentinised harzburgite
- “High-T” – subsurficial conditions – 100-200 °C
- *Serpentine (Srp) is transformed into smectite and provides Mg<sup>2+</sup> in the liquid phase*
- *Precipitation of quartz in veins with carbonates suggest high SiO<sub>2</sub> contents in the circulating fluids ?*



- **High efficiency:** >80% of the Mg<sup>2+</sup> in serpentine is released without pre-treatments.

## 2. Hydromagnesite – **serpentinised dunite**

- Meteoric water with CO<sub>2</sub> interacted with serpentinised dunite
- “Low-T” – surficial conditions – 10-20 °C
- *Brucite dissolutions directly provides Mg<sup>2+</sup> in the liquid phase and maintain an alkaline environment*

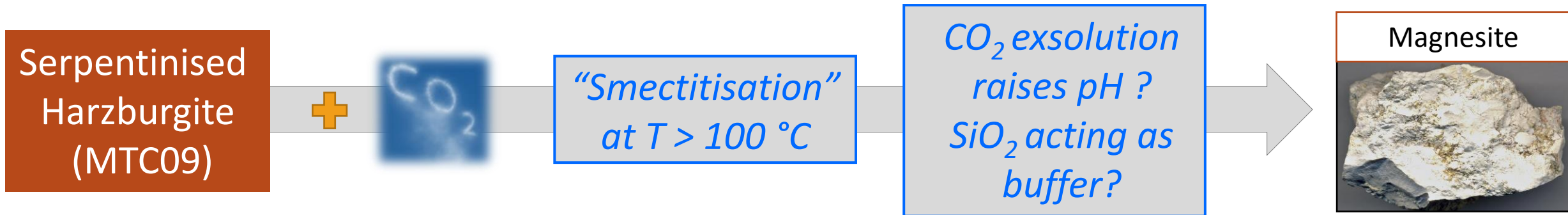


- **Spontaneous carbonation:** the entire dunite deposit react at outcrops scale under low T in a few weeks.

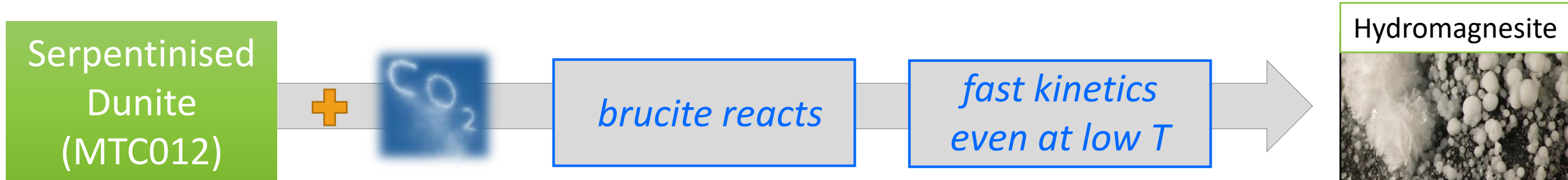
# FROM NATURAL ANALOGUE TO EXPERIMENTAL TASK

## *Inputs for experimental runs:*

- High  $T$  *serpentinised harzburgite* carbonation through “smectitisation” (i.e. serpentine- $\rightarrow$ smectite transformation)



- Low  $T$  *serpentinised dunite* carbonation



# PRELIMINARY HIGHLIGHTS FROM EXPERIMENTAL RUNS

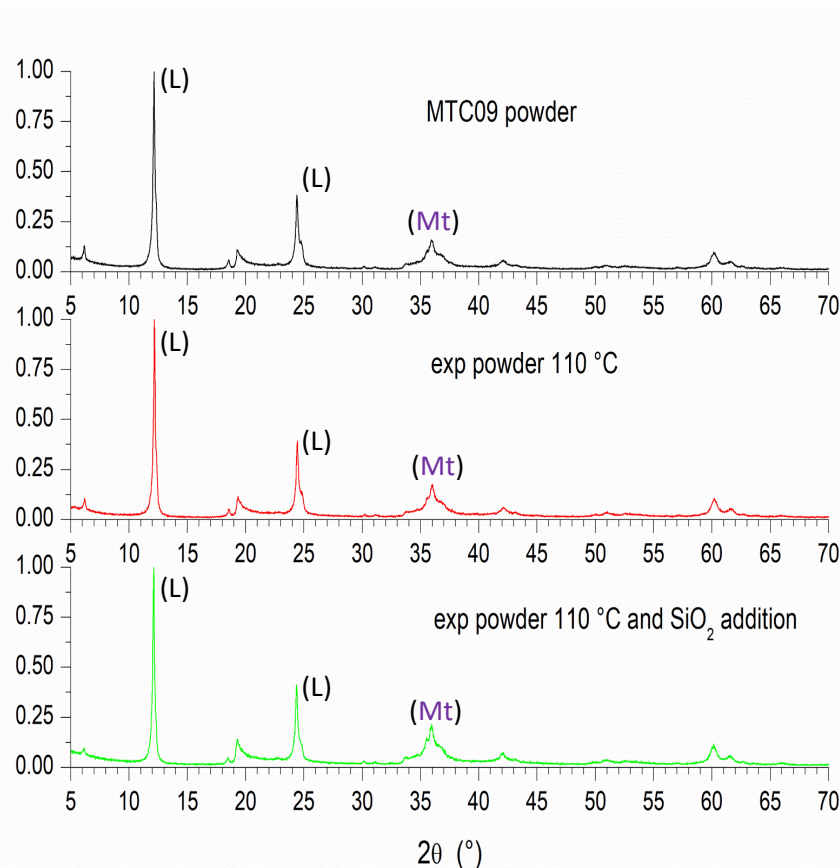
## MTC09 (serpentinised former harzburgite)

- XRD spectra of powder before and after the experiments very similar, indicating very low reactivity.
- Leach from lizardite (L) of  $\text{Mg}^{2+}$  in solutions, no precipitation of magnesite despite higher contents in solutions with respect to MTC012 experiments.

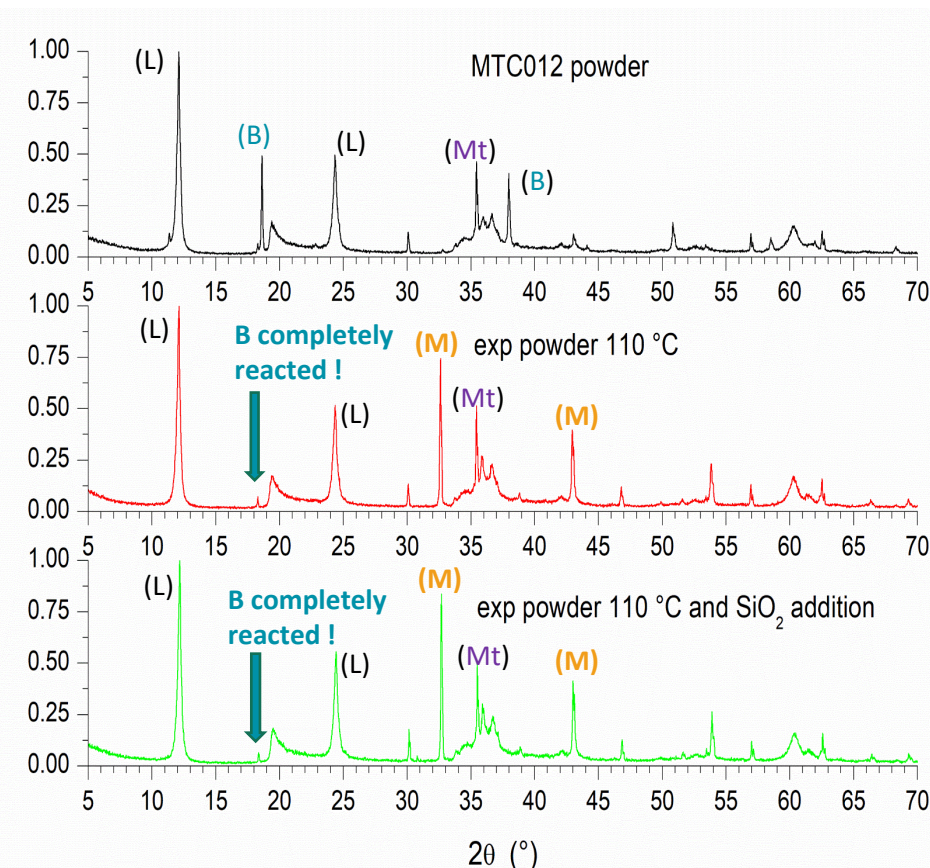
## MTC012 (serpentinised former dunite)

- brucite **B** –  $\text{Mg}(\text{OH})_2$  is almost completely consumed to form magnesite **M** –  $\text{MgCO}_3$ .
- High contents of  $\text{Mg}^{2+}$  and  $\text{HCO}_3^-$  in solutions still present after magnesite precipitation.
- Magnetite (**Mt**) relatively poorly reactive at these conditions (low amounts of Fe in solutions).
- **No differences between the experiments with and without adding  $\text{SiO}_2$  (400 ppm in solution that is the saturation contents for amorphous silica at 110 °C).**
- **Lizardite -> smectite transformation still not observed at 110 °C.**

Experiments performed with 5-day of duration,  $\text{P}=22\text{-}25$  bar  $\text{CO}_2+\text{H}_2\text{S}$  (98-2 %),  $\text{T}=110$  °C



$\text{pH}=6.6$   $\text{Mg}^{2+}=299\text{-}440$  mg/L  $\text{HCO}_3^-=1075\text{-}1580$  mg/L



$\text{pH}=7.0$   $\text{Mg}^{2+}=226\text{-}238$  mg/L  $\text{HCO}_3^-=1100\text{-}1150$  mg/L

# CONCLUDING REMARKS

- ✓ Owing to the **fluid reinjection** activity, carbonate precipitation is prevented by the low Ca and Mg contents both in the rock samples and dissolved in solution and the acidic pH, which is not favourable to carbonate formation.
  - Preliminary results highlighted that H<sub>2</sub>S controls the reaction pathways with phyllites and micaschists, allowing the formation of small amounts of pyrite in a wide range of P-T conditions, inducing a selective removal of Fe from the solution.
  - The mineral phases are more likely leached to release ions in solutions than reacted (except for biotite in micaschists) to form new mineral phases.
- ✓ Experiments with **ultramafic rocks** has been performed by using (1) serpentinised harzburgite and (2) serpentinised brucite-rich dunite in order to identify the most reactive lithology for mineral **carbonation**.
  - Preliminary data (experiments at 110 °C) show that CO<sub>2</sub> sequestration (magnesite precipitation) is strongly enhanced by the presence of brucite compared to lizardite only, but further experiments are required to establish the most efficient reaction conditions.
  - Higher temperature (up to 200 °C) experiments with serpentinised harzburgite are planned in order to reproduce lizardite -> smectite transformation observed in the natural analogues, which is believed to be a key step to obtain the high carbonation efficiency seen in natural analogues.
  - Low temperature experiments (15-20 °C) will be attempted to reproduce the hydromagnesite formation after the reaction between serpentinised brucite-rich dunite, meteoric water and atmospheric CO<sub>2</sub>.