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In situ CO₂ mineralization in mantle-derived ultramafic basements: Insights from laboratory experiments and field studies (Oman ophiolite)

Marguerite Godard^{a,*}, Philippe Gouze^a, Pascale Benezeth^b, Isabelle Martinez^c, Sofia Escario^a, Thierry Decrausaz^a, Richard Leprovost^a, Delphine Roubinet^a, Philippe Pézard^a

^aGéosciences Montpellier, CNRS, University of Montpellier, Place Eugène Bataillon, 34095 Montpellier, France

^bGéosciences Environnement Toulouse-CNRS, IRD, University of Toulouse, 14 Avenue Edouard Belin, 31400 Toulouse, France

^cInstitut de Physique du Globe de Paris, Université Paris Diderot, 75005 Paris, France

Abstract

Carbon trapping in ultramafic (UM) and basaltic basements is one of the options explored to mitigate industrial CO₂ emissions in the Earth's atmosphere. UM rocks and basalts comprise silicates rich in divalent cations (Mg, Ca, Fe) that are dissolved to form carbonates when in contact with CO₂-rich fluids, thus trapping CO₂ over geological time scales. UM rocks have the highest concentrations in divalent cations and thus they have the highest potential for carbon trapping by CO₂-mineralization. Nevertheless, because of their low permeability, UM basements have been overlooked for possible *in situ* CO₂ storage in favor of basaltic basements. Recent research shows that CO₂-mineralization is active and efficient in UM basements, and that it is associated to potential benefits, such as the production of H₂. However, the hydrodynamic, physical and chemical mechanisms driving CO₂-mineralization whilst sustaining fluid flow are still poorly understood and numerous scientific and technological challenges remain before implementing industrial CO₂ geological storage in UM basements. Here we present an overview of our recent results on CO₂-mineralization in UM rocks combining (i) laboratory experiments, and (ii) field studies of carbonated UM basements with a focus on the Semail ophiolite (Sultanate of Oman), in relation to the recently completed ICDP (International Continental Scientific Program) Oman Drilling Project.

Keywords: CO₂ mineralization; ultramafic rocks; peridotites; scientific drilling; laboratory experiments, borehole monitoring, pilot injection site

1. Introduction

In situ CO₂ storage in mantle-derived ultramafic (UM) and basaltic basements is one of the options explored to mitigate excess CO₂ emissions produced by industrial activities, and limit the steady increase of greenhouse gases in the Earth's atmosphere [1]. UM rocks (peridotites, serpentinites) and basalts comprise abundant silicates rich in divalent cations (Mg, Ca, Fe) that are dissolved to form carbonates when in contact with CO₂-rich fluids (CO₂-mineralization), thus potentially trapping CO₂ over geological time scales [2-3]. Basalts compose most of the oceanic seafloor as well as oceanic islands (e.g., Iceland) and peridotites and serpentinites are accessible in several regions around the world at the limits of tectonic plates in both oceanic and continental environments (Fig. 1, [4]).

* Corresponding author. Email *address:* Marguerite.Godard@umontpellier.fr

Oceanic peridotites are exposed where mantle is tectonically exhumed along oceanic slow and ultra-slow spreading ridges (e.g., Mid-Atlantic Ridge; Southwest Indian Ridge; American-Antarctic Ridge; Gakkel Ridge) and along hyper-extended avolcanic continental passive margins (e.g., the Iberia and Newfoundland margins), in deeps along the fast spreading East Pacific Rise and in some fore-arcs (e.g., Izu Bonin Mariana, South Sandwich). Continental peridotite massifs outcrop along ancient to still active orogenic belts. They preserve relics of subcontinental mantle (orogenic massifs, e.g., Ronda, Beni Bousera, Pyrenees -including Lherz-) and oceanic lithosphere (ophiolites, e.g., Philippines, Bay of Island, California, Internal Ligurides in the Western Alps, Troodos). Some of these massifs, such as the Oman and New Caledonia ophiolites, are several km thick and outcrop over 10's of km², and are exploited today for metals, such as copper, manganese, chromium and nickel.

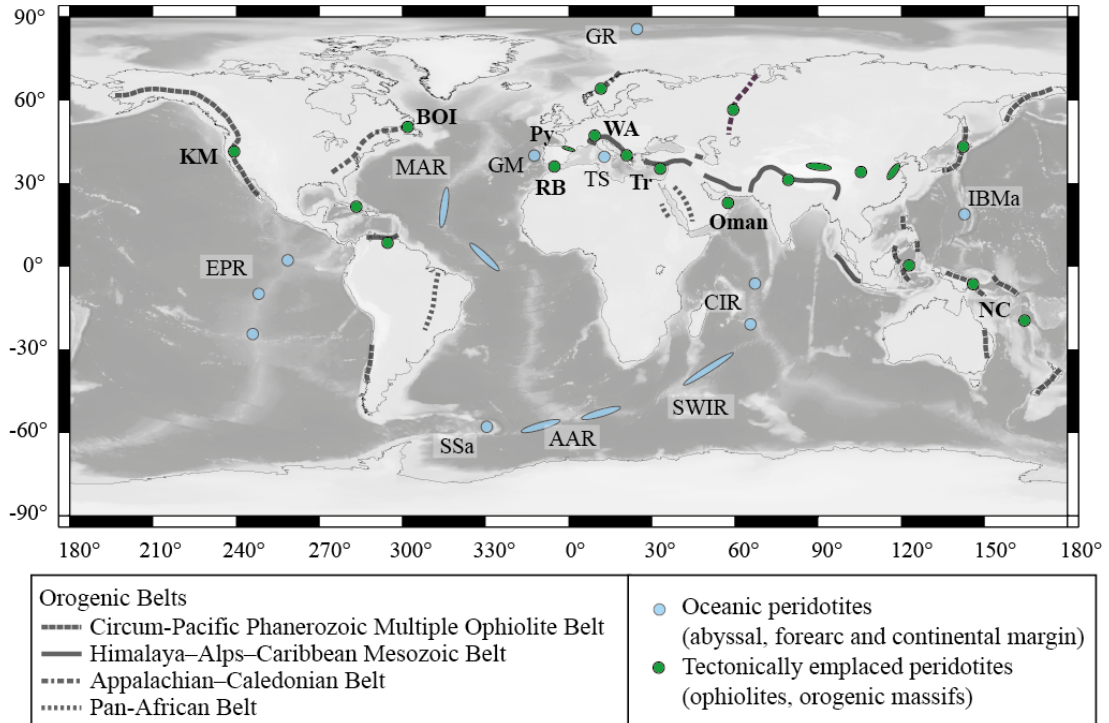


Fig. 1. Location of main peridotite occurrences mentioned in the text. (after [4]). Oceanic peridotites: *Fast-spreading ridge systems*: EPR—East Pacific Rise. *Slow-spreading ridge systems*: MAR—Mid-Atlantic Ridge; CIR—Central Indian Ridge. *Ultraslow-spreading ridge systems*: SWIR—Southwest Indian Ridge; American-Antarctic Ridge; Arctic Ocean (GR—Gakkel Ridge). *Supra-subduction settings*: SSa—South Sandwich Arc-Basin system; IBMa—Izu–Bonin–Mariana Forearc; TS—Tyrrhenian Sea. *Continental Margins*: GM—Galicia Margin and Gorrige Bank; Tectonically emplaced peridotites: Orogenic massifs (sub-continental mantle): Pyr—Pyrenees, southern France; RB: Betico-Rifean Neogene belt : Ronda, Betic Cordilleras, southern Spain & Beni Bousera, Rif Mountains, northern Morocco: Main ophiolitic belts and massifs: *Circum-Pacific Phanerozoic Multiple Ophiolite Belt* (450–0 Ma): KM—Klamath Mountains (Trinity and Josephine, western USA); NC—New Caledonia; *Himalaya–Alps–Caribbean Mesozoic Belt* (150–80 Ma): Oman (=Semail ophiolite), Sultanate of Oman and Unites Arab Emirates; Tr—Troodos, Cyprus; WA—Western Alps (Internal Ligurides, Lanzo). *Appalachian–Caledonian Belt* (450 Ma): BOI—Bay of Islands, Newfoundland. *Pan-African Belt* (750 Ma).

Field studies provide abundant evidences of natural CO₂ mineralization in basaltic and UM basements with the common occurrence of carbonates in basalts (e.g., [5]) and serpentinized peridotites (e.g., [6,7]) in both continental and oceanic environments. Enhancing this process could provide long-lasting and safe storage of CO₂ [1-3]. Peridotites and serpentinites have the highest potential for CO₂ mineralization, with divalent cation oxides typically representing more than 45% of their mass (e.g. [4]).

Enhanced *in situ* CO₂ mineralization requires efficient fluid flow to renew the reactants at the fluid-rock interface. The main issue for achieving efficient CO₂ mineralization in UM basements is the low porosity and permeability of

peridotites ($10^{-21} - 10^{-17} \text{ m}^2$; e.g., [8-9]) that limits fluid flow. Furthermore, the CO_2 mineralization reaction itself involves the precipitation of low density carbonates and hydrous phases at the expense of dense mantle minerals, therefore clogging flow paths [10]. For these reasons, UM basements had initially been overlooked for possible *in situ* CO_2 storage in favor of highly permeable basaltic basements (e.g., CARBFIX project; www.or.is/en/projects/carbfix [3]). Recent research shows that CO_2 -mineralization is active and efficient in the oceanic UM basements (e.g., [6, 11]) and in continental peridotite massifs (e.g., [7, 12]), and that it is associated to potential benefits, such as the production of H_2 , therefore requiring further investigations of their potential for enhanced *in situ* CO_2 mineralization.

We present an overview of our recent research realized as part of several research projects: ANR-CO2FIX (2008-2012, www.anr.fr/Project-ANR-08-PCO2-0003) and LISZT (2018-2023, www.anr.fr/Projet-ANR-18-CE01-0014), FP7 ITN ABYSS (2013-2018) and the ICDP Oman Drilling Project [13] (OmanDP 2017-2018; www.icdp-online.org/projects/world/asia/oman/ and www.omandrilling.ac.uk/). These studies aim to identify and measure the physical and chemical mechanisms driving CO_2 -mineralization whilst sustaining fluid flow in UM basements. They involve a dual approach combining (i) field studies of carbonated UM basements with a focus on the Semail ophiolite (Sultanate of Oman) and (ii) laboratory experiments to quantify the efficiency and sustainability of CO_2 -mineralization over the range of pressure, temperature, compositional and flow rate conditions characterizing natural environments and expected for industrial applications.

Nomenclature

Mantle	Dense, ultramafic layer underlying the Earth crust; the upper mantle is composed of peridotites.
Ultramafic	Composed of >90% of Mg-Fe-rich minerals (mafic minerals) such as olivine, orthopyroxene, clinopyroxene and serpentine.
Olivine	Mineral solid solution between end-members forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4); its composition in most peridotites sampled at the surface of the Earth is ($\text{Mg}_{1.8}\text{Fe}_{0.2}\text{SiO}_4$).
Serpentine	Hydrous sheet silicate group with Mg-end member $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$
Peridotite	Ultramafic rock containing more than 40% olivine; <i>herzolite</i> (> 5% clinopyroxene), <i>harzburgite</i> and <i>dunite</i> (>90% olivine) are peridotites.
Serpentinite	Ultramafic rock composed mainly of serpentine resulting from the hydrothermal alteration (<i>serpentinization</i>) of peridotites.
Listvenite	Rock composed quartz and magnesite (\pm dolomite, more rarely calcite) and minor hydrous silicates and oxides. It is also spelled <i>listwaenites</i> .
Carbonation	Formation of carbonates by hydrothermal reaction of CO_2 with silicates; the carbonates produced are variously Fe-bearing magnesite (MgCO_3), calcite (CaCO_3) and/or dolomite ($\text{MgCa}(\text{CO}_3)_2$); it is also called <i>carbonatization</i> , <i>CO_2 mineralization</i> and <i>carbon mineralization</i> .
Obduction	Tectonic emplacement of fragments of oceanic crust and upper mantle onto a continental margin; it occurs at zones of convergence between tectonic plates, typically in relation to <i>subduction</i> where one tectonic plate is thrust beneath the other.

2. CO_2 mineralization in peridotite basements

2.1. Insights from field studies : the Semail Ophiolite

The Semail Ophiolite (Sultanate of Oman) preserves a section of Tethyan oceanic lithosphere obducted onto the Arabian peninsula (Fig. 1). Its mantle section is variably serpentinized and it hosts several H_2 -rich alkaline springs suggesting that serpentinization is still active today (e.g. [12, 14]) and carbonate-rich areas that can be used as analogues of CO_2 geological storage [2].

Carbonate-rich areas are most commonly observed as outcrops of several 10s to 100s m^2 along dry wadis. One of the most spectacular outcrops, set in the Wadi Dima area (south of Muscat), exposes partially altered to highly serpentinized harzburgites cross-cut by a high density (> 20 Vol%) carbonate vein network (Fig. 2a and b; [7]). The

vein network is composed of carbonates of variable Mg/Ca compositions, from dolomite to calcite, locally intermingled with serpentine. The majority of carbonate veins have serpentinite selvages (Fig. 2c). Carbonates were formed over several stages of veining and hydrothermal alteration. The onset of carbonation occurred as a fine diffuse network of dolomite and Mg-calcite penetrative into the serpentinized harzburgite, replacing olivine relics and, locally, co-precipitation with proto-serpentine (Fig. 2d-e). Analyses of carbon species and carbon isotopes indicate that minor fractions of reduced solid carbon species precipitate during this incipient stage of carbonation. This first step is followed by a sequence of veining during which carbonation occurred as a suite of dissolution/precipitation reactions at the expense of serpentine and early carbonates; locally, these processes replaced almost completely the harzburgite basement (Fig. 2b). Trace element analyses combined with oxygen and carbon isotope data indicate that carbonation reactions were triggered by interactions with CO₂-bearing fluids of different compositions (salinity, cationic content, pH) and over temperatures ranging from hydrothermal (150-200°C) to ambient temperatures. Similar to serpentine veins [14], the field scale orientation of carbonate veins reflects the mantle fabric, suggesting that influx of CO₂-bearing fluids occurred along preexisting serpentine veins and that these structural heterogeneities acted as fluid pathways throughout the different stages of carbonation and veining. Carbonation likely started as the oceanic mantle lithosphere was cooling during the onset of obduction (end of Cretaceous), and continued during the ophiolite uplift until today.

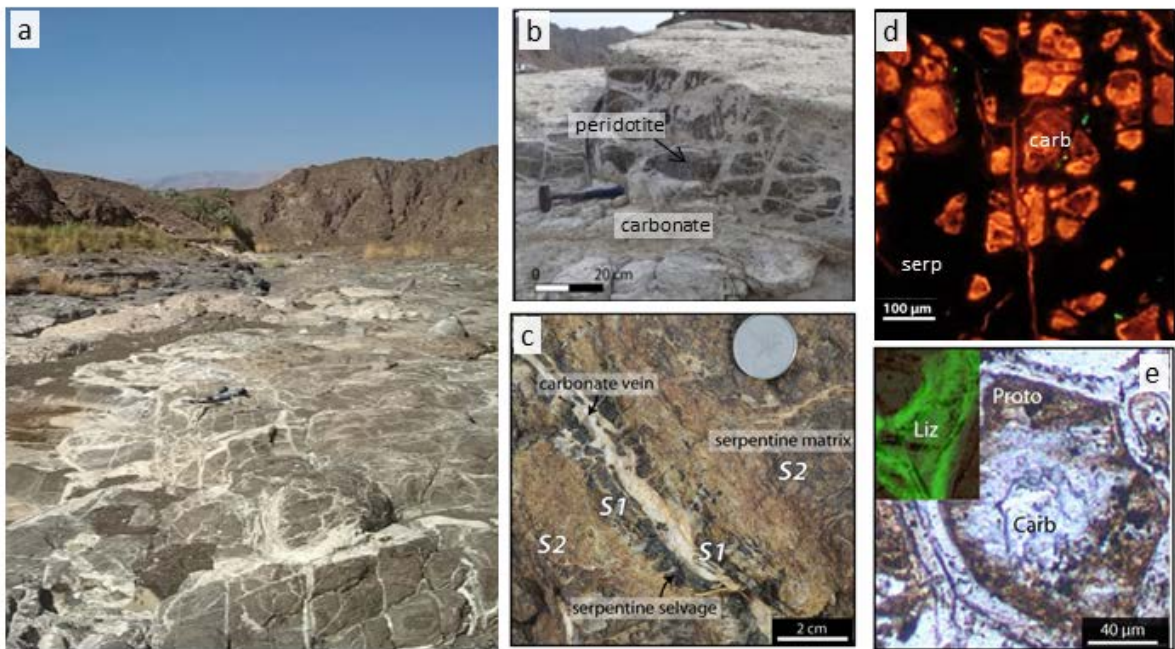
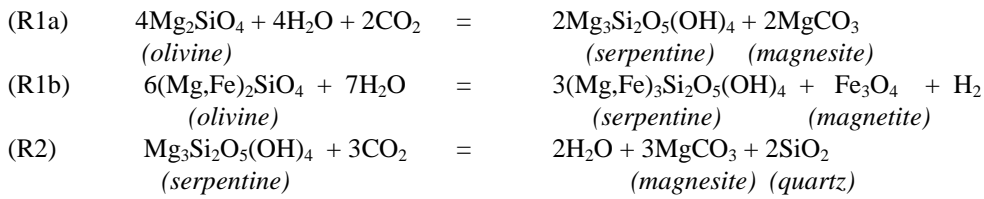


Fig. 2. Photographs of peridotite-hosted carbonate vein networks showing vein density, carbonate morphologies and relationships with serpentinized basement at different scale, in the Wadi Dima area (Oman ophiolite). (a, b) Photographs of Wadi Dima outcrops; (c) Close-up on a carbonate vein cross-cutting the serpentinized peridotite basement: serpentinitized selvages are observed (S1, S2) in which carbonation and secondary serpentinization occurs; (d) carbonate cores in S1 serpentinized matrix (cathodoluminescence); (e) Proto-serpentine (proto) and carbonate (carb) replacing olivine in S2 serpentinized matrix – Liz : Lizardite background serpentine identified using Raman spectroscopy. (c, d, e from [7,15])

The Semail ophiolite exposes along its basal thrust a second type of carbonated peridotites, the listvenites (e.g., [16]). These UM-derived rocks are composed of quartz and magnesite (\pm dolomite) and minor hydrous silicates and oxides [17]. Listvenites outcrop in association to the metamorphic sole and/or to the serpentinite melange that characterizes the transition from the ophiolite to the underlying sedimentary lithologies. One of the largest exposures, set in Wadi Mansah (South of Muscat), was cored as part of OmanDP. Hole BT1B sampled a sequence

of carbonated serpentinites and listvenites atop a series of meta-basalts composing the ophiolite metamorphic sole at this site [18]. The detailed petro-structural and geochemical study of the cores indicates that Hole BT1B listvenites formed after highly serpentinized basal peridotites by a sequence of carbonation reactions triggered by the influx of batches of sediment- and/or slab-derived fluids of different compositions, all enriched in CO₂ [19-21]; carbonation reactions occurred at temperatures ranging from hydrothermal (150-250°C) to ambient temperatures [21]. Mass balance calculation shows that listvenites preserve the composition of their protolith except for (i) the addition of CO₂ (up to 43% of their mass), fluid mobile trace elements (e.g., Li, Pb, Cs) and, more rarely, Ca, and (ii) the complete loss of water initially contained in the hydrous minerals forming the serpentinite. These reactions produce an increase in mass and volume (30-55 vol. %) [20]. The basal thrust acted as the main fluid pathway as well as the main deformation zone throughout the carbonation sequences; listvenites are characterized by intense veining and brittle deformation, from the mineral to the borehole scale, with locally the development of cataclasite. This intense deformation facilitated the accommodation of volume changes and the development of multiple fluid pathways parallel to the ophiolite basal thrust. The formation of listvenites is interpreted as associated to the ophiolite emplacement and cooling along its basal thrust, from the incipient stages of subduction to the ophiolite uplift (e.g., [16, 22]).

The carbonated peridotites exposed at these two sites derive from a roughly similar precursor, a variably serpentinized peridotite. They formed over a complex sequence of carbonation reactions occurring over the same range of temperatures, as the result of the cooling of the ophiolite during obduction. Yet, carbonation followed significantly different pathways. For simplicity, these two pathways can be summarized as:



The first carbonation pathway is closely linked to serpentinization (R1a-b) and produced the Wadi Dima carbonated peridotites. The second pathway produced the BT1B listvenites: it is namely a de-hydration reaction (R2). These results suggest that the differences in the Wadi Dima and Hole BT1B carbonation sequences result, at least in part, from differences in (i) the structure of the peridotite basement and distribution of fluid pathways, and (ii) the composition of the CO₂-bearing fluids triggering carbonation reactions, seawater-derived to meteoritic in Wadi Dima, slab-derived and CO₂-rich at Hole BT1B. It is however difficult to test this hypothesis solely from field observations, considering the complex and strongly coupled processes (tectonics, fracturing, hydrodynamics, devolatilization at depth, fluid rock-interactions...) involved in the continuous or intermittent development of these different reaction pathways over geological time periods.

2.2. Laboratory experiments: Preliminary results

The efficiency and kinetics of carbonation reactions in the Oman peridotites has been investigated by laboratory experiments using (i) batch reactors, in order to constrain the physical and chemical parameters controlling carbonation reactions independently of hydrodynamic and structural parameters; (ii) the ICARE Lab reactive percolation rig to study the coupling between fluid fluxes, elemental transport and reaction kinetics.

- *Batch experiments*: This experimental work was conducted to quantify the reactions of carbonation of peridotites as a function of temperature (90-210°C) and CO₂ partial pressure (15-40 bar), and to understand the mobility and fate of the trace metals (Cr, Mn, Ni) involved in the overall process. A series of one-month long experiments was carried out with a Ti-batch reactor using a partially serpentinized Oman harzburgite. We studied the chemical evolution of NaCl aqueous solutions at equilibrium with CO₂ during the interaction with the rock powder and analyzed the solid samples at the end of each experiment (Fig 3). The highest extents of carbonation (20-30 %) were achieved between 120 and 150 °C, with the appearance of abundant Fe-bearing magnesites and amorphous silica precipitation, whereas at higher temperature rapid Fe-oxidation reactions and the formation of secondary silicates, such as talc, strongly limited the formation carbonate minerals and minimized the aqueous concentrations of Mn and

Ni. The collected data, including the results from Mg-isotope analyses of the fluid samples, will allow a precise determination of the reaction sequence involved in peridotite listvenitization and should help to develop more effective strategies of CO₂ storage in the subsurface.

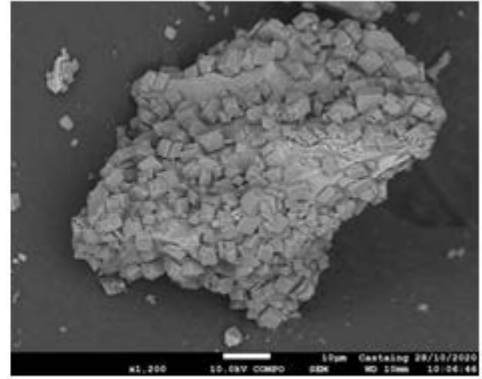
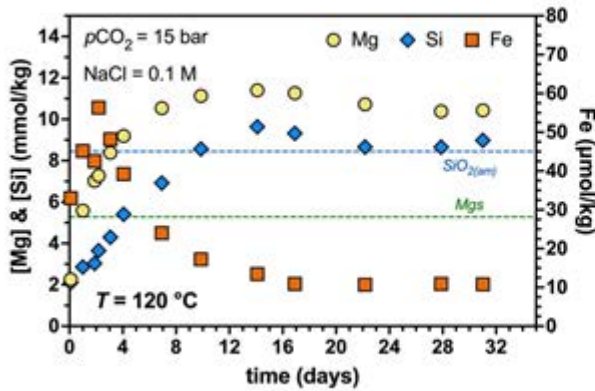


Fig. 3. Chemical evolution of the aqueous fluid (Mg, Si, Fe) during the interaction of Oman harzburgite with a NaCl solution at equilibrium with $p\text{CO}_2 = 15$ bar and at $T = 120$ °C (left). The rapid decrease of Fe concentration after 2 days is consistent with the precipitation of abundant ferrous magnesite observed in the solid product after the experiment (right). The dashed lines on the plot refer to equilibrium conditions relative to magnesite (Mgs) and amorphous silica ($\text{SiO}_2(\text{am})$).

• *Reactive flow experiments:* This experimental work was conducted to quantify the efficiency and sustainability of CO₂-mineralization over the range of pressure, temperature, fluid composition and flow rate conditions characterizing natural environments and expected for industrial applications. The kinetics of carbonate precipitation is strongly dependent on temperature but also on fluid chemistry, the precipitation for Mg-carbonates (magnesite) being sluggish compared to Ca-carbonates (e.g., calcite) [23-25]. Reactive-flow experiments revealed an additional control by the coupling between fluid flow, serpentinization and carbonate-forming reactions at the pore-scale that leads to a heterogeneous distribution of carbonates in peridotites percolated by CO₂-bearing fluids (e.g., [26]): Mg-carbonates develop preferentially in low flow zones where fluid composition is controlled by silicate dissolution, whilst the composition of carbonates in the main fluid pathways are controlled by that of the inlet fluids [27-28]. These linkages result in complex reactive systems controlled by pore-scale changes in redox, fluid compositions (pH, solutes,...) and by heterogeneities in the structure and mineralogy of reacting peridotites. Recently, Peuble et al [29] showed that the development of these pore-scale redox domains was also strongly dependent on the $p\text{CO}_2$ of the injected fluid with reduced solid carbon species developing at low $p\text{CO}_2$ whilst solely carbonates precipitated when high $p\text{CO}_2$ fluid is injected. These pore-scale processes could explain the occurrence of reduced carbon in the Wadi Dima peridotites. These early experimental studies were realized on peridotite analogues (sintered or compressed olivine core). As part of the ANR LISZT project, we investigated a more complex system and conducted a series of reactive percolation experiments designed to investigate carbonation reactions in a fractured peridotite basement, similar to the Semail ophiolite.

The first set of experiments consisted in injecting CO₂ rich saline solutions (0.5 M NaCl) with $p\text{CO}_2$ values of 20 MPa and 2 MPa into artificially fractured partially serpentinized harzburgite cores (Oman ophiolite) at constant flow rates of 6 mL/h, except for one experiment realized at 2.4 mL/h. The experiments were conducted at constant temperature (170°C) and pressure (25 MPa) and lasted 6 to 11 days [30].

All experiments displayed outlet fluids characterized by high pH and high Si, Mg, Fe and Ca concentrations compared to inlet fluids hence revealing the dissolution of silicate minerals. At the end of experiments, reaction zones with strong evidences of dissolution (e.g., voids formation, etch-pits and saw-toothed textures) were observed along fractures in all samples (Fig. 4). Two reaction zones were systematically observed: the first, adjacent to the fracture (darker zone), denotes a highly porous area characterized by extensive dissolution and the second, more diffuse, further from the fracture denotes a less reacted slightly porous reacted zone (lighter grey areas). Both

reacted zones show the alteration of olivine and pyroxenes into hematite (a ferric iron oxide), and precipitation of Si-rich phase (i.e., amorphous silica). Away from the fracture, the reacted zone displays also abundant carbonates indicating changes of the fluid reactivity as it migrates into the peridotite matrix.

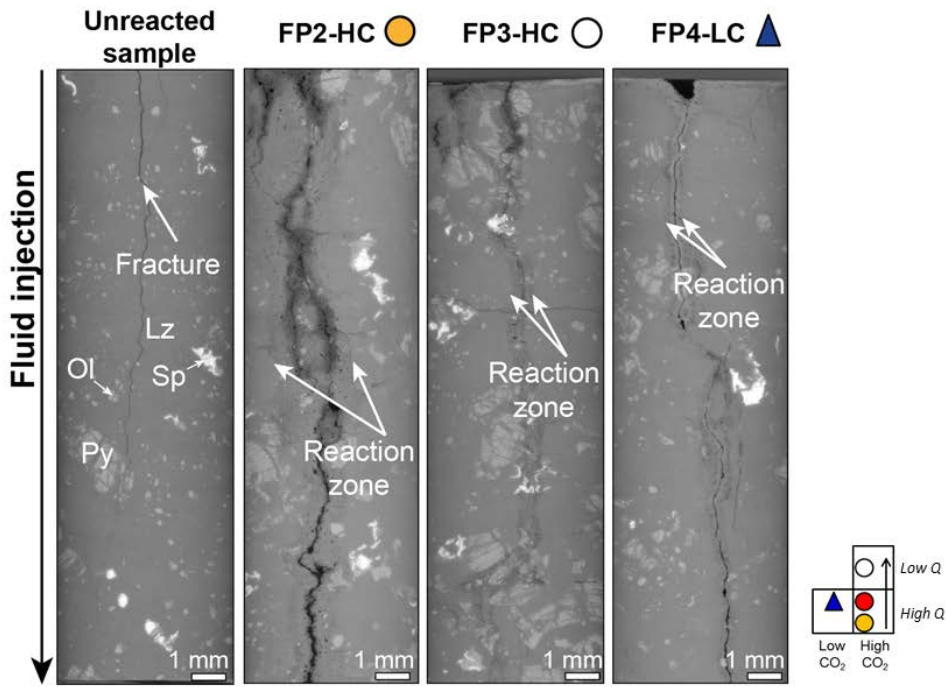


Fig. 4. X-ray microtomography images (XMT) acquired with a resolution of 2.2 microns on fractured peridotite cores before (unreacted sample) and after reactive percolation experiments at $p\text{CO}_2=20$ MPa (FP2-HC; FP3-HC) and $p\text{CO}_2=2$ MPa (FP4-LC). The peridotite cores sample a serpentinized peridotite from the Oman ophiolite; their initial mineralogy is lizardite (Lz), olivine (Ol), pyroxene (Px) and minor spinel (Sp). (After [30])

Detailed investigations of the mineralogy and mass balance calculations based on the chemistry of the outlet fluid time series indicate differences in reaction paths and reaction rates depending on $p\text{CO}_2$ and solute transport conditions. At low $p\text{CO}_2$, olivine and pyroxenes are slightly altered to (Ca)-magnesite, hematite and (Ni-Fe) oxides and, at high $p\text{CO}_2$, olivine, pyroxenes and lizardite are strongly altered to (Fe)-magnesite, hematite and amorphous silica. At constant $p\text{CO}_2$ values, carbonation is more efficient at high injection rates. This investigation provides a preliminary basis for the evaluation of UM fractured reservoirs as potential ways for safety CO_2 -storage.

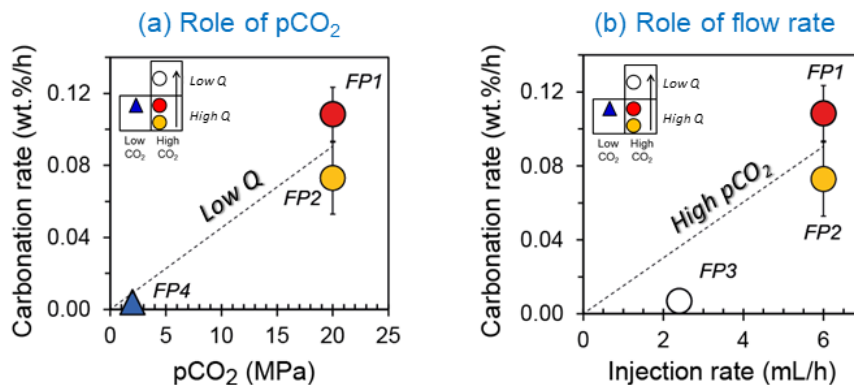


Fig. 5. Carbonation rates (wt.%/h) vs (a) $p\text{CO}_2$ (MPa) and (b) injection rate Q (mL/h). (After [30])

3. Discussion and conclusions

Combining field studies with laboratory experiments provides insights on the strongly coupled processes that control natural CO₂-mineralization in UM basements.

The petrostructural, mineralogical, and geochemical (elemental chemistry, C and O isotopes) study of the Semail ophiolite shows that it underwent widespread serpentinization induced by the ingress of seawater-derived fluids in Wadi Dima and by slab-derived fluids in Wadi Mansah. Carbonation reactions are closely associated with serpentinization, but show different reaction pathways. Carbonation reactions produce (i) Mg-carbonates (and quartz) and act as an efficient de-hydration process (de-serpentinization) in Wadi Mansah and (ii) Ca-Mg-carbonates co-precipitating with serpentinites and (possibly abiotic) formation of minor fractions of reduced-carbon species in Wadi Dima. The two reaction pathways are also distinguished by the remobilization of critical metals (Mn, Cr, Li, Pb,...) in Wadi Mansah and by evidences of H₂-rich alkaline fluids in Wadi Dima. Carbonation reactions occur over the same range of temperature at both sites. This suggests that the composition of incoming fluids (salinity, pH, solute concentrations ...) and, in particular, their CO₂ concentration (high in Wadi Mansah compared to Wadi Dima), is critical in the development of these two different reaction pathways. Such variations in the fluid composition are expected at an industrial CO₂-injection site, with the fluid CO₂-contents decreasing away from the injection borehole, therefore studies of different carbonation analogues can contribute to provide guidance to predict the impact of CO₂-injection in UM basements. However, because of the complex tectonic history of ophiolites, studies of carbonated UM basements provide little information on the kinetic and efficiency of carbonation reactions. These processes and specifically the role of the complex interactions between the chemical changes, rock microstructure evolution and hydrodynamic properties are better quantified by experimental studies where conditions are controlled and mass transfers monitored. Our results suggest that the (evolving) CO₂ content of percolating fluids is critical in the development of variable serpentinization and carbonation reaction paths by promoting (localized) dissolution/precipitation of hydrous phases and carbon species (Mg- or Ca-carbonates, reduced carbon) that, in turn, control the porous network (porosity, tortuosity) and thus the sustainability of the fluid flow (permeability...), the elemental spreading of the reactants over long distances and the local mixing that controls the reactions [26-31].

This research is a first step in the evaluation of the feasibility of industrial *in situ* CO₂ mineralization and of its possible environmental and economic impacts. Numerous scientific and technological challenges remain before implementing industrial CO₂ geological storage in UM basements; one of these challenges is improving knowledge on the linkages between hydrodynamic and (bio-)geochemical processes, at the scale of a borehole, in a region where serpentinization and carbonation are active.

A “Multi-Borehole Observatory” (MBO) was developed as part of OmanDP in an area of active weathering in the Semail ophiolite [32]. MBO is the first and unique site where the geochemistry, mechanics, and hydrology of peridotite alteration can be investigated *in situ*. It consists in 6 boreholes (including 3 cored holes), set mostly in a 500m x 500 m area, thus allowing for the first time a continuous acquisition of flow and (bio-)geochemical time series on UM hydrothermal alteration. Comparing the petro-structure and composition of drilled cores to downhole borehole physical and hydrodynamic measurements will provide a unique dataset to identify the reactive transport mechanisms and characterize the links between the basement structure, fluid flow, chemical fluxes, effective reaction rates and the deep biosphere during CO₂ mineralization in natural environments. Investigations are still in progress. The results of these studies will be critical for developing pilot test sites for CO₂ storage in UM basements.

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