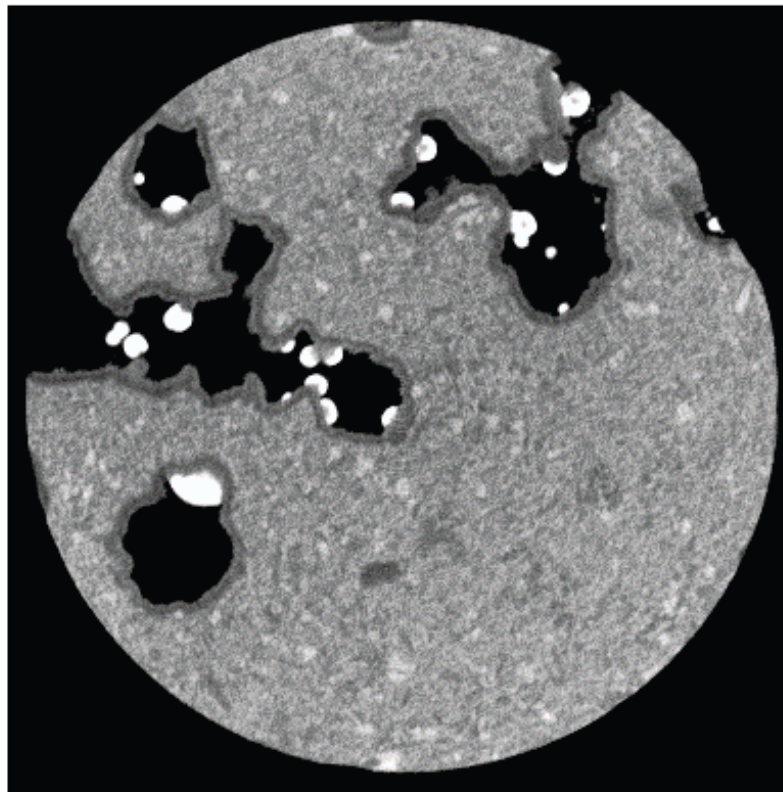




InCarbon

Carbonatação Mineral *In Situ*

Benchmarking of CO₂ Sequestration by mineral carbonation



**XCT image from basalts rock:
Wallula test site (Mc Grail et al. 2017)**

Date: October 2020

Project ID: PTDC/CTA-GEO/31853/2017



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October 2020

Objective

The objective of this report is to present and discuss the state-of-the-art relative to mineral carbonation in mafic and ultramafic rocks and their implication as an alternative for to CO₂ geo-storage.

Abstract

In Carbon geo-sequestration (CGS), CO₂ is captured from stationary emitter units and injected into subsurface as solution to mitigate climate change. The conventional method is to store the CO₂ in sedimentary rocks as the porous structure of these formations allows them to trap fluids (water, oil, gas) for long periods of time. The technology requires the presence of an impermeable caprock to contain the injected CO₂ from upward leakage due to buoyancy of the free-phase CO₂. The option requires geophysical and chemical monitoring during the life scale of the operation. Carbon mineralization in mafic and ultramafic rocks has been proved an alternative, both in laboratory experiments (*ex situ* and *in situ routes*) and field tests (specifically in Carbfix and Big Sky Sequestration Partnership), that offer a safe solution for CO₂ storage. In fact, laboratory experiments indicated that carbonation of igneous rock occurs within several hours at high $p\text{CO}_2$, pressure and temperature, and in days scale at moderate temperature and $p\text{CO}_2$. Field injection tests demonstrate total carbonation of the injected CO₂ in two years. The deployment of CO₂ in mafic and ultramafic rocks at industrial scale requires the multiplication of test sites, including in plutonic rocks.

1. Introduction

CO₂ sequestration in geological formations is regarded as one of the portfolio solutions to mitigate the increase of greenhouse gas emissions in the atmosphere. However, carbon geological storage (CGS) needs to gain public acceptance through proven safe storage technologies. The conventional geological reservoirs (saline aquifers, depleted oil and gas fields and uneconomic coal seams, Fig.1), rely on four trapping mechanisms: (1) structural trapping below a sealing impermeable caprock, (2) residual trapping, where free-phase CO₂ is retained in isolated pores and rendered immobile due to phase discontinuity, (3) solubility or aqueous trapping as CO₂ dissolves in pore-water, losing the ability to ascend by buoyancy; (4) mineral trapping, in which the dissolved CO₂ reacts with rock and water to precipitate as minerals.

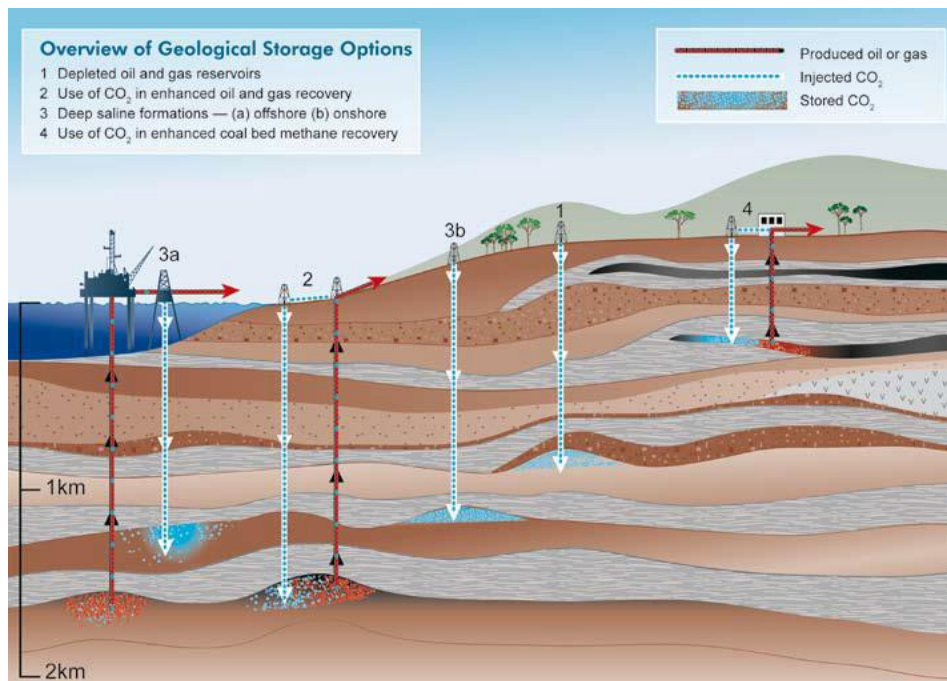


Figure 1: Schematic showing the different CO₂ storage reservoir in sedimentary rocks (IPCC, 2007).

Mineral trapping represents the most stable and safer storage, as the CO₂ is immobilised in the solid phase. However, in conventional reservoirs is seen as a meaningful trapping mechanism at very long time scales (centuries to millennia) (Fig.2a). The most limiting factor of mineral trapping in sedimentary rocks is the presence in small amount or the absence of silicate-bound divalent metals cations triggering the carbon uptake into carbonates minerals (Snoebjörnsdóttir *et al.*, 2020). In situ carbon mineralization in mafic and ultramafic igneous rocks is proposed as alternative to overcome the Ca-Mg-Fe rich rock limitation in sedimentary reservoir. Mafic and ultramafic rocks are known to contain high amounts of divalent metals cations and are reactive in presence of CO₂ (Wolfff-Boenisch *et al.* 2006; Kelemen and Matter, 2008).

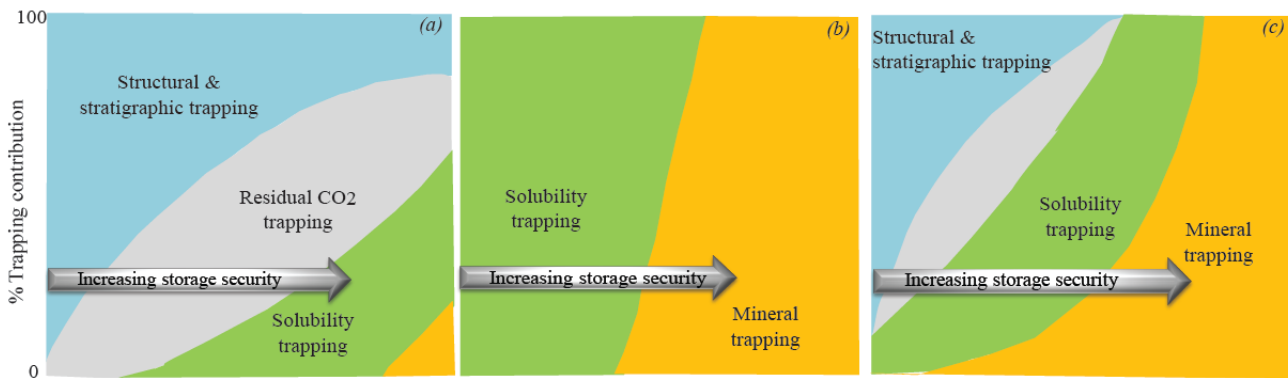


Figure 2: CO₂ trapping mechanisms and capacities in conventional and non-conventional geological environments. (a): sedimentary rocks (IPCC, 2007); (b): basalt reservoir with water dissolved CO₂ representing the Carbfix project (Snoebjörnsdóttir *et al.* 2020); (c): basalt reservoir with supercritical CO₂ representing Big Sky project (McGrail *et al.*, 2014).

In this review, we analyse the recent findings published in the regard of *ex situ* and *in situ* carbonation in unconventional reservoirs storage in mafic and ultramafic rock.

1.1. Potential of mineral trapping in mafic and ultramafic rocks

Mafic silicates are uncommon in sedimentary rocks. In sedimentary basins, the dominant rocks are sandstones, siltstones, limestones and shales. Therefore, the CO₂ conversion into stable minerals is an uncommon process in such environments (Xu *et al.* 2004). Mafic rocks (containing 45-52% SiO₂ and near 40 % MgO-CaO-FeO) and ultramafic rock (containing less than 45% SiO₂ and more than 45% MgO-CaO-FeO), have a greater potential for mineral trapping (Xu *et al.* 2004, Matter and Kelemen,

2009). For instance, basalt rocks (containing up to 20 wt% of Ca, Mg and Fe) constitute the most common igneous group of rocks but peridotite with MgO concentration up to 50% by weight, has the highest carbonation capacity (Farooqui *et al.*, 2009). Rich metal cation silicates (olivine, pyroxene, plagioclase and serpentine series, the most common minerals) are highly reactive in presence of CO₂ (Metz *et al.* 2005 and Esposito *et al.* 2011). These rocks are widespread (Fig.3), and cover more than 10% of the Earth (Matter *et al.* 2016).

Carbon mineralization in mafic and ultramafic rock is a natural process and has been studied in many area of the world including the Semail Ophiolite in Oman. The annual carbonation rate from atmospheric CO₂ is in the order of 40000 t_{CO2}/yr (Kelemen and Matter, 2008) and the worldwide estimate of natural CO₂ uptake on basalts and serpentine ophiolites is 0.18 Gt_{CO2}/year. As reported by Kelemen *et al.* (2011), enhanced weathering or *in situ* carbonation conditions multiply the natural carbonation rate by 6 orders of magnitude. Moreover, the large igneous provinces mainly in land include continental flood basalts: CFBs, Ophiolite, (according to McGrail *et al.* 2006) can be used in CO₂ storage because apparently have the characteristics and the appropriate permeability to support geologic sequestration. For instance, Goldberg and Slagle (2009) estimated storage capacities of 500-2500 billion tons at British Columbia River Basalt Group, and 1000-5500 billion tons in Caribbean flood basalts (McGrail *et al.* 2006). These estimates indicate that the CO₂ storage capacity by mineral carbonation is higher than the 700 billion tons of CO₂ emitted to the atmosphere by industrial activities since 1850 (Kelemen and Matters, 2008).

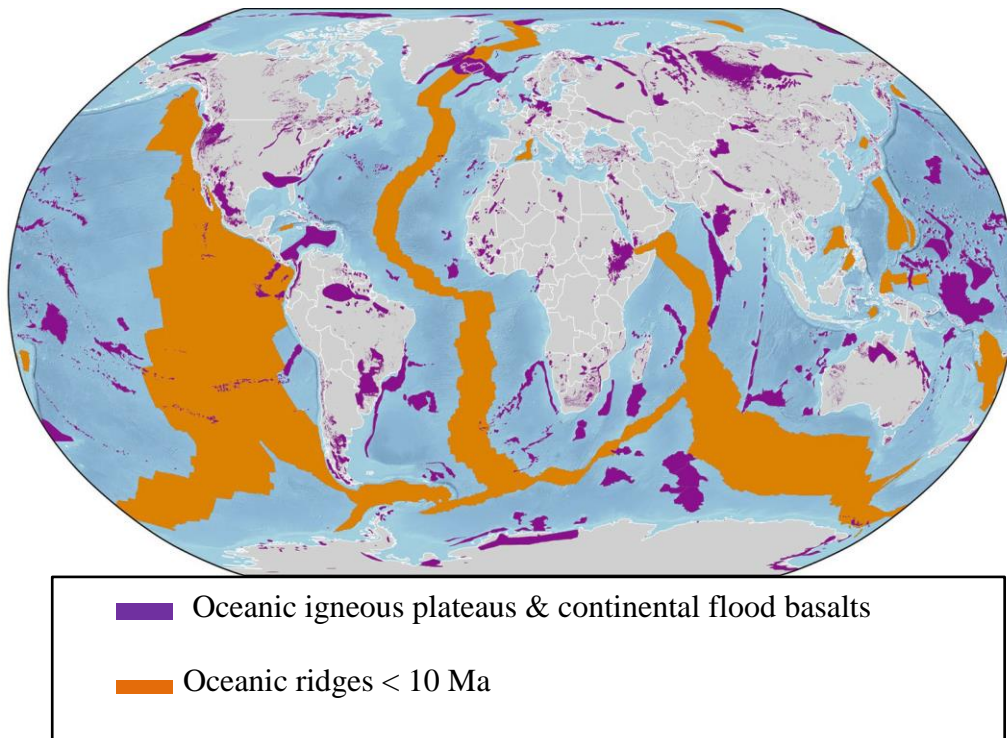


Figure 3: Global distribution of geological formations suitable for carbon mineralization. The map shows the potential onshore and offshore targets for in situ mineral storage of CO₂. Oceanic ridges younger than 10 Ma are shown in orange, and oceanic igneous plateaus and continental flood basalts are shown in purple (Snoebjörnsdóttir *et al.*, 2020).

1.2. Geochemistry of mafic and ultramafic rock – dissolution-precipitation processes

The carbonation potential in mafic and ultramafic rocks is stated depends on reaction processes and on the solute transport mechanisms that need to be well known. The sustainable transport (either by advection, diffusion or dispersion) of solute into the pore space brings aqueous CO₂ and chemical species into contact, making reactions possible (Andreani *et al.* 2009, Peuble *et al.* 2015, Peuble *et al.* 2019), with cations being released into the pore water. The first step of carbon mineralization consists on CO₂ solubility in the aqueous phase. The physico-chemical process depends on Henry constant described in Duan and Sun (2003). Figure 4 shows the relation between the CO₂ solubility as a function of pressure and temperature. As the reservoir pressure increases, CO₂ solubility increases, but decreases slowly with the increase in temperature and salinity.

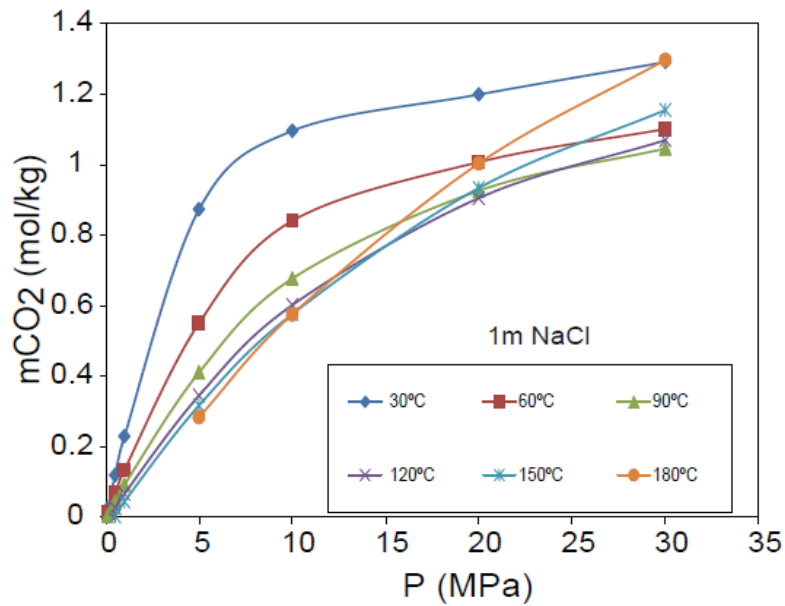
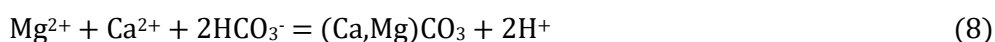
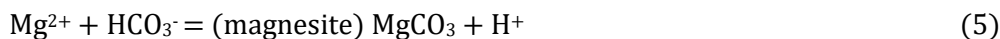
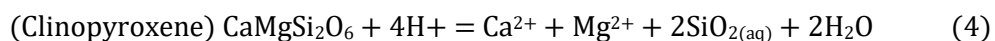
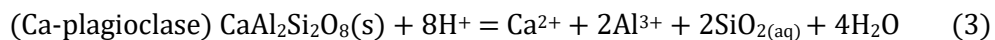
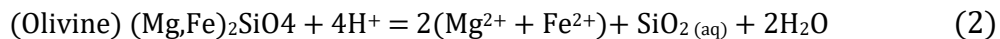


Figure 4: CO₂ solubility (mol/kg water) in 1 mole of brine, as function of Pressure and Temperature according to Duan and Sun model, (2003).

The dissociation of carbonic acid (formed by the interactions between aqueous CO₂ with water) releases protons (H⁺) in the water (eq.1). The dissolution rate of the Mg-Ca-Fe rich silicates and precipitation of carbonates depends on the activity of proton H⁺ and therefore the evolution of the fluid pH. When CO₂ is injected into the host rock, water pH is lowered due to the dissociation of carbonic acid. Consequently, the divalent ion-rich silicate releases Mg, Fe and Ca in the pore water increasing the pH (5~8) to values promoting carbonate precipitation.



The CO₂ consumption starts by the formation of nucleus containing Mg, Fe and Ca with carbonates ions. The nucleus grows into carbonate minerals namely magnesite, siderite, calcite, dolomite and ankerite or Mg-Ca-carbonates with other secondary phases such as zeolites, clays and silica, (for example. eq.2-7).

2. Background: Mineral carbonation routes

2.1. *Ex situ* Mineral Carbonation Technology


Ex situ CO₂ mineralization is a CO₂ storage option yielding to produce stable and valuable carbonates and to protect the environment. The technology consists of quarrying and transporting the silicates rocks near CO₂ source units, grinding the rocks to µm grain size (35 - 70 µm) and reacting it with fluid at high pCO₂ and elevated temperature. The suitable feedstocks consist mainly of mafic and ultramafic silicates containing significant amounts of Ca²⁺, Mg²⁺, and Fe²⁺. The feedstocks-CO₂ conversion efficiency (R_{CO2}), stands for the mass of the mineral needed to react and precipitate a unit mass of CO₂. The lower the ratio, the more efficient is mineral carbonation in that rock type (table 2).

Table 1: Composition of various typical rocks suitable for mineral carbonation and their storage characteristics (Lackner *et al.*, 1995; Olajire, 2013)

Rock (Mineral)	MgO (wt%)	CaO (wt%)	R _{CO2} (ton _{Rock} /ton _{CO2})
Dunite (olivine)	49,5	0,3	1,8
Serpentine	40	0	2,3
Wollastonite	0	35	3,6
Basalt	6.2	9.4	7.1

When available, industrial Ca/Mg rich solid residues or asbestos-mining tailings, electric arc furnace (EAF) dust, steel-making slag, cement-kiln dust, waste concrete, coal fly ash (Gerderman *et al.*, 2007), can also be used as carbonation feedstock.

Ex situ dry phase carbonation is widely neglected whereas aqueous phase is seen to produce significant amounts of carbonates through direct or indirect methods (Sanna *et al.*, 2014):

-  **Direct aqueous carbonation**, consists of pouring the raw materials in aqueous solution to obtain a suspension phase, that promotes the release of divalent cations



and accelerate CO₂ sorption and carbonates precipitation. To prevent the use of strong acid, the amount of CO₂ added must be efficient to dissolve the raw silicates and release significant concentration of Mg, Fe and Ca cations. The optimal temperature considered at $p\text{CO}_2 = 13 \text{ MPa}$ is between 70°C and 180°C (O'conor *et al.* 2001; Bearat *et al.*, 2006). This means, direct aqueous carbonation requires a proper selection of thermodynamic conditions (Pressure, Temperature, $p\text{CO}_2$) and the control of reaction rates. Based on previous works, solution composed with one mole (M) of sodium chloride (NaCl) and 0.64 M of sodium bicarbonate (NaHCO₃) is mostly used to balance the system and control the pH (Oconor *et al.*, 2001). Of course, minerals dissolution occurs with low pH whereas carbonates precipitation takes in transition at neutral to basic pH.

- **Indirect aqueous carbonation** increases Mg-Fe-Ca rich silicates dissolution rate in several steps. First step consists of adding a strong acid (hydrochloric acid: HCl) to obtain a cation hydrated complex with chlorine, the magnesium dichloride dihydrate (MgCl₂.2H₂O) at standard temperature. The following steps of dechlorination and hydroxylation-dehydroxylation produce pure magnesium carbonate (MgCO₃) obtained after the CO₂ addition at temperature higher than 400°C (Zevenhoven *et al.*, 2008). Organic additives (ammonia-water (NH₃.H₂O), ammonium bisulphate (NH₄HSO₄)) promote the formation of hydrated carbonates minerals complexes at ambient temperature (magnesium carbonate trihydrate: MgCO₃.3H₂O), moderate temperature (4MgCO₃.Mg(OH)₂.4H₂O at 50-100°C) and pure magnesite at high temperature (MgCO₃, T > 100°C) (Kemache *et al.*, 2017). More other strong acids (sulfuric (H₂SO₄) and phosphoric acid (H₃PO₄)) are used to dissolve efficiently the serpentine (70 – 90%) and increase the specific surface area (Maroto-Valer *et al.*, 2005).

2.2. In Situ Mineral Carbonation Technology

In situ mineral carbonation route is a developing technology as an alternative for conventional CO₂ storage and is suitable for both large-scale and isolated emitters (Sana *et al.*, 2012; Olajire, 2013). The process consists of CO₂ injection underground aiming to produce rapid reaction between injected CO₂ with alkaline-minerals present in the geological formation (Sipilä *et al.*, 2008). CO₂ sequestration by the mineralization route has the advantages to be a permanent trapping mechanisms without need of costly monitoring, with the benefit to reduce the upwards migration

(Gislason and Oelkers, 2014). In situ CO₂ mineralization is at an early development stage and evaluation of the effectiveness is based mostly on laboratory tests, numerical simulation and field testing.

2.2.1. Laboratory experiments

Rock types suitable for large-scale CO₂ mineralization are those containing Mg²⁺, Fe²⁺, or Ca²⁺ cations as presented in Figure 5. Dunite and peridotite consist principally of the magnesium iron silicate mineral olivine ([Mg,Fe]₂SiO₄), and serpentinite consists principally of the magnesium end-member serpentine-group pseudo-morphs antigorite, lizardite, and chrysotile (Mg₃Si₂O₅[OH]₄). Basalt consists principally of plagioclase (anorthite-albite, CaAl₂Si₂O₈-NaAlSi₃O₈), pyroxene minerals ([Ca,Mg,Fe]₂Si₂O₆), and olivine. Locally, very quickly chilled basaltic lava forms amorphous glass (Chizmeshya *et al.*, 2007; Daval *et al.*, 2011; Sissmann *et al.*, 2013), which has available Mg²⁺, Fe²⁺, and Ca²⁺ cations, rather than a crystalline rock.

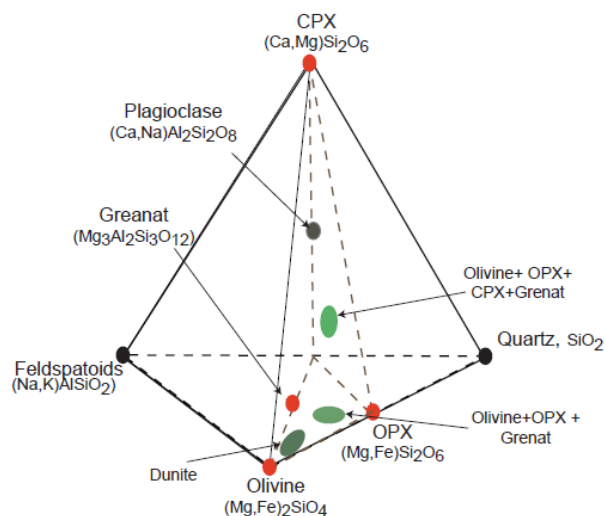


Figure 5: Tetrahedral representation of basalts rich magma showing the distribution of mafic and ultramafic minerals (Adapted from Yoder and Tilley 1962).

2.2.1.1. Batch experiments

Numerous lab experiments have been conducted during the last decade to study the reactivity of olivine, pyroxene, serpentine and amphibole with CO₂ at *in situ* storage conditions. Most of them conducted under batch reactor, thus without reactants

renewal based on the pioneer works developed by the Albany research center (O'Connor *et al.*, 2001; Bearat *et al.*, 2006; Stockman *et al.*, 2010; Shaefi *et al.*, 2013). Batch experiments consisted to crush and pour micron-sized mineral grains (35-200 μm) inside a closed reactor where temperature, pressure, CO_2 partial pressure and fluid composition are controlled. The authors argued that optimal conditions in term of temperature and $p\text{CO}_2$ ranged respectively between 155°C to 185°C and 11.5 MPa to 19 MPa (O'Connor *et al.*, 2001; Bearat *et al.*, 2006; Gerdermann *et al.*, 2002; 2007; Kelman and Matters, 2008). As in *ex-situ* carbonation, NaHCO_3 is often added in the reactor to boost the carbonation reaction by increasing the bicarbonate concentration (O'Connor *et al.*, 2001). The results showed significant mineral carbonation up to 50%-70% in few hours (O'Connor *et al.*, 2001, 2004; Schaefer *et al.*, 2013). Nevertheless, ultramafic and mafic rocks are assemblage of minerals having pore networks, different composition and dissolution rate, thus crushed sample is not representative of the bulk reservoir rock. The cited results are mostly representative of *ex situ* mineralization rather than *in situ* carbonation because underground conditions cannot be optimized as in laboratory experiments. However, they provide data on the cation release rate from primary minerals and thereby the carbonation rate (Giammar *et al.*, 2005; Hanchen *et al.*, 2006). The experiment conducted by McGrail *et al.*, (2006), on uncrushed basalt sample, under supercritical conditions confirms the rapid chemical reaction of CO_2 -saturated pore water with basalts to form stable carbonate minerals. Carbonation batch experiments on coarse grains (0.8 to 2 mm) was also conducted by Schaefer *et al.*, 2009 in worldwide basalts representing formations from North America, India and Africa. The optical images of post-reacted basalt grains after 230 days of testing (10.3 MPa CO_2 ; 100°C), showed large interporal Ca-carbonates and redish carbonates around the unreacted basalts.

2.2.1.2. Flow through experiments

Because in basaltic and peridotites aquifers, water is under hydrodynamic flow, Andreani *et al.*, (2009), Peuble *et al.*, (2015), and Peuble *et al.*, (2019) conducted flow through laboratory experiments, on sintered grains of dunite. The packed cylindrical samples (80 μm grains sintered using an isotropic press (Peterson, 1990), favoured a controlled porosity and permeability. The permanent flow is used to promote reactants renewals towards the fresh unreacted surface where metal-cation rocks continue dissolving and Mg-Ca-Fe carbonates precipitates at the water-rock interfaces. The



authors used mineral water with composition similar to the downhole brine (e.g. Volvic, a natural mineral groundwater from a volcanic environment) or pre-equilibrated after 64 days (Kanakiya *et al.*, 2017). Peuble *et al.*, (2019) noticed the reduction of the rock permeability by the carbonation and secondary phase's precipitation. Such permeability decrease (5 times with respect to the initial permeability) was interpreted as the consequence of carbonation occurring at dead-end zones where transport is diffusion-controlled, whereas slight porosity increase was observed throughout the sample at the flowing zone. Conversely a quick and slight increase in permeability (1.1 times) during the first hour of injection, corresponding to a short transitional period (Andreani *et al.*, 2009), is related to the setting up of a dispersion-induced chemical gradient in the inlet water followed by a steady state along the experiment time. A significant increase on Mg, Ca and the Si concentration, followed by a steady release was observed simultaneous with the permeability increase resulting on the rock dissolution and void increase. In the outlet fluid, Si was highly enriched whereas Mg-Ca concentration was depleted. This discrepancy indicates the non-stoichiometric dissolution leading to silica formation. The steady state observed in both permeability and effluent chemistry was explained by the growth of a passivation layer composed by amorphous silica. Such amorphous materials impede the reactants to reach the reactive surface. Fe was absent in the effluent due to the neo-formation of iron oxide (Fe_2O_3) and less amount of siderite (FeCO_3) associated to the Ca enriched Magnesite ($\text{Ca}_{0.1}\text{Mg}_{0.9}\text{CO}_3$) and calcite precipitation. Peuble *et al.*, (2019) observed rapid increase in Fe, and Si concentration in the outlet fluid followed by a quick breakthrough (during day 1) before steady state, while Mg and Ca are trapped in the system as highlighted by the negative dissolution rate. The excess of Si in the solution (Mg/Si ~ 0.1) was reported by (Porkovsky and Scott, 2000) for experiment performed in batch reactor.

In Peuble *et al.*, (2015), the permeability dropped significantly about two to three orders magnitude, and the samples seemed to be clogged ($k = 0.5 \times 10^{-18} \text{m}^2$). Outlet fluid was enriched in Si and Fe for lesser extent and depleted in Mg and Ca after three to seven hours injection. The negative concentration difference (ΔC) for Mg and Ca indicates the precipitation of Ca-Mg carbonates. In term of microstructure changes, Andreani *et al.*, (2009) observed magnesite separated with olivine in nanometer scale porous layer filled with nano-grains of siderite and poorly crystallized phyllosilicates. The authors noticed the development of cracks on diopside cleavage line, increasing the reaction surface (promoting further mineral dissolution) and creating nano flow

pathways. The inlet zone of the sample ($z \sim 6$ mm) was the most reacted area. This was observed in several flow-through experiments (Abdoulghafour *et al.*, 2016, Noiriél *et al.*, 2007 and Gouze *et al.*, 2003). Such phenomenon was linked to the dispersion-controlled fluid through preferential paths, named longitudinal dispersion. Reactions were efficient in this area and the occurrence in silicates dissolution and carbonate precipitation was derived by μ Raman and SEM. Micro-silica grains and iron oxide were also seen as reaction products (Peuble *et al.*, 2015). Carbonates precipitation was large enough in the $50 \mu\text{m}$ scale at the inlet zone. Up to 7 mm length towards the outlet zone, loose materials apparent to phyllosilicates have been observed confirmed later by transmission electron microscopy images (TEM). As observed in flow-through experiments (Peuble *et al.*, 2015), inter and intra-granular porosity was filled with magnesite type minerals ($10 \mu\text{m}$ pore throats) and characterized using μ Raman and SEM-TEM images. According to EDX analysis and mass balance, the magnesite was Fe-Ca enriched. Etch-pits structures (or dissolution rough surfaces) are observed on the olivine surface, and were filled with magnesite. At sub-micron scale, TEM images showed micro veinlets (channels) filled with amorphous silica in its outer parts and magnesite in the inner parts. Smaller etch-pits (150 nm wide and below) have been filled homogenously with poorly crystallized serpentine. In both flow and batch experiments based studies, Ca rich zeolites were observed to compete with carbonates precipitation to reduce calcium concentration. This competition has consequence on the carbonation capacity in the system CO_2 -brine-rock.

Table 2: Hydrodynamic changes as function of the dissolution/precipitation of the primary minerals.

Reference	Experimental conditions	Observations
Andreani <i>et al.</i> , 2009	CO_2 water flow = 0.6 mL.mn^{-1} $P = 12 \text{ MPa}$, $T = 160^\circ\text{C}$, $P_{\text{CO}_2} = 11 \text{ MPa}$, $t = 6\text{h}$	<ul style="list-style-type: none"> - Secondary minerals : Magnesite + (few amounts siderite, TOT phyllosilicates) - Carbonation efficiency is controlled by the reactant renewals and pore structure heterogeneity - Decrease in porosity in diffusion controlled area <p>Sustainable injection promoted by moderate flow</p>
Peuble <i>et al.</i> , 2015 Peuble <i>et al.</i> , 2019	CO_2 water flow = 0.1 mL.h^{-1} $P = 12 \text{ MPa}$, $T = 180^\circ\text{C}$, $P_{\text{CO}_2} = 10 \text{ MPa}$, $t = 60\text{h}$	<ul style="list-style-type: none"> - - Rapid increase in Fe and Si in the effluent Ca and Mg depletion in the effluent due to Magnesite and dolomite precipitation - Strong decrease in permeability [0.05 to 0.001 mD] and minor changes in porosity due to pore network heterogeneity
Menefee <i>et al.</i> , 2018	<ul style="list-style-type: none"> - CO_2 saturated water flow = 1ml/h, $t = 12 \text{ h}$ - $P = 20 \text{ MPa}$, $T = 100\text{-}150 \text{ }^\circ\text{C}$ <ul style="list-style-type: none"> - $p_{\text{CO}_2} = 10 \text{ MPa}$ - $[\text{NaHCO}_3]$ effect 	<ul style="list-style-type: none"> - Carbonation at diffusion-controlled zones (dead end fracture), Mg-Fe carbonate increased with $[\text{NaHCO}_3]$ and clays precipitate at the main fracture - - Constant permeability during the experiment, controlled by the moderate rate and clays precipitation zone.

2.2.2. Numerical modelling

Numerous numerical codes have been developed and enable scientists to study the underground complex interplay of rock matrix with fluids circulating through the porous media. Time-independent equilibrium speciation, reaction paths and phase stability has been calculated with increasing CO_2 fraction (Holland & Powell 1998, in Kelemen *et al.*, 2011). With this purpose, Holland & Powell (1998) simulated the phase's stability scheme when reacting Mg-olivine with CO_2 at increasing temperature. They concluded that the mineral trapping in peridotites occurs in a series of hydration-dissolution-precipitation reactions. Olivine hydration results in the formation of serpentine, talc, and brucite which in turn converted into magnesite (Fig.6).

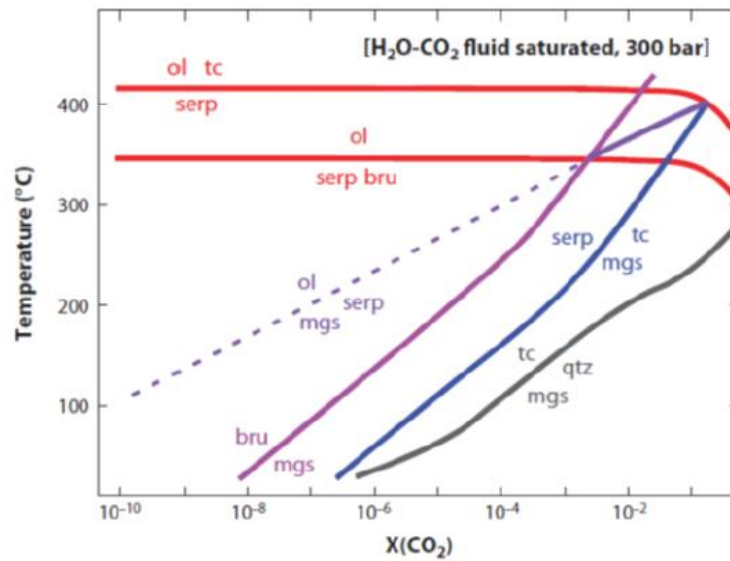


Figure 6: Phase diagram for reactions involving olivine (ol), brucite (bru) quartz (qtz), serpentine (serp), talc (tc) and magnesite (mgs) in $\text{MgO-SiO}_2\text{-H}_2\text{O-CO}_2$ at increasing temperature (Holland & Powell 1998 in Kelemen *et al.*, 2011)

Rosembaur *et al.*, (2012) conducted a series of thermodynamic equilibrium modelling on basalts at thermodynamic conditions range from 50-200°C and 300 bars, using CHILLER code (Reed, 1982). In these simulations the fluid was first equilibrated with basalt at the stated conditions, then CO_2 added incrementally and equilibrium recalculated at each step. The primary carbonates mineral assemblage is magnesite, as dolomite and ankerite were intentionally impeded to precipitate. These minerals are supposed to inhibit calcite and magnesite precipitation. When allowing all minerals to precipitate, calcite appears first after reaction with 40g CO_2 followed by dolomite, ankerite siderite and dawsonite.

Using GEMS code package, Gysi (2017) simulates the carbonation of basalts glass by incrementally adding basalt mass in a reactor containing a concentration of CO_2 ($p\text{CO}_2 = 2 \text{ MPa}$, in the case of fig.6) at supercritical conditions. Successive equilibriums are reached during the titration experiments leading to pH changes and secondary minerals in four different stages (1-4, Fig7).

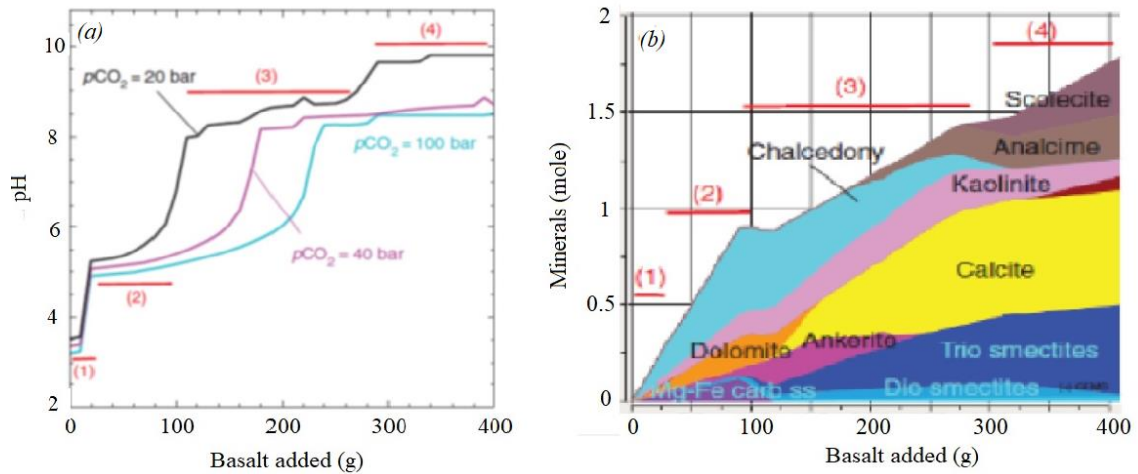


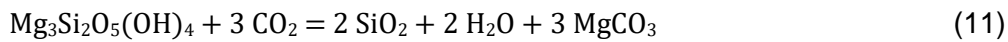
Figure 7: Titration model showing the simulated pH and secondary mineralogy as a function of basaltic glass added at 50 °C and pCO₂ of 20 bars. The numbers indicate different pH buffered conditions: (1) CO₂-water-buffered; (2) SiO₂ + kaolinite + Ca-Mg-Fe carbonate solid solutions; (3) SiO₂ + kaolinite + smectites + Ca-(Fe)-carbonates; (4) SiO₂ + kaolinite + smectites + zeolites + calcite.

In parallel, other simulation works focused mainly on the reaction path using the kinetic aspects of the relevant minerals rather than minerals assemblage at thermodynamic equilibrium (e.g. McGrail *et al.*, 2006, Rosembaur *et al.*, 2012, Gysi and Stefansson, 2011). The later used the dissolution-precipitation kinetics data from literature to run the models. The simulations are based on the theory that CO₂ dissolution into pore water is time and reactive surface-dependent. Divalent cations release is a function of temperature and pH which is in turn function of dissolved CO₂. Thus, the calculation of carbonates mineralization requires solving together all reactions and kinetics equations involved in the system. In phase assemblage (equilibrium) the focus is the reaction end-point and thermodynamic conditions. Cipolli *et al.*, 2004, simulated CO₂ sequestration in serpentine rocks (Genova, Italy) using EQ3/6 code (Wollery and Daveler, 1992). They considered the average dissolution rate of serpentine at 25°C to 10⁻⁹ mol.m⁻².s⁻¹. The activation energy was assumed to be 70±10 KJ/mol and the dissolution rate follows the transition state theory (Lasaga, 1981):

$$R_m = \mp A_m k_m (\prod a_n) \left| \left(\frac{Q_m}{K_{eq}} \right)^n - 1 \right|^m \quad (9)$$

$$k_T = k_{25} \text{Exp} \left[\frac{E_a}{R} \left(\frac{1}{298.15} - \frac{1}{T} \right) \right] \quad (10)$$

The calculated rate at 60°C and $p\text{CO}_2 = 250$ bars was $1.93 \times 10^{-8} \text{ mol.m}^{-2}.\text{s}^{-1}$. In this mono-mineral rock system, pH increased from 3.3 to 4.5 and was associated to the precipitation of amorphous silica produced simultaneously with the precipitation of magnesite. Magnesite precipitation at such low pH contrasts with the published simulation and experiments indicating that carbonation occurs at pH above 5.5 and becomes stable for pH > 6.5 (Gysi and Stefanson, 2011 and 2012; Moita et al., 2020). Nearly 3 moles of magnesite and 2 moles of chalcedony are produced for 3 moles of dissolved CO_2 in the aquifer.



The production of SiO_2 and magnesite with time induced the increase of rock volume in about 19%, leading to the decrease in porosity.

We performed and present hereby the result of a reactive transport simulation aiming to reproduce Andreani *et al.*, 2009 experiment. The simulation was run by upscaling the core sample from mesoscale to meter scale. The multi-components reactive transport software, CrunchFlow (Steeffel & Lasaga, 1994; Steeffel, 2001; Giambalvo *et al.*, 2002; Knauss *et al.*, 2005; Maher *et al.*, 2006; Li *et al.*, 2008) has been used for this purpose. The theoretic sample consists of 1-meter long column of dunite composed of 97% of olivine and 2% of diopside, with initial porosity of 24% (sintered rock). The simulation conditions were 100°C, 10 MPa of $p\text{CO}_2$, and total pressure of 12MPa considered to be in the range of the optimized conditions. The simulation has the purpose of understanding the mineral carbonation mechanisms focusing on reaction pathways and their associated kinetics and the feedback between geochemical reactions and aqueous transport. Through the 1-D geometry model, they considered the propagation of the carbonation reaction front under different boundary conditions, such as flow rate and aqueous CO_2 concentrations. After CO_2 injection pH dropped to 3.5, and volume fraction changes were updated to follow the change in porosity. Ten years simulation showed carbonation abundance (magnesite precipitation and in less extent dolomite, ankerite, calcite and siderite) within 20 cm distance picked at the first 7 cm. The simulation results showed 20% of magnesite, 5% of dolomite and approximately 5% of cumulative ankerite, calcite and siderite. Amorphous silica (15%)

was the abundant non carbonate secondary phase. These results indicate the rapid carbonation potential of the dunites rock. In fact, twenty years of simulation might result on 40-60% of carbonates, 20-30% of amorphous silica and 50% in average of the rock simulation but are in the same range of the reservoir simulation results presented by Zhang and Dipaolo (2017) in Nagaoka basalt sands reservoir (see below).

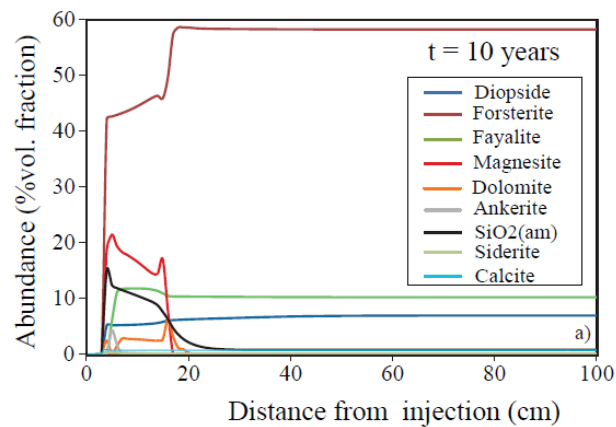


Figure 8: Numerical simulation of the injection of CO₂ rich fluid into dunite rock minerals assemblage after 10 year injection based on Andreani *et al.*, 2009 experiment

Recently Zhang and Depaolo (2017) conducted a reservoir simulation capturing the spatial and temporal variation of the CO₂-rock interaction on Nagaoka volcanogenic sediments (Japan) and Etchegoin (volcanic rock, California, US). The simulation has been conducted with TOUGHREACT at 75°C for reservoir located at 2000 m depth and having 40 m extension. The porosity and permeability are respectively 0.185 and 65 *mD*. The model uses a first order formulation for mineral dissolution and precipitation kinetics as shown in eq.8. They observed carbonation to occur after fifty years and get total carbonation of the injected CO₂ after three hundred years. One of the most influencing parameter of the carbonation is the specific area as the higher the SSA the first the release of metals ions promoting carbonates saturation. Nagaoka rock was observed to be much more reactive than Etchegoin basalts.

2.2.3. Pilot test sites

In-situ carbonation of Mg-Fe-Ca rich silicates is currently implemented in several pilot sites around the world for the testing of permanent and safe CO₂ sequestration in the form of solid and stable minerals.

2.2.3.1. Carbfix pilot project

Before the Carbfix projects studies (e.g. Matter *et al.*, 2016), published studies postulated that meaningful CO₂ precipitation in the form of minerals might take thousands of years to occur. The developed models based essentially on traditional targets suggested that CO₂ trapping occurs by physical means within hundreds of years, during which aqueous CO₂ and rock interact and provide necessary divalent metallic cations to neutralize CO₂. The CarbFix pilot project, launched in Iceland near the Hellisheidi geothermal power plant, demonstrated revolutionary results in CO₂ sequestration projects. The pilot was designed to inject CO₂ into basaltic lavas topped with hyaloclastites at targeted depth ranges between 400 m and 800 m. Two injection phases, respectively in January to March 2012 (175 tons of pure CO₂) and in June to August 2012 (73 tons of CO₂-H₂S gas mixture) were conducted. The novel strategy consisted of injecting water dissolved CO₂ (CO₂ volume fraction = 3.5%, Matter *et al.*, 2011, Fig 9a) selected to promote the CO₂ solubility the triggering the basalts dissolution rate and eliminate the fluid buoyancy. The monitoring technique consisted of chemical and isotopic tracers (carbon 14 tackles the interactions of CO₂ with the rock and 20sulphur with hexafluoride (SF₆) and trifluoromethyl pentafluoride (SF₅CF₃)), to track the gas plume. The results revealed that approximately 95% of injected CO₂ has been mineralized in less than two years. Interestingly mafic and ultramafic rock carbonation can be very fast and safe process than initially predicted. At the Carbfix2 injection site located at 1.5 km north of Helisheidi power plant, gas mixture (4526 tons of water dissolved CO₂ and 2536 tons of water dissolved H₂S) was injected from June 2014 and terminated in July 2015. The target reservoir depth is located around 2.9 to 2.2 km and the formation temperature estimated to be 255 – 266°C. Because of the density difference, the cold gas-charged water was expected to sink once in the reservoir temperature promoting rapid reaction with basalts. After the two years of injection-monitoring, 0.84 m³ of calcite and 0.7 m³ of pyrite precipitated respectively for

one ton of CO₂ and one tone of H₂S injected. The other interesting result is the constant permeability demonstrating the long term viability of CO₂ mineralization at reservoir scale regardless the carbonates volume. Carbfix rapidly developed to a semi-industrial project and the obtained results can be replicated elsewhere.

2.2.3.2. Big Sky Carbon Sequestration Partnership (BSCP) pilot project at Wallula

The BSCP pilot project near Wallula (a township in Washington State) aims to test the concepts of *in situ* conversion of basalt into stable carbonates minerals at supercritical conditions . The Wallula field pilot region is part of the Miocene Columbia River Basalts Group (CRBG), covering over 200000 km² and having an estimated storage capacity from 10 to 50 Gt_{CO₂}. The hydraulic tests of the geological reservoir indicated aquifer transmissivity ranging from 0.9 to 1.8 m²/day implying higher permeability ranged from 1.22 to 2,49 D. Low permeability caprock was also characterized and ranged from 0.01 to 0.1 μD. 977 metric tons of supercritical CO₂ at depth interval between 828 and 887 m was injected within three interconnected basalts breccia reservoir from July 17, 2013 to August 11, 2013. After injection completed, CO₂ spreading was monitored to study the CO₂ migration and chemical reaction (between host rock divalent cations and scCO₂, Fig.9b) based on residual saturation tools (RST) logging, pore water sampling and surface soil gas monitoring. Any leakage along the injection or monitoring wells has been noticed, indicating that CO₂ remained in place and progressively dissolved in pore water. For instance, fluid and gas samples collected from the injection zone show strongly elevated concentrations in Ca, Mg, Mn, and Fe that might promote CO₂ carbonation. Core sampling within the delimited zone might provide knowledge about the carbonation. Also, the next injection tests should include chemical monitoring using carbon 14 and tracers. That, monitoring system helps to quantify the amount of CO₂ fixed as mineral by the mafic rocks (Matters *et al.*, 2016).

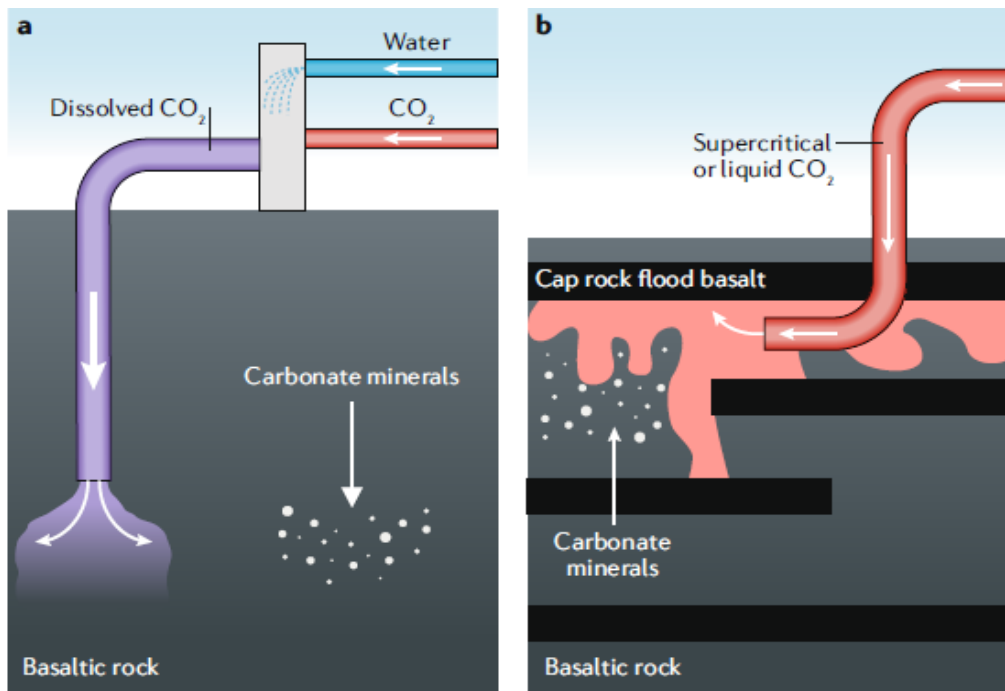


Figure 9: Comparison in CO₂ injection form and the behaviour of the plume in each state (a: CO₂ mixed with CO₂ at Carbfix. Note the homogenous distribution of the plume. B: Supercritical CO₂ injected in Wallula site. Note the plume fingering and the accumulation below the caprock, Snæbjörnsdóttir *et al.*, 2020).

2.2.3.3. Shallow CO₂ injection experiment in Newark basalts (New York)

A shallow depth injection site has been developed at the Newark basin (Pallisade Sill outcrop) in the New York state. The Newark super-group is formed with Triassic sedimentary lacustrine sequence, imbedded within three flood basalts formation. The Newark basalts are obvious sequestration rocks having 10 to 20% porosity providing enough reactive-surface for CO₂ mineralization. Matters and others (2007) conducted an injection experiment (amount of CO₂-saturated water ≈ 1400 liters) in reservoir located at 230 m with a reservoir thickness of 8 m. The acid was neutralized within hours, and the release rates of Ca²⁺ and Mg²⁺ available for mineralization were comparable to laboratory experiments. Beside this experimental study, the Newark basin is subject of several works studying the storage capacity and leakage assessment with the objective of large scale CO₂ storage. The basin has the potential

to support both traditional (in sedimentary reservoir) and less traditional options (in mafic reservoir).

Table 3: Summary of the important published works about *In situ* CO₂ mineralization

Reference	Characterizing method	Main observations
Bearat <i>et al.</i> , 2006 Agreawal & Mehra (2020)	Batch experiments: crushed olivine (1 mol NaCl, 0.64 mol NaHCO ₃ , T =185°C. Characterization: micro-Raman spectroscopy, X-ray diffraction, and scanning electron microscopy	Carbonation of the aqueous olivine grain + growth of fractured amorphous silica layer. Agreawal & Mehra observed magnesite precipitation quickly after 7 days and continues up to 30 days.
Schaief <i>et al.</i> , 2010	Batch experiments in flood basalts rock samples (USA, India, and South Africa. T = 100°C, P = 10.34 MPa, $p(\text{CO}_2/\text{CO}_2+\text{H}_2\text{S}) = 6.72 \text{ MPa}$	All basalts samples were observed to react with CO ₂ . Basalt from Newark (New-York) was the most reactive and sample from Karoo (SA) the least. Both CO ₂ + H ₂ S were observed to increase the reactivity of Karoo.
Gysi & Stefanson 2012	Batch experiment in basalts glass at 40°C and variable $p\text{CO}_2$	Poorly crystalline Ca-Mg-Fe carbonates,
Gysi and stefanson 2011	Numerical simulation (phreeqc) in basalt glass: effects of $p\text{CO}_2$ on, basaltic glass dissolution kinetics and minerals assemblage	Competition between Ca-Mg-Fe carbonates with Ca zeolites and Ca-Mg-Fe Clays namely smectites.
Andreani <i>et al.</i> , 2009	Flow through experiment on dunite	Steady release in Mg and Fe before decreasing. SiO ₂ and clay contents favour the incongruent dissolution (few amount of Si in solution)
Matter <i>et al.</i> , 2016 Gunnarsson <i>et al.</i> , 2018	Shallow aquifer (T = 50°C,)Deep aquifer (T = 240-250°C) The novel injection method: water dissolved CO ₂ , gas mixture co-injection	Nearly 92% of CO ₂ carbonated in two years Sulphur uptake as pyrite Cost-effective methods
Mc Grail <i>et al.</i> , 2014 and 2017	Field test in Wallula: lqCO ₂ or scCO ₂ into brecciated basalts at 800-900 m depth topped with caprock	- Proof of CO ₂ mineralization within two years Carbonates nodules = ankerite + calcite veins - Significant amount of injected CO ₂ remains in free phase or dissolved

<p>Xu <i>et al.</i>, 2004</p>	<p>Numerical simulation (glauconite sandstone and dunite: olivine)</p>	<p>The trapped carbonates and abundance is function of the original rock:</p> <ul style="list-style-type: none"> - For glauconite, CO₂ trapped as ankerite, siderite and few dolomite and dowsonite - For dunite, CO₂ trapped as magnesite and siderite with large trapping capacity (100kg/m³).
<p>Zhang and Depaolo 2017</p>	<p>Reservoir Simulation in Nagaoka (volcanogenic sediments, Japan) and Etchegoin (volcanic rock, California)</p> <p>Software: TOUGHREACT</p>	<ul style="list-style-type: none"> - Carbonate precipitation conditions: pH 4.5-6, fluid velocity 5m/year, time after injection > 50 years. - CO₂ mineralization at Nagaoka = 90 Mt~80% of the injected CO₂ after 300 years for SSA = 50 cm²/g and ~ 20% of CO₂ mineralization for SSA = 2cm²/g.

2.3. Biotechnological mineral carbonation routes

Biom mineralization is the process by which living organisms' synthesise minerals. The process is controlled by environmental parameters such as the temperature, salinity, water pH. Well over 90% of the carbonate sediments found in geological environment are biological in origin and form under aqueous conditions (Milliman, 1974; Wilson, 1975; Sellwood, 1978; Tucker and Wright, 1990). Thus, several microorganisms present in marine, lacustrine and terrestrial ecosystems including cyanobacteria and plants have the capacity of CO₂ sequestration through biom mineralization. In recent years, biom mineralization is explored among the solutions to sequester CO₂ from industrial emitters. The process is based on the common reaction described in eq. 1, where calcification is a common biotic process.



The Microbially-mediated calcium carbonate precipitation is controlled by five metabolic processes including: (1) urea hydrolysis, (2) activity of carbonic anhydrase, (3) microbial reduction of Fe(III), (4) photosynthesis by cyanobacteria fixes CO₂, and (5) sulphate reducing bacteria. Ureolysis-driven CaCO₃ precipitation has been investigated experimentally by Mitchell *et al.* (2010) with application in both wellbore materials sealant and caprock microfracture and enhancing mineral trapping.

Interesting results have been observed as dissolved calcium was completely precipitated to calcite and the increase in urea concentration from 1 to 5 g/L induced an increase of CaCO_3 from 8.3% to 31%. Fortin et al. 1997 (among others) pointed the role of the bacterial urea hydrolysis in the precipitation of high amount of carbonates. In fact the implication of the bacterial enzyme is characterized by the ability to create an alkaline environment and the ability of the bacterial charged surface to fix the positively charged ions and resulting in Ca-carbonates. Biomimetic of CO_2 storage has been explored as a potential solution of CO_2 mineralization based on biocatalysts activities namely the carbonic anhydrase (Bond et al. 1999 and 2001; Lee et al. 2010, Sahoo et al. 2012, Yadav et al. 2012). The technology consisted of using carbonic anhydrase (CA) in the gas stream from a coal-fired power plant (in artificial sea water) to convert CO_2 to HCO_3^- triggering CaCO_3 precipitation (Bond et al., 1999). Sahoo et al. (2012) and Yadav et al. (2012) studied the effect of temperature and pH on the CA activities of CO_2 hydration. Both studies agree that for CA driven carbonation, alkaline pH and low temperature are required. Power et al. (2009), suggested that geoengineering facilities with cyanobacteria and sulfato reducing bacteria might constitute better environment for CO_2 biomineralization. However the overall technologies of CO_2 biomineralization remained poorly understood and must be studied deeper before it deployment.

3. Discussion of the experimental observations

3.1. Factors affecting dissolution and precipitation rates

Rapid CO_2 neutralization by the conversion of olivine, pyroxene, plagioclases and amphiboles rich-rocks into carbonates minerals is an alternative to the CO_2 storage in sedimentary rocks. In fact, in sedimentary rocks, silicates are free of divalent cations, a key factor for CO_2 mineralization. Such cations (Mg^{2+} , Fe^{2+} , Ca^{2+} concentration > 20 wt%) are however abundant in mafic and ultramafic rocks, widely distributed across the globe (Schaefer *et al.*, 2010, Rosenbaur *et al.*, 2010, Gislason and Oelkers, 2014). Due to the large volume of basalt in the Columbia Ridge basalts ($200,000\text{km}^3$), McGrail *et al.*, (2006), estimated the Columbia River basalts itself to have over 100 Gt of CO_2 storage capacity. Similarly Goldberg *et al.*, (2008) and Goldberg *et al.*, (2010), estimated the large storage capacities of sea-floor basalts in Washington and British Columbia, and in Caribbean offshore flood basalts to more than 2000 Gt_{CO_2} . Kelemen and Matter 2008, demonstrated that worldwide peridotite mass and mantle peridotite have neutralizing capacity of 77 trillion of CO_2 . According to these theoretical estimates

and the insights provided by natural carbonation, storage capacities are not a limitation and *in situ* mineralization can balance the CO₂ atmospheric 700 Gt emitted to the atmosphere since the onset of the industrial revolution. Beside the cost of the technology, the control of the injection rate, the injection fluid properties, the CO₂ solubility and the rocks dissolution rate are to be considered. All of these key parameters have been studied handled in recent years through laboratory and field experiments.

In laboratory tests, the major challenge consists of reproducing the optimal conditions yielding to accelerate the dissolution rate and maximize the amount of divalent cations that can precipitate with CO₂ and minimize the associated secondary minerals, including clays and silicates. Figure 10 is a conceptual model summarizing the dissolution-precipitation mechanisms leading to Mg-Ca-Fe carbonates and amorphous silica.

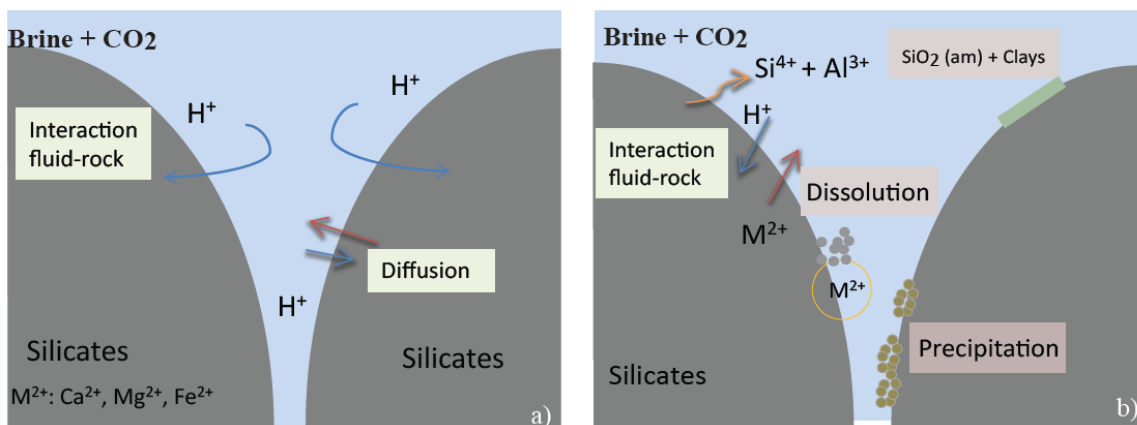


Figure 10: Factors involving in dissolution of ultramafic rock and precipitation of carbonates and secondary phases. Dissolution is governed by the lower fluid pH, and adsorption capacity of H⁺ by the silicate rock, while precipitation is promoted by oversaturation properties of cations at the fluid rock interface and the pH increase.

Gislason *et al.*, 2010 listed four key factors likely to enhance the basalts dissolution rate and optimize carbonation, including:

The rock compositions imply the relative concentration of SiO₂ and divalent cations present in the rock. The high concentration in SiO₂ and Al₂O₃ decreases the dissolution

rate. This is the case of quartz, K feldspar and some clay minerals such as kaolinite, whereas basic rocks dissolve faster (Fig.5).

The reactive surface area plays an important role in the dissolution rate as it exposes the available rock surface to the fresh CO₂: the higher the specific surface, the faster the dissolution rate, as a consequence of the direct scaling of reactive surface with the general rate law. Still, the reactive surface is the most uncertain parameter in the rate estimate because its definition is based on approximations. This limitation may lead to an inaccurate estimate of the pore structure evolution, the amount of secondary minerals, and the overall porosity and permeability.

Temperature and CO₂ partial pressure need to be optimized in order to enhance the dissolution rate. Many experimental works reported the important role of temperature ranges from 70 to 200°C. This temperature range is probably present in high geothermal gradient zones but not common in shallow CO₂ storage reservoirs. Gunnarson et al., 2018 recorded a positive feedback at Carbfix2 injection site in high reservoir temperature (240-250°C) where rapid CO₂ mineralization occurred. Injecting cold gas-charged water was required to sink large amounts of CO₂-H₂S in the reservoir, and the high local temperature to promote dissolution rate (Eq. 6).

Fluid composition also affects the rock dissolution rate. In fact, the higher the proton activity, the faster the dissolution rate (Eq.5). Higher dissolution rate mobilizes the divalent cations increasing the fluid pH to values where carbonates are stable. Consequently, mafic and ultramafic rock dissolution rate is a direct function of the fluid pH (Fig.11)

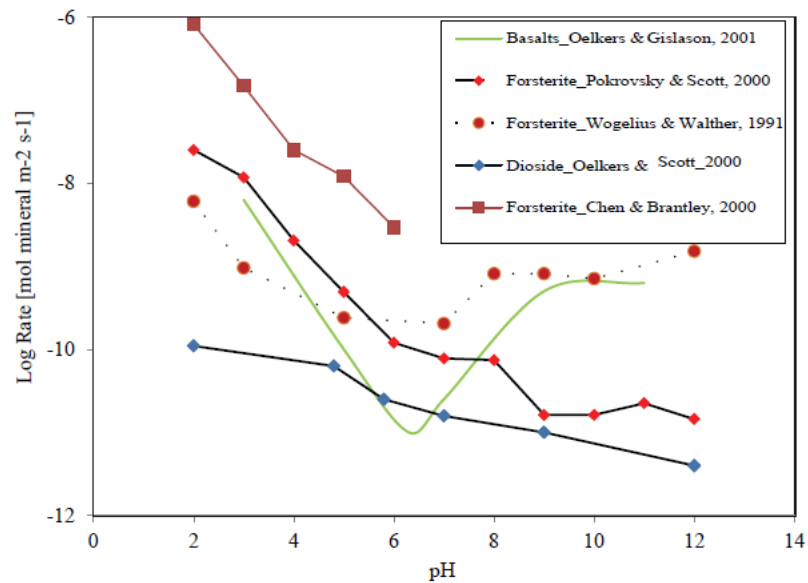


Figure 11: Dissolution rate from common minerals, basaltic glass as a function of the fluid pH at 25 °C. The forsterite dissolution rate was measured by Chen and Bentley, 2000 at 65°C (Palandri and Kharaka. 2004)

All the influencing parameters are studied at laboratory experiments in batch reactor and flow-through reactors and currently tested in fields.

3.2. Dissolution mechanisms and microstructure changes during CO₂ mineralization

As observed in many reviews (Andreani *et al.*, 2009, Gysi and Stefansson, 2011), carbonation rate decreases with carbonation and therefore inhibits the dissolution rate. Porosity, another factor influencing the mass transfer, is estimated from the difference in molar volume between carbonated and initial sample obtained by the mean of mass balance (Andreani *et al.*, 2009, Peuble *et al.*, 2015). Carbonates precipitation with secondary phases increase rock volume and progressively decrease the sample porosity. The decrease in porosity and the sample coating by passivation layers have the same impact to inhibit or decrease the dissolution rate. In this case, flow and reaction properties should be properly controlled to optimize carbonates precipitation while restricting SiO₂ growing. While magnesite-calcite precipitation front increase toward the inner olivine crystal (case of dunite samples, Peuble *et al.*, 2015), serpentine appears as valley in the boundary of olivine. This supposes that

serpentinization (hydration of olivine and formation of serpentine, talc and brucite mineral assemblage) takes place in olivine bound prior to the carbonation. The limit between the carbonated and unreacted olivine constitutes an irregular surfaces (etch-pits) rich in magnesium and calcium. The carbonates growth behind the dissolution surface increases the internal stresses, creating micro-channels or veinlet (Peuble *et al.*, 2019). These sub-microstructures connect the fresh CO₂ with the inner olivine and carbonation continues. Stockman *et al.*, (2010) observed, that calcite precipitation rate from basalt glass, was constant with time, invalidating the claim of dissolution rate inhibition by calcite growth. The incongruent dissolution reported by Bearat *et al.*, (2006) and Andreani *et al.*, (2009), resulted on growth-foliation and regrowth of a glasslike fracture at the silica layer during carbonation. Continues cracking of this so-called passivation layer is the consequence of the continue conversion of olivine to magnesite while the exfoliation was induced to the stress in the interface between the SiO₂ layer and fresh olivine due the difference in molar volume. Based on studies focusing on crystal growths and involved energy and stresses (Correns 1949, Correns & Steinborn 1939) Kelmen *et al.*, 2011 explain that volume increase by CO₂ sorption induces the rock microcracking and the increase of the reactive surface. Clearly, the carbonation of Ca-Mg-Fe rich silicates minerals implies the competition between sustainable transfer of solutes and their interactions with the unreacted rocks under kinetics or conditions near the equilibrium.

CarbFix field experiments demonstrate that *in situ* carbonation do not require additive or if used might be an expensive method. At CarbFix field scale (1&2), carbonation was observed to be far faster (almost the whole injected CO₂ was converted into calcite in less than two years) than initially predicted (e.g. Han, 2008). Numerous keys processes enable the rapid carbonation of basalts in CarbFix project. The use of water dissolved CO₂ having high density (Fig9.a) prevented buoyancies and leakage and also promoted the faster dissolution of the host rock. The rapid dissolution rate provided the required Mg, Ca, Fe ions for carbonation. Water dissolving CO₂ is therefore practicable technique especially when caprock is assessed to be insufficient to tackle CO₂ capillary breakthrough. The injected CO₂ broke out the local equilibrium at the onset injection increasing the fluid pH that promoted the carbonation of the dissolved basalts.

4. Risks assessment and Challenges in CO₂ storage.

There are several risks and challenges associated with CO₂ storage, from the risks associated with the installations to the risks associated with CO₂ storage in geological reservoirs. The risks of CO₂ storage in a geological reservoir can be divided into different categories (Damen *et al.*, 2006, Fig.10):

- ⦿ CO₂ leakage: CO₂ migration out of the reservoir to other formations, from where it may escape into shallower drinking aquifers and the atmosphere;
- ⦿ Seismicity: the occurrence of (micro) earth tremors caused by CO₂ injection;
- ⦿ Ground movement: Subsidence or uplift of the earth surface as a consequence of pressure changes induced by CO₂ injection;
- ⦿ Displacement of brine: Flow of brine to other formations (possibly sweet water formations) caused by injection of CO₂ in open aquifers.

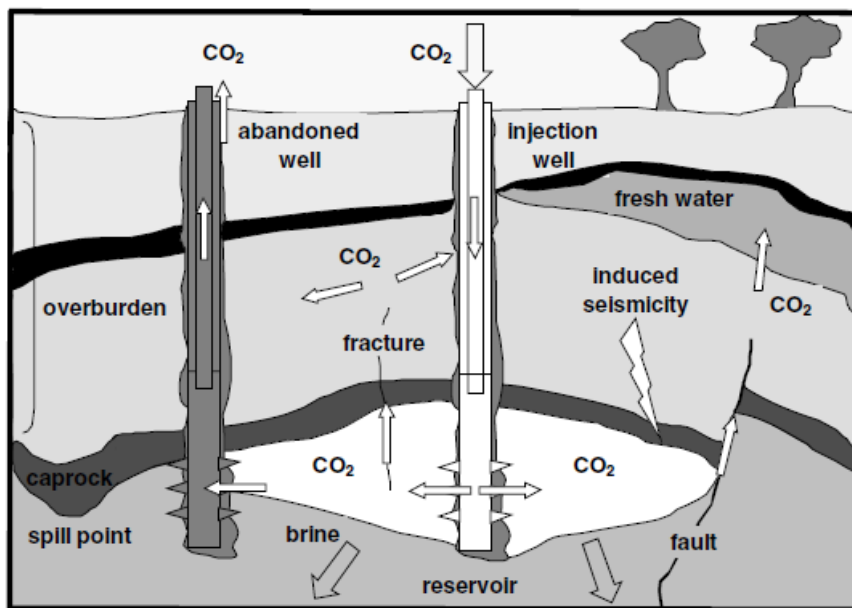


Figure 10: Risks of underground CO₂ storage. Black arrows represent CO₂ flows (along fractures, abandoned wells and faults). White arrows represent brine displacement as a consequence of CO₂ injection (adapted from Damen *et al.*, 2006).

4.1. CO₂ Leakage

CO₂ injected into geological reservoirs can potentially migrate upwards and laterally through the overburden formations and eventually leak into the atmosphere /

biosphere. The leakage rate depends on the integrity of the well cement / reservoir, the cap rock and the trapping mechanism (Damen *et al.*, 2006; Bachu and Celia, 2009; Iglauer *et al.*, 2015a, Yang *et al.*, 2015). As discussed previously, free CO₂ (gaseous or supercritical) has migration potential due to the buoyancy effect and in the case of caprock failure, leakage can occur. Free CO₂ is mostly prevalent in hydrocarbon depleted or coal seam reservoirs because of the high CO₂-wettability. At saline aquifers, models showed that CO₂ may stay at supercritical state for hundreds of years and the complete sink is predicted around 5,000-100,000 years (Ennis-King and Paterson, 2003; Lindeberg and Bergmo, 2003). Drinking water contamination risk is associated with CO₂ leakage along caprock and applies to both conventional storage as well as for CO₂-mineralization storage. CO₂ and H₂S (in the case of gas mixture), leakage might dissolve contaminants such as heavy metals loading (Pb,Cd, Hg..) and cause drinking water toxicity.

As we mentioned previously from Carbfix project and Big Sky projects, CO₂ sequestration in mafic and ultramafic rock will decrease prevent the potential leakage.

4.2. CO₂ induced seismicity

High CO₂ injection rate or the injection of large amount of fluids into the reservoir induces pressure build up. The increase of pore pressure modifies the reservoir mechanical state that might cause fracturing or faults reactivation triggering micro-seismicity events. Such events might cause surface installations damage, earth surface subsidence or uplift, and most likely damages on caprock and wellbore materials triggering CO₂ leakage. High CO₂ injection pressure might also cause brine displacement with potential consequence or drinking water salinization. The control of the CO₂ injection pressure enables to master the risk of induced micro seismicity.

4.3. Ground movement and brine displacement

Land subsidence and groundwater displacement are respectively the consequences of pore water withdrawal and CO₂ injection. Non-wetting fluid injection namely CO₂ displaces the formation brine into the small pore networks or upward to the shallow fresh aquifers, increasing the charge and contaminating the drinking water. Conversely the brine withdrawal might induce pore pressure disequilibrium leading to ground subsidence/uplift. Both geomechanic and chemical phenomena are avoidable

in subsurface mineral storage as CO₂ can be injected in dissolved water and injection pressure can be controlled.

4.4. Cost of Mineral Carbonation

The climate goals defined in the Paris agreement involved CCS as one of the most-effective GHG mitigation technology to limit global warming below 2°C. Yet, CCS cost is the main challenge for CCS deployment at industrial scale. CO₂ capture accounts for more than 75% of the CCS costs. New technologies are in development to lower these costs, but are not sufficient to lower the cost of electricity (COE). Recently, studies reported that if CCS is included in the global solution of climate mitigation, the overall cost is lowered for about 30%. This means, without CCS more costly methods are needed to reduce the targeted atmospheric CO₂ concentration. Many methods have been developed to control the COE when CCS is implemented as part of a power plant. A compliance option is to produce power by burning natural gas in combined cycle power plant. This option allows emitting lower amount of CO₂ and takes advantage in the low cost of natural gas. For coal fired power plants more options can be considered to reduce emissions. A First option is the capture about 50 - 75% of the gas stream and to vent the remaining CO₂ or to build plant that emit limited amount of CO₂ annually (Fowler *et al.*, 2012). These options might increase the COE costs to 13% when EOR is planned and to 19% if no EOR is considered. Note that the capture method using organic absorbents or solvents, has significant influence on the capture cost. To overcome these limitations, Gunnarsson *et al.*, 2018 proposed an upscaling of CCS technology that lowers substantially the CCS costs. The cost estimates is based on the success of the rapid carbon and sulphur mineralization into basalts rocks at the Carbfix pilots (Matter *et al.*, 2016; Gunnarsson *et al.*, 2018; Snoebjörnsdóttir *et al.*, 2020), where CO₂-H₂S gas mixture was simultaneously captured and co-injected. The approach consisted of an integrated process that water was used to dissolve the gas mixture (from Helishedi geothermal power plant), and then directly inject the gas charged water into basalt at deeper reservoirs. The interaction between condensate water and the gas mixture forms water-soluble gas captured in single step. As no gas separation was required, the capture cost was estimated to US \$21.3/ton. The considerable part of that cost results from the gas-water pressurizing at 6 bar and 9 bars within the scrubber and the amount of water to be used. The studies report that 25

tons of water are required to solubilise 1 ton of CO₂ (Snoebjörnsdóttir et al., 2020), with the advantage of rapid solubility trapping (Fig8a).

The global on-site CCS cost was estimated to US \$24.8 (including capture, transport and injection). An additional cost was introduced when new injection well is drilled, leveling the global CCS cost to 42 US\$. These estimates are significantly lower compared to the conventional CCS cost when pure and dry CO₂ is captured (38 to 140 US\$; Global CCS Institute, 2011; Rubin et al., 2015; Gunnarsson *et al.*, 2018). The capture and storage approach developed at Helisheidi present substantial cost advantages and can be applied to another potential injection sites if presents similar rocks and fluid properties. Such properties include high CO₂ concentration in the gas mixture, water availability and Mg-Ca-Fe rich rock having high permeability and porosity.

5. Conclusion and Perspectives

Mineral carbonation is accepted as a complementary alternative to conventional CO₂ storage, in the goals of reducing the atmospheric CO₂ concentration. Thus, the field of mineral sequestration is rapidly growing into many routes. Ex situ mineral carbonation is suitable for small-medium scale if the available feedstocks (e.g. mafic and ultramafic rocks and industrial alkaline residues) are located close to the CO₂ emitters. The advantages of using industrial wastes are the landscape environment preservation and the avoided costs of mining and transporting. Using ex-situ mineral carbonation at large scale, requires the design of new plants equipped with the appropriate CCS infrastructures.

In situ carbonation of mafic and ultramafic rocks has the benefits to overcome most of the *ex-situ* mineral carbonation issues. This includes large storage capacity and the *in situ* thermodynamic conditions. In this respect, the reservoir controls the energy and the kinetics conditions involved in the reaction rates that prevent the use of external energy. However, most of the experimental data claimed that optimal temperature for Mg, Ca, Fe-rich silicates carbonation is about 185°C and 16 MPa. This means CO₂ is preferably injected in high geothermal gradient sites or the or preheated and injected at high flow rate. This method has the inconvenient, to be unproductive and therefore affect the CO₂ mineral sequestration effectiveness. However, even at normal

geothermal gradient site (Wallula test site), injected CO₂ was in supercritical state (injection depth ≈ 880 m), and rapid carbonation evidence was proved from core samples [ankerite, Ca(Fe,Mg, Mn)(CO₃)₂ and calcite] and isotopic analysis. Similar rapid carbonation (after two years injection since the injection stop) has been geochemically monitored in shallow and deep basalt lavas storage reservoirs at CarbFix. The results of both field works challenges the common view that carbonation occurs only under higher temperature and higher PCO₂.

For instance, the two tests performed at the Carbfix project dissolved gas mixture with water before injection into basaltic lava located respectively at 500 m and 2000 m where pore water pH ranged from 8.0 - 9.6 and temperature of 18 to 33°C for Carbfix1 and 266 to 277°C for Carbfix2. The results indicate that over 95% of the CO₂ injected was mineralized in less than two years and H₂S fixed as pyrite. In laboratory, the conversion of hosted rock to stable carbonates was conducted using mineral suspension or crushed rock mostly in batch reactor, with chemical additive. More than 50% of the tested grains were carbonated in less than one hour. The, working procedure based on single mineral or crushed rock is representative of the ex-situ carbonation rather than in situ case, but the use of sintered samples with dynamic fluid is close to the field reality, when conducted at realistic temperature, pressure and P_{CO_2} . Few reactive-(transport) simulations in the context of mafic and ultramafic carbonation under storage conditions have been performed (Rosembaur *et al.*, 2012; Gysi, 2017; Gysi and Stefanson, 2011; Xu *et al.*, 2004; Aradóttir *et al.*, 2012; Zhang and Diapolo 2017; Moita *et al.*, 2020). Most of these studies focused on phase assemblage in equilibrium (i.e. olivine serpentinization) and kinetics aspects and few of them focused on coupled transport and reaction at reservoir scale.

In situ CO₂ mineral carbonation has been significantly studied for basalts and peridotites rocks. However, gabbro and diorites have not yet been addressed for the purpose of CO₂ mineralization, constituting a good challenge for research. To be interesting as hot-rocks, these rocks types have to be fractured enough to allow the CO₂ to be injected at reasonable pressure and enable solutes to reach fresh unreacted surface.

6. References

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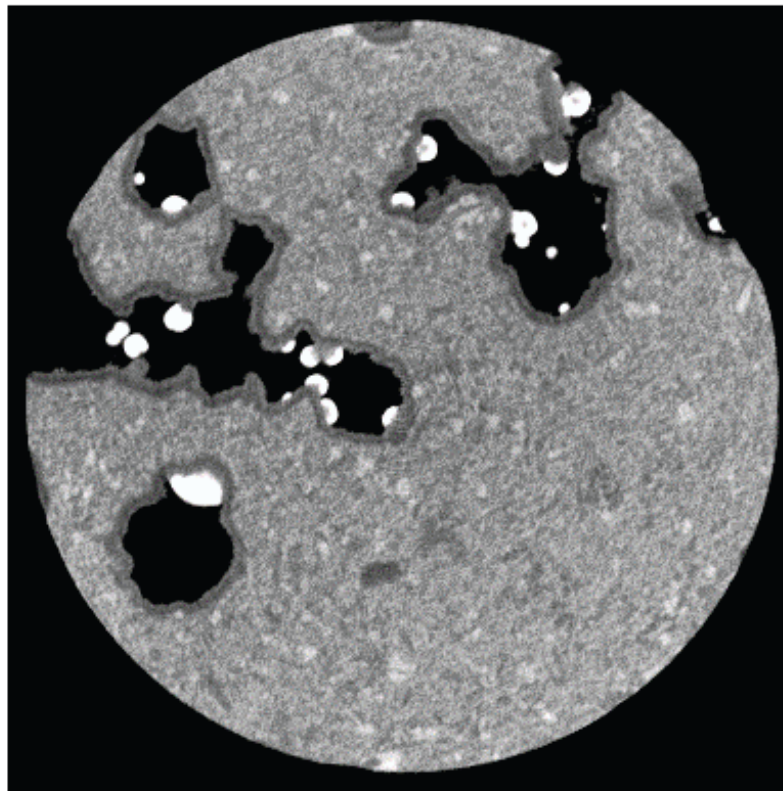
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InCarbon

Carbonatação Mineral *In Situ*

Benchmarking of CO₂ Sequestration by mineral carbonation



**XCT image from basalts rock:
Wallula test site (Mc Grail et al. 2017)**

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