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CO_2 Mineralization potential in mafic and ultramafic rocks in Central Italy

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Abstract

Reduction of CO_2 emissions is crucial for achieving sustainability goals and to do that, concrete methods of long-term carbon storage should be implemented. The most common way is geological storage, in which CO_2 is kept in underground formation to ensure that does not escape in the atmosphere on geological time scales. Among all the solutions, mineralization is the one of the most secure techniques that converts CO_2 into solid carbonate minerals. This method is particularly appropriate solution since the final product is not a buoyant liquid that must be pumped back into underground formations.

This thesis provides an in-depth investigation into the process of mineralization, its working principles, and the feasibility of its application in Central Italy. It summarizes the main chemistry (what leads to the reactions and how quickly they take place), the contribution of the water-rock interactions and the fractures, and the primary methods of conducting the process in situ. Lessons from international projects are used to set realistic expectations for reaction rates, monitoring, and containment.

It examines the environment of Central Italy where reactive mafic and ultramafic rocks exists. It discusses the impact of their mineralogy and texture on the potential storage capacity along with the role of structural and petrophysical properties in controlling injectivity and carbonate precipitation. The results of the thesis indicate that there exist both strong points, such as the large number of reactive minerals and the high-quality subsurface data, but also practical issues such as non-uniformity of fracture connectivity, high demand of water in dissolved-CO_2 approaches, geochemical spikes early in time, and the complexity of monitoring fractured media.

In the last part of this thesis, a simplified screening logic is provided which explains the connection between mineral capacity and fracture-mediated fluid access, as well as design pointers to keep

reactions off the wellbore and toward storage-beneficial volumes.

This thesis concludes that CO_2 mineralization seems to be an effective, sustainable complement to the emission reductions, and a plausible route, supported by the experience of the world community and the local experimentation, for the case of Central Italy.

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1. Introduction

The near-term climate targets require the complementary elimination of carbon dioxide and propose storage solutions since the swift decarbonisation will not be sufficient to achieve the mitigation targets ((2023)., 2023). One of the existing methods of CO2 storage is the in-situ carbon mineralisation which is the process of reacting rock minerals with injected CO_2 to form stable carbonates. This has become a crucial part of the underground geological storage. This method is thermodynamically stable, and has a less risk of leakage, compared to buoyant fluid storage. In addition, according to the actual projects, including the CarbFix experiments in Iceland, as well as laboratory and numerical analyses, is proved that even significant part of CO_2 mineralisation can be achieved within couple of years by adjusting the injection chemistry and flow parameters. However, the transition between these pilot tests to wide-scale implementation needs a clearer insight into how reservoir structure particularly the geometry and connectivity of the fracture system influence the parameters of storage such as the injectivity, reactive efficiency, and the long-term stability of storage [1].

Mafic and ultramafic lithologies containing olivine and pyroxene-bearing rocks, basaltic glass, and serpentinite have Mg-, Ca-, and Fe-bearing silicates that can be dissolved in CO_2 -bearing fluids. This reaction causes release of divalent cations that are in turn precipitated as carbonates of magnesites, calcite and siderites. By this, the trapping of solubility is quickly improved, and long-term trapping in the mineral is attained as stable carbonate phases are developed (Boschi, C., Dini, A., & Dallai, L, 2013). The efficiency of mineralisation in general is not just determined by the thermodynamic potential, but also by the reaction kinetics and transport. At low pH, the dissolution of silicate is increased and may be able to temporarily mobilise trace metal, though at higher pH, when buffering reactions occur, secondary carbonate phases form and immobilise dissolved species. The distribution of these reactions is important in space where the deposition of carbonates in large fractures assists in maintaining storage of carbon without closing the system but the accumulation of carbonates in small apertures or throats of pores can greatly decrease permeability. Consequently, the use of coupled thermo-hydro-mechanical-chemical models that represent the feedback between the dissolution, precipitation and stress development is essential to understand the behaviour of systems.

In this context, a natural analogue and a research opportunity is represented by the large mafic and ultramafic terranes of the Ligurian-Piedmont ophiolites. Such geological units, in Central Italy, may be of interest, in which screenings of reactive rock distributions have identified Tuscany and Liguria as key areas to be a priority in carbon capture and mineral storage. Such tests insist that site selection must consider not only the mineralogy but also other parameters such as porosity, permeability degree, degree of serpentinization, reservoir geometry, and degree of connectivity between faults. It is important to note that ophiolitic exposures between Siena, Pisa, and Grosseto possess favourable traits of mineralisation (Boschi, C., Dini, A., & Dallai, L, 2013). As an illustration, the Montecastelli Ophiolite Complex is rich in naturally carbonated, brucite-bearing serpentinites, which document carbonation at low temperatures, which would be a useful model in engineered processes within the same conditions.

Analogues of such coupled fluid-rock processes also can be observed in natural analogues in Tuscany under field based structural conditions. A single case example is the Malentrata system of the Larderello geothermal system whereby serpentinites are clearly altered by silicification and formation of prolific magnesite-dolomite veins. Field observations and petrographic analysis indicate that two-stage evolution is necessary that must include: a period of pervasive disintegration and enrichment of silica that increase or maintaine rock permeability and a period of open-space carbonate precipitation that is in the process of occurrence principally along fractures and pore spaces. These aspects, when compared with the fault-controlled structure of the area, point out an important exploration parameter in Central Italy, where the previous ultramafic rocks are most prospective where the flow through fractures can be sustained, and where precipitation is channeled to areas favourable with increased storage capacities. Nonetheless, it also seems that, at the initial stages of interaction between water, rock, and injected CO_2, the interactions should be described with caution to predict the short-term mobilization of solutes.

Considering all of the above and according to the international research, mineral carbonation offers a geochemically stable form of carbon storage, whereas regional data of Central Tuscany demonstrate the possibilities and the challenges specific to that location for employing such methods. Based on this, this thesis combines global and regional data , as well as screening and environmental design of the mineralization potential of Central Italy.

2. CO_2 Mineralization: Principles and Framework

Geological storage of carbon dioxide uses several physical and chemical techniques to keep injected carbon in place for long time periods. These processes are also known as the trapping mechanisms. There are 4 known trapping methods including: stratigraphic trapping, residual trapping, mineral trapping and solubility trapping. Each mechanism acts in a different way for storing carbon in underground formations (Nisbet, Kelemen, & Oelkers, 2024). As an example, in case of stratigraphic trapping mechanism, the effective trapping of CO_2 depends on layers of rock which block the upward movement of CO_2, while in residual and solubility trapping carbon is mixing with water in the reservoir. However, since these mechanisms keep CO_2 in a gas, supercritical, or dissolved form, there is still some possibility of leaks or movement over time.

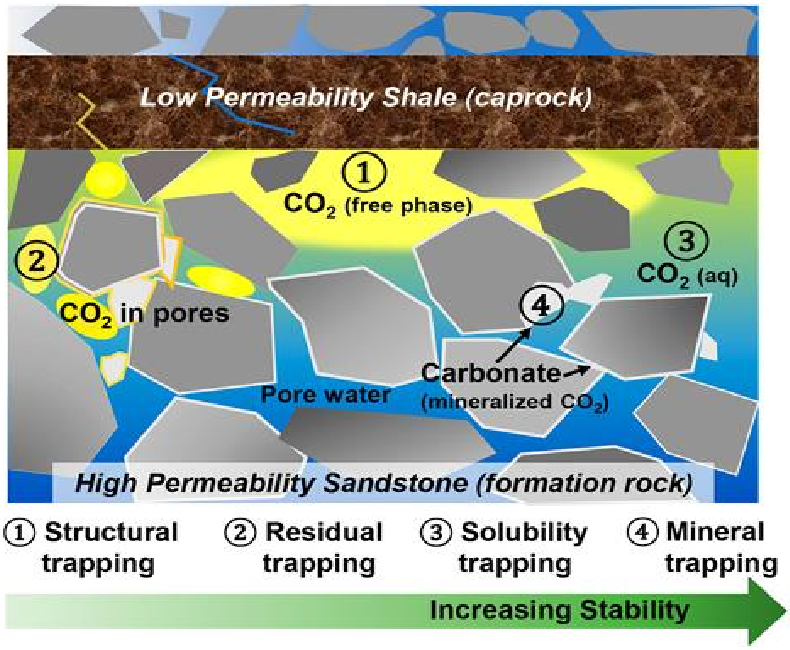

Figure 1 CO_2 trapping mechanisms (Neil, Matter, Oelkers, & Snæbjörnsdóttir, 2024)

In comparison to other trapping mechanisms, one of the most durable is mineral trapping where carbon is stored in a more secured way. The process can be explained by the reaction of injected CO_2 with host-rock minerals. As a result of these reactions solid carbonate phases are formed. The minerals such as magnesite, calcite, and siderite become non-buoyant and stable in thermodynamics point of view once they are formed. The formation of these minerals significantly reduces the risk of upward migration or in other words, leakage. Consequently, mineral trapping is a permanent sequestration pathway that does not depend on the reservoir characteristics and it is not controlled by reservoir pressure or by monitoring of caprock integrity (Ye, Li, Wang, & Zhao, 2025).

2.1 CO_2 Storage in Mafic and Ultramafic Rocks

One of the most used mineralization technique so-called in-situ mineral carbonation particularly in mafic and ultramafic rocks is a promising technique for CO_2 immobilization over time. What makes these lithologies even more suitable for better mineralization are their composition which involves silicate minerals. The composition of these silicate minerals involves divalent cations including olivine, pyroxene, plagioclase, serpentine and basaltic glass. As the interaction occurs between these minerals and CO_2-rich fluids, these minerals undergo dissolution-precipitation processes followed by the formation of the stable carbonate minerals as magnesite ($MgCO_3$), calcite ($CaCO_3$), and siderite ($FeCO_3$). Thus, permanent transformation of the injected CO_2 into solid mineral phases occur, which generates a long-lasting and secure storage channel (Boschi, Dini, Dallai, & Nisi, Natural carbonation of brucite-bearing serpentinites: Implications for in-situ CO_2 mineralization, 2020). Accordingly, figure 2 demonstrates the global distribution of ultramafic and mafic rock types and multiscale approaches for mineralisation phase of CO_2.

The composition of ultramafic rocks, particularly peridotite and serpentinite are rich in magnesium oxide (MgO), which often surpass 40% weight of total formation. In addition to that, having high Mg concentration provide these rocks with the highest theoretical CO_2 storage capacity per unit mass among typical lithologies.

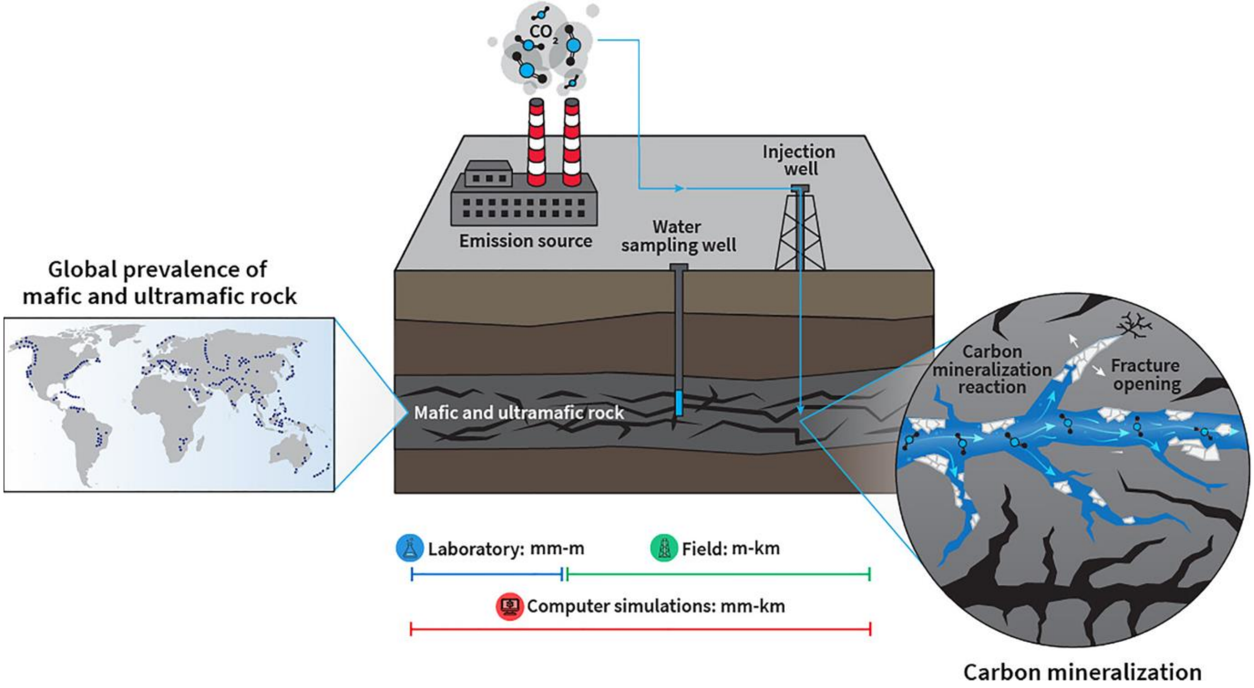

Figure 2 Illustration of carbon mineralization in mafic and ultramafic rocks (Nisbet, Kelemen, & Oelkers, 2024)

In contrast, mafic rocks including basalt and gabbro, have less divalent cations. However, these bodies have strong characteristics for CO_2 storage in terms of increased permeability and injectivity, particularly within jointed or vesicular flow zones. In addition, table 1 compares the reservoir features of basaltic and ultramafic host lithologies related to CO_2 mineralization.

Overall, characteristics such as high chemical reactivity and fracture-controlled fluid circulation of both mafic and ultramafic rocks make them suitable for permanent geological carbon storage through mineral trapping (Chen, Zhang, & Xu, 2024).

Table 1 Hydrological-structural controls on in-situ CO_2 mineralization by host lithology (Giammar, Wang, & Peters, 2023)

Host lithology	Reservoir architecture	Hydrologic behaviour & injectivity	Design focus for mineralization	Principal risk	Useful diagnostics
Basalts	Inter-flow porosity; vesicles; pervasive joint/columnar fracture networks	High injectivity, large fluid-rock contact area → rapid mineralization potential	Dissolved CO_2 injection; control rate/residence time to distribute reaction down-gradient	Near-well carbonate clogging if oversaturation occurs	Injectivity trend vs. time; pH-DIC profiles; tracer tests; porosity/sonic logs
Ultramafics	Low matrix porosity, flow primarily in natural/engineered fractures	High intrinsic reactivity but low fracture-controlled flow; base injectivity often limited	Fracture access management, controlled rates to avoid proximal precipitation	Permeability loss from near-well carbonate precipitation, fracture self-sealing	Pressure-transient analysis

2.2 Methods and Technological Approaches

This part of the thesis deals with the engineering aspects of mineralization in order to accelerate the process and also compares their strengths, limitations and monitoring requirements. Approaches of mineralization can be divided into in-situ methods where reaction takes place within reactive formations and ex-situ methods which describes the interaction of CO_2 with mined or industrial alkaline solids.

2.2.1 In-situ Mineralization Strategies

In-situ mineralization which is the main focus of this thesis can be explained by injecting CO_2 (preferably dissolved) into fractured, Ca-Mg-bearing host rocks (basalt, peridotite/serpentinite) so that carbonates precipitate within the reservoir. The most mature example is the dissolved-CO_2 approach (CarbFix): CO_2 is first dissolved into water/brine at the surface and injected as a single-phase fluid into permeable basalts (Figure 3) (Nisbet, Kelemen, & Oelkers, 2024).

A fluid which is acidified can primarily enhance the dissolution of silicates which lead to the increase in down-gradient pH and causes the precipitation of calcite (±Mg-carbonates). In its turn precipitated calcite itself traps the carbon dioxide for longer time periods. Field tracers and mass balances showed that there was 95 % mineralization in less than 2 years, thus, making it a benchmark of permanence in in-situ techniques.

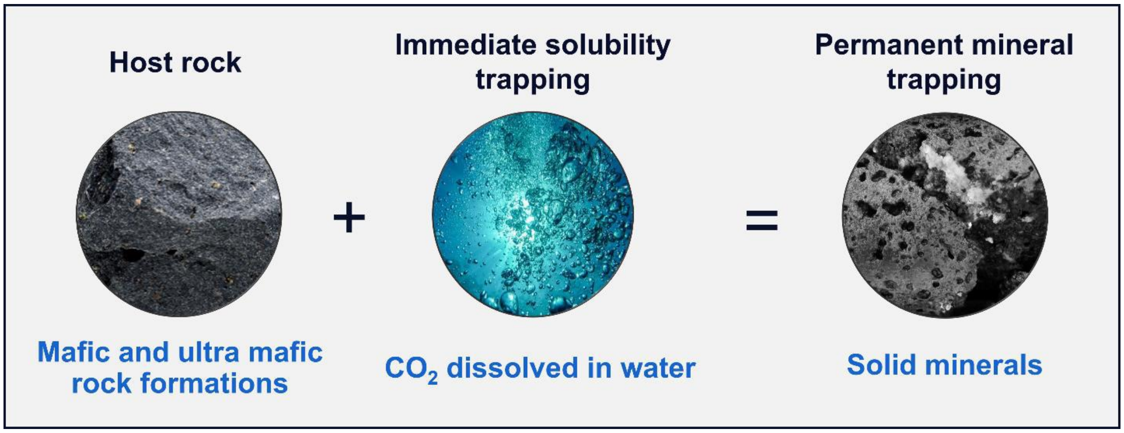

Figure 3 Simplified diagram of in-situ carbon mineralization (Ye, Li, Wang, & Zhao, 2025)

Co-injection variants can lower freshwater requirement and provide co-sequestration of impurities. For example, when CO_2 was co-injected with H_2S in basaltic formation, an identical trapping of sulfur as sulfides and carbon as carbonates was observed with operational geochemistry being monitored using observation wells.

Recirculation/doublet schemes (push-pull or injector-producer) enhances the overall efficiency by increasing the time for residence and sweep efficiency along with the variations of the moderate transient pressure. This pressure basically helps in verification with the repeat geochemistry and pressure-transient analysis. increase residence time and sweep efficiency while moderating pressure transients. CarbFix injections is one of the examples of this method which is successfully applied (Snæbjörnsdóttir, S. Ó., Sigfússon, B., Marieni, C., Goldberg, D., Gíslason, S. R., & Matter, J. M., 2020).

Design notes. The dissolved-CO_2 pathway trades water for optimal contact and non-buoyant behavior. Pressure windows vary from tens to 100 bar which helps to maintain solubility while avoiding fracture reactivation. It is crucial to choose correct injectivity technique for preventing precipitation away from the wellbore.

2.2.2 Ex-situ Mineralization

Direct aqueous carbonation (slurries). Finely divided alkaline solids-steel/cement slags, kiln dusts, Mg-rich tailings, ultramafic fines are brought into contact with CO_2 in fluidized slurries at moderate $p\mathrm{CO}_2$and temperature (typically 1-20 bar, 25-90 °C). Large conversions on hours-days time scales are obtained in process control. Products which are carbonated can be redeemed as aggregates or supplementary cementitious materials (SCMs), improving unit economics.

Mine tailings and near-site carbonation. Mg-silicate tailings (Ni/Cr/PGM operations) offer large and low-cost feedstocks for near-site field carbonation. Strategic evaluations by IEA GHG highlight techno-economic potential, logistics, and maturity across tailings types; ambient operations trade speed for scale, while mild activation reducing the kinetic deficit (Boschi, Dini, Dallai, & Nisi, Natural carbonation of brucite-bearing serpentinites: Implications for in-situ CO_2 mineralization, 2020).

Indirect (two-step) routes. A lixiviation step (acids, salts, or chelants) extracts Ca/Mg into solution; controlled pH swing and CO_2 dosing then precipitate carbonates with tunable polymorphs (e.g., aragonite/magnesite). Indirect routes counter passivation and can co-recover metals from wastes, at the cost of reagent handling and recycle loops.

Trade-offs. Ex-situ techniques is characterized by close control of the processes and product revenue, but with the penalties in terms of energy / material handling along with the permission and siting for solid flows.

2.3 Geochemical Principles of Mineral Carbonation

As described in above sections mineral carbonation is a chemical interaction between CO_2-bearing fluids and silicate minerals which contain divalent cations. As a result of such interaction, conversion of CO_2 into solid carbonate phases occur. The process described by 2 interconnected steps, which are:

- Dissolution of silicate minerals in acidic CO_2-charged water, which liberates cations such as Mg^{2+}, Ca^{2+}, and Fe^{2+}
- Precipitation of carbonate minerals once alkalinity increases and carbonate ions become available.

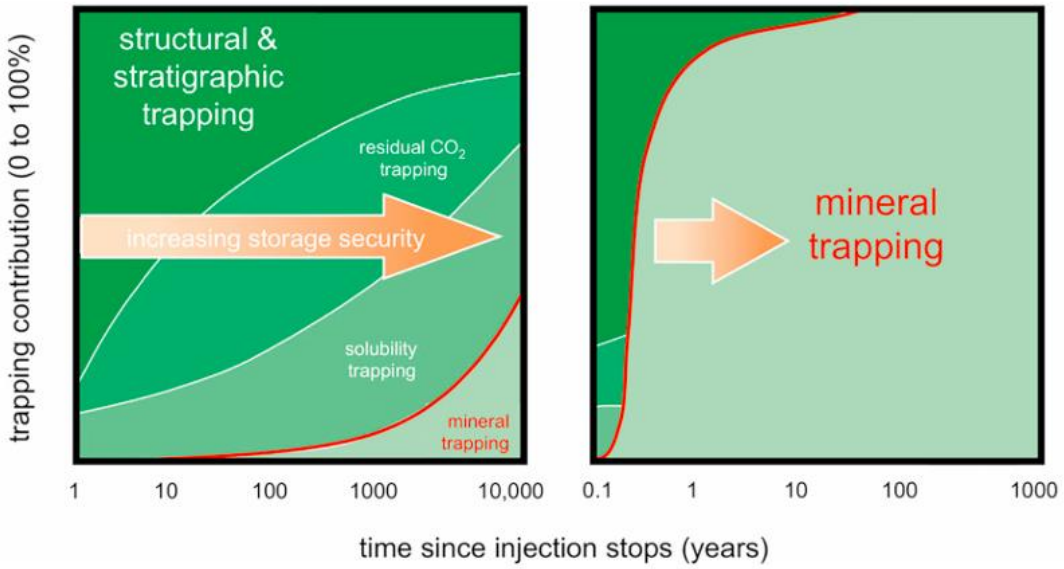

Figure 4 Evolution of the extent of CO2 trapping mechanisms with time (Nisbet, Kelemen, & Oelkers, 2024)

In reservoir settings, geochemical processes work in tandem with physical trapping mechanisms such as structural, stratigraphic, and capillary retention (Matter J. M., 2009). Over time, storage security shifts from physical confinement to chemical fixation. This occurs through CO_2 dissolution and mineral trapping by carbonate precipitation. Figure 4 depicts this trend, emphasising the growing stability of geochemical trapping modes as time since injection stops.

2.3.1 Reaction Pathways and Thermodynamic Basis

The interactions during the carbon mineralization can be explained by dissolution of carbon dioxide in water where, because of this reaction, carbonic acid is generated (H_2CO_3). In the next steps generated carbonic acid itself breaks down into bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) species. During silicate mineral dissolution, aqueous carbon species interact with divalent cations, resulting in solid carbonate minerals such as calcite ($CaCO_3$), magnesite ($MgCO_3$) as described in Figure 5, and siderite ($FeCO_3$) (Sanna, Uibu, Caramanna, Kuusik, & Maroto-Valer, 2024).

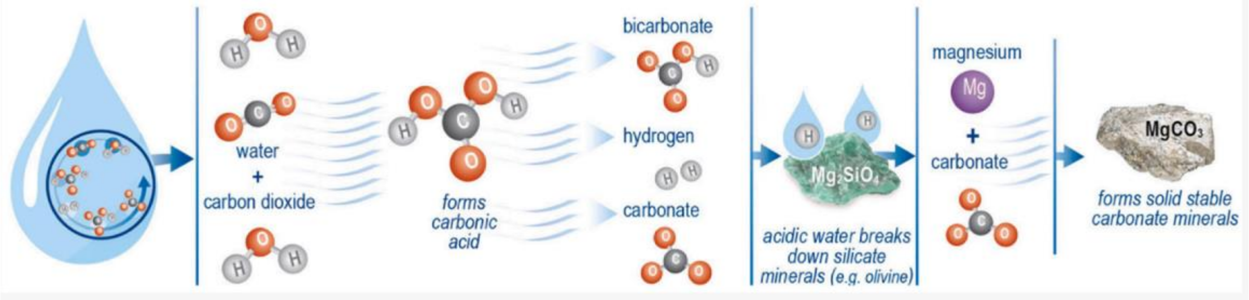

Figure 5 Schematic illustration of CO_2 mineralization in Basalt (Chen, Zhang, & Xu, 2024)

The resultant reactions are exothermic and significantly thermodynamically favoured, implying that once created, carbonate phases are extremely stable under geological conditions. Mineral carbonation is effective for long-term and permanent CO_2 storage because of its high stability (Neil, Matter, Oelkers, & Snæbjörnsdóttir, 2024).

Representative reactions include:

Forsterite (Mg_2SiO_4):

$$Mg2SiO4 + 2\,CO2 \rightarrow 2\,MgCO3 + SiO2$$

Serpentine ($Mg_3Si_2O_5(OH)_4$):

$$Mg3Si2O5(OH)4 + 3\,CO2 \;\rightarrow\; 3\,MgCO3 + 2\,SiO2 + 2\,H2O$$

Brucite ($Mg(OH)_2$):

$$Mg(OH)2 + CO2 \;\rightarrow\; MgCO3 + H2O$$

Ultramafic lithologies are particularly attractive because of their high MgO content, while mafic rocks also contribute Ca^{2+} and Mg^{2+} from plagioclase, pyroxenes, and basaltic glass.

2.3.2 Kinetic Controls and Mineral Reactivity

Although the thermodynamics of carbonation strongly favour the creation of stable carbonate minerals, reaction kinetics determine both the rate and overall mineralisation efficiency. The geochemical environment changes gradually during CO_2 injection. CO_2 enriched water has a low pH (about 3-5) after injection, causing reactive silicate minerals to dissolve quickly.

Table 2 Relative reactivity of key phases relevant to CO_2 mineralization (Chen, Zhang, & Xu, 2024)

Phase	*Qualitative reactivity*	*Design relevant note*
Basaltic glass	Very high	Rapid Ca-Mg release; consider near-well carbonate occlusion risk
Olivine	High	Efficient Mg source for magnesite; requires fracture-mediated access
Sarpentine	Moderate-low	Often benefits from thermal/chemical activation and longer residence time
Brucite	Very-high	Near-instant carbonation; manage to avoid proximal self-sealing

As the process develops, protons are consumed and carbonate species build, progressively raising the pH and providing circumstances conducive to carbonate precipitation. Reactivity of minerals changes systematically with composition and structure, as seen in Table 2 above (Chen, Zhang, & Xu, 2024).

Temperature is critical factor for increasing the dissolution rates of silicate minerals, whereas higher reactive surface area provides faster total reaction development. These kinetic correlations explain why some engineered injection strategies are frequently used to accelerate mineral carbonation. These strategies may include changing the acidity of the injected fluid or gradually increasing its temperature. Apart from that, by optimising these parameters CO_2-rock interaction rate also increases, which results more faster conversion of dissolved carbon into stable mineral phases (Management, 2025).

2.3.3 Hydrological and Structural Coupling

The chemical composition of the host minerals influences the level of carbonation along with the efficiency of fluid circulation within the reservoir. Mineralization requires CO_2-rich fluids to contact with a high reactive surface area, which is determined by the porosity, permeability, and fracture network of the corresponding rock. Mafic formations, such as basalt, typically include both interflow porosity and fracture permeability, allowing for fluid access. However, ultramafic rocks rely on tectonically produced fractures to provide these paths (Boschi, Dini, & Dallai, Low-temperature in situ carbonation of ultramafic rocks at Montecastelli, Tuscany: Mineralogical evidence and CO_2 uptake potential, 2017).

Carbonate precipitation can have different effects on reservoir behaviour. On one hand, it contributes favourably to CO_2 sequestration by filling open cracks and blank areas with stable carbonate minerals, essentially trapping carbon in solid form. On the other side, precipitation within pore throats or restricted fracture apertures may reduce permeability and block fluid movement. These reactive feedbacks between chemical and mechanical processes emphasize how important is using coupled thermo-hydro-mechanical-chemical (THMC) models that account for mineral dissolution, carbonate precipitation, stress redistribution, and fracture evolution (Jun, Y.S.; Zhang, L.; Min, Y.; Li, Q., 2017).

2.4 Thermodynamics and Reaction Stoichiometry

2.4.1 Carbonate stability and aqueous speciation

As discussed before in mineral carbonation, the CO_2-containing liquids come in contact with silicate minerals in order to produce stable carbonate minerals. In water-based systems, carbonic acid is formed due to the chemistry between the dissolved CO_2 and water which lead to the formation carbonic acid (H_2CO_3) and its conjugate bases, bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}). However, the presence of carbonate minerals depends on carbonate ions (CO_3^{2-}) and those metal cations (Mg^{2+}, Ca^{2+}, Fe^{2+}). It is most favourable condition once the pH has recovered after initial dissolution which is driven by protons with the fugacity of CO_2 (fCO_2 or pCO_2) remaining sufficiently high to retain the dissolved inorganic carbon (DIC) while the fugacity of CO_2 (fCO_2 or pCO_2) remains high enough to sustain dissolved inorganic carbon (DIC) (Figure 6) (Xu, 2014).

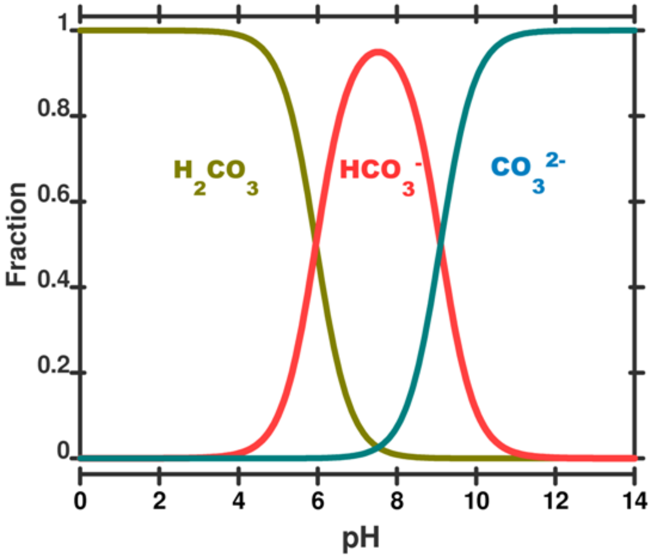

Figure 6 Carbonate system speciation vs pH (Xu, 2014)

Formations of minerals such as calcite, magnesite, and siderite from their corresponding silicates has a negative free-energy change at surface pressure-temperature environments. These phases of carbonate are thermodynamically stable and can stay over long geological periods and it is permanent and energy-efficient CO_2 sink.

Two practical consequences follow:

- The saturation of carbonates rises along the fluid flow paths when the protons are absorbed in process of silicate weathering. This pH rebound improves the carbonate precipitation at a distance from the injection point, which is consistent with field data in basaltic reservoirs.

- Higher fCO_2 shifts competition between secondary mineral phases, favouring carbonate formation over clays or zeolites. The objective of the injection techniques is keeping the CO_2 dissolved while maintaining carbonate supersaturation in the reactive zone.

2.4.2 Thermodynamic parameters

Calcite or magnesite production from silicate minerals is exothermic ($\Delta H < 0$) and spontaneous ($\Delta G < 0$) under normal crustal settings. Crystallization of carbonate phases ensures long-term

CO_2 storage. Injecting CO_2-water solutions improves the conversion route by allowing for solubility trapping to occur before mineral trapping. However, this strategy necessitates large amounts of water, which can become a practical limitation. In contrast, adding supercritical CO_2 reduces water demand but leads in slower mineralization rates (Kelemen P. B., 2008).

The ideal reservoir design balances CO_2 fugacity (fCO_2), pH evolution, and temperature to enhance carbonation efficiency. Elevated temperatures increase reaction kinetics but decrease CO_2 solubility in the fluid phase. This creates a trade-off between reaction rate and carbon availability in the reservoir system.

2.5 Factors Influencing the Efficiency of Mineral Carbonation

In the preceding sections, we outlined the fundamental principles of CO_2 mineralization and various approaches to implementing this process. We now examine the key variables and interdependencies that influence how efficiently mineral carbonation proceeds in mafic and ultramafic rocks. These factors include properties of the solid reactants and of the reacting fluid as well as external conditions and process parameters. Understanding each of these factors is crucial for designing effective carbon storage strategies and for interpreting differences between laboratory kinetics and field performance. In particular, mafic volcanic rocks and ultramafic rocks can exhibit widely varying carbonation rates depending on their texture and geochemical environment (Kelemen, Matter, & Streit, Reaction pathways and energetics of peridotite carbonation for CO_2 storage, 2023).

2.5.1 Mineral Surface Area and Grain Size

Surface Area: The degree of interaction area between reactive minerals and CO_2-bearing fluids is a crucial factor in determining how fast mineralization process going. In case of finer-grained materials, reaction kinetics improved due to having a much higher surface area-to-volume ratio. In practice, pulverized mine tailings or crushed basalts have a substantially higher reactive surface area than complete rock cores and so carbonate much faster under equivalent conditions (Kelemen P. B., 2008). Based on the previous research it has been clarified that that reducing the size of particle of silicate minerals improves CO_2 uptake.

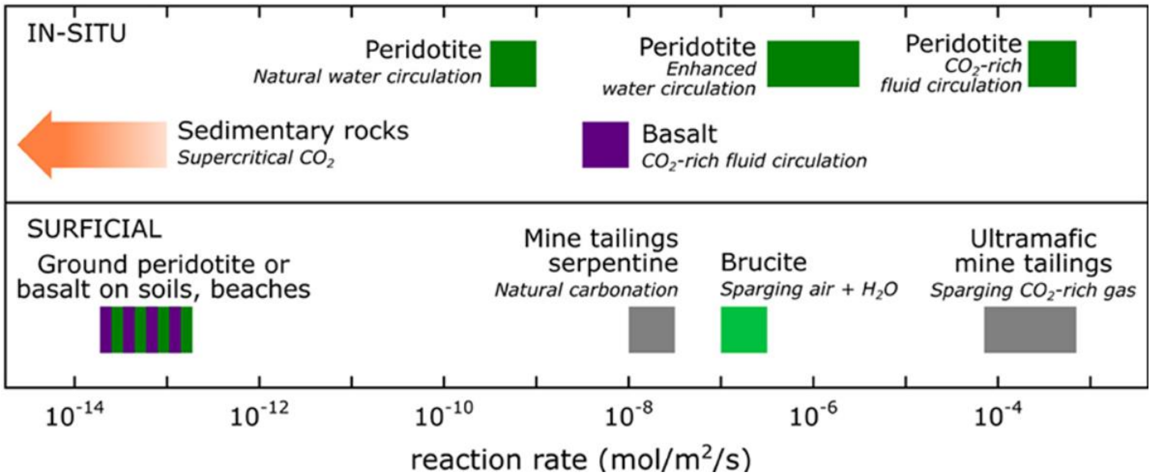

Figure 7 Reaction rate in-situ and surficial mineralization of CO2 using mine tailings or rocks as the source of alkalinity (Kelemen P. B., 2008)

Based on the research have been made, figure 7 shows the reaction rates (in units of mol · m^{-2} · s^{-1}) for various mineral or rock-based pathways for the sequestration (mineralization) of CO_2 which is separated into in-situ (within the subsurface) and surficial (near-surface) settings.

Grain Size in Situ: In the context of in situ carbonation, the grain size of the rock is the factor which depends on the geology, but it has an influence on reactivity (Figure 8).

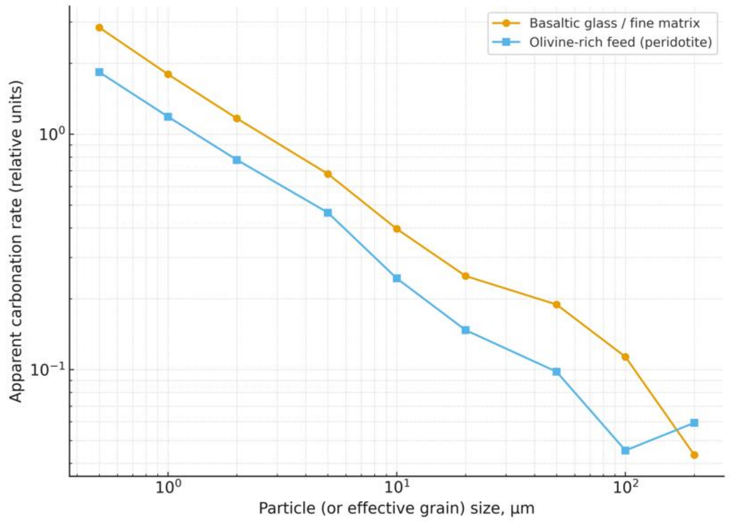

Figure 8 Affected grain size on apparent CO_2 mineralization rate (Sanna, Uibu, Caramanna, Kuusik, & Maroto-Valer, 2024)

Due to a fine-grained composition of basalts, they typically consist of a fine-grained groundmass that can dissolve relatively fast in compared to other formations. In terms of the composition of periodites, they may have coarser grains of olivine and pyroxene.

2.5.2 Temperature and pressure

Temperature controls. In general, increasing the Temperature makes reaction faster for both dissolution and carbonate formation as shown in Figure 9. Calcite nucleates efficiently at near-ambient conditions, whereas magnesite is kinetically inhibited at low T due to the strong hydration of Mg^{2+}; elevated T (or catalytic chemistry) is typically required for rapid Mg-carbonate formation. Because CO_2 solubility in water decreases slightly with T, designs aim for an intermediate range that preserves a high dissolved CO_2 inventory while accelerating kinetics.

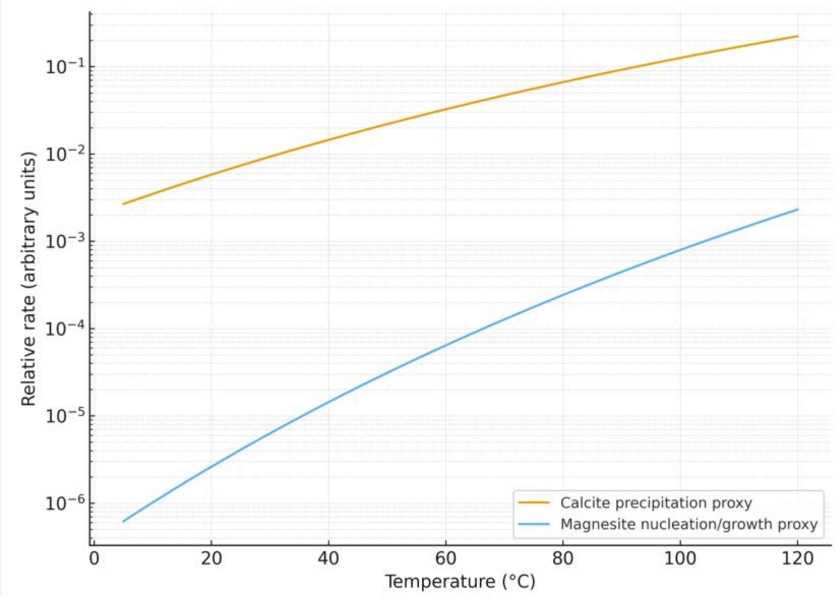

Figure 9 Temperature dependence of carbonate formation kinetics (Sanna, Uibu, Caramanna, Kuusik, & Maroto-Valer, 2024)

Figure 9 illustrates these contrasting responses: the calcite proxy rises steadily from low T; the magnesite proxy is flatter at low T and steepens at higher T, reflecting its larger effective activation barrier (Ye, Li, Wang, & Zhao, 2025).

Pressure controls. At fixed T, increasing pCO_2 raises dissolved CO_2 and carbonic-acid activity, enhancing silicate dissolution and pushing fluids toward carbonate supersaturation (Chen, Zhang, & Xu, 2024). In practice, two operational regimes are relevant:

Dissolved-CO_2 injection (0.5-3 MPa): CO_2 remains fully in solution, maximizing fluid-rock contact and enabling rapid down-gradient carbonation without a buoyant gas phase.
Supercritical CO_2 (greater than 7.38 MPa): water use is lower, but mineralization relies on subsequent dissolution into formation waters; near-well precipitation or reduced contact area can slow net conversion if not managed.

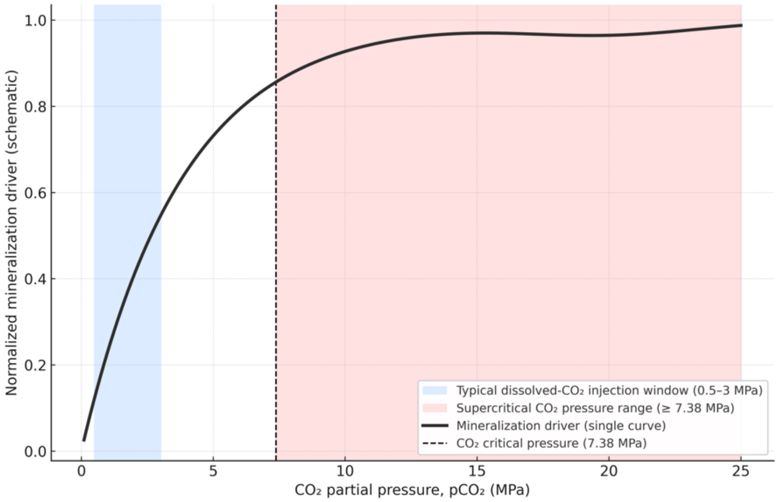

Figure 10 Schematic illustration of effect of CO_2 partial pressure on a normalized “mineralization driver” ((2023)., 2023)

It has been described in figure 10 that saturating increase with pCO_2. The light-blue band marks the dissolved-CO_2 window; the dashed line marks the CO_2 critical pressure (7.38 MPa); the light-rose band indicates supercritical pressures (Ye, Li, Wang, & Zhao, 2025).

2.5.3 Mineralogy and Crystallinity of Host Rock

Mineralogical composition and crystallinity of the host rock actually determine the efficiency of the carbonation process, as each mineral reacts with CO_2 at a different rate. The most frequently used rocks in storing CO_2 are mafic and ultramafic rocks, which are primarily enriched with reactive silicates, including calcium, magnesium, and iron, which are capable of trapping CO_2 in carbonates. However not all silicates are identical, some are much more reactive. Olivine ([$(Mg,Fe)_2SiO_4$] and pyroxenes ([$(Mg,Fe,Ca)SiO_3$ family]) are the major constituents of these rocks, feldspar plagioclase (a Ca/Na aluminosilicate) is the secondary element, and there is also secondary material such as brucite [$Mg(OH)_2$] or serpentine [$Mg_3Si_2O_5(OH)_4$] in ultramafics.

Concisely, mineralogy determines the rate as well as quantity of carbonation that occurs. The dream candidates are those rocks that are full of divalent cation silicates (olivine, brucite, Ca plagioclase, or glass alterations), whereas rocks with more inert minerals such as quartz or clay alterations are less efficient. By the descending order of the reactivity of common silicates with CO 2 (largest to smallest) you have: brucite > olivine > basaltic glass. Ca -feldspar > pyroxene > serpentine > Mg clays. Thus, when the target formation is put in the right combination, carbonation is likely to sink at an alarming rate as the environment is not harsh.

2.5.4 Implications for reservoir design

Injection mode. Water-intensive, dropping in dissolved-CO_2 accelerates mineralization. The supercritical CO_2 reduces water consumption, but tends to slow the rate of carbonate formation and relies more on dissolution and flow.

Water-rock interactions & monitoring. At the low-pH stages Al, Fe and trace metals detach to solution. The target carbonates may be completed by secondary phases such as Fe-carbonates, clays/zeolites as the pH rebounds

3. International Case Studies of CO_2 Mineralization

In this chapter, international and real practical applications of CO_2 mineralization in both mafic and ultramafic rock formations have been discussed.

3.1 CarbFix Iceland: Reactive Injection in Basalt

The worldwide projects provide us with an excellent perspective of various geological contexts, technology solutions, and lessons to learn in transforming the trapped CO_2 into consistent carbonates which you can store up long-term. The checkouts of projects in Iceland, Oman and the US provide insight into how different types of rocks, design options, research objectives advance our understanding of carbon mineralization around the world. In the next sections also advantage and limitations of each project has been described (Snæbjörnsdóttir, S. Ó., Sigfússon, B., Marieni, C., Goldberg, D., Gíslason, S. R., & Matter, J. M., 2020).

3.1.1 Site and Geological Setting

The injection point is in southwest Iceland in Hellisheidi geothermal field located within the Hengill central volcano complex as illustrated in Figure 11. It is at the overlap of the Western Rift Zone and the Reykjanes volcanic zone. The bottom layers are geologically dominated by olivine-tholeiite basalts (approximately 50% SiO_2). The primary phenocrysts are olivine, plagioclase, and clinopyroxene in addition to certain Fe-Ti oxides (Snæbjörnsdóttir, 2020).

The formation is characterized by extensive hydrothermal changes. Near the surface formations of zeolites and smectite dominates while in deeper zones in which temperature is over 200°C there are assemblages of chlorites, epidotes and quartz. Calcite is distributed quiet extensively in the zones where temperature is less than 300°C. This formation contains an approximate of 1.6 x 10^9 tonnes of naturally stored CO_2.

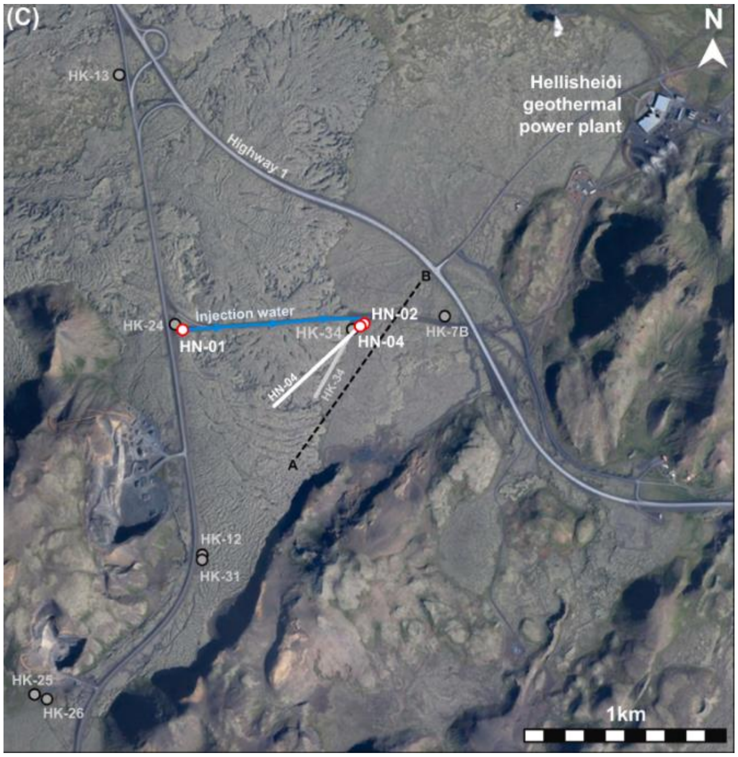

Figure 11 Satellite image of CarbFix project (Snæbjörnsdóttir, S. Ó., Sigfússon, B., Marieni, C., Goldberg, D., Gíslason, S. R., & Matter, J. M., 2020)

The primary injection well, HN16, which is in the Husmuli reinjection zone on the north side of the volcano, the distance from the power plant is around 1.5 km from south with the elevation of 270 m. It is a directional well, extending down to approximately 2,200 m, cased to approximately 660m, and injected into fractured basalt between 800 and 2,200m. It also has three monitoring wells: HE-31, HE-48, and HE-44 with approximate distance of 1-1.5 km at approximately 570 m above the ground. The geothermal field consists of over 60 production wells and 17 reinjection wells.

3.1.2 Process Design and Operational Framework

In contrast to the supercritical CO_2 injection method, CarbFix uses a fully dissolved method which is preventing the phenomenon of gas buoyancy and plume migration. At the wellhead, the fluid pH initially is around of 5.4 but decreases to 4.7 due to the increased rate of injection.

The CarbFix injection system is shown more detailed in Figure 12. The CO_2-H_2S gas mixture is delivered by pipeline and co-injected with water into well HN-02, where gas dissolves at depths of around 350-500 m. The design also depicts the arrangement of monitoring and injection wells (HN-01, HN-02, HK-34, and HN-04), as well as the reactive flow paths and stratigraphic layering that allow for in-situ carbonation in the basaltic aquifer.

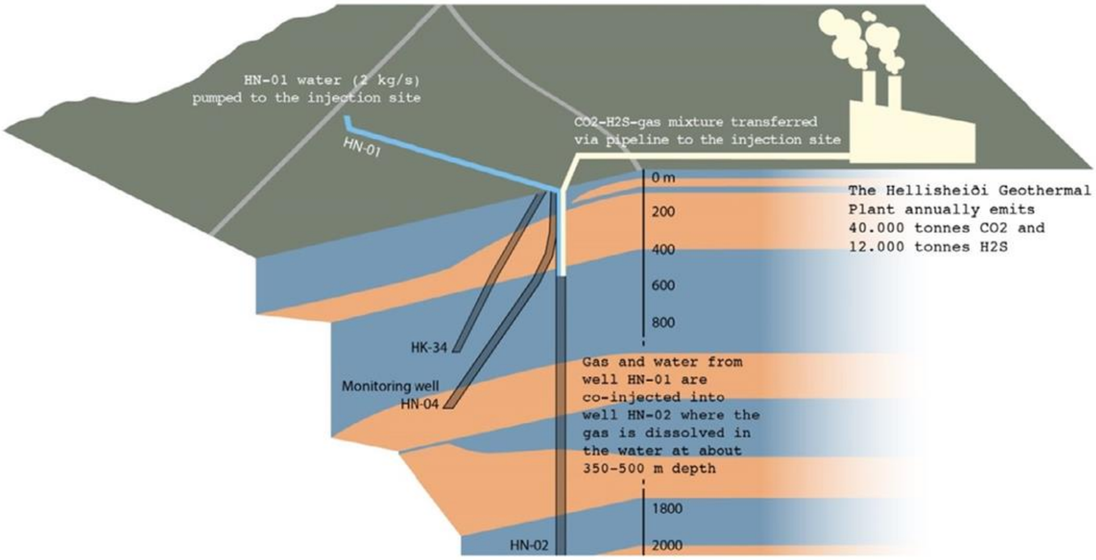

Figure 12 Infrastructure and geological cross-section of the CarbFix injection site (Snæbjörnsdóttir, S. Ó., Sigfússon, B., Marieni, C., Goldberg, D., Gíslason, S. R., & Matter, J. M., 2020)

In addition to that, the dissolved inorganic carbon concentrations increase up to 50 mM. The injection pressure at the surface is around 9 bar whereas the pressure at the bottom of the hole is approximately 60 bar. The project added approximately 23,200 t of CO_2 approximately a third of the CO_2 emissions of the plan (Snæbjörnsdóttir, S. Ó., Sigfússon, B., Marieni, C., Goldberg, D., Gíslason, S. R., & Matter, J. M., 2020).

Once the low-pH injected, dissolution of basaltic glass starts and releasing of ions involving Ca^{2+}, Mg^{2+}, and Fe^{2+} occurs. Such ions are then washed off as carbonate and sulfide minerals as the pH increases along the flow path. This reaction front maintains the porosity in and around the wellbore intact, in addition to the reservoir in further spots. Geochemical models illustrate that equilibrium in terms of injection fluid changes to a state of being supersaturated in minerals, i.e. calcite and sulfides. This is done with using the infrastructure including compressors, scrubbers, as well as booster pumps. The water with gas is transported to the point of injection by a pipeline, which is connected to an additional steel tubing to maintain the pressure and regulate the mixing of the fluids deep within the borehole. The open-hole part below approximately 700 m allows the fluid to have a direct contact with reactive basalt.

3.1.3 Results and Long-Term Storage Performance

The pilot studies were successful since the 95% of CO_2 was converted into solid carbonate within just two years. The below plots involve monitoring the dissolved inorganic carbon and the radiocarbon in the monitoring wells prior to the CO_2 injection and after the injection (Figure 13). The grey (observed) values are falling behind the red (predicted) as time passes. In other words, the variance in the expected and measured values reflects the quick process of dissolved CO_2 into solid carbonate minerals throughout in-situ mineralization (Snæbjörnsdóttir, 2020).

CarbFix2 project is active from 2014-2017 and it was recorded that about half of the CO_2 injected mineralized in a matter of months and about 60% mineralized in 4-9 months once the rate of injection increased.

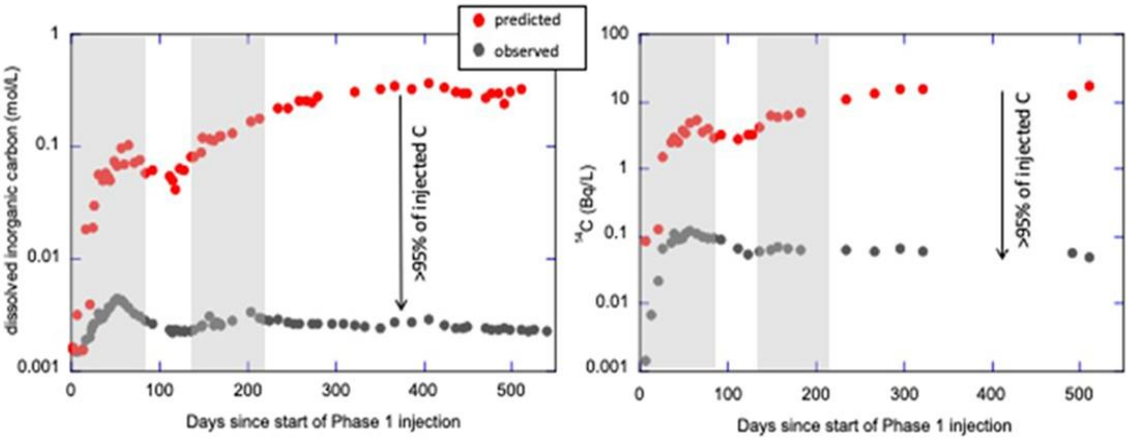

Figure 13 Dissolved Inorganic Carbon Concentration and Isotopic Evidence of CO_2 Mineralization at the CarbFix1 Site (Snæbjörnsdóttir, 2020)

By 2025, CarbFix had permanently mineralized approximately 100,000 tonnes of CO_2. The Icelandic government by that time issued the first EU-compliant onshore storage license of up to 100,000 tonnes CO_2 annually. The geothermal plant and its DAC units are to be covered by a long-term objective of storing 3.2 million tonnes of CO_2 in 30 years. Observation during the past couple of years has ensured that injectivity remains constant and no accumulation of pressure is observed. Core samples and geochemical tracers indicate that carbonate (calcite, dolomite, siderite) and sulfide minerals were formed in-situ and not only at the wellbore. The presence of radiocarbon-labelled calcite in well parts is also evidence that the carbonate is firmly seated. When fixed, the CO_2 becomes geochemically stable over geologic times, and it is virtually impossible to be re-mobilized, even during the occurrence of seismic conditions.

3.1.4 Advantages, Limitations and Lessons Learned

Advantages: There are several advantages of CarbFix's in-situ basalt approach which involves:

- Fast and permanent CO_2 mineralization with the minimized risk of leakage
- No need to caprock formation to block the CO_2 upward movement
- Large potential of deployment due to the global availability of basalts

Limitations:

- High demand to water (25 tonnes of water per ton of stored CO_2)
- Conditions of sufficient permeability and hydraulic connectivity
- Potential clogging of pore-space due to the increased solid volume in process of precipitation

Lessons Learned: The CarbFix experience provides that basalt carbonation is viable in considering both technical and economical terms. The crucial lessons involve the significance of the comprehensive characterisation of the reservoir and strict regulation of geochemical and mechanical parameters. Among these technical parameters injection design is crucial to manage porosity. Operationally, CarbFix showed that injecting into the same well for years is feasible. Economically, co-injection process makes gas capture process much simpler and reduces costs. Economic assessments show that costs are less than $30 per tonne of stored CO_2, which is quite competitive in economic point of view.

Considering all, CarbFix project has thus established a scalable model for rapid and verifiable CO_2 mineralization, combining high injectivity, favorable kinetics, and permanent trapping. This operation has been successful and therefore has affected other pilot studies in the world as well as offering a conceptual framework on CO_2 storage in other basaltic provinces.

3.2 Samail Ophiolite: Natural and Enhanced Carbonation

3.2.1 Geological and Geochemical Background

The Samail Ophiolite in Oman composes one of the largest and best-preserved pieces of the obducted oceanic lithosphere on earth . It also has a full Penrose-type stratigraphy of sedimentary cover, pillow basalts, layered gabbros and ultramafic rocks including harzburgite and dunite. Serpentinized peridotite is found in the lower part of the ophiolite which is characterized by its high content in magnesium and being very reactive to the CO_2-bearing fluid. Figure 14 illustrates the geological extent of the Samail Ophiolite and the principal field sites involving Wadi Dimah, Al Qaryatayn, and Listvenite.

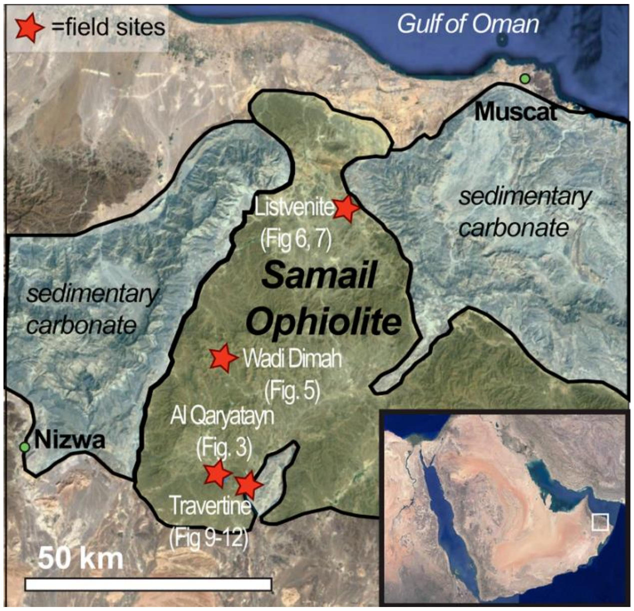

Figure 14 Field locations within the Samail Ophiolite, Oman (Giammar, Wang, & Peters, 2023)

The widely distributed natural carbonation can be observed in the area. The serpentinized peridotite is usually cut by carbonate veins, which are usually white magnesite or calcite, and these veins are evidence of long-term passive mineralization of CO_2. The listvenites, the Mg - carbonates and quartz rocks, formed during the obduction process when the CO_2 rich fluids percolated through the peridotite are particularly notable. These natural counterparts prove the possibility of the formation to hold large amounts of carbon. In addition, research estimates that already the Samail Ophiolites hold 1-2 gigatonnes of naturally mineralized CO_2.

Based on the geology it has been determined that there is a high capacity for even more CO_2 storage. It has been also indicated that rock mass is a kilometers-wide mass that is below the surface, but it is well fractured and faulted. This also shows that mineralization was not complete in the test area of the single well and there is a decreasing trend of reactivity as the distance increase from the borehole. To take into all consideration, in order to increase the extend of reactivity it is the crucial to consider factors such as fracture connectivity, fluid delivery, and a continuous injection.

3.2.2 Experimental and Field-Based Carbonation Studies

The pilot project in Oman also followed the concept of CarbFix and used a push-pull injection method. This technique implied the introduction of CO_2-rich water into shallow fractures which was approximately 300 m deep into peridotite, and 45 days later, the mixture was removed and chemically and isotopically analyzed. The injected solution was completely in the dissolved state, so there was no exsolution and gas-free accumulation. Acidic CO_2 solution was introduced to the alkaline groundwater which caused the promotion of olivine/brucite dissolution and release of Mg^{2+} and Ca^{2+} ions (Figure 15). Following that, these ions then precipitated as calcite-dolomite complexes on the fracture boundaries and pores (Sanna, Uibu, Caramanna, Kuusik, & Maroto-Valer, 2024).

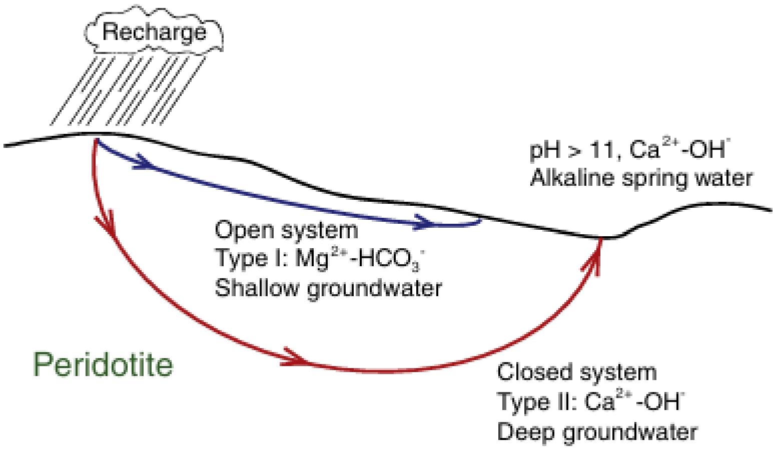

Figure 15 Flow path schematic illustration of groundwater evolution in the peridotite aquifers of the Samail Ophiolite (Matter J. M., 2009)

The mineralization was also exceptionally high and based on the analyses made it was established that approximately 88 % of the injected CO_2 had been transformed into solid carbonates in six weeks.

It can be seen from Figure 16 that geophysical borehole and core logs from the Oman Drilling Project reveal a pervasive fracture and vein network. Data collected from borehole BA1B includes a lithostratigraphy log (OmanDP Multi-Borehole Observatory), wireline borehole resistivity log, and downhole plots of discrete sample measurements of porosity and vein types (25 meters average) as well as a summary of the estimated hydraulic conductivity of discrete intervals based on pumping tests. The data shows that the permeability decreases with depth, relating to a decrease in alteration and crack/vein density.

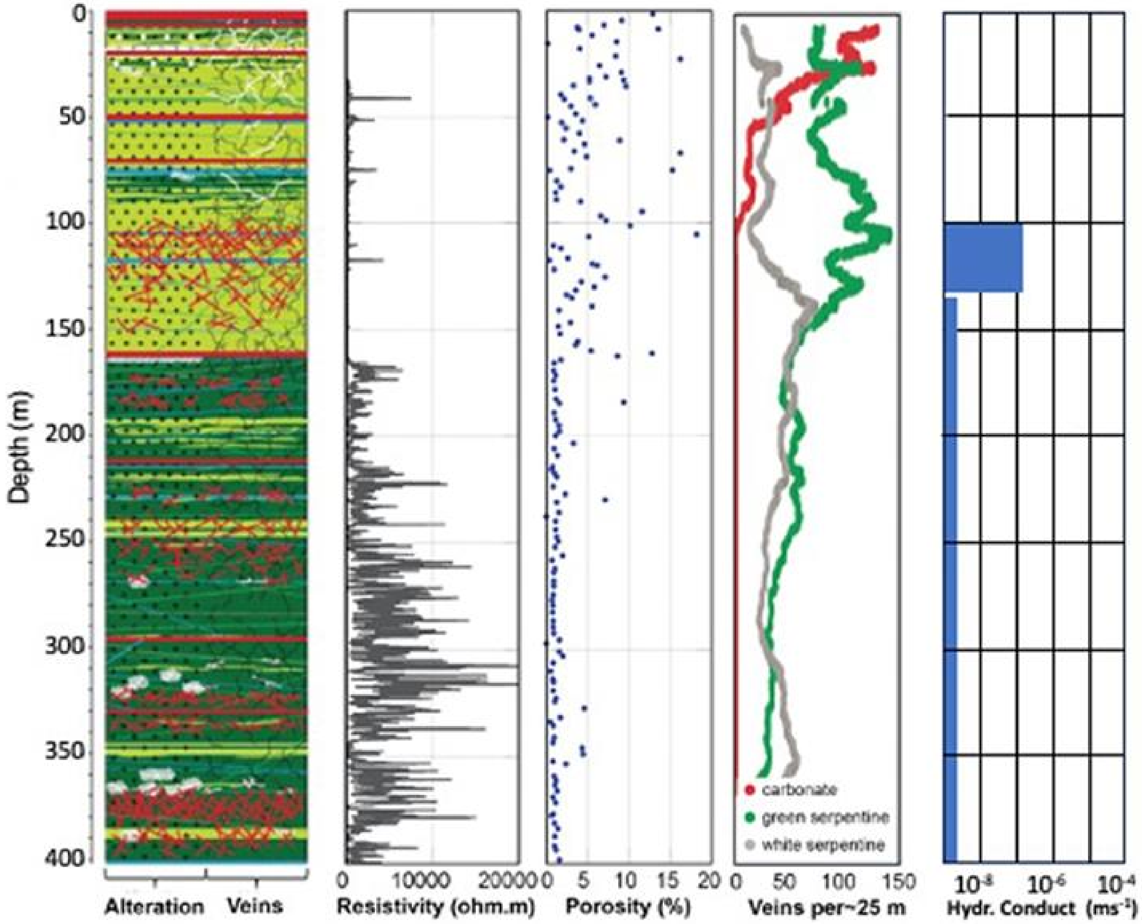

Figure 16 Geophysical borehole and core logs (Matter, Stute, Snæbjörnsdóttir, & al., 2016)

Apart from that, dissolution of silicate was indicated by the rise in the concentrations of Mg and Si, whereas the decrease in Ca, alkalinity, and dissolved inorganic carbon indicated the formation of carbonate. Even carbon isotope shifts also demonstrated that lighter carbon was more favored in the new minerals. These findings demonstrated that, the ultramafic peridotites can trap CO_2 at an extremely fast rate in ambient conditions (Boschi, Dini, Dallai, & Nisi, Natural carbonation of brucite-bearing serpentinites: Implications for in-situ CO_2 mineralization, 2020).

3.2.3 Advantages, Limitations, and Technological Insights

Advantages:

- Availability of site to store CO_2 permanently
- Production of stable carbonates because of exothermic reaction of peridotite with CO_2
- Quiet high storage potential of CO_2

Limitations:

- Very low primary porosity and permeability of unaltered peridotite
- In addition to the fracturing pressurization or stimulation may be necessary during injection
- Increased volume of solid which may lead to the blockage of flow paths, thus affecting injectivity
- Reduced reaction rate with time

Lessons Learned: According to the field tests conducted in Oman, the most important consideration is that tectonic fracturing is the key to the circulation of fluids and mineralisation. Introduction of dissolved CO_2 inhibits the gas breakthrough and enhances the reaction rate. Together with the geothermal operations or direct air capture would be useful to increase economic viability. The success of the pilot in Oman provides us with a ground in view of larger mineralisation operation in ultramafic terrains in some parts of the world. The Samail Ophiolite still remains one of the most prospective natural laboratories to investigate and develop CO_2 mineralisation in ultramafic rock and its experiences can be utilised in similar geological outcrops like in the Alps, California and ophiolite belts in southern Europe.

3.3 Wallula Project (USA)

3.3.1 Site and Geological Framework

The Wallula Basalt Pilot Project is located in southeast Washington and is essentially the first successful example of CO_2 mineralization in continental flood basalts. It belongs to Columbia River Basalt Group (CRBG), a vast Miocene lava area whereby basalt layers are piled one over the other. Initially, the Grande Ronde Formation is chosen to inject the CO_2 in due to flow interiors and break zones whereby the gas enters and is then chemically trapped.

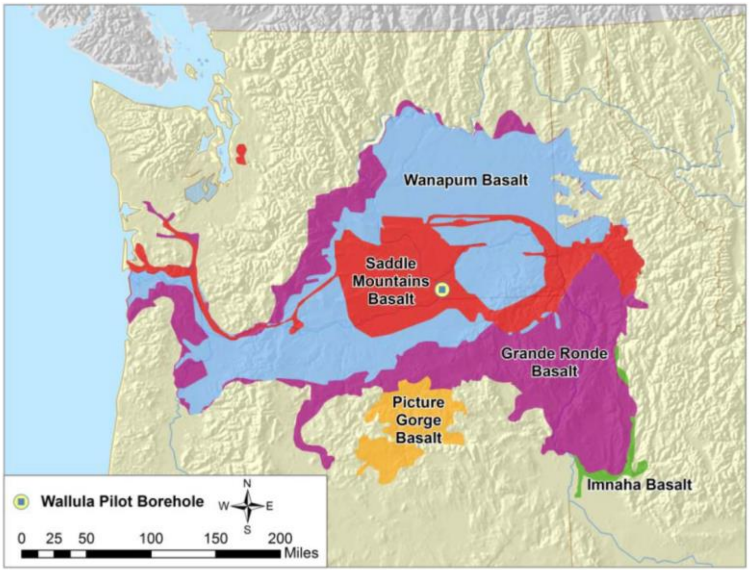

Figure 17 Surface distribution of the Columbia River Basalt Group basalts and location of the Wallula Pilot well (B. P. McGrail, 2014)

The injection well was perforated inside a stack of these layers of basalt, SCFT2 and SCFT1 interflow areas are targeted. These are permeable, vesicle-filled layers, which allow the CO_2 to pass through and react in depth from 830 to 890 meters. The formation density log and design schematics were used to visualize the casing of the well and the process of getting the supercritical CO_2 past. Such a section of the rock is an ideal one in which vesicles can be injected with ease and thick, sealed flow interiors can serve as natural barriers.

A larger picture is demonstrated in a regional map (Figure 17). The Wallula Pilot Borehole is located at the Saddle Mountains Basalt. The CRBG actually encompasses large portions of WA, OR and ID, and such groups as Wanapum, Grande Ronde, Picture Gorge, and Imnaha Basalts all appear to be promising locations of long-term CO_2 storage.

3.3.2 CO_2 Injection Strategies and Monitoring Results

In 2013, nearly 1000 metric tonnes of supercritical CO_2 injected in the SCFT1 and SCFT2 flow-top areas, and this has been done through employing directional borehole which measures approximately 890 m in depth. It has been adopted that depth as it is the depth that provides us with porosity on the tops and then have a thick cap of basalt above that can keep the CO_2. The well infrastructure had solidified casing up to some 765 meters and an open hole of 12.25 inches up to the bottom of the injection zone. Apart from that, wireline logs have been used and thus, hydrological data received to plot the levels and determine which ones were the best to inject (Figure 18).

Figure 19 depicts a cross-sectional diagram of the spreading of the various layers of basalt around the well, and indicates the two-layer barrier of the solid minerals and the physical rock. Observation of covered baseline and post-injection hydrology, core sampling and geochemistry.

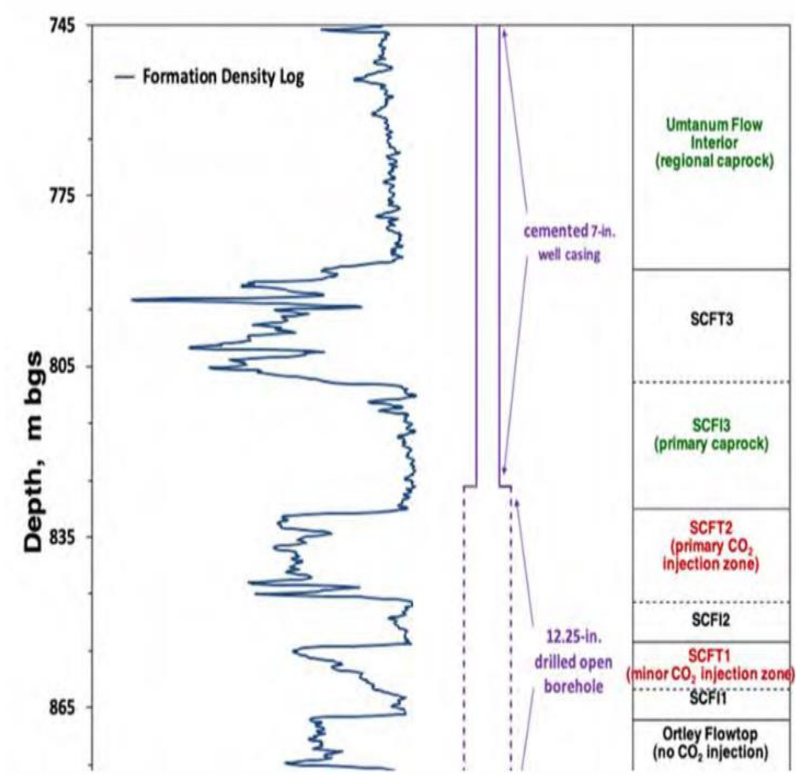

Figure 18 CRB stratigraphy and injection interval based on formation density and wireline log data (B. P. McGrail, 2014)

The cores two years later contained fine carbonate minerals, mainly ankerite and siderite, sticking to the vesicles and microfractures in those basalt areas. The tests relied on isotopic and petrographic tests proved that the carbonates were formed out of the injected CO_2, i.e. in-situ mineralization had been successful (Figure 19).

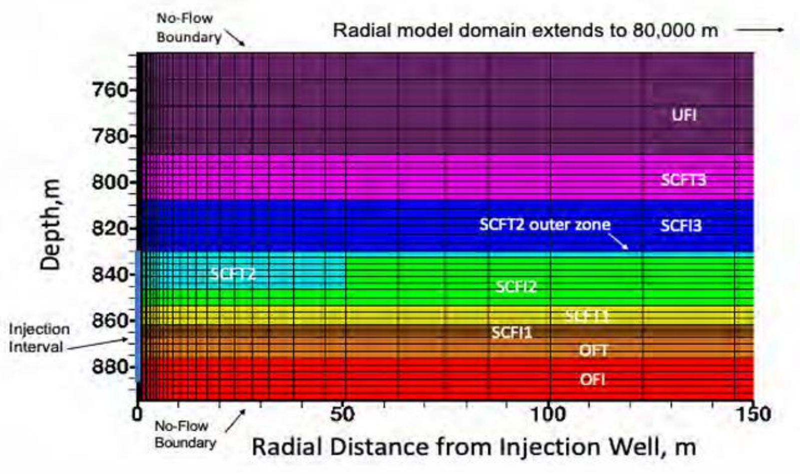

Figure 19 Radial Model Domain and Injection Interval (Snæbjörnsdóttir, 2020)

3.3.3 Mineralization Efficiency and Storage Stability

Shallow soil gas samples collected around the injection well for over a year post-injection show (Figure 20) a variable CO_2 concentration trend on an annual cycle driven by soil temperature. These values were unaffected by the injection and are related to microbial activity in the sawdust fill used to prepare the site. Discrete soil-gas PFT measurements near the well-head showed background levels of about 25 ppqv before injection. Unfortunately, during introduction of the tracer, pipe leaks and an accidental spill of the liquid PFT on the ground near the well head caused a 4,000-fold increase in soil-gas PFT levels. Over time, these levels have decreased at a quasi-first order rate (B. P. McGrail, 2014).

Further releases of tracers must have come as a result of inevitable venting of CO_2 during later insertion/extraction of the downhole fluid sampling tool. The surface release had affected the viability of the tracer in detection of leaks in the site despite the fact that the peak in concentration of the tracer in the soil gases is dissipating with time.

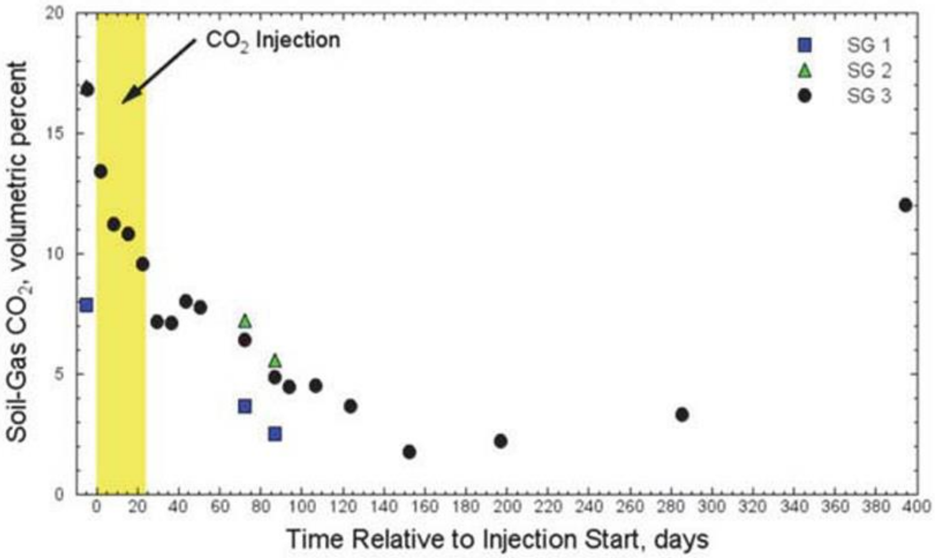

Figure 20 Soil gas monitoring data from locations around the injection well (B. P. McGrail, 2014)

It is found that some 60-65 % of the CO_2 was entraped in solid carbonate minerals within two years after the injection. The cover of the carbonate nodules occupied a proportion of 4% of the pore space in the SCFT2 layer by the cores. Hydrology and chemical models show that the mineralization was mainly taking place during the reaction of the supercritical CO_2 with the silicates of Ca, Mg and Fe in basalt. This would be excellent because it would trap the CO_2 and limit its circulation, which would increase the long-term security. It is worth mentioning that all of the CO_2 that emerged through the injection point has not been detected therefore the geologic system is performing as expected. Despite the fact that the permeability was slightly decreased with the precipitation of carbonate, injectivity was good during the period of the operations. It is because the CRBG possesses a large number of reactive sites that are easy to scale up, through the cautious characterization of every single site. The Wallula pilot proved that flood basalts have the capability of converting CO_2 to stable carbonate minerals, based on the fact that they can be storage forms. This accelerates the transformation of the temporary storing of CO_2 into a permanent immobilisation stage, reducing the risks of having mobile CO_2. The approach has the possibility to maximize the CO_2 storage over sedimentary basins due to the abundance of basaltic in the world (Boschi, Dini, Dallai, & Nisi, Natural carbonation of brucite-bearing serpentinites: Implications for in-situ CO_2 mineralization, 2020).

However, the project revealed significant technological obstacles. While the rate of mineralisation was encouraging, the injection volume (1000 tonnes) was insufficient for climate-scale implementation. The variable permeability of basaltic strata, particularly differences between flow tops and interflows, needs detailed site characterisation. Furthermore, carbonate precipitation might gradually reduce the main rock parameter permeability and may potentially restrict injectivity during extended operations. Scaling up injection while maintaining fluid flow remains a significant engineering challenge (Chen, Zhang, & Xu, 2024).

3.3.4 Advantages and Limitations

Advantages:

- High mineralization potential over short time periods
- Large volume CRBG with reactive chemistry
- The lower risk of leakage due to existence of natural caprock and basalt layers
- High safety due the storage of CO_2 in a solid state

Limitations:

- Very heterogenous basalt flow tops which makes it crucial to have close subsurface information
- Risk of plugging of pores due to the precipitation; need to manage flow and pressure
- Potential of decrease in reaction pace due to the dry CO_2 injection which can be prevented by adding water

4. Assessment of CO_2 Mineralization Potential in Italy

Due to the diversified geology, Italy is a good candidate in the CO_2 mineralization since the country has large mafic and ultramafic formations owing to ophiolites as well as volcanic provinces. According to the recent surveys, it was revealed that there is an enormous storage potential in many Italian regions. Most of these regions, such as Toscana, Liguria, Lazio among others, have large areas of suitable formations of mineral carbonation. This chapter is dedicated to central Italy and specifically Tuscany and Lazio considering where there is availability for CO_2 mineralization in mafic/ultramafic rocks, what is the potential of mineralization and what are the relevant projects or studies regarding the CO_2 mineralization in the discussed areas.

4.1 Geological Context and Distribution of Mafic and Ultramafic Formations

The geology of central Italy includes evidence of the Jurassic Tethyan oceanic crustal material which was pushed against the Apennine chain during the Alpine-Apennine orogenesis. In Tuscany, the remnants in the form of ophiolitic complexes are made up of ultramafic and mafic rocks. They are known as Ligurian Units in the Northern Apennines, which are traditionally divided into Internal and External Ligurian Units (Figure 21) (Boschi, Dini, Dallai, & Nisi, Natural carbonation of brucite-bearing serpentinites: Implications for in-situ CO_2 mineralization, 2020).

The Internal Ligurian sequences have a basement of oceanic serpentinized peridotites, including some gabbros and basalts which is then covered by Jurassic-Camretaceous deep-sea sediments. The External Ligurian units, on the other hand, consist predominantly of sedimentary (calcareous-marly turbidites) material with less ophiolite inclusions. The greatest exposures of ultramafic in Tuscany are of the Internal Ligurian realm and are grouped together in the middle of the country between Pisa and Siena with Grosseto and the Tyrrhenian coast (Brogi, Liotta, Dini, & Rielli, 2023).

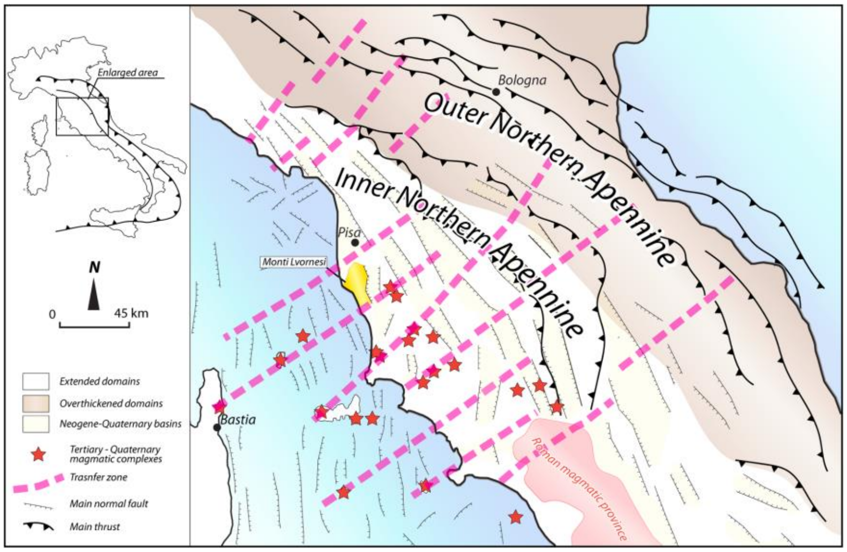

Figure 21 Tectonic sketch of the central-northern Apennine orogen (Nisbet, Kelemen, & Oelkers, 2024)

These volcano-sedimentary complexes cannot be called ophiolites, but their basaltic sequences (including lava flows and pyroclastics) contain calcium- and magnesium-bearing minerals similar to those employed in the CarbFix basalt carbonation strategy. It is also notable that the Vulsini/Vico region (around Lake Bolsana) has large deposits of basaltic tuff and flows, with a few ultramafic mantle xenoliths being reported in the local tuffs (e.g. clinopyroxeneamphibole peridotite nodules). Such mafic structures in Lazio also offer more sites to be mineralized in situ to generate CO_2, but with geological conditions other than the ultramafic peridotites of Tuscany (Management, 2025).

The geological map of Tuscany (Figure 22) shows the spatial distribution of ophiolitic rocks, magnesite deposits, and associated ore occurrences throughout the region. The map illustrates that ophiolitic units, depicted in green, are mostly concentrated between the Larderello, Micciano, and Malentrata area-regions, which contain multiple natural carbonation sites.

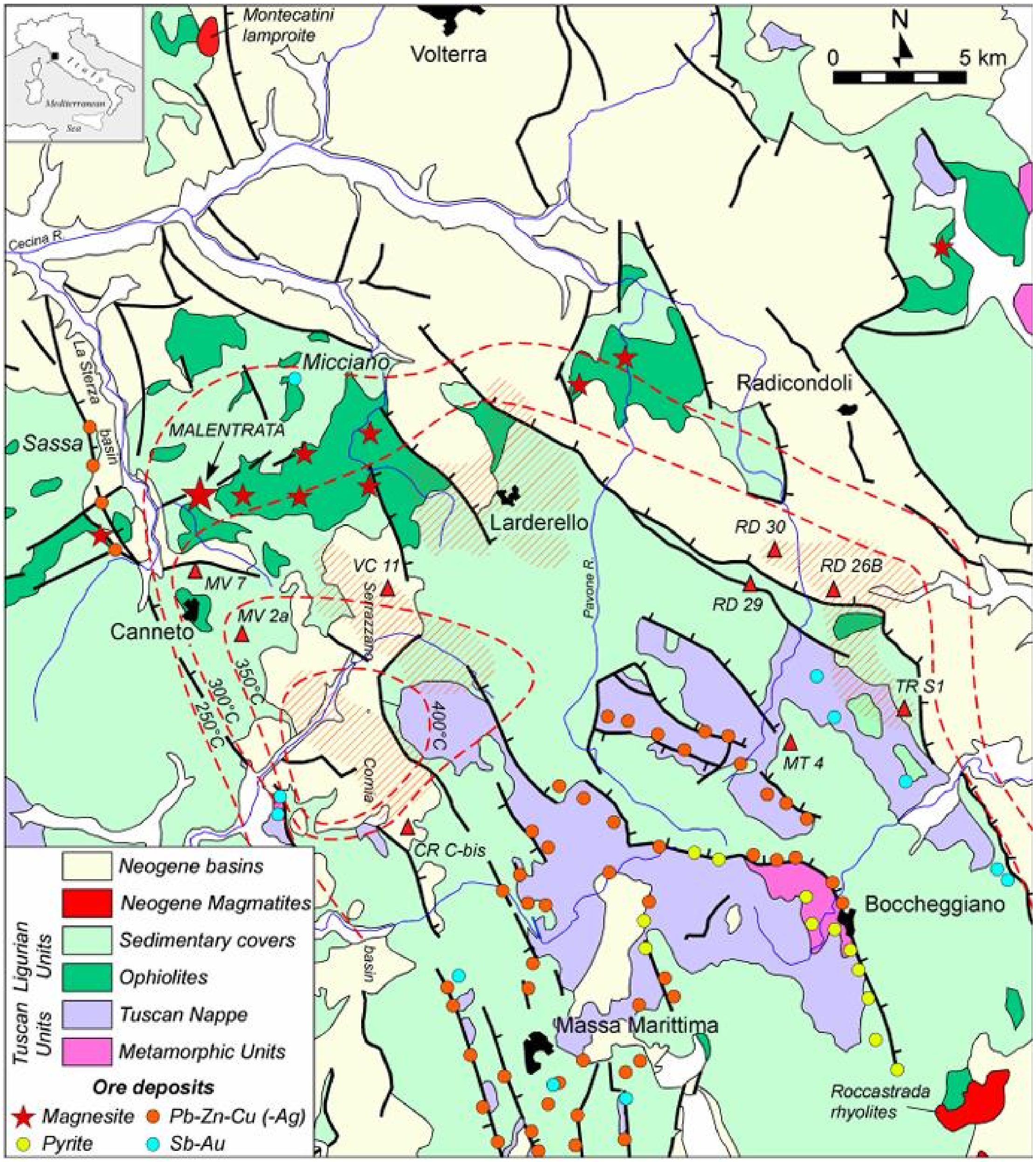

Figure 22 Geological map of Tuscany (Boschi, Dini, & Dallai, Low-temperature in situ carbonation of ultramafic rocks at Montecastelli, Tuscany: Mineralogical evidence and CO_2 uptake potential, 2017)

Besides, most of the Roman Magmatic Province, which consists of the Vulsini, Vico, Sabatini, and Colli Albani volcanic complexes, is composed of basalts, trachybasalts, with minor basaltic-andesitic lavas (Figure 23). These volcanic products are mineralogically enriched in plagioclase (labradorite to bytownite), clinopyroxene (augite, diopside), olivine and Fe-Ti oxides that contain divalent cations (Ca^{2+}, Mg^{2+}, Fe^{2+}) which reacts readily with dissolved CO_2 to form stable carbonate minerals.

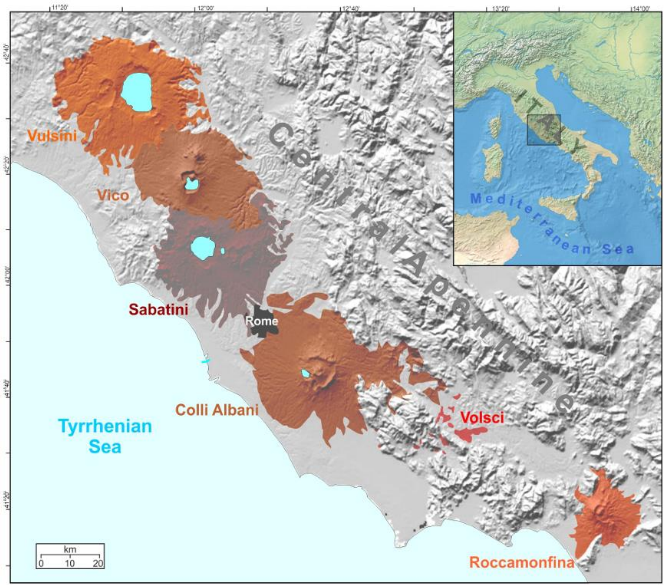

Figure 23 Geological map of Roman Magmatic Province (Boschi, et al., 2020)

4.2 Mineralogical and Geochemical Suitability of Target Lithologies

The ophiolites of Tuscany are ultramafic rocks, and are mostly peridotites, ancient mantle rocks composed of olivine and pyroxenes which have variously undergone serpentinization (Figure 24). On the surface they present themselves as serpentinites, dark green or grey, or rather black, with scaly or blocky surfaces, since they have been struck by water and changed to serpentine. It is typically quite widespread, serpentinizing 70-100 % of the original minerals, although some original minerals remain in some areas. An example is the dunite of Montecastelli, an olivine-dominant peridotite, which contains relic cores of forsteritic olivine, enclosed in a serpentite-bastite net, and exhibiting the change as being already well-advanced, but not yet complete (Boschi, et al., 2017).

The original minerals in such peridotites were magnesium-rich olivine (forsterite) and pyroxenes such as enstatite, and a Cr-spinel. In case of serpentinization, the mentioned minerals become serpentine group minerals: mostly lizardite and chrysotile at lower temperatures and occasionally antigorite when it is hotter, as well as some by-products such as magnetite (Fe_3O_4) and brucite ($Mg(OH)_2$.

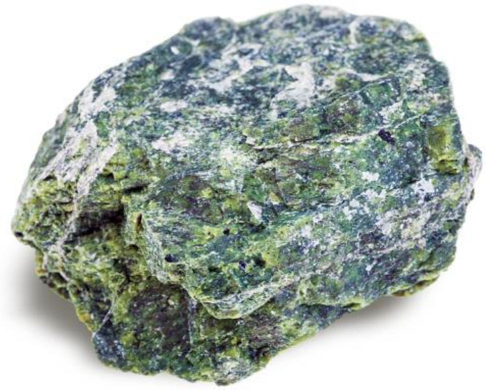

Figure 24 Sarpentinized periodite (Boschi, Dini, & Dallai, Low-temperature in situ carbonation of ultramafic rocks at Montecastelli, Tuscany: Mineralogical evidence and CO_2 uptake potential, 2017)

The fact that the mineral composition of serpentinites is of paramount importance to CO_2 reactivity. Brucite develops in olivine-rich systems, when silica activity is low and this component is particularly reactive to the CO_2. The brucite constituent of Montecastelli dunite serpentinized forms a large part of the rock and has the ability to rapidly sequester CO_2 to form Mg-carbonates conditions. In fact, one of the processes that promote rapid CO_2 uptake there is brucite to provide carbonation (Dini, Rielli, Di Giuseppe, Ruggieri, & Boschi, 2024).

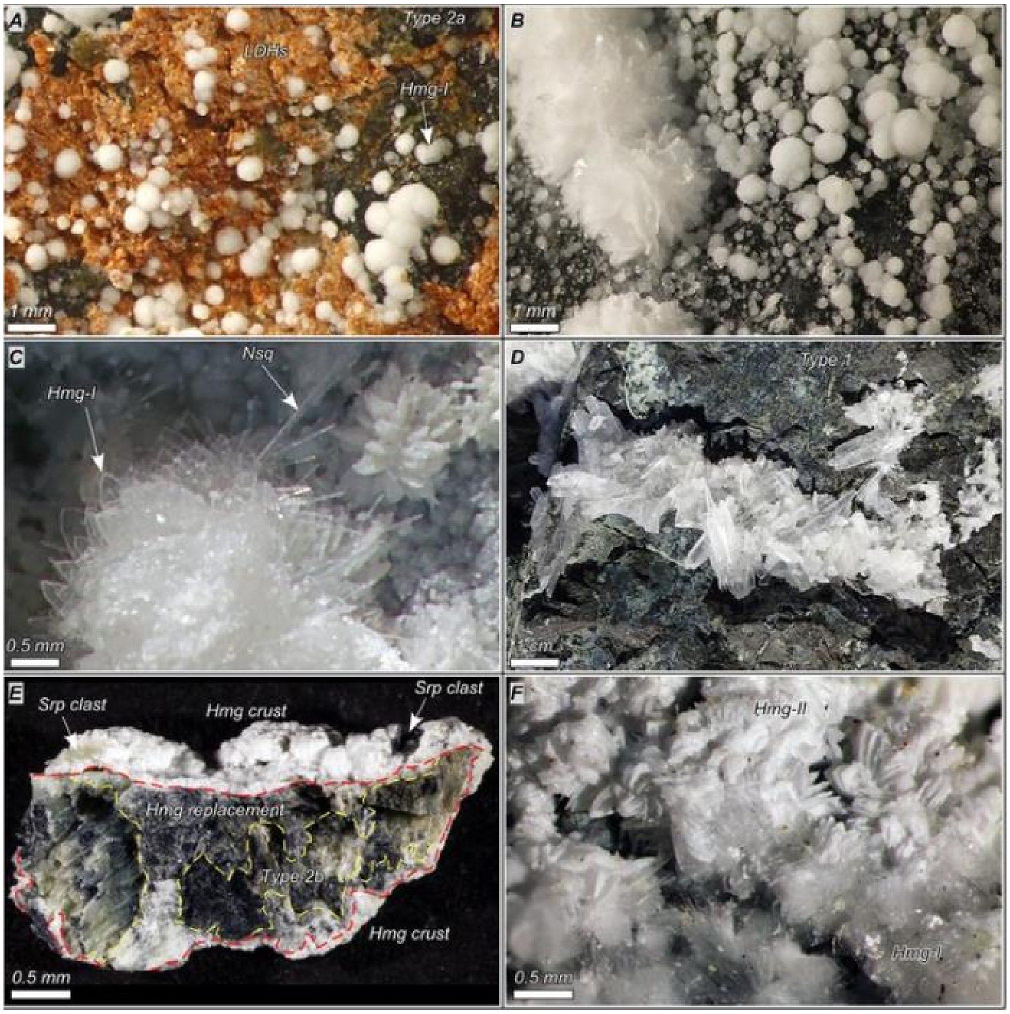

Figure 25 (a-f) Macroscopic images of idiomorphic crystals/aggregates of carbonates from Montecastelli (Boschi, et al., 2017)

Other typical alteration minerals are the talc and clay minerals in shear zones and the carbonate minerals in veins. Their little mafic accompaniment: gabbros and basaltic (which are usually considered to be pillow lavas or dikes), are themselves altered: gabbros (initially a mixture of plagioclase and pyroxene) can be saussurized and chloritized, and basaltic lavas can be spilitized (albitized) and veined with calcite and zeolites (Figure 25). These mafic rocks contribute additional Ca, Fe and Mg which can produce calcite or dolomite at the expense of the CO_2 but on the whole are a minor proportion of the Tuscan ophiolites in comparison with the serpentinite. Structurally the peridotite massifs in Tuscany are fractured and faulted due to their tectonic origins (Boschi, Dini, & Dallai, Low-temperature in situ carbonation of ultramafic rocks at Montecastelli, Tuscany: Mineralogical evidence and CO_2 uptake potential, 2017). As the Apenninic nappe toppled and fell along the extensional faults thereafter, the ophiolites disintegrated into blocks and slices of lenses. That formed a lunatic chain of fractures, breccias and shear zones within the ultramafics (Boschi, et al., 2017).

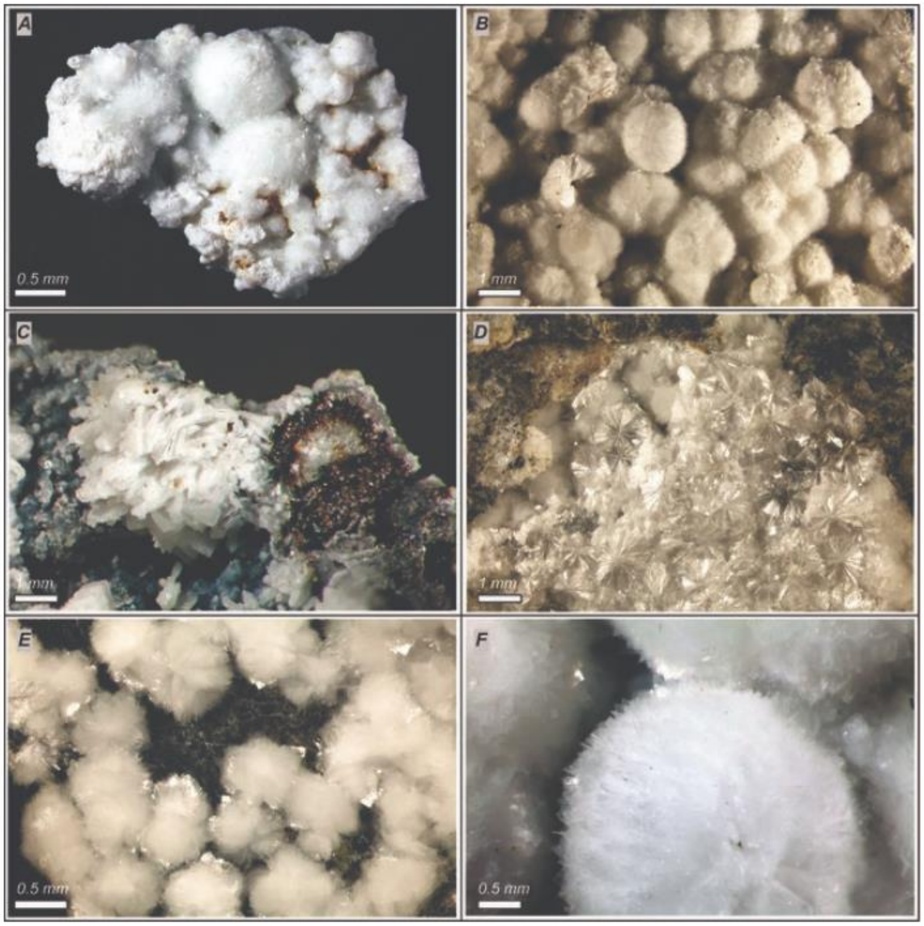

Figure 26 (a-f)Additional macrophotos of aggregates of hydrous Mg carbonates from Montacastelli (Boschi, Dini, Dallai, & Nisi, Natural carbonation of brucite-bearing serpentinites: Implications for in-situ CO_2 mineralization, 2020)

The field mapping and subsurface data reveal that the bodies of serpentinite typically contain many fracture pores that are concentrated in the faults systems and lithological contacts. Indicatively, Montecastelli geology is intersected by low-angle detachment faults and steep transfer faults forming a patchwork of blocks that are separated by both crushed serpentinite gouge and open fractures (Figure 26). These fracture systems increase the bulk permeability of the otherwise low-porosity ultramafics- good news on CO_2 mineralization. Injections of fractures and vein networks assist injected fluids to enter the rock and to react at depth.

Actually, the natural groundwater in serpentinites exploits these routes, and many springs and small travertine formations can be found along faulted contacts in the region (indicating the discharge of CO_2-enriched water). Further, even the serpentinization process, itself, may produce a fracture: once peridotite is transformed into serpentinite, the volume swells and the micro-cracks form that in their turn may be fluidified in the future to form a fluid passage. Most of the cracks are aligned to serpentine or magnetite, though some remain open partially or become reactivated due to later tectonic movements (Boschi, C., Dini, A., & Dallai, L, 2013). As an example, the field images in Figure 27 (a, b) show well-developed carbonate-silica veins cutting through altered serpentinites at Malentrata. These veins indicate where CO_2-rich hydrothermal fluids interacted with the host rock, resulting in localized silicification and carbonation.

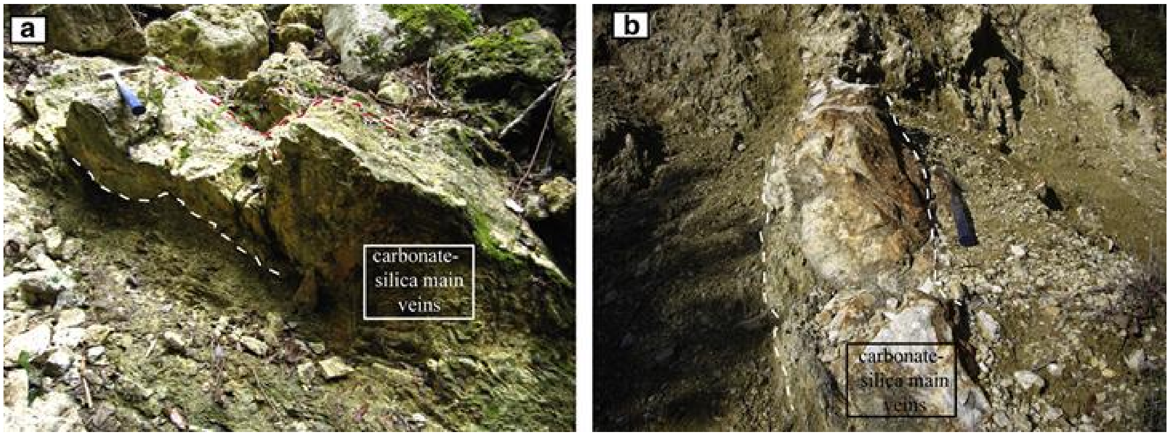

Figure 27 a, b) Representative examples of carbonate–silica veins hosted by silicified, carbonated and argillified serpentinites at Malentrata (Chen, Zhang, & Xu, 2024)

In addition to that, it can be observed that the porosity and permeability of dense peridotite are practically negligible, whereas in rocks that are completely serpentinized, porosity may develop within micro-fractures. The majority of the flow of fluid is however in the fault-related conduits. Petrophysically, that implies that the CO_2-containing fluids are able to pass through the serpentinites provided that the pressure is sufficient. Fractured ophiolitic rocks have been demonstrated to have the capacity to support fluid flows at depth by the geothermal drilling in

Tuscany. As an example, wells at the Larderello-Travale region have been penetrating into fractured horizons of serpentinite that serve as conduits of hydrothermal fluids- and they were notoriously known to cause massive wastages of drilling fluids (Boschi, Dini, & Dallai, Magnesite–hydromagnesite precipitation from serpentine-derived waters in the Larderello geothermal field (Tuscany, Italy): An example of CO_2 sequestration from natural fluids, 2009).

The ultramafic bodies present in central Italy solid have all these characteristics: lots of reactive minerals (in particular, Mg-silicates, such as olivine, serpentine, and brucite), and permeable fracture networks, and are thus good in-situ mineralization of CO_2.

4.3 Structural and Petrophysical Controls on Injectivity and Reactivity

The geochemical performance of mineralization of CO_2 is directly connected with the structural fabric and petrophysical properties of the ophiolitic formations, in particular, the serpentinites of the Internal Ligurian Units. Such structures are the widely serpentinized pieces of the Tethyan oceanic lithosphere that have been periodically overriding as well as experiencing the varied Alpine-Apennine orogenic cycles and subsequently shedding off during the Miocene extensional detachments. Their complex deformation history has formed a discontinuous structure that not only offers a pathway of permeability to move fluid in the store but also increases the surface area of reactive components to respond to carbonation. In these conditions, structural preparation serves two purposes: tectonic fracturing enhances the accessibility of mineral surfaces, and changes induced by deformation enhances the creation of carbonation receptive mineral phases such as brucite and serpentine. The location of the ultramafic blocks has been indicated in both the mapping and the borehole data in the area such as Montecastelli site to be separated by detachment faults of low angle with steeply inclined transfer faults (Boschi, Dini, & Dallai, Low-temperature in situ carbonation of ultramafic rocks at Montecastelli, Tuscany: Mineralogical evidence and CO_2 uptake potential, 2017). These edifices are outlines of harsh tectonic lenses of serpentinite parted by fault gouge lands, ruined breccia and exposed or half-sealed fracture conduit. All these properties increase bulk permeability and balance the natural low matrix porosity (less than 1%) of dense peridotite. The formation of serpentinite out of peridotite in these massifs (Montecastelli, and others of the same kind) in respect of textual structure is intimately connected with microfracturing, and with the mineralogical modification (Brogi, Liotta, Dini, & Rielli, 2023).

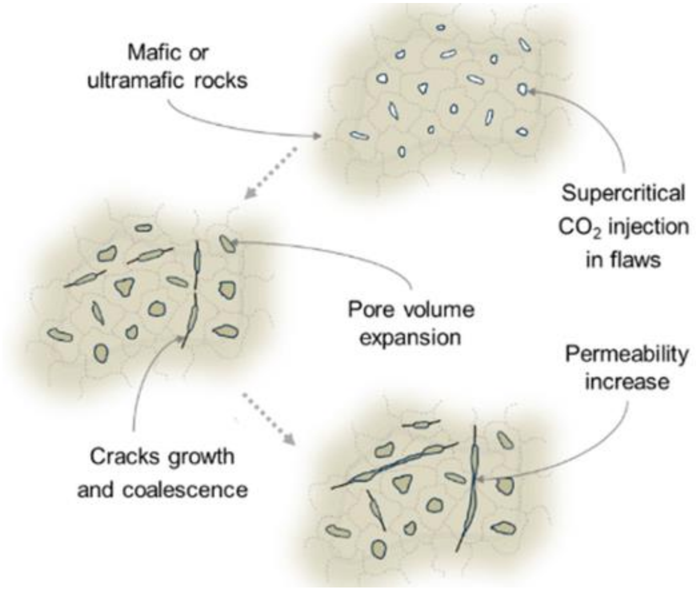

Figure 28 Schematic of crucial micro-scale mechanisms responsible for the change of rock volume and fracture connectivity (Ye, Li, Wang, & Zhao, 2025)

Serpentinization is what leads to volumetric expansion (around 20-40%), a process responsible for the creation of a network of microcracks that may or may not be closed in later deformation. These microfractures are more likely to follow chlorite-magnetite-serpentine seams and are unremedied fluid conduits (Figure 28) (Ye, Li, Wang, & Zhao, 2025). A petrographic study and on-site surveys reveal that carbonation is concentrated around such microstructural features whereby magnesite and dolomite is deposited in veins created or formed during deformation. Through those channels, injected fluids with high CO_2 content can be spread efficiently across the reactive ultramafic volume. In addition to this, there are indications of the development of secondary pores at different scales in some of the ultramafic bodies in

Tuscany as in Miemo and Murlo. Modification of the shear zones by talc and clay minerals, along with serpentine-carbonate veins and mineral cores of relics within fine-grained alteration halos are also contributing to a petrophysical characterization that allows protracted but slow interaction between rocks and fluids. Inclusion of brucite particularly in the protolith (olivines) like the Montecastelli dunite, has led to a high reactivity of brucite as fast reactive at ambient temperatures to dissolved CO_2 to form hydrous magnesium carbonates. Spatial distribution of brucite can be associated with fronts of serpentinization as well as locally raised pH that means that the reaction front can be used in order to optimize mineralization. Geothermal drilling of Larderello-Travale also confirms the hydrogeologic nature of serpentinites as a carrier of fluids. Boreholes through serpentinite, horizontal planes in this region have identified high permeability levels that not only carried the hydrothermal fluids but also caused a lot of loss of drilling fluids, indicating an open and interconnected system of fractures in the depth. The inference made based on this empirical fact is that injection of CO_2-bearing fluids with controlled pressure conditions can take place in tectonic fractured serpentinites. But on the contrary, a different regime is found in the mafic Lazio at least in the Vulsini-Vico-Bolsena volcanic complex (Boschi, Dini, & Dallai, Magnesite–hydromagnesite precipitation from serpentine-derived waters in the Larderello geothermal field (Tuscany, Italy): An example of CO_2 sequestration from natural fluids, 2009).

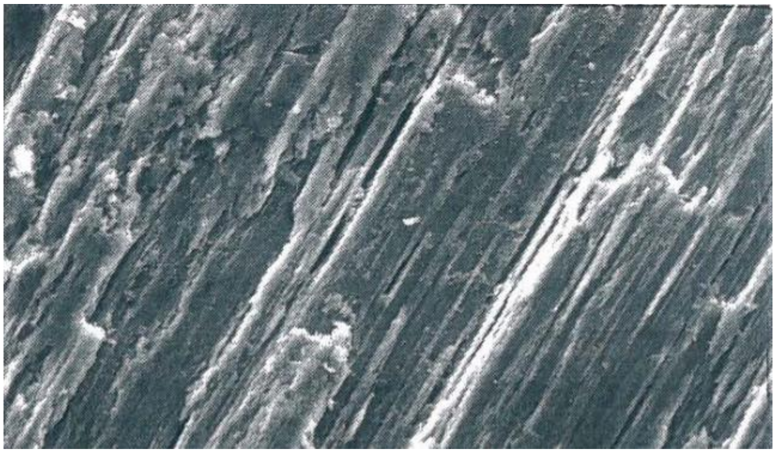

Figure 29 Microfissures developed from the gabbro (Xu, 2014)

The matrix (vesiculation, cooling fissures) of the basaltic lava flows and interflow horizons, as well as scoria layers are porous (Figure 29). Even though the ophiolitic domains are structurally more complex, these mafic lithologies contain an interconnected system of pores and flow-top breccias that further enhances the lateral continuation of permeability. Their mineralogical composition with high content of Ca- and Mg-carrying pyroxenes and feldspars allow them to be involved in the carbonation reactions, although the reactions may be slower than those of the ultramafics. Moreover, the occurrence of mantle peridotite nodules in xenoliths in such deposits of volcanism shows that there were possible ultramafic sources in the area, but that they were transient and small scale (Geology, 2021).

Table 3 MMV Requirements Under EU and Italian Frameworks (Snæbjörnsdóttir, 2020)

Effect	Risk	Mitigation Strategy
Induced Fracturing	Overpressure	Pressure control, reservoir modeling
Early Wellbore Sealing	Carbonate clogging	Pulsed injection, fracture staging
Fault Reactivation	Seismicity	Stress mapping, injection throttling
Porosity Loss	Rapid mineral growth	Flow modulation, alternate well design

The table 3 identifies the main monitoring, measurement and verification (MMV) requirements of an EU regulatory and Italian regulatory framework, including the possible risks of operation such as overpressure, seismicity and carbonate clogging, and the specific control measures such pressure control, stress mapping and pulsed injection to safely and efficiently mineralize CO_2.

Depending on the carbonation reactions, solid carbonate phases may form in the fractures and space between pores which induces local permeability losses especially near the wellbore. However, the observation of the Tuscany region in nature implies that flow path self-regulation is possible due to the repeated reactivation of fractures and the gradual mineralisation over time. This feedback demonstrates the need to ensure that injection regimes are kept in check in order to prevent the premature clogging and long-term reactivity.

However, in Lazio the vesicular and fine-grained and glassy nature of most RMP basaltes gives a large surface area of reactive sites, increasing the rate of dissolution and carbonate precipitation reactions in CO_2-bearing aqueous environments. The geochemical and field researches point out that volcanic aquifers in Lazio are already in the natural CO_2-water-rock reactions, as the chemistry of thermal and carbonated springs of the Lake Bolsana, Vico, and Bracciano demonstrate. The calcium-bicarbonate-rich waters indicate the continued natural carbonation of mafic minerals, which is akin to the processes occurring early-stage in engineered systems such as CarbFix in Iceland. The occurrence of hydrothermal alteration assemblages such as calcite, zeolites, and clays in these volcanic layers, contribute to the possibility of enhanced trapping of minerals in situations where injection was controlled. Petrophysically, the mafic sequences of Lazio have fracture permeability and vesicular porosity, which are due to volcanic degassing and cooling contraction as well as interflow brecciation. All these characteristics promote the circulation of fluids and efficient diffusion of CO_2-saturated fluids. These basaltes are more permeable in the matrix compared to dense ultramafic serpentinites, so no artificial stimulation is necessary. Additionally, the overlying welded tuffs and massive lava units mechanical integrity might act as natural seal, which reduces vertical CO_2 migration and enhances long-term containment. The Ca- and Mg-enriched silicates in mafic rocks have reactive carbonation routes in terms of reactivity. Plagioclase and pyroxenes change to calcite and dolomite faster than magnesite in ultramafic systems, which results in the efficient sequestration of CO_2 over working time frame. Although the overall carbon storage of mafic formations is less than peridotite-dominated ophiolites, they have a kinetic advantage and are readily accessible hydrogeologically, and are the focus of pilot-scale projects in Central Italy. Also, these volcanic regions lie close to some of the largest industrial sources of CO_2 emitters, including geothermal and energy plants of Viterbo and Civitavecchia, which may justify integrated capture-and-store approaches with less transportation needs (Oelkers, Matter, Gislason, & Aradóttir, 2023134).

4.4 Comparative Insights from Global Mineralization Projects

When determining the viability of CO_2 mineralisation in ultramafic and mafic lithology in Central Italy, it can be useful to examine what large-scale international projects have discovered. The most helpful analogs are the CarbFix project in Iceland, The Wallula Basalt Pilot in Washington State (USA) and field measurements on the Semail ophiolite in Oman. These locations provide us with opposite ideas regarding the strategy of injection, the reactivity of minerals, the interaction of fluid and rock and the control of permeability all of which play a vital part in the designing and evaluating of the risk in the future deployments in Tuscany and Lazio.

Comparative synthesis underscores that, despite differences in lithology and climate, key success factors recur across sites:

- fracture-mediated permeability
- availability of highly reactive Mg- or Ca- bearing minerals (e.g., brucite, olivine, basaltic glass)
- fluid chemistry management (pH, DIC), and (iv) structural containment

Central Italy's serpentinites and basalts display many of these characteristics in different proportions. For example, Montecastelli and Larderello combine high Mg content (including brucite) with fractured geometries that facilitate fluid access-more akin to the Oman and CarbFix sites than to Wallula's homogenous basalts.

4.5 Advantages, Limitations, and Site-Specific Uncertainties

The mineralisation of CO_2 on the ophiolitic chasses of Central Italy especially, Tuscany has several advantages, owing to the favourable lithological, structural and geochemical peculiarities. However, when implemented in large quantities, big data should be given a second consideration in its regard to constraints and location-related ambiguity.

Advantages:

- Most of the serpentinites of the internal Ligurian Units consist of Mg -bearing silicates such as forsterite, serpentinite and brucite-all of which are the very reactive phases of the carbonation reactions. One of them is Montecastelli dunites that are comprised of brucite-laden domains and can thus absorb CO_2 rapidly during moderate subsurface conditions.
- The Apennine tectonic evolution has created extensive faulting and brecciation such that the ultramafics of that hitherto low-porosity have become more penetrable. High

fracture network density along the fracture line, shear and serpentinite gouges lines that can provide fluid penetration and enhance the area of reactive cause Montecastelli, Murlo and Miemo to be characterised.

- Natural carbonation is naturally observed in the Malentrata region of the Larderello geothermal field in which silica is gradually substituted and the magnesite dolomite veins appear. This indicates that the geology and chemistry in Central Tuscany are ideal to ensure that CO_2 is trapped in the minerals on a long-term basis.
- The considered locations are quite close, in terms of emission centres including cement, steel and geothermal power plants in Tuscany and Lazio. This makes the deployment of piloting logistically feasible and reduces the amount of emissions associated with transportation.
- The locations under consideration are not far away in terms of emission centers such as cement, steel and geothermal power plants in Tuscany and Lazio. This ensures that piloting deployment is logistically viable and has low transportation-related emissions.

Limitations:

Despite of the fracturing of the region, the distribution of permeability is spatially heterogeneous. A portion of the peridotite bodies can be enclosed by secondary mineralisation or low-strain domains, restricting the uniform dispersal of CO_2 rich fluids. Carbonation in-situ, particularly via a CarbFix-style dissolved CO_2 system, needs extensive quantities of water. In the Mediterranean climate regions where summer droughts are common, and industries and agriculture are competing with to pass the water, the question of sustainable water is one. Multiscale fracture networks and lithological variability make the tracking and verification of the plumes difficult. Perhaps, seismic imaging and downhole sampling can lower resolution in heterogeneous, anisotropic serpentinites, and augment costs and uncertainty in MMV. Trace metals (e.g., Ni, Cr, Co) may also be present in serpentinites and these may be dissolved temporarily at low pH. Although they can be immobilised with eventual precipitation, to control this geochemical risk, it is imperative to characterise the baseline and process control (Jun, Y.S.; Zhang, L.; Min, Y.; Li, Q., 2017).

Site-Specific Uncertainties:

- In Montecastelli, Monterufoli, and Livornesi bodies, there is a considerable range of serpentinisation. Variations in the abundance of brucite, leftover amount of olivine, and the polymorphs of serpentinite have an influence on the reaction rates and the CO_2 capacity.
- There is limited high-resolution data on the thermal gradient, in-situ stress fields, and fluid regimes at depth across many ophiolitic massifs. This makes it difficult to optimize injection strategies and predict reaction front propagation.
- Several target sites fall within areas of ecological or cultural significance (e.g., geothermal parks, nature reserves, archaeological zones). Permitting may be delayed or rejected due to land-use restrictions or public opposition.While Central Italy benefits from extensive geological data and geothermal infrastructure, no field-scale CO_2 mineralization trials have been conducted to date. This absence of empirical data introduces uncertainties in upscaling lab-derived parameters to operational systems.

4.6 Results and Discussion

According to the multidisciplinary analysis in this chapter, Central Italy was considered to be geologically and strategically favorable territory to conduct in-situ CO_2 storage through mineralization, particularly in the case of specific ultramafic and mafic lithologies. The ultramafic Tuscany massifs that worth the attention include Montecastelli, Murlo, and Miemo, which are richin brucite, extensively serpentinized, and have well-developed fracture networks. These structural and petrological aspects directly increase the injectivity as well as the carbonation reactivity needed in the effective storage of CO_2.

The most interesting aspect of the comparison between Tuscany and well-known examples such as Oman or Iceland is how naturally the Montecastelli and Malentrata systems have already in the geological past, exhibitesd similar interactions between fluids and rocks. On shorter time scales, carbonate-filled veins, travertine deposits, and even naturally altered serpentinites serve as analogues for what an engineering system might reproduce. These natural phenomena may support the technical viability of CO_2 mineralization in the region.

At the same time, it is necessary not to underestimate the complementary value that mafic provinces in Lazio. Although the Vulsani and Vico volcanic complexes might lack the desirable brucite chemical composition of the Tuscan ophiolites, the basaltic flows and pyroclastics of these complexes do still contain reactive mineral substrates, which in certain aspects are analogous to the CarbFix hosts rocks in Iceland. The fact that these mafic rocks are more porous and less structurally complex may even make injection planning easier, particularly the dissolved CO_2 case. Reaction kinetics may however be slower than in ultramafics and the total carbonation capacity per unit volume may be less.

Both lithological domains in Central Italy, including ultramafic and mafic formations, are characterized by uncertainties. These uncertainties are due to the lack of field-scale injection practices, heterogenous permeability of the fracture systems and environmental risks. A suitable future approach would be creating a pilot-scale injection project within one of the most promising serpentinite massifs, such as Montecastelli. This could allow the calibration of the reactivity models as well as the MMV protocols under real field conditions. Parallel projects may be launched in the Lazio volcanic territory to determine the most suitable adaptation of the aqueous carbonation methods for basaltic media.

5. Conclusions

This thesis assesses the permanence of CO_2 storage through mineral carbonation in Central Italy, based on the critical synthesis of peer-reviewed studiesand project reports. Two complementary opportunities emerge. First, the Internal Ligurian ophiolites of Tuscany (e.g., Montecastelli, Miemo, Murlo) combine highly reactive lithologies-serpentine, forsteritic olivine and locally abundant brucite-with fracture networks generated by Alpine-Apennine compression and later extensional faulting. These features jointly satisfy the core requirements for mineral trapping: sufficient cation supply and connected flow paths. Second, the basaltic provinces of northern Lazio (Vico–Vulsini) offer Ca-Mg–bearing mafic hosts with interflow/vesicular architectures analogous to those exploited successfully in basalt projects, supporting rapid aqueous carbonation when injection chemistry is properly managed.

Across both settings, performance depends less on thermodynamic favorability than on engineered control of reaction fronts in fractured media. The design imperative is to promote dissolution near the injector to mobilize divalent cations and shift carbonate precipitation down-gradient so solids accumulate in storage-beneficial volumes (open fractures, vesicles) rather than sealing near-well porosity. In Tuscan serpentinites this requires using the reactivity of brucite-bearing domains without inducing early self-sealing; in Lazio basalts it favors dissolved-CO_2 strategies that sustain high DIC while allowing pH/alkalinity rebound along the flow path and careful water stewardship. Natural analogues in Tuscany (e.g., Malentrata, Castiglioncello) demonstrate long-lived CO_2-water-rock interaction and the permanence of carbonate trapping in veins and fracture fills, while international pilots (CarbFix, Wallula; ultramafic studies in Oman) calibrate expectations for rates, monitoring signals, and containment behavior. These analogues reduce uncertainty but cannot replace local demonstration.

The principal constraints identified in the literature are practical: heterogeneous fracture connectivity at the operational scale affects injectivity; high-water demand for dissolved-CO_2 schemes in a Mediterranean hydro-climatic context; transient mobilization of trace metals (Cr, Ni) during early low-pH stages in serpentinites; and MMV complexity in anisotropic fractured media. Countervailing factors include proximity to CO_2 sources (cement, geothermal, industry), subsurface knowledge from geothermal operations, and a regulatory environment that recognizes mineral trapping and requires robust MMV.

In conclusion, Central Italy offers a credible, strategically advantageous platform for mineral-based CO_2 storage because it co-locates brucite-rich ultramafics and reactive basalts within a mature industrial context. The logical next step is a staged, well-instrumented pilot in a serpentinite target (e.g., Montecastelli), coupled with a smaller dissolved-CO_2 trial in a Lazio basalt interflow. Each should integrate high-resolution fracture characterization, controlled-pressure injection with acidity management, reactive tracers, and post-injection coring to verify mineral products and distribution, alongside water-recycling plans and environmental thresholds. If these pilots confirm predicted injectivity and mineralization rates, Central Italy could progress rapidly from bibliographic promise to demonstrated, permanent CO_2 storage at climate-relevant scale.

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