International Society for Rock Mechanics and Rock Engineering
Norwegian Group for Rock Mechanics

ISRM International Symposium
Eurock 2025 – Expanding the Underground Space
Trondheim, Norway, 16-20 June
ISBN 978-82-8208-079-8

Fundamental Study on Chemical Reaction of Rocks with CO_2: Implication for Carbonate Precipitation

Xiurong Yang, Hiroaki Ito, Atsushi Sainoki
Faculty of Advanced Science and Technology, Kumamoto University, Kumamoto, Japan
yangxiurong66@gmail.com

Kazuya Shimana, Yuto Nakamichi
Department of Civil and Environmental Engineering and Architecture, Faculty of Engineering, Kumamoto University, Kumamoto, Japan

Abstract

CO_2 emissions have surged in recent decades due to rising global power generation demands, complicating efforts to limit temperature rise to below 2°C, as per the Paris Agreement. This underscores the urgent need for large-scale CO_2 reduction measures, including underground engineering projects. However, these projects pose risks of inducing earthquakes and unexpected surface leakage, requiring new mitigation technologies.

This study explores the chemical reaction between rocks and CO_2 to induce rapid carbonate precipitation for CO_2 sequestration. We assessed the impact of minerals in sandstone, serpentinite, peridotite, basalt, and silicified andesite on CO_2 immobilization, considering factors like injection pressure, mineral elution, and incubation period.

Essential cations necessary for carbonate mineralization were found to elute within a week, varying by rock type and immersion time. Peridotite, basalt, and serpentinite were identified as significant sources of cations, such as Ca, Fe, Mg, and Ni, which promote carbonate precipitation. Notably, serpentinite was found to facilitate rapid carbonate precipitation within one week upon reacting with CO_2, suggesting immediate stabilization of injected CO_2 as carbonate.

These findings support the potential of targeted rock types in enhancing the efficiency of carbonate sequestration technologies.

Keywords

Carbon storage and earthquake, mineral composition, carbonate precipitation, underground engineering, serpentinite

1 Introduction

In recent years, the increased demand for thermal power generation following nuclear power plant accidents has resulted in a rise in CO_2 emissions. The target set by the Paris Agreement—to keep the global average temperature increase well below 2°C above pre-industrial levels and ideally limit it to 1.5°C—has become increasingly difficult to achieve. Consequently, there is a growing need for large-scale CO_2 reduction measures worldwide. To address this, various underground engineering projects aimed at CO_2 reduction have been developed. New methods for utilizing the subsurface, such as shale gas extraction, Carbon Capture and Sequestration (CCS), and geothermal energy production, have been advancing (Boot-Handford et al., 2014). For instance, of the approximately 700 billion m^3 of natural gas produced annually in the United States, around 140 billion m^3 comes from shale gas extraction. This advancement has positioned the U.S. as the world's leading natural gas producer since 2009. The IPCC has set a goal of reducing CO_2 emissions by 50% by 2050, with CCS expected to contribute 17% of this target.

In conventional CCS projects, CO_2 is injected into a permeable geological layer composed of porous sandstone, such as deep saline acquirers and petroleum reservoirs (Patruno et al., 2024). The geological layer needs to be overlain by an impermeable layer composed of rock masses with low permeability, such as shale and mudstone. Under such conditions, the injected CO_2 is expected to be trapped in the permeable layer permanently with four mechanisms: structural, residual, solubility, and mineral trapping. The structural trapping pertains to the impermeable layer overlaying the porous layer to which CO_2 is injected, whilst residual trapping is related to microscopic pore spaces in the permeable layer as well as the displacement of brine and CO_2 (Zhang et al., 2024). The solubility trapping is the dissolution of the injected CO_2, affected by the temperature, salinity, and diffusion of the CO_2 plume. Importantly, CO_2 trapped by these three mechanisms could become unstable when the in-situ conditions, such as temperature, pressure, and rock mass physical conditions, undergo change. For example, if seismic events caused by CO_2 injection form fractures in the caprock, the structural trapping is no longer effective and CO_2 plume could escape to upper geological layers, which would change reservoir pressure as well, leading to further CO_2 leakage.

In contrast, the mineral trapping is stable, not affected by changes of the in-situ conditions, because injected CO_2 is transformed to carbonate minerals (Hanifa et al. 2023). This makes it possible to store injected CO_2 almost permanently, even if the in-situ pressure and temperature gradually change for a long period of time. However, it is well known that the mineral trapping requires long geological time periods, meaning that CO_2 leak-off can take place, if the in-situ condition changes prior to the occurrence of mineralization. To overcome this limitation, many studies have been conducted recently in order to enhance CO_2 fixation and mineralization by taking advantage of rock-CO_2 chemical interaction. This technology involves the chemical reaction of rocks and pore water in reservoirs with dissolved CO_2.

Previous studies on CO_2 mineralization have predominantly investigated basalt-CO_2-H_2O reactions because basalt is known to release cations, such as Ca^{2+}, Mg^{2+}, and Fe^{2+}(Iglauer et al., 2020). Such cations react with carbonate ions, resulting in the formation of carbonate minerals. It is to be noted that such experiments are predominantly conducted at very high temperature more than 100°C, with the aim of injecting CO_2 into a very hot rock, such as volcanic regions and geothermal reservoirs, because the dissolution rate of such minerals in basalt is increased with temperature. Hence, the knowledge accumulated in previous studies cannot be directly applied to CCS projects, where temperature basically ranges from 40°C to 60°C.

In light of the aforementioned situations, this study aims to develop CO_2 mineralization technology that can be applied to CCS projects. To this end, we investigate the influence of CO_2 pressure and exposure time on carbonate precipitation for various types of rocks, including serpentinite, basalt, sandstone, peridotite, and andesite. Then, fundamental knowledge has been accumulated on the dissolution of minerals from the rocks as well as the potential for CO_2 mineralization under temperature ranges much lower than previous studies.

2 Experimental procedure

The general outline of the experimental procedure is illustrated in Figure 1. The process begins with selecting and collecting rock samples for the experiment. For the leaching test, the rock samples are immersed in water. After the test, the samples are retrieved, and their pH and electrical conductivity

(EC) are measured. The elemental concentrations are then analysed, and the elemental composition of the samples obtained from the leaching test is examined. Subsequently, a high-pressure sealing test and thermogravimetric analysis are performed on serpentinite to qualitatively assess its CO_2 fixation capabilities. Detailed explanations of these experimental procedures are provided in the following sections.

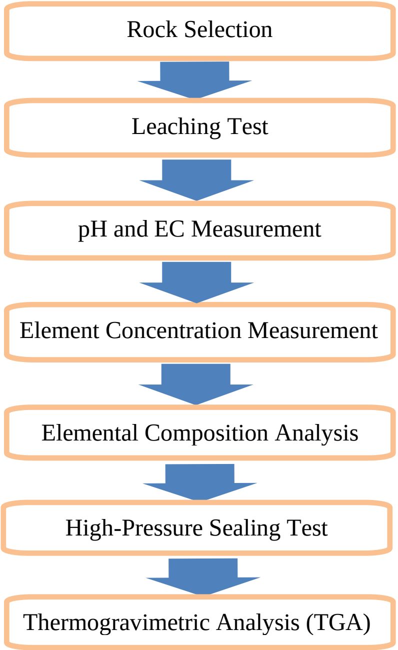


Fig. 1 Overview of the Experimental Procedure

2.1 Selection of Rock Samples

In this study, we used several types of rocks for CO_2 fixation experiments:

Sandstone: Kimachi sandstone (Fig. 2a) was chosen various types of sandstone. It is composed of andesite fragments, pyroxene, hornblende, plagioclase, with small amounts of quartz, orthoclase, and granitic rock fragments. Much of its composition, like that of conglomerate, originates from the andesite in the lower layer of this formation. Kimachi sandstone is known for its distinctive natural qualities, featuring a soft texture and a warm surface feel.

Serpentinite: A metamorphic rock formed from the hydration of peridotite, an ultrabasic rock, under high-temperature conditions (Fig. 2b). This process results in a ligher rock, often found at the Earth's surface due to its instability at greater depths. Serpentinite is rich in magnesium ions (Mg) and is often associated with highly alkaline groundwater, making it highly reactive with CO_2 solutions (Popall, et al. 2023). It primarily consists of minerals from the serpentine group, such as chrysotile, lizardite, and antigorite. Its main elements include magnesium (Mg), silicon (Si), oxygen (O), and hydrogen (H), with trace amounts of iron (Fe), nickel (Ni), aluminum (Al), and other elements.

Fig. 2 Rock samples (a. Sandstone, b. Serpentinite, c. Peridotite, d. Basalt, e. Silicified andesite)

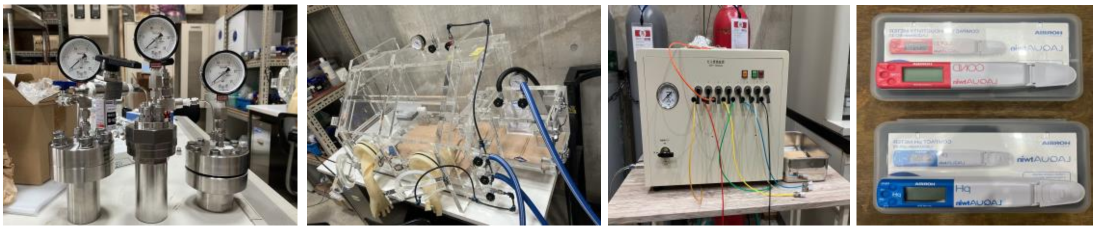
Peridotite: Composed mainly of olivine and pyroxenes, peridotite is characterized by low silica (SiO_2) and high magnesium oxide (MgO) content. This rock was selected for its high metal content and potential for reacting with CO_2 (Fig. 2c).

Basalt: A widely distributed rock commonly used for CO_2 fixation due to its large volume and high concentration of divalent cations (Fig. 2d).

Silicified Andesite: Consisting of over 90% silica, these rocks undergo metamorphosis into leaching-type and accretion-type silicified forms. The accretion-type used in this study is dense and characterized by microcrystalline quartz filling its fissures (Fig. 2e).

2.2 Leaching Test

The rock samples were initially crushed into powder using a hammer and mortar. The powdered rock, CO_2, and deoxygenated water were then combined in a pressure vessel (Fig. 3a). Afterward, the pressure vessel was removed from the glove box (Fig. 3b), and three additional cycles of vacuum degassing and mixed gas injection were carried out using the gas substitution apparatus (Fig. 3c) to replace the mixed gas in the pressure vessel with CO_2 (0.6 MPa and 0.6×10^{-2} MPa).). The rock samples were then left to elute elements over a specified period. After this, the solution was collected again under anaerobic conditions, and its pH and EC were measured using a pH and EC meter (Fig. 3d). During the solution collection, additional rock samples and solutions were also gathered as needed for concentration measurements. A blank test, without rock samples, was conducted to compare the results.



(a) High-pressure vessel (b) Glove box (c) Gas substitution apparatus (d) pH and EC meter

Figure 3 Leaching testing equipment

2.2.1 Short-Term Leaching Test (1 week)

Samples were collected immediately after mixing and subsequently at 1day, 3days, and 7 days to measure pH and EC. The purpose of this test was to examine the amount of precipitation over a short period of 1 week.

2.2.2 Long-Term Leaching Test (6 months or longer)

The solutions were collected and the pH and EC were measured after at least 6 months had passed since mixing. Due to the limited number of containers, this test was conducted only with siliceous andesite and serpentine rocks. The siliceous andesite samples were collected after 6 months, while the serpentine rock samples were collected after 8 months. This experiment aimed to investigate potential mineralization based on these results.

The collected samples were returned to high-pressure containers, and after injecting CO_2, samples were stored at room temperature. During this experiment, the solution was periodically collected, and the pressure vessel was opened under anaerobic conditions to visually inspect for mineralization.

2.2.3 Measurement of pH and EC

The pH and EC were measured whenever the solution from the leaching test was collected. The pH was measured to determine the ratio of cations to anions in the solution. EC, expressed in millisiemens per centimeter (mS/cm), indicates the total amount of water-soluble salts present and serves as an indicator of salt concentration. Measuring EC helps determine the amount of ions precipitated over time, which can provide a reference for the duration of the cultivation test.

2.2.4 Elemental Analysis Method

Qualitative evaluations were performed using the Electron Probe Microanalyzer (EPMA-1720). First, carbon tape was applied to the holder to secure the powdered sample with its adhesive properties. To improve conductivity and facilitate elemental analysis, the holder with the sample was placed in an ion sputtering device, where the surface was coated with a thin layer of gold. The holder was then mounted in the EPMA, and an electron beam was directed at the sample. The interaction between the beam and the atoms in the sample produced characteristic X-rays, which were detected to confirm the elemental composition of the sample surface.

2.2.5 High-Pressure Sealing and Mineralization Experiment

The high-pressure sealing experiment begins with preparing and loading serpentinite powder and water into a high-pressure vessel (Fig. 3a) under a CO_2 pressure of 9 MPa, ensuring the vessel is securely sealed to prevent leakage. After one week, the samples are dried and analyzed using thermogravimetric analysis (TGA). The mineralization experimental setup involves heating powdered serpentinite in a muffle furnace or TGA at temperatures ranging from 0–1000°C to monitor temperature and weight changes. The reactions are conducted in controlled gas environments, such as air, inert gases, or CO_2-rich atmospheres.

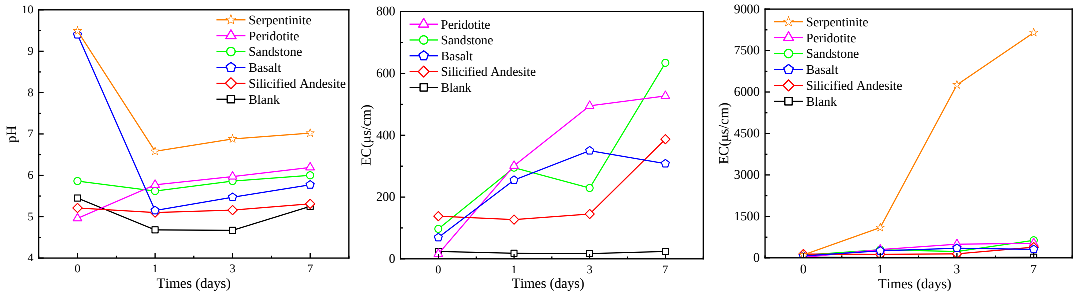
3 Experimental results

3.1 pH and EC Measurement Results

The results of the leaching tests for pH and EC are summarized for both short-term and long-term durations.

3.1.1 Short-term Leaching Test (1 week)

The pH measurement results are presented in Figure 4(a). It is observed that the pH values for all rocks, except serpentinite, converge between 5.0 and the low 6.0. However, serpentinite maintains a relatively high pH, even in the presence of CO_2.



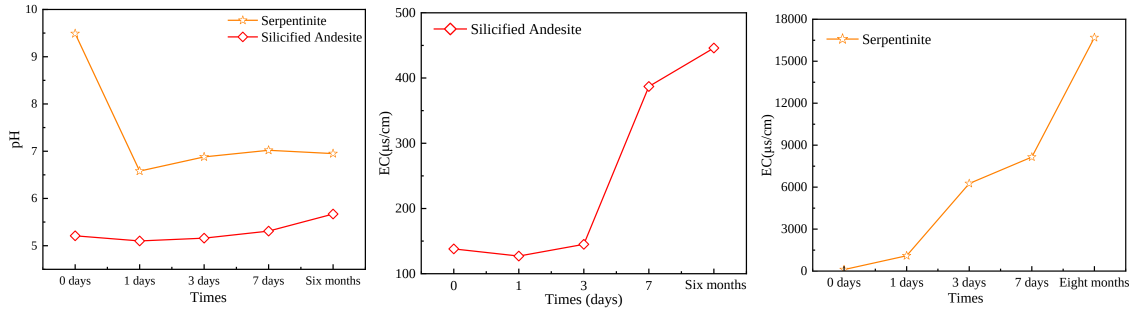
(a) pH measurement results (b) EC measurement results without Serpentinite (c) EC Measurement Results with Serpentinite

Figure 4 Short-term leaching test results

The EC measurement results are shown in Figures 4(b) and 4(c), with two separate graphs provided due to the divergence in EC values for serpentinite. From these graphs, it can be seen that the EC values for peridotite and basalt increased significantly up to the third day, with little further change thereafter. Conversely, sandstone, silicified andesite, and serpentinite exhibited a notable rise in EC values starting from the third day.

3.1.2 Long-term Leaching Test (6 months or more)

The pH values remained relatively stable throughout the long-term test, with no significant changes observed. Consistent with the short-term results (Figure 4a), the pH of the silicified andesite fluctuated between 5.0 and 6.0, while the pH of the serpentinite ranged between 6.0 and 7.0, except immediately after mixing (Figure 5a). No notable differences were found when compared to the short-term results.



(a) pH measurement (b) EC measurement of Silicified Andesite (c) EC measurement of Serpentinite

Figure 5 Long-term leaching test results

The EC results are shown in Figures 5(b) and 5(c). Due to the variation in EC values for serpentinite, separate graphs are provided for silicified andesite and serpentinite. Although the graphs cover a period of over six months, the silicified andesite samples were collected after six months, while the serpentinite samples were collected after eight months.

The silicified andesite samples displayed a trend toward convergence after several weeks, whereas the serpentinite continued to show significant increases in EC even after one week. Unlike the convergence observed in peridotite and basalt, as noted in Figure 4(b), serpentinite did not show such convergence.

3.2 Element Analysis Results

3.2.1 Short-term Leaching Test

The results of the elemental analysis for the original serpentinite are presented in Figure 6. In the original serpentinite, elements such as oxygen (O), magnesium (Mg) and silicon (Si) were found to be widely distributed. However, elements essential for mineralization, including metal ions like carbon (C), calcium (Ca), iron (Fe), and nickel (Ni), were scarcely present.

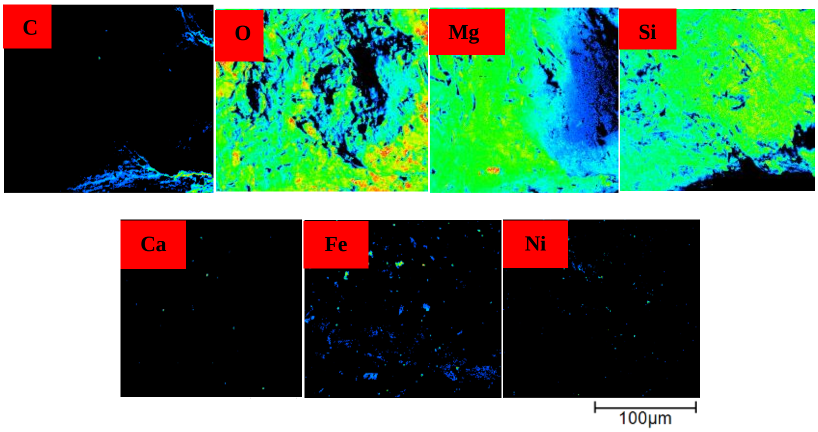


Figure 6 Elemental analysis for the original serpentinite: (a) C, (b) O, (c) Mg, (d) Si, (e) Ca, (f) Fe, (g) Ni

Figure 7 shows the results of the elemental analysis after a one-week leaching test on serpentinite. The distribution of magnesium (Mg) and silicon (Si) remained similar to their distribution in the natural state, with no significant localized precipitation; these elements were broadly dispersed. Additionally, Figure 7 indicates that five elements—carbon (C), oxygen (O), calcium (Ca), iron (Fe) and nickel (Ni) —precipitated together in specific localized areas.

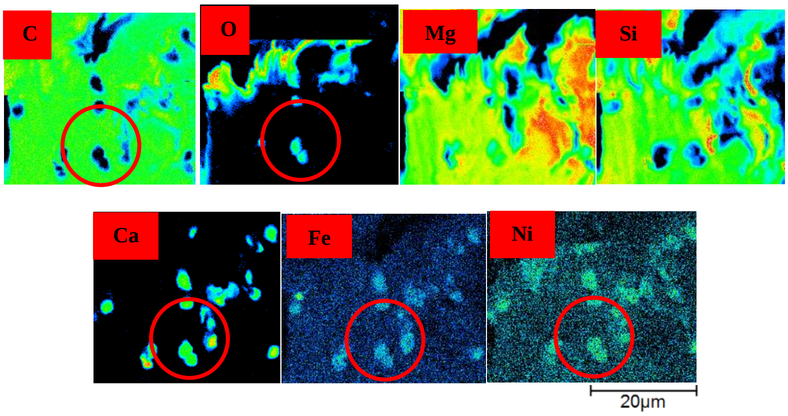
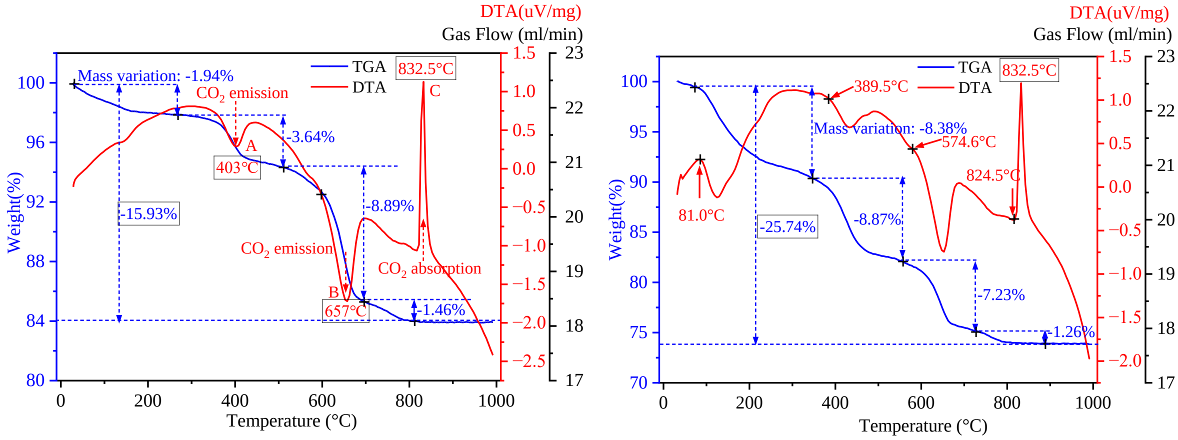


Figure 7 Elemental analysis after a one-week leaching test on serpentinite: (a) C, (b) O, (c) Mg, (d) Si, (e) Ca, (f) Fe, (g) Ni

3.3 Composition Changes During Thermal Decomposition

Differential Thermal Analysis (DTA) is a thermoanalytical technique used to measure the temperature difference between a sample and an inert reference material as they are subjucted to the same thermal cycle. The output of a DTA experiment is a plot of the temperature difference (ΔT) as a function of the sample temperature or time.

DTA revealed that the thermal decomposition of calcium carbonate occurs in two stages: Point A, between 300 °C and 400 °C, and Point B, between 600 °C and 700°C (Figure 8a). The maximum weight loss, observed in the TGA at approximately 15.93% for serpentinite before reacting with CO_2 and water, is attributed to the release of gaseous carbon dioxide (Dash, et al., 2000). At 800°C, the weight loss is complete. Beyond this temperature, calcium carbonate decomposes into CaO and CO_2. In contrast, the maximum weight loss for serpentinite after reacting with CO_2 and water is approximately 25.74% (Figure 8b). This increase in weight loss after reactions is likely due to the formation of new carbonate phases (such as magnesite or dolomite), which would produce distinct exothermic peaks related to their decomposition. These thermal effects indicate the presence of newly formed carbonates.



(a) Before (b) After

Figure 8 TGA-DTA thermogram of serpentinite before and after reaction with CO_2 and water

All DTA curves display a sharp exothermic peak, consistently occurring between 820°C and 840°C (Viti, 2010). The presence of these sharp peaks indicates that the serpentine samples undergo recrystallization processes within this temperature range (Karunadasa et al., 2019). According to MacKenzie and McGavin (1994), heating in air atmosphere results in the complete oxidation of iron before dihydroxylation occurs at approximately 800°C.

The DTA of serpentinite before and after reaction with CO_2 and water shows clear differences in thermal peaks associated with dehydration, dihydroxylation, and decomposition of mineral phases. Before the reaction, serpentinite exhibits typical thermal behavior, primarily from carbonates. After the reaction, additional thermal peaks appear due to the decomposition of newly formed carbonates and structural changes in the serpentine minerals. These variations reflect the carbonation and hydrothermal processes that have altered the serpentinite.

3.4 Observations and Analysis in Serpentinite

Visual inspections were conducted at regular intervals to monitor for signs of mineralization. A yellow colloidal substance was consistently observed in all samples containing serpentinite, as well as a white precipitate in the serpentinite samples. Figure 9 provides data on the yellow colloid observed in the serpentine samples, along with the blank test data. Figure 10 illustrates the white precipitate observed in the serpentine sample.

(a) Blank (b)Serpentine

Figure 9 Leaching test after one week

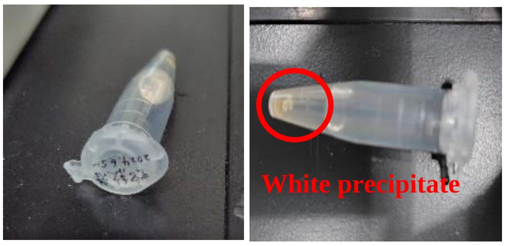


Figure 10 White precipitate in serpentine

The formation of the yellow colloidal substance could be attributed to several factors, depending on the chemical composition and environmental conditions. Potential causes include the presence of iron hydroxides or oxides, colloidal sulfur and silica colloids (Schwarzenbach et al., 2013).

4 Conclusions

In the short-term leaching test under a CO_2 pressure of 600 kPa, the pH values for sandstone, peridotite, and basalt remained stable between 5.0 and 6.0, while serpentinite stabilized between 6.0 and 7.0. During the long-term test, the pH values showed no significant changes, remaining relatively stable throughout the duration of the experiment.

The duration of element leaching varied by rock type. Peridotite and basalt exhibited significant leaching within approximately three days, while sandstone and silicified andesite showed substantial leaching over a period ranging from one week to six months. In contrast, serpentinite continued to leach elements consistently over an extended period of up to eight months.

In serpentinite samples subjected to a one-week leaching test, elements such as C, Ca, Fe, and Ni were found to be more widely distributed compare to the original serpentinite. The co-precipitation of these cations (Ca, Fe, Ni) with anions (C, O) at specific sites suggests the formation of carbonates. These findings underscore the potential of certain rock types, particularly serpentinite, to promote rapid CO_2 sequestration through carbonate precipitation.

5 Acknowledgement

This work was supported by JSPS (Postdoctoral Fellowships for Research in Japan (Standard)) as well as JST FOREST (JPMJFR225S).

References

Boot-Handford ME, Abanades JC, Anthony EJ, et al. (2014) Carbon capture and storage update. Enegry & Environmental Science, 7(1), pp.130-189.

Dash S, Kamruddin M, Ajikumar, PK. (2000) Nanocrystalline and metastable phase formation in vacuum thermal decomposition of calcium carbonate. Thermochimica Acta, 363(1-2), pp.129-135.

Hanifa M, Agarwal R, Sharma U, et al. (2023) A review on CO_2 capture and sequestration in the construction industry: Emerging approaches and commercialised technologies. Journal of CO_2 Utilization, 67, 102292.

Iglauer S, Al-Yaseri AZ, Wolff-Boenisch D. (2020) Basalt-CO_2-brine wettability at storage conditions in basaltic formations. International Journal of Greenhouse Gas Control, 102, 103148.

Karunadasa Kohobhange S. P., Manoratne C. H., Pitawala H. M. T. G. A., et al. (2019) Thermal decomposition of calcium carbonate (calcite polymorph) as examined by in-situ high-temperature X-ray powder diffraction. Journal of Physics and Chemistry of Solids, 134, pp.21-28.

MacKenzie K.J.D. and Meinhold R.H. (1994) Thermal reactions of chrysotile revised: A29Si and 25Mg MAS NMR study. American Mineralogist, 79, 43–50.

Patruno S, Green A, Corcoran J, et al. (2024) A conceptual CO_2 fill-and-spill mega-fairway in the UK Southern North Sea: A new approach to identify and optimise large-scale underground carbon storage (CCS). International Journal of Greenhouse Gas Control, 133, 104092.

Popall Rabja Maria, Postec, Anne, Lecoeuvre, Aurelien, et al. (2023) Metabolic challenges and key players in serpentinite-hosted microbial ecosystems. Frontiers in Microbiology, 14, 1197823.

Schwarzenbach Esther M., Lang Susan Q., Frah-Green Gretchen L., et al. (2013) Sources and cycling of carbon in continental, serpentinite-hosted alkalinesprings in the Voltri Massif, Italy. Lithos, 177, pp.226-244.

Viti Cecilia. (2010) Serpentine minerals discrimination by thermal analysis. American Mineralogist, 95(4), pp.631-638.

Zhang HY, Arif M. (2024) Residual trapping capacity of subsurface systems for geological storage of CO_2: Measurement techniques, meta-analysis of influencing factors, and future outlook. Earth-Science Reviews, 252, 104764.