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Experimental Evaluation of CO_2-Rich Water Interaction with Paleogene Basalt Samples for Mineral Carbonation Potential, Malaysia

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Abstract

CO_2 is the leading anthropogenic greenhouse gas (GHG) responsible for global warming. Mitigating the effect of anthropogenic CO_2 emission is among the priority. As Malaysia is one of the largest CO_2 emitters among the four ASEAN countries, identifying a potential geological formation for CO_2 storage is compulsory in order to minimize the environmental effect of emitted CO_2. Hence, fundamental research in which fluid-rock interaction of Paleogene basalt samples was assessed in the context of Malaysia's need to identify any potential host rock for mineral carbonation. For this purpose, laboratory experiments were conducted, including CO_2 injection using high pressure and high temperature (HPHT) reactor, geochemical analysis on water samples (leachates) using atomic absorption spectroscopy (AAS), and mineralogical analysis on the reacted rock samples using X-Ray Diffraction (XRD) techniques. During the fluid-rock interaction experiment, the water chemistry and mineralogical changes in the rock samples were evaluated at 914 psi and 3133 psi pressures and 100ºC and 120ºC temperature conditions. The concentration of Ca, Mg, and Fe released into the solution increased when the pressure of CO_2 applied increased. Yet, the concentration of these elements showed a non-consistent trend with the rise of the experimental temperature. These results were influenced by the reaction of silicate and carbonate minerals during the experiment. This finding may provide clues into the pressure and temperature values required for geological CO_2 sequestration in the Malaysian geological settings.

Keywords: *CO_2 storage; Mineral carbonation; Basalt; Malaysia.*

1. Introduction

The increasing threat of global warming and climate change has called for more attention and discussion of global environmental issues [1]. Carbon dioxide (CO_2) is a principal leading greenhouse gas (GHG) among other gases that are responsible for global warming and climate change [1-4]. Figure 1 is showing greenhouse gas emission in percentage and CO_2 as the principal emitter. It is recorded that Malaysia, a developing country is the largest CO_2 emitter among four Association of Southeast Asian Nations (ASEAN) countries (Indonesia, Thailand, Malaysia, and the Philippines) from 1970 to 2013 [5]. Other than that, Malaysia has discovered a gas field with a high content of CO2 that reaches up to 70% [6-7]. When many developed countries have successfully reduced GHGs emissions, Malaysia continues to increase its emission level [8]. It is necessary to store CO2 away from the atmosphere. Therefore, a long-term reduction of CO_2 emissions will be needed as a significant solution.

Carbon dioxide capture and storage (CCS) is one of the methods for global CO_2 emission reduction. Where industrial and energy-related CO_2 is captured and transported for sequestration procedure as long-term isolation from the atmosphere [9-10]. This research focuses on mineral carbonation, a safe technique that able to minimize the global environmental issue. It mimics the natural silicate weathering process of silicate minerals with CO_2 in fluid, resulting in solid carbonate minerals to form such as calcite ($CaCO_3$), dolomite ($CaMgCO_3$), magnesite ($MgCO_3$), and siderite ($FeCO_3$) [11-16].

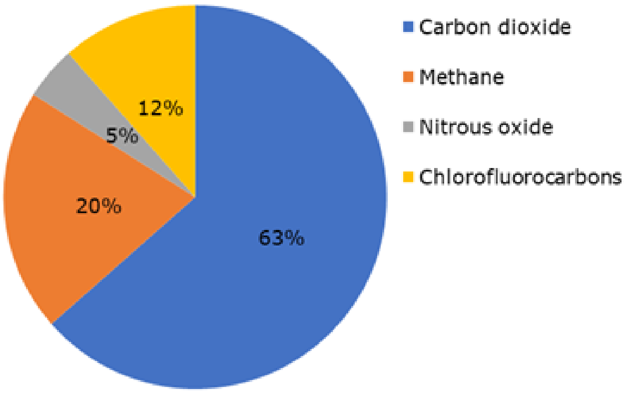

Figure 1. Contribution to global warming by greenhouse gas emissions from anthropogenic sources from the pre-industrial time, modified from [2]

Mineral carbonation technologies are divided into two, which are ex-situ and in-situ mineral carbonations. Ex-situ mineral carbonation happens on the aboveground using the natural minerals and industrial alkaline wastes via an industrial chemical process involving a combination of a pre-treatment and sequestration process [17]. The in-situ mineral carbonation approach will inject the CO_2 directly into the geological formation, where it can directly react with the minerals in the geological formation [18]. However, the storage rock must contain minerals that can easily dissociate and produce metal cations (Ca, Mg and Fe) to allow the mineral carbonation process to occur [17-19].

In most mineral carbonation scenarios, it starts with the reaction of CO_2 and water to form carbonic acid H_2CO_3 (Eq. 1), and the carbonic acid later will dissociate to bicarbonate HCO_3^- (Eq. 2) and carbonate CO_3^{2-} (Eq. 3) [18]. The metal cations from silicate mineral dissolution (Eq. 4), through a coupled reaction with carbonate, precipitate a metal carbonate (Eq. 5) [18]. The silicate-phase dissolution rates are slower than the corresponding carbonate precipitation rate in most cases, so quickening the dissolution is the key to optimization [18].

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \qquad (1)$$
$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \qquad (2)$$
$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \qquad (3)$$
$$Mg_2SiO_4 + 4H \rightarrow 2Mg^{2+} + SiOH4_4 \qquad (4)$$
$$Mg^{2+} + CO_3^{2-} \rightarrow MgCO_3 \qquad (5)$$

In this paper, Malaysia's Paleogene ultramafic rock samples were used for a hydro-geochemistry experimental study to observe CO_2-rich water interaction with the rock samples at variable temperatures and pressures. The fluid-rock interaction is believed to be affected by the applied pressure and temperature. Thus, four experiments at varying pressure (914 and 3133 psi) and temperature (100°C and 120°C) were conducted for further comparison. This work presents the water chemistry and the mineralogical changes on the rock samples to assess the mineral carbonation potential of the Paleogene basalt within the experimental hours.

2. Materials and methods

2.1. Materials

Malaysia's Paleogene basalt rock samples used for interaction with CO_2-rich water experiment were prepared as a plug with a diameter of 5 mm and height of 25 mm. The rock samples were placed into the HPHT reactor containing ultra-pure water. The ratio of the rock sample to water in this experiment was set to 1:5 by weight. After closing the cell tightly, the heater was switched on, and the temperature was set to 100°C. CO_2 was injected into the reactor until it reaches 914 psi. In this paper, this CO_2 injection experiment will be referred to as a batch experiment. The batch experiment was run and monitored constantly for 10 days. This closed system experiment containing injected CO_2, pure water, and the rock sample was carried out separately for 240 hours repeated at 914 psi and 3133 psi pressures; at 100°C and 120°C temperatures (Table 1). The temperature and pressure were set while considering the compatibility of the reactor used and within the range of several geological storage sites.

After conducting the batch experiment, the solution samples and the reacted rock samples were collected. The solution samples were filtered using filter paper, and the collected rock samples were pulverized and subsequently sieved to obtain particles with grain sizes of <63µm. Standardizing the grain size is important to prevent biased results on elements in those grains, and reducing the grain size will enhance the precision during mineralogical analysis [20-21]. The grain size was determined by MASTERSIZER-2000 from Malvern Instrument.

Table 1. Malaysia's Paleogene basalt interaction with CO_2-rich water experimental conditions

Sample ID	Duration (hours)	Pressure (psi)	Temperature (°C)	Rock to water ratio by weight
PB-01	240	914	120	1:5
PB-02	240	3133	120	1:5
PB-03	240	914	100	1:5
PB-04	240	3133	100	1:5

2.2. Geochemical analysis

By using Atomic Absorption Spectrometers (240FS AA) from Agilent Technologies, flame atomic absorption spectroscopy (AAS) was conducted to determine the concentration of metal elements (Ca, Mg and Fe) in the collected solution samples after performing a batch experiment. Before measuring the elements in the collected solution samples, three (3) different concentrations of standard solutions of Ca, Mg, and Fe elements along with pure water were prepared to produce the calibration curves for each element. This procedure used to ensure the accuracy of the measured results of the solution samples is within the AAS detection range for each element. Based on the calibration curves produced, the concentration detection limit for Ca and Mg measurement were 0 - 5 ppm while 0 - 1 ppm was for Fe. Four solution samples were analyzed using this method. The raw solution samples and the diluted solution samples were analyzed and compared to ensure the analyzed concentration of Ca, Mg, and Fe were within its measurable range of the calibration curves. The elemental concentration in the diluted solution samples was calculated using Eq. (6).

$$M_1V_1=M_2V_2 \qquad (6)$$

where: M_1 concentration of the element in diluted solution by mass; V_1 volume of the diluted solution; M_2 concentration of the element in actual solution by mass; V_2 volume of the actual solution.

2.3. Mineralogical analysis

The mineralogical identification on the pulverized rock samples was conducted by using X'Pert³ Powder from Malvern Panalytical Instrument for X-Ray Diffraction (XRD) analysis in order to identify the mineral changes in the rock samples. Four (4) samples that were listed in Table 1 and their unreacted and reacted samples were analysed at variable temperature and pressure experimental conditions to identify its possible mineralogical changes during the experimental hours.

3. Results

3.1. Geochemical analysis

The result of each element was shown in the produced column charts in Figures 2-4. The column charts were showing the concentration of the elements, Ca, Mg, and Fe, increased when the pressure was increased. However, the leaching of the elements into the pure water was not consistent when increasing the temperature. When the experimental temperature increased from 100°C to 120°C, the concentration of Ca in pure water decreased (Figure 2), but Mg concentration in the pure water increased (Figure 3). However, the changes of Fe concentration at 914 psi and 3133 psi pressure were not consistent when increasing the experimental temperature from 100°C to 120°C (Figure 4).

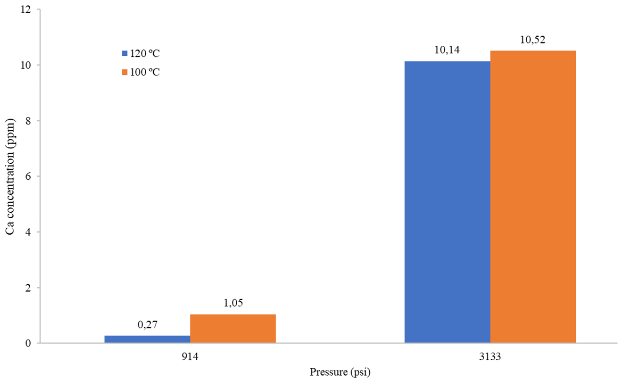

Figure 2. Ca concentration released into the solution at different temperature and pressure experimental conditions

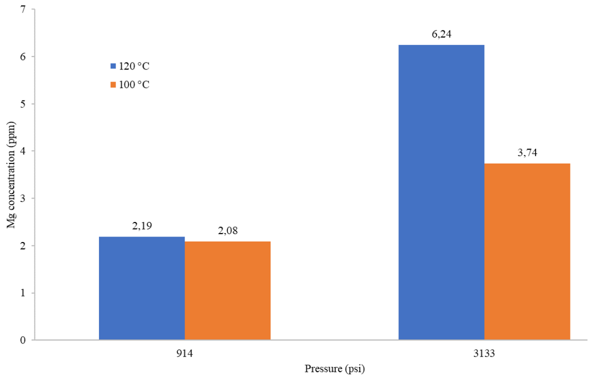

Figure 3. Mg concentration released into the solution at different temperature and pressure experimental conditions

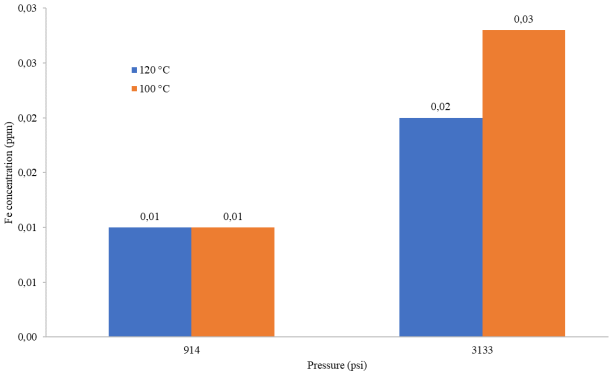

Figure 4. Fe concentration released into the solution at different temperature and pressure experimental conditions

3.2. Mineralogical analysis

The XRD spectrums of the reacted and unreacted samples of Malaysia’s Paleogene basalt were shown in Figures 5-8. All the XRD spectrums of unreacted and reacted samples were detected the presence of fayalite, forsterite, enstatite, augite, sudoite, microcline, orthoclase, anorthite, rutile, hypersthene, analcime, and calcite minerals except for the reacted samples PB-02 (Figure 6) and PB-04 (Figure 7) as there were no calcite mineral detection on them.

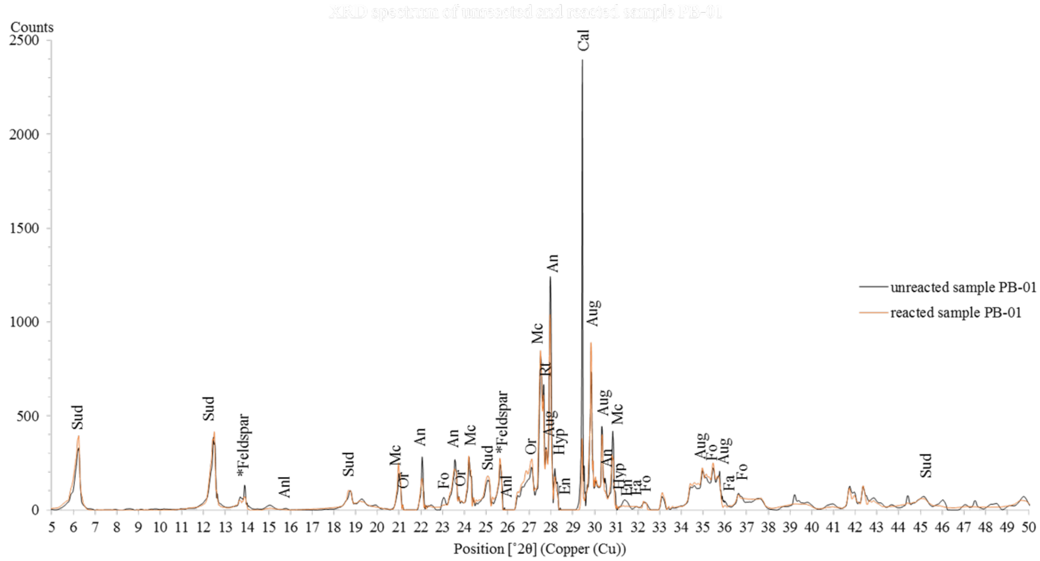

Figure 5. XRD spectrum of unreacted and reacted sample PB-01 (Sud=Sudoite, *Feldspar=Common feldspar group peak, Anl=Analcime, Mc=Microcline, An=Anorthite, Fo=Forsterite, Or=Orthoclase, Rt=Rutile, Aug=Augite, Hyp=Hypersthene, Cal=Calcite, En=Enstatite, Fa=Fayalite)

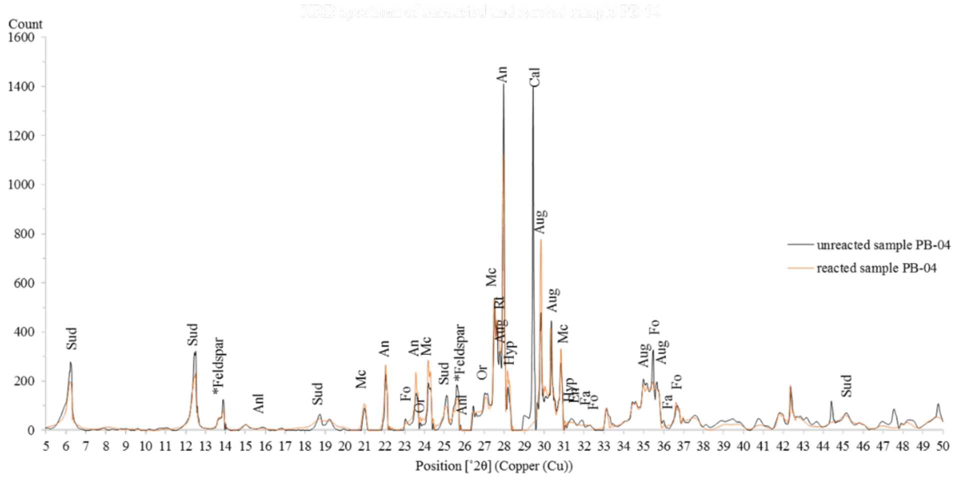

Figure 6. XRD spectrum of unreacted and reacted sample PB-02

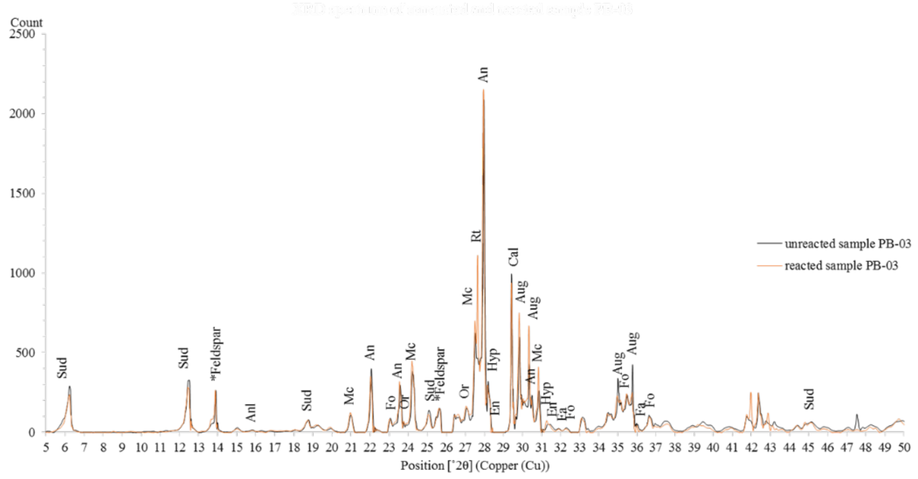

Figure 7. XRD spectrum of unreacted and reacted sample PB-03

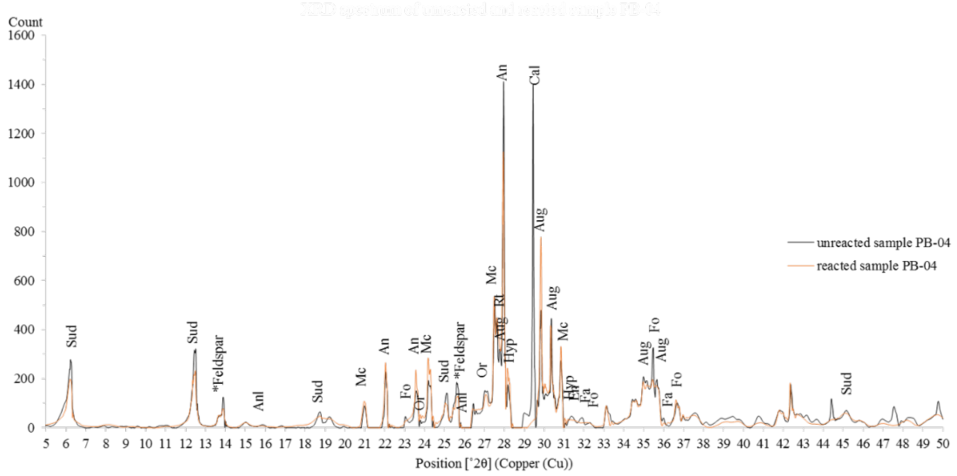

Figure 7. XRD spectrum of unreacted and reacted sample PB-04 (Sud=Sudoite, *Feldspar=Common feldspar group peak, Anl=Analcime, Mc=Microcline, An=Anorthite, Fo=Forsterite, Or=Orthoclase, Rt=Rutile, Aug=Augite, Hyp=Hypersthene, Cal=Calcite, En=Enstatite, Fa=Fayalite)

4. Discussion

4.1. Effect of pressure on the dissolution of the Paleogene basalt samples

Referring to produced column charts in Figures 2-4, the elements of Ca, Mg, and Fe were released into the solution during the fluid-rock interaction for 240 experimental hours. When increasing the pressure from 914 psi to 3133 psi, the concentration of Ca, Mg, and Fe in solution were increasing. This was because CO_2 solubility into the solution increased when the applied pressure was increased, and more carbonic acid was formed. The dissociated carbonic acid might be reacting with calcite ($CaCO_3$), enstatite ($MgSiO_3$), forsterite (Mg_2SiO_4), fayalite (Fe_2SiO_4), and augite ($(Ca,Na)(Mg,Fe,Al)(Si,Al)_2O_6$) and dissolution happened thus releasing Ca, Mg and Fe elements in the solution. Fayalite and forsterite are members of the olivine group, while enstatite and augite are in the pyroxene group. The olivine and pyroxene are the potential minerals for mineral carbonation [15, 22-24]. From the result, the Fe element was the least reactive and hardly been dissociated from the rock samples. The Ca concentration released into the solution might be influenced by the presence of calcite mineral in the basalt samples. As shown in Figures 6 and 8, the calcite peak at 2θ position of 29.4º after applying 3133 psi pressure could not be detected anymore as the calcite was dissolved completely into the solution. This explains that the carbonate mineral was more soluble with increasing the pressure from 914 psi to 3133 psi than any other silicate minerals such as enstatite, forsterite, fayalite, and augite. However, the dissolution of calcite was not the intended scenario in the process of mineral carbonation. Thus, in order to preserve the calcite minerals in these samples while allowing the silicate minerals dissolution, controlling the pressure to the optimum is important. However, if there were only silicate minerals to be extracted as the feedstock for the ex-situ mineral carbonation process, increasing the pressure would have increased the dissolution of silicate minerals and released Mg and Fe elements into the solution, which will be potentially carbonated to form magnesite and siderite by reacting with carbonate (CO_3^{2-}). Since the increased pressure of CO_2 which is accompanied by a high proton activity, the minerals are preferably dissolved [25].

4.2. Effect of temperature on the dissolution of Paleogene basalt samples

The Ca, Mg, and Fe elements released into the solution showed a non-consistent pattern when increasing the temperature from 10°C to 120°C (Figures 2-4). When increasing the temperature, only Mg showed an increasing concentration in the solution. It is possible that the Mg was released from enstatite and forsterite, which could be related to the more soluble trend showed by those two minerals at the higher temperature (Figure 3). Fe was hardly dissociated from the rock samples. However, it showed a slight decrement in concentration or remained constant at increased experimental temperature. Thus, it was assumed fayalite was the least reactive to release Fe element into the solution samples compared to enstatite and forsterite minerals. Ca showed a decreasing concentration when increasing the temperature from 100°C to 120°C. This is because calcite is more soluble at low temperature, thus at 120°C, it can maintain more calcite than at 100°C. Resulting from this experiment, CO_2 was observed to be less soluble at high temperature (120°C) than at the low temperature (100°C) during the experimental hours. From the experimental observation, the dissolution of silicate minerals was favored by high temperature. This is because the temperature rises only favored endothermic reaction which needs additional heat that is the dissolution of silicate minerals [25]. Yet, the dissolution of carbonates is an exothermic reaction [25]. Therefore the solubility of carbonate mineral is less favorable with increasing temperature [25].

4.3. Mineral carbonation potential of Paleogene basalt

In order to allow mineral carbonation in any rock formation to happen, the selection of the host rock is a prerequisite. The rock/s must contain elements that are able to form stable carbonate mineral/s. For this process to happen, it involves several chemical reactions of CO_2-water-rock/minerals (See Eqs. 1-5). Calcite detection in this Paleogene basalt samples had proven that it had already undergone the natural mineralization process as it was exposed to the atmosphere. However, there are still several reactive minerals (e.g., enstatite, forsterite, fayalite, and augite) which are available for mineralization into carbonate mineral/s. This study had proven the dissolution of these silicate minerals and the fulfillment of the prerequisite to forming carbonate mineral/s. However, to preserve the calcite in the basalt samples while allowing the dissolution of other reactive silicate minerals, the optimum temperature, and pressure selection during the fluid-rock interaction process is crucial to enhance the mineral carbonation process in these basalt samples. From this experiment, low pressure (914 psi) and high temperature (120°C) conditions were preferable, as this may enable the dissolution of the silicate minerals while sustaining calcite mineral in the rock.

5. Conclusion

The required minerals for the mineral carbonation process are found in Malaysia's Paleogene basalt; hence conducting the experiment using the basalt samples has enabled us to observe the fluid-rock interaction at the selected temperature and pressures conditions. The reaction between the Paleogene basalt samples and CO_2-rich water in the batch experiment at the stated temperatures and pressures showed that the mineral dissolution process had occurred during the experimental hours. The elements of Ca, Mg, and Fe that were released from the silicate minerals into the solution during the experimental hours will able to form carbonate minerals. The findings of this experimental study give an idea of the consequences for Malaysia's Paleogene basalt or rocks of similar composition during the mineral carbonation process if it is to serve as a potential geological storage for CO_2 by in-situ mineral carbonation. It may provide clues into the pressure and temperature values required for geological CO_2 sequestration in Malaysian geological settings.

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