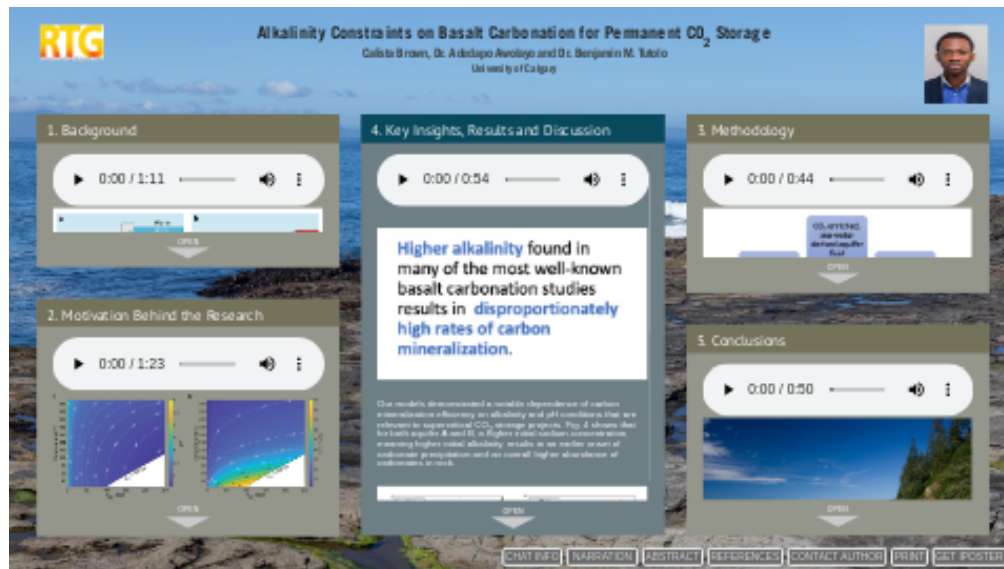


# Alkalinity Constraints on Basalt Carbonation for Permanent CO<sub>2</sub> Storage



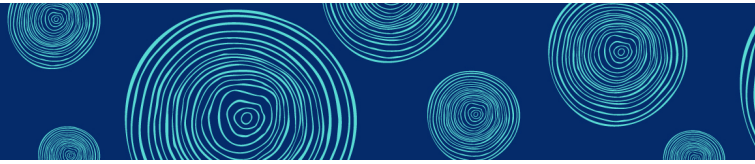
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University of Calgary



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## 1. BACKGROUND

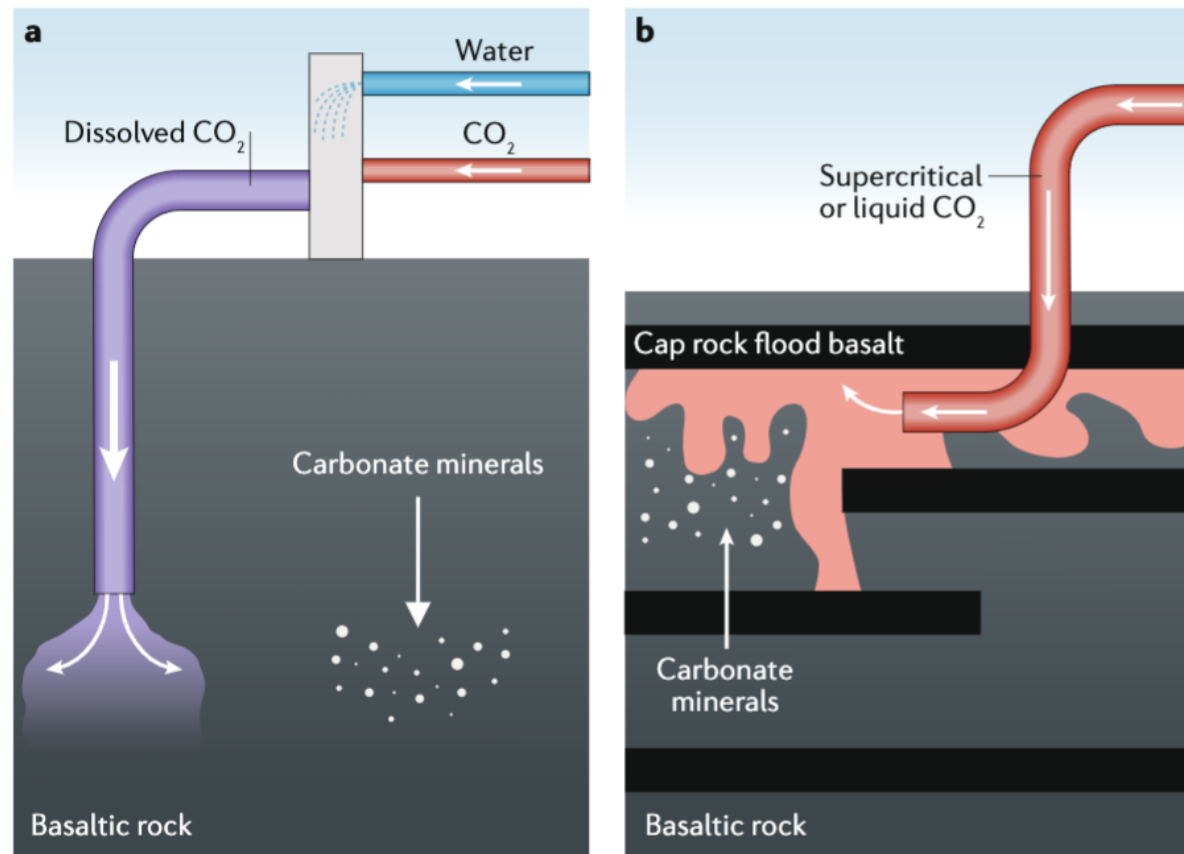
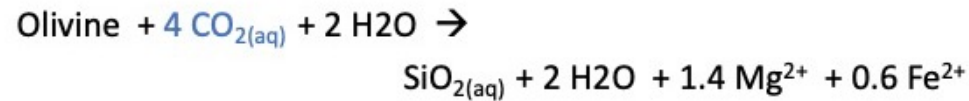
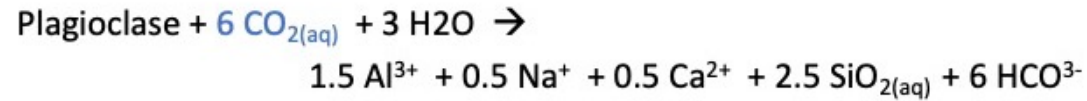


Figure 1. Two methods of basalt carbonations. a| Injection of dissolved CO<sub>2</sub> into the basaltic rock. This was the method used for Carbfix. b| Injection of supercritical CO<sub>2</sub> into the basaltic rock. Many basalt CO<sub>2</sub> storage projects will likely use this method as the injection of supercritical CO<sub>2</sub> is less energy-intensive. The figure is not to scale. (Figure is taken from Snæbjörnsdóttir et al., 2020).

Mineral carbonation is a climate mitigation-strategy that mimics mineral weathering and stores atmospheric CO<sub>2</sub> in a geologic reservoir by converting CO<sub>2</sub> gas into carbonate minerals (Fig. 1). Mineral carbonation proceeds through the reaction of water containing dissolved CO<sub>2</sub> with rock. Mafic basalt is an ideal lithology for mineral carbonation due to its large abundance as the most common

rock at the Earth's surface, the high concentration of cation-rich silicate minerals and its porosity, permeability and injectivity<sup>1,2</sup>. Water charged with CO<sub>2</sub> will be acidic and the dissolution of plagioclase (e.g., Ca<sub>0.5</sub>Na<sub>0.5</sub>Al<sub>1.5</sub>Si<sub>2.5</sub>O<sub>8</sub>) and olivine (e.g., Mg<sub>1.4</sub>Fe<sub>0.6</sub>SiO<sub>4</sub>) will be promoted:



The dissolution of plagioclase and olivine generates alkalinity through the consumption of acidity. Once secondary clays and carbonates become supersaturated they will precipitate and begin to reduce the ability of the dissolution of primary minerals to produce alkalinity. Once secondary clays and carbonates begin to precipitate, alkalinity generation depends on both the rate of dissolution of the primary minerals and the rate at which secondary clays and carbonates remove the primary minerals donated ions from the solution.

The dissolution of plagioclase and olivine promotes mineral carbonation by increasing the pH and alkalinity, significant drivers of mineral carbonation, and by releasing cations that can react with dissolved CO<sub>2</sub> to form carbonate minerals, permanently fixing CO<sub>2</sub> as a stable solid mineral phase<sup>3</sup>. This type of fixation is appealing as it is less prone to leakage and has a longer residence time than CO<sub>2</sub> storage in sedimentary basins<sup>4,5</sup>.

## 2. MOTIVATION BEHIND THE RESEARCH

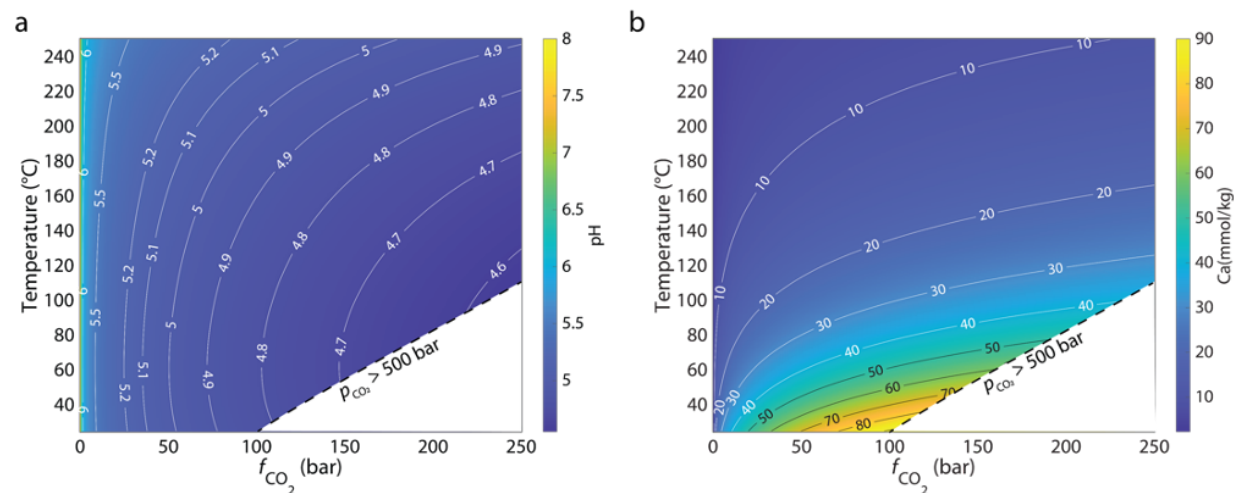


Figure 2. pH and calcite solubility in calcite-saturated seawater as a function of temperature and fugacity of  $\text{CO}_2$ . At higher  $\text{CO}_2$  fugacities, as would be seen in most  $\text{CO}_2$  storage projects, it can be seen that the pH is lower than 5.5. Calcite solubility is higher at lower temperatures, higher  $\text{CO}_2$  fugacities, and lower pH meaning carbonate precipitation will decrease in these conditions.

There are two renowned large scale carbon mineralization field experiments, the Wallula Washington experiment<sup>6</sup> and the Carbfix experiment in Iceland<sup>7</sup>. In both experiments,  $\text{CO}_2$  was injected underground and the progress of  $\text{CO}_2$  mineralization was monitored. Carbfix found over 95% of the injected  $\text{CO}_2$  was mineralized within two years<sup>7</sup> whereas the Wallula experiment also resulted in mineralization but as of yet has not been quantified<sup>6</sup>.

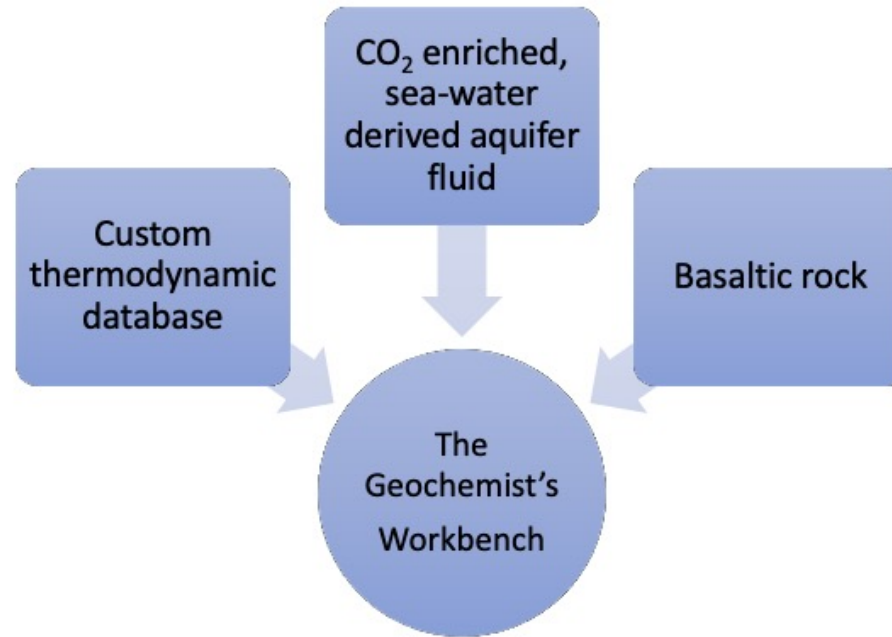
Both experiments had pH ranges that fell within the range of **8.4-9.8**<sup>7,8</sup>. This is an abnormally high pH range for  $\text{CO}_2$  enriched aquifer water which has a pH of approximately **5.5**<sup>9,10</sup>. Many lab experiments also have abnormally high pH ranges due to the use of  $\text{NaHCO}_3$  as a pH buffer and  $\text{CO}_2$  source.  $\text{NaHCO}_3$  adds both sodium and bicarbonate to the water and artificially increases alkalinity<sup>11</sup>.

Most  $\text{CO}_2$  storage projects will likely inject supercritical  $\text{CO}_2$  rather than dissolved because it is less energy-intensive<sup>5</sup>. The injection of supercritical  $\text{CO}_2$  will result in lower alkalinity and pHs than the field and experimental studies. As seen in Fig 2., higher pH values result in higher solubility of calcite. This

shows that a high pH (and consequently high alkalinity) is a significant driver of carbon mineralization meaning the promising results of these field and lab experiments may not be applicable to a broader suite of environments.

This possible oversight is what prompted our research by bringing up the important question: How efficiently can natural CO<sub>2</sub>-water-rock interactions increase the pH and alkalinity of high-pCO<sub>2</sub> reservoirs? We hope to assess the efficiency of mineral carbonation in a wider array of environments by examining how alkalinity in a system affects carbon mineralization.

### 3. METHODOLOGY



To explore the dependency of carbon mineralization efficiency on alkalinity (and pH) we modelled the interaction of basalt with two different CO<sub>2</sub> enriched, seawater-derived aquifer fluids. The composition of Aquifer A is from Juan de Fuca Ridge Site 1301<sup>12</sup> and the composition of Aquifer B is from Luhmann et al's direct carbonation experiment<sup>13</sup>.

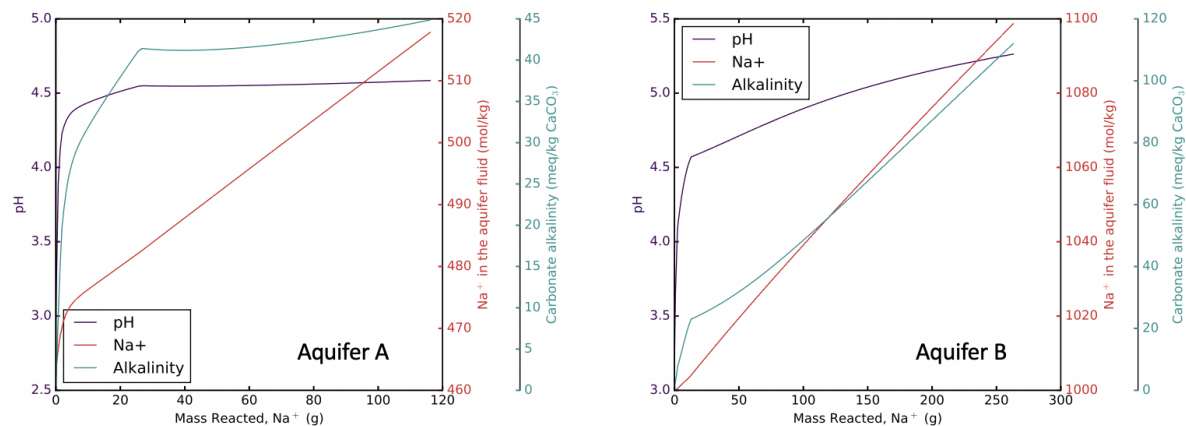


Figure 3. pH, carbonate alkalinity, and sodium concentration as a function of the total mass of sodium reacted. As more sodium reacts, the concentration of sodium, pH and carbonate alkalinity all increase.

The initial alkalinities were varied by changing initial sodium concentration by 5-10% (Fig. 3). The model was run at 60°C with a CO<sub>2</sub> fugacity of 100 bar and used a custom thermodynamic database that incorporated updated thermodynamic data for the relevant primary and secondary minerals. Kinetics were applied to the dissolution of the primary minerals and the oxidation of ferrous iron.



#### 4. KEY INSIGHTS, RESULTS AND DISCUSSION

**Higher alkalinity** found in many of the most well-known basalt carbonation studies results in **disproportionately high rates of carbon mineralization.**

Our models demonstrated a notable dependence of carbon mineralization efficiency on alkalinity and pH conditions that are relevant to supercritical CO<sub>2</sub> storage projects. Fig. 4 shows that for both aquifer A and B, a higher initial sodium concentration, meaning higher initial alkalinity, results in an earlier onset of carbonate precipitation and an overall higher abundance of carbonates in rock.

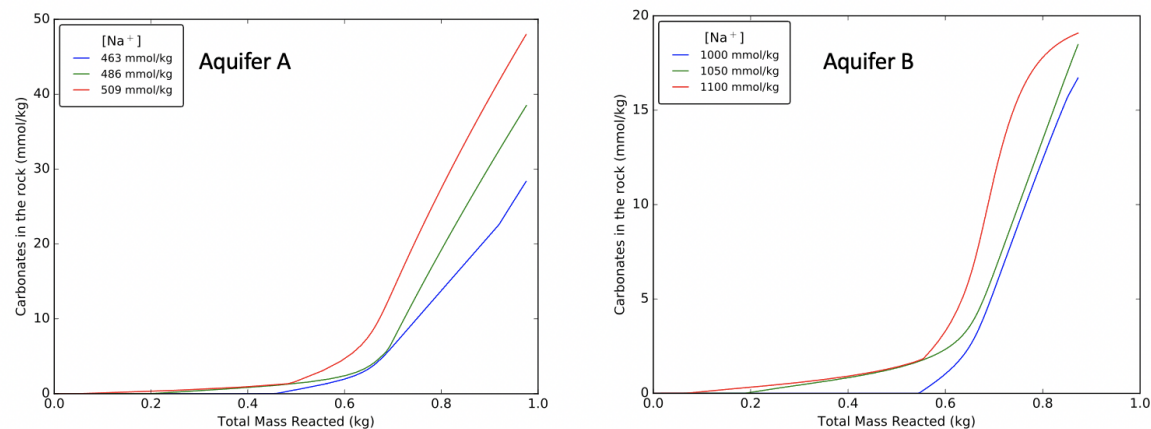


Figure 4. Carbonates in the rock as a function of total mineral mass reacted.

The 5 and 10% increases in alkalinity resulted in proportional increases in carbon mineralization. This demonstrates that higher pH ranges will result in more efficient mineral carbonation. Therefore, it can be concluded that the high pH ranges that are found in most well-known basalt carbonation studies result in disproportionately high rates of carbon mineralization. The increased rates frame carbon mineralization as a highly efficient and rapid CO<sub>2</sub> sequestration method.

The slow rate of CO<sub>2</sub> dissolution becomes significantly more important when supercritical CO<sub>2</sub> is injected rather than dissolved CO<sub>2</sub>. Projects that use supercritical CO<sub>2</sub> injection will result in carbon mineralization, however, it will likely take much longer and may be less effective overall than is insinuated by popular studies.

## 5. CONCLUSIONS



Figure 5. Image of Juan de Fuca trail beach. (Figure is taken from Wikimedia Commons).

Popular mineral carbonation studies often have a pH range that is much higher than the expected pH of 5.5 for CO<sub>2</sub> enriched aquifer water. Therefore, the high alkalinities found in these scenarios do not apply to CO<sub>2</sub> storage projects that inject supercritical CO<sub>2</sub>. Most CO<sub>2</sub> storage projects will likely use supercritical CO<sub>2</sub> injection over dissolved CO<sub>2</sub> because it is less energy-intensive to inject and uses less water.

Through modelling, we demonstrated that changes in alkalinity proportionally changed the efficiency of mineral carbonation. This means that the high pH range found in popular studies results in higher efficiency of mineral carbonation than would be found in projects with lower pH ranges.

# ABSTRACT

Basalt carbonation has gained traction as a key technology for avoiding the worst consequences of human-driven climate change. However, our understanding of this method's promise is likely inflated by the specialized conditions used in many of the most well-known laboratory studies and demonstration projects. For technological, hydrogeologic, and energetic simplicity, many basalt CO<sub>2</sub> storage projects will likely inject supercritical, not dissolved, CO<sub>2</sub>. Thus, fluids in these systems are likely to have low alkalinity and low pH, in contrast to many experimental and demonstration studies. Here, we present a series of geochemical models that explore the dependence of carbon mineralization efficiency on alkalinity and therefore pH at conditions relevant to these proposed operations. We modelled the interaction of basalt with CO<sub>2</sub> enriched, seawater-derived aquifer fluid with varying initial alkalinities at 60°C using a custom thermodynamic database incorporating updated thermodynamic data for relevant primary and secondary minerals. The results reinforce the notion that alkalinity is an important driver for carbonate precipitation, ultimately because carbonate minerals are up to an order of magnitude more soluble at pH <5 than they are at pH >6. Alkalinity increases of 5 to 10% proportionally increase carbonate precipitation in the models. Our results thus demonstrate that the elevated alkalinity found in many of the most well-known basalt carbonation studies yield disproportionately high rates of carbon mineralization, which, in turn, frames basalt carbonation as an extremely rapid and exceptionally effective CO<sub>2</sub> storage method. Although supercritical CO<sub>2</sub> injection operations such as those we explore here are likely to achieve high fractions of CO<sub>2</sub> mineralization over their lifetimes, this will likely take considerably longer and potentially be ultimately less effective, due to sluggish rates of CO<sub>2</sub> dissolution and alkalinity generation.

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Picture references:

Figure 1 - Snæbjörnsdóttir, S. Ó., Sigfússon, B., Marieni, C., Goldberg, D., Gislason, S. R., & Oelkers, E. H. (2020). Carbon dioxide storage through mineral carbonation. *Nature Reviews Earth & Environment*, 1(2), 90–102.  
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Figure 5 - Wikimedia Commons. (2007). Retrieved from  
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