

Alkalinity Constraints on Basalt Carbonation for Permanent CO₂ Storage

Calista Brown¹, Dapo Awolayo¹, and Benjamin Tutolo¹

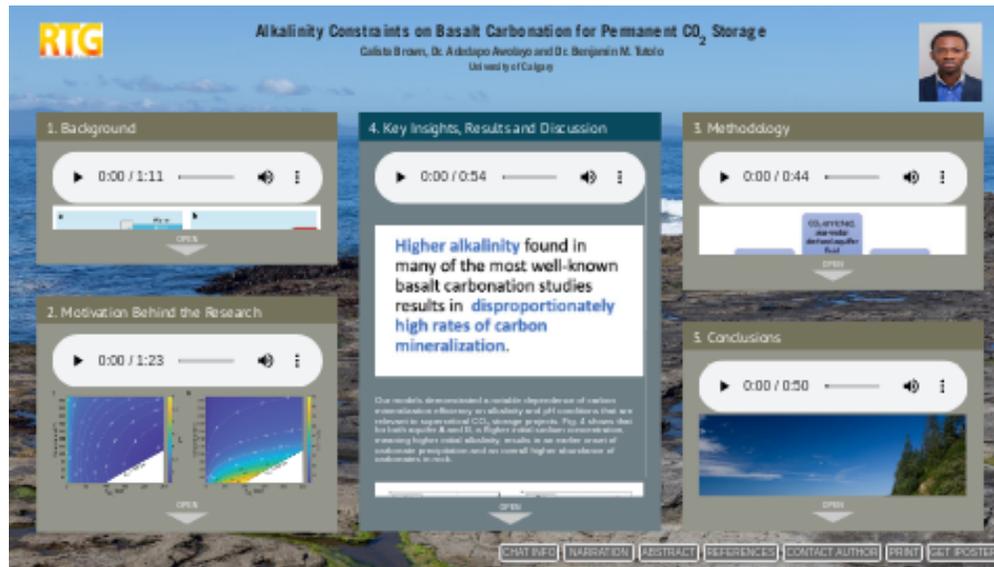
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Abstract

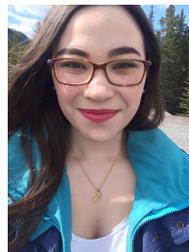
Basalt carbonation has gained traction as a key technology for avoiding the worst consequences of human-driven climate change. However, our understanding of this method's promise is likely inflated by the specialized conditions used in many of the most well-known laboratory studies and demonstration projects. For technological, hydrogeologic, and energetic simplicity, many basalt CO₂ storage projects will likely inject supercritical, not dissolved, CO₂. 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 CO₂ 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 CO₂ storage method. Although supercritical CO₂ injection operations such as those we explore here are likely to achieve high fractions of CO₂ mineralization over their lifetimes, this will likely take considerably longer and potentially be ultimately less effective, due to sluggish rates of CO₂ dissolution and alkalinity generation.

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1. BACKGROUND

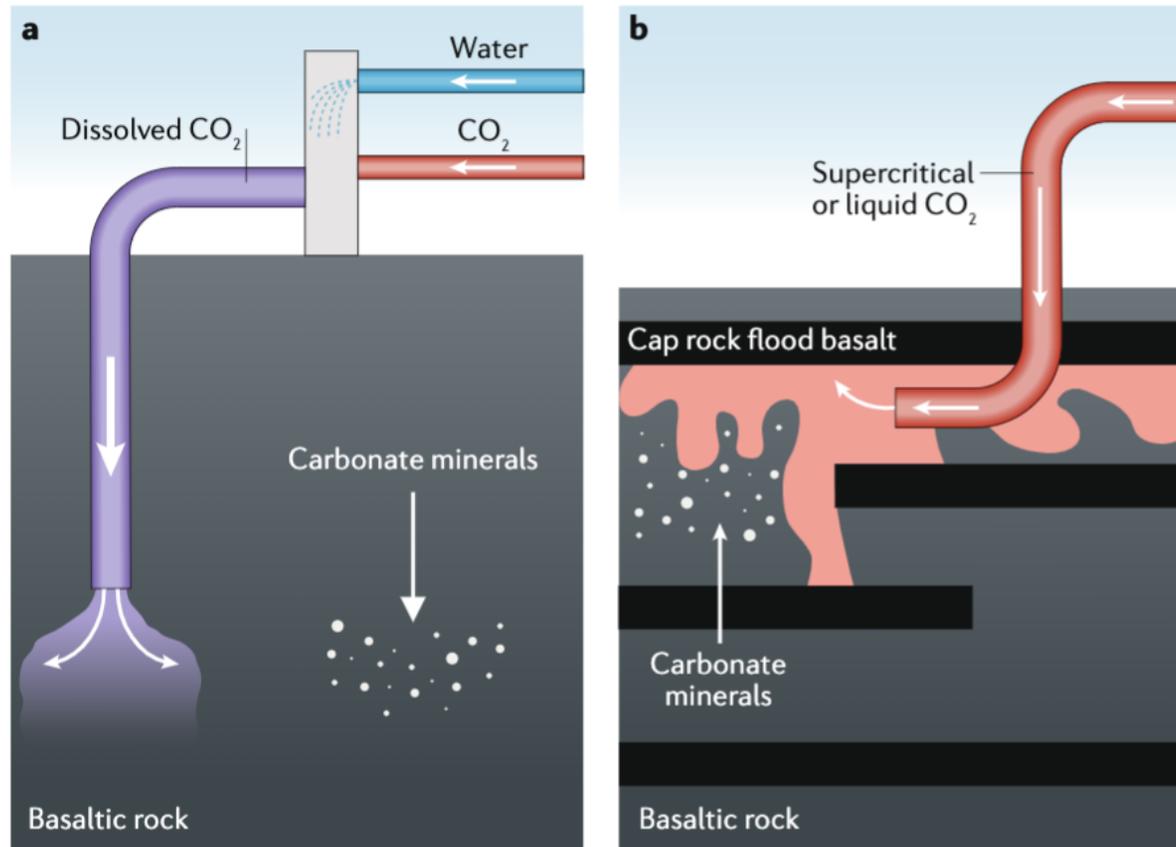
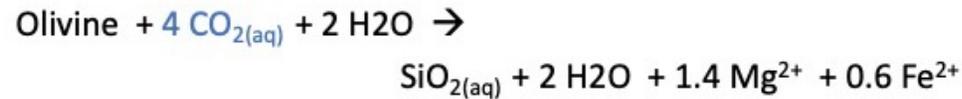
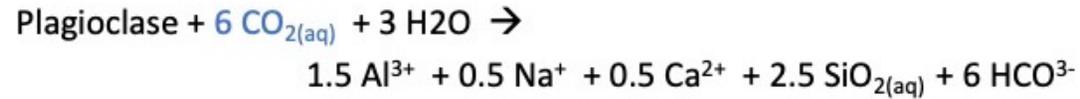


Figure 1. Two methods of basalt carbonations. a) Injection of dissolved CO₂ into the basaltic rock. This was the method used for Carbfix. b) Injection of supercritical CO₂ into the basaltic rock. Many basalt CO₂ storage projects will likely use this method as the injection of supercritical CO₂ is less 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 CO₂ in a geologic reservoir by converting CO₂ gas into carbonate minerals (Fig. 1). Mineral carbonation proceeds through the reaction of water containing dissolved CO₂ 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^{1,2}. Water charged with CO₂ will be acidic and the dissolution of plagioclase (e.g., Ca_{0.5}Na_{0.5}Al_{1.5}Si_{2.5}O₈) and olivine (e.g., Mg_{1.4}Fe_{0.6}SiO₄) 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 CO₂ to form carbonate minerals, permanently fixing CO₂ as a stable solid mineral phase³. This type of fixation is appealing as it is less prone to leakage and has a longer residence time than CO₂ storage in sedimentary basins^{4,5}.

2. MOTIVATION BEHIND THE RESEARCH

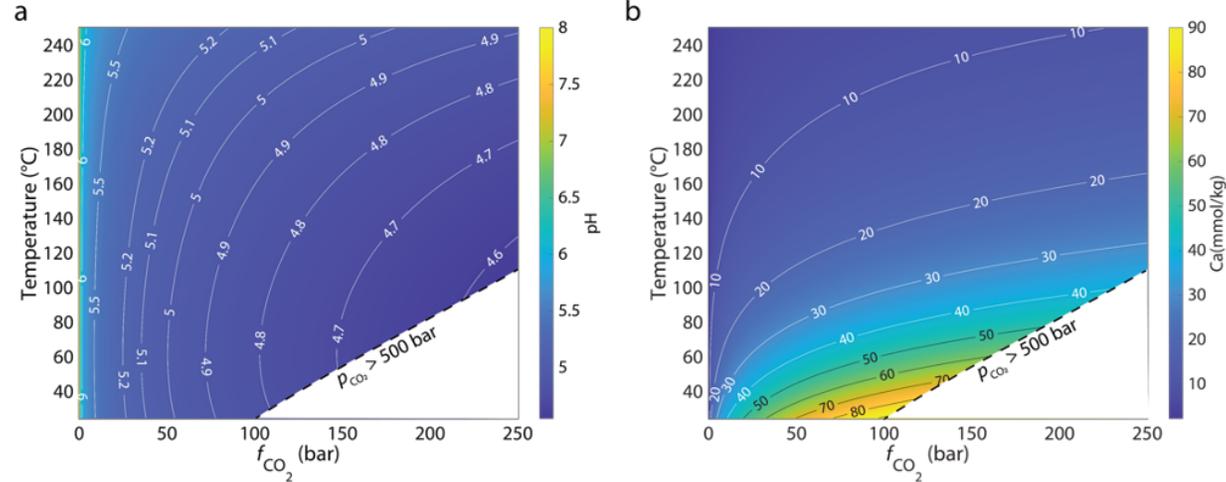


Figure 2. pH and calcite solubility in calcite-saturated seawater as a function of temperature and fugacity of CO₂. At higher CO₂ fugacities, as would be seen in most CO₂ storage projects, it can be seen that the pH is lower than 5.5. Calcite solubility is higher at lower temperatures, higher CO₂ fugacities, and lower pH meaning carbonate precipitation will decrease in these conditions.

There are two renowned large scale carbon mineralization field experiments, the Wallula Washington experiment⁶ and the Carbfix experiment in Iceland⁷. In both experiments, CO₂ was injected underground and the progress of CO₂ mineralization was monitored. Carbfix found over 95% of the injected CO₂ was mineralized within two years⁷ whereas the Wallula experiment also resulted in mineralization but as of yet has not been quantified⁶.

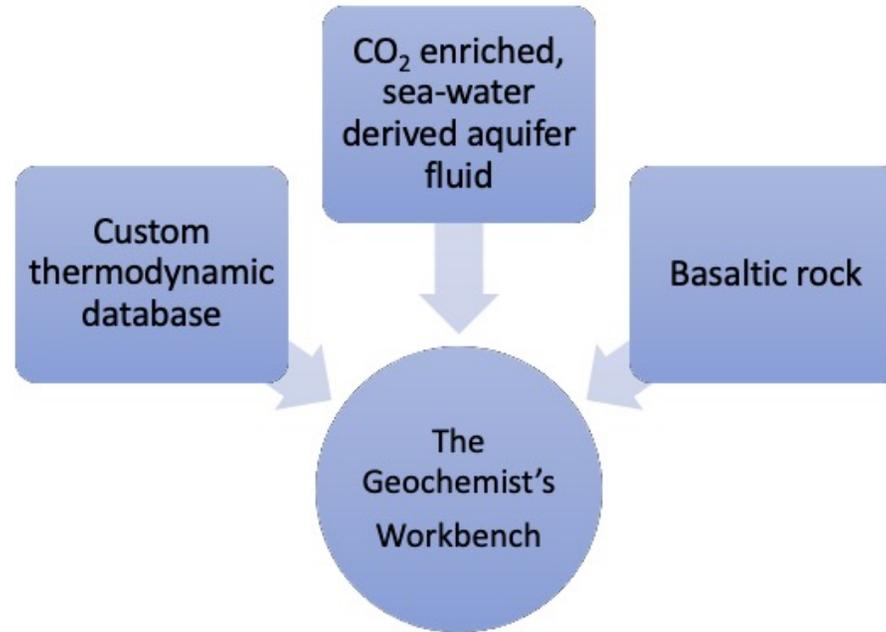
Both experiments had pH ranges that fell within the range of **8.4-9.8**^{7,8}. This is an abnormally high pH range for CO₂ enriched aquifer water which has a pH of approximately **5.5**^{9,10}. Many lab experiments also have abnormally high pH ranges due to the use of NaHCO₃ as a pH buffer and CO₂ source. NaHCO₃ adds both sodium and bicarbonate to the water and artificially increases alkalinity¹¹.

Most CO₂ storage projects will likely inject supercritical CO₂ rather than dissolved because it is less energy-intensive⁵. The injection of supercritical CO₂ 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 CO₂-water-rock interactions increase the pH and alkalinity of high-pCO₂ 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 CO₂ enriched, seawater-derived aquifer fluids. The composition of Aquifer A is from Juan de Fuca Ridge Site 1301¹² and the composition of Aquifer B is from Luhmann et al's direct carbonation experiment¹³.

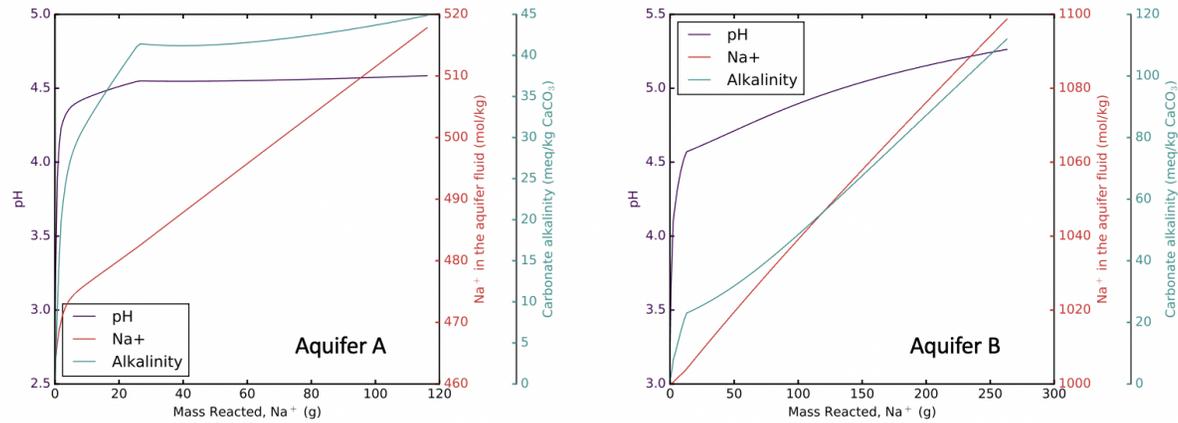


Figure 3. pH, carbonate alkalinity, and sodium concentration as a function of the total mass of sodium reacted. As more sodium reacts, the concentration of sodium, pH and carbonate alkalinity all increase.

The initial alkalinities were varied by changing initial sodium concentration by 5-10% (Fig. 3). The model was run at 60°C with a CO₂ 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 CO₂ 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.

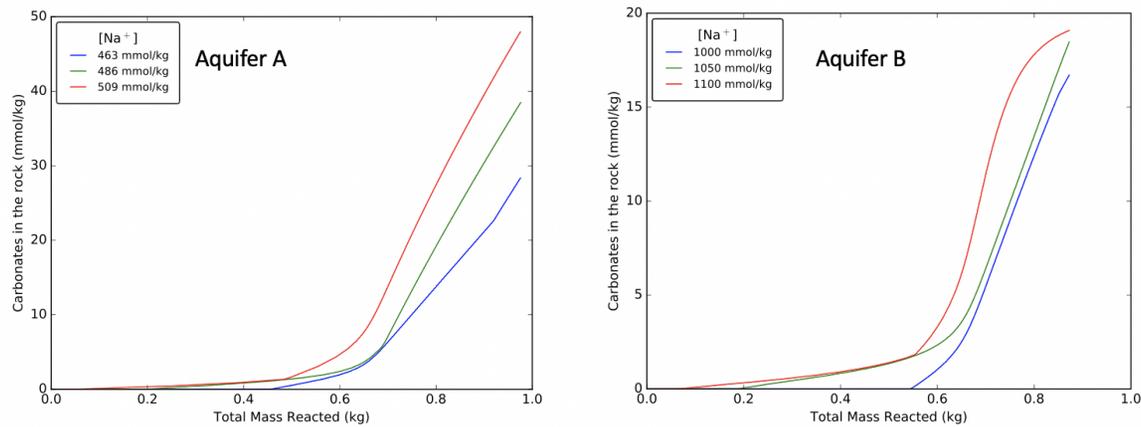


Figure 4. Carbonates in the rock as a function of total mineral mass reacted.

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 CO₂ sequestration method.

The slow rate of CO₂ dissolution becomes significantly more important when supercritical CO₂ is injected rather than dissolved CO₂. Projects that use supercritical CO₂ 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 CO₂ enriched aquifer water. Therefore, the high alkalinities found in these scenarios do not apply to CO₂ storage projects that inject supercritical CO₂. Most CO₂ storage projects will likely use supercritical CO₂ injection over dissolved CO₂ 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 CO₂ storage projects will likely inject supercritical, not dissolved, CO₂. 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 CO₂ 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 CO₂ storage method. Although supercritical CO₂ injection operations such as those we explore here are likely to achieve high fractions of CO₂ mineralization over their lifetimes, this will likely take considerably longer and potentially be ultimately less effective, due to sluggish rates of CO₂ dissolution and alkalinity generation.

REFERENCES

In-text references:

1. Gislason, S. R., & Oelkers, E. H. (2014). Carbon storage in basalt. In *Science* (Vol. 344, Issue 6182, pp. 373–374). American Association for the Advancement of Science. <https://doi.org/10.1126/science.1250828>
2. Goldberg, D., & Slagle, A. L. (2009). A global assessment of deep-sea basalt sites for carbon sequestration. *Energy Procedia*, 1(1), 3675–3682. <https://doi.org/10.1016/j.egypro.2009.02.165>
3. Marieni, C., Matter, J. M., & Teagle, D. A. H. (2020). Experimental study on mafic rock dissolution rates within CO₂-seawater-rock systems. *Geochimica et Cosmochimica Acta*, 272, 259–275. <https://doi.org/10.1016/j.gca.2020.01.0044>
4. Goldberg, D. S., Takahashi, T., & Slagle, A. L. (2008). Carbon dioxide sequestration in deep-sea basalt. *Proceedings of the National Academy of Sciences of the United States of America*, 105(29), 9920–9925. <https://doi.org/10.1073/pnas.0804397105>
5. 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. <https://doi.org/10.1038/s43017-019-0011-8>
6. McGrail, B. P., Schaef, H. T., Spane, F. A., Horner, J. A., Owen, A. T., Cliff, J. B., Qafoku, O., Thompson, C. J., & Sullivan, E. C. (2017). Wallula Basalt Pilot Demonstration Project: Post-injection Results and Conclusions. *Energy Procedia*, 114, 5783–5790. <https://doi.org/10.1016/j.egypro.2017.03.1716>
7. Matter, J. M., Stute, M., Snæbjörnsdóttir, S., Oelkers, E. H., Gislason, S. R., Aradóttir, E. S., Sigfússon, B., Gunnarsson, I., Sigurdardóttir, H., Gunnlaugsson, E., Axelsson, G., Alfredsson, H. A., Wolff-Boenisch, D., Mesfin, K., Taya, D. F. D. L. R., Hall, J., Dideriksen, K., & Broecker, W. S. (2016). Rapid carbon mineralization for permanent disposal of anthropogenic carbon dioxide emissions. *Science*, 352(6291), 1312–1314. <https://doi.org/10.1126/science.aad8132>
8. Alfredsson, H. A., Oelkers, E. H., Hardarsson, B. S., Franzson, H., Gunnlaugsson, E., & Gislason, S. R. (2013). The geology and water chemistry of the Hellisheidi, SW-Iceland carbon storage site. *International Journal of Greenhouse Gas Control*, 12, 399–418. <https://doi.org/10.1016/j.ijggc.2012.11.019>
9. Kharaka, Y. K., Cole, D. R., Hovorka, S. D., Gunter, W. D., Knauss, K. G., & Freifeld, B. M. (2006). Gas-water-rock interactions in Frio Formation following CO₂ injection: Implications for the storage of greenhouse gases in sedimentary basins. *Geology*, 34(7), 577–580. <https://doi.org/10.1130/G22357.1>
10. Tutolo, B. M., Kong, X. Z., Seyfried, W. E., & Saar, M. O. (2015). High performance reactive transport simulations examining the effects of thermal, hydraulic, and chemical (THC) gradients on fluid injectivity at carbonate CCUS reservoir scales. *International Journal of Greenhouse Gas Control*, 39, 285–301. <https://doi.org/10.1016/j.ijggc.2015.05.026>

11. Menefee, A. H., Giammar, D. E., & Ellis, B. R. (2018). Permanent CO₂ Trapping through Localized and Chemical Gradient-Driven Basalt Carbonation. *Environmental Science and Technology*, 52(15), 8954–8964.

<https://doi.org/10.1021/acs.est.8b01814>

12. Hulme, S. M., & Wheat, C. G. (2019). Subseafloor Fluid and Chemical Fluxes Along a Buried-Basement Ridge on the Eastern Flank of the Juan de Fuca Ridge. *Geochemistry, Geophysics, Geosystems*, 20(11), 4922–4938.

<https://doi.org/10.1029/2019GC008408>

13. Luhmann, A. J., Tutolo, B. M., Tan, C., Moskowitz, B. M., Saar, M. O., & Seyfried, W. E. (2017). Whole rock basalt alteration from CO₂-rich brine during flow-through experiments at 150 °C and 150 bar. *Chemical Geology*, 453, 92–110.

<https://doi.org/10.1016/j.chemgeo.2017.02.002>

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.

<https://doi.org/10.1038/s43017-019-0011-8>

Figure 5 - Wikimedia Commons. (2007). Retrieved from

https://commons.wikimedia.org/wiki/File:Juan_de_Fuca_trail_beach.jpg