

THE PREDICTED FATE OF CO₂ INJECTED INTO BASALTIC ROCK

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ABSTRACT

A number of recent studies have advocated the injection of CO₂ into basaltic rocks to promote mineral carbonation due to their abundance in divalent metal cations and their high reactivity. This study assesses this possibility through a set of reactive path modeling calculations. Two gas mixtures were considered 1) pure CO₂ and 2) a 75%-24.2%-0.8% mixture of CO₂-H₂S-H₂. It is assumed that these gases are dissolved into a representative basaltic groundwater prior to their injection into the subsurface. The injected water is assumed to have a temperature of ~25 °C and is equilibrated with ~25 bar pressure of the CO₂ gas, and ~14 bar pressure of the CO₂-H₂S-H₂ mixture. The injected fluid will have a total CO₂ concentration of ~0.8 and a pH of 3.7 for the pure CO₂ gas and total CO₂ concentration of ~0.42 and a pH of 4.0 for the gas mixture. Model calculations reacted these fluids with basaltic glass, the most abundant constituents of many basalts.

Reaction path modelling shows that 1-2 moles of basaltic glass are needed to lower the CO₂ concentration of each liter down to natural pre-injection concentrations, but less than 1 mole is needed for the H₂S rich fluid. Major carbonates formed were Ca-Mg-Fe-carbonate and dolomite at pH <5, whereas ankerite and calcite formed later at higher pH. Associated minerals at lower pH were chalcedony, kaolinite and iron hydroxide, followed by smectite and zeolites at higher pH. Modelling result suggest that the first sulfur bearing phase to precipitate is elemental sulfur, followed by greigite and mackinowite upon further basaltic glass dissolution.

1. INTRODUCTION

1.1 Mineral carbonation in basaltic rocks

One solution to challenge of anthropogenic CO₂ emission induced global warming is carbon capture and storage (Lackner, 1995; Broecker and Kunzig, 2008; Oelkers and Cole, 2008). Among the commonly proposed CO₂ storage techniques, much attention has been paid to the injection of anthropogenic CO₂ into deep geologic formations (e.g., Bachu et al., 1994; Holloway, 2001; Metz et al., 2005; Oelkers and Cole, 2008; Benson and Cole, 2008). One way to enhance the long-term stability of injected CO₂ is through the mineral carbonation. Mineral carbonation provides a long lasting, thermodynamically stable and environmentally benign carbon storage host. Carbon-dioxide mineralization could be enhanced by its injection into reactive silicate rocks rich in divalent metal cations such as basalts and ultra-mafic rocks (McGrail et al., 2006; Goldberg et al., 2008; Kelemen and Matter, 2008; Garcia et al., 2010; Schaef et al., 2010). This possibility is currently being pursued as part of the CARB-FIX project, which is

ongoing in Iceland (Alfredsson et al., 2008, 2012; Gislason et al., 2010; Matter et al., 2011; Aradóttir et al., 2011, 2012)

1.2 Basaltic weathering and CO₂

Numerous studies have been conducted on low temperature basalt weathering, including field observations and laboratory experiments (e.g. Jakobsson and Moore, 1986; Gislason and Eugster, 1987a,b; Gislason et al., 1993; Neuhoff et al., 1999; Stefansson and Gislason, 2001; Stroncik and Schmincke, 2001, Gislason et al., 2002; Frolova et al., 2005; Franzson et al., 2010). The first basaltic glass alteration product is often referred to as palagonitization (Jakobsson and Moore, 1986 and references therein). Palagonite is distinguished by the presence of amorphous and/or crypto-crystalline alteration-rims on glass surfaces (Stroncik and Schmincke, 2001). Common secondary products in this process are Mg-Fe-smectites, Ca-zeolites and calcite (e.g. Neuhoff et al., 1999).

In the presence of elevated CO₂ pressure, the identity of secondary products changes. Rogers et al. (2006) showed that Fe/Mg-carbonates, dolomite with minor ankerite solid solutions and finally calcite, sequentially formed in the Nuussuaq, a basalt hosted petroleum reservoir in Greenland. The partial pressure of CO₂ decreased over time, with calcite forming at the lowest partial pressure. Gysi and Stefansson (2011) concluded from experiments and modelling that CO₂-water-basalt interaction provokes the sequential precipitation of Mg/Fe-carbonates, Ca-Mg-Fe-carbonates, then calcite. Associated minerals were Ca-Mg-Fe(III) smectite at low pH, followed by Ca-Mg-Fe(II) smectite, iron hydroxide, and zeolites. Other common secondary minerals found in the modelling calculations were quartz/chalcedony, and Al-Si-minerals. Schaef et al. (2010) performed supercritical CO₂-water-basalt interaction experiments at 60-100°C and 62-103 bars. They observed the precipitation of Ca-Mg-Fe-(Mn)-carbonate solid solutions, where Ca was the dominant cation.

2. METHODS

All calculations presented in this study were performed using PHREEQC (Parkhurst and Appelo, 1999). The standard PHREEQC database with additional data from Gysi and Stefansson (2011) was used for these model calculations.

3. RESULTS

Two gas compositions were considered: i) 100% CO₂ and ii) 75% CO₂, 24.2% H₂S and 0.8% H₂. These gases were dissolved into a fluid having the composition of a typical Icelandic ground water (HN-1 water; Alfredsson et al., 2012) at 25°C and 25 bar injection pressure. The CO₂ (aq) and H₂S (aq) concentrations, and pH of the resulting fluids are 835 mmole/L, 0.00 mmole/L, and 3.74, and 418 mmole/L, 135 mmole/L, and 4.03, respectively for the HN-

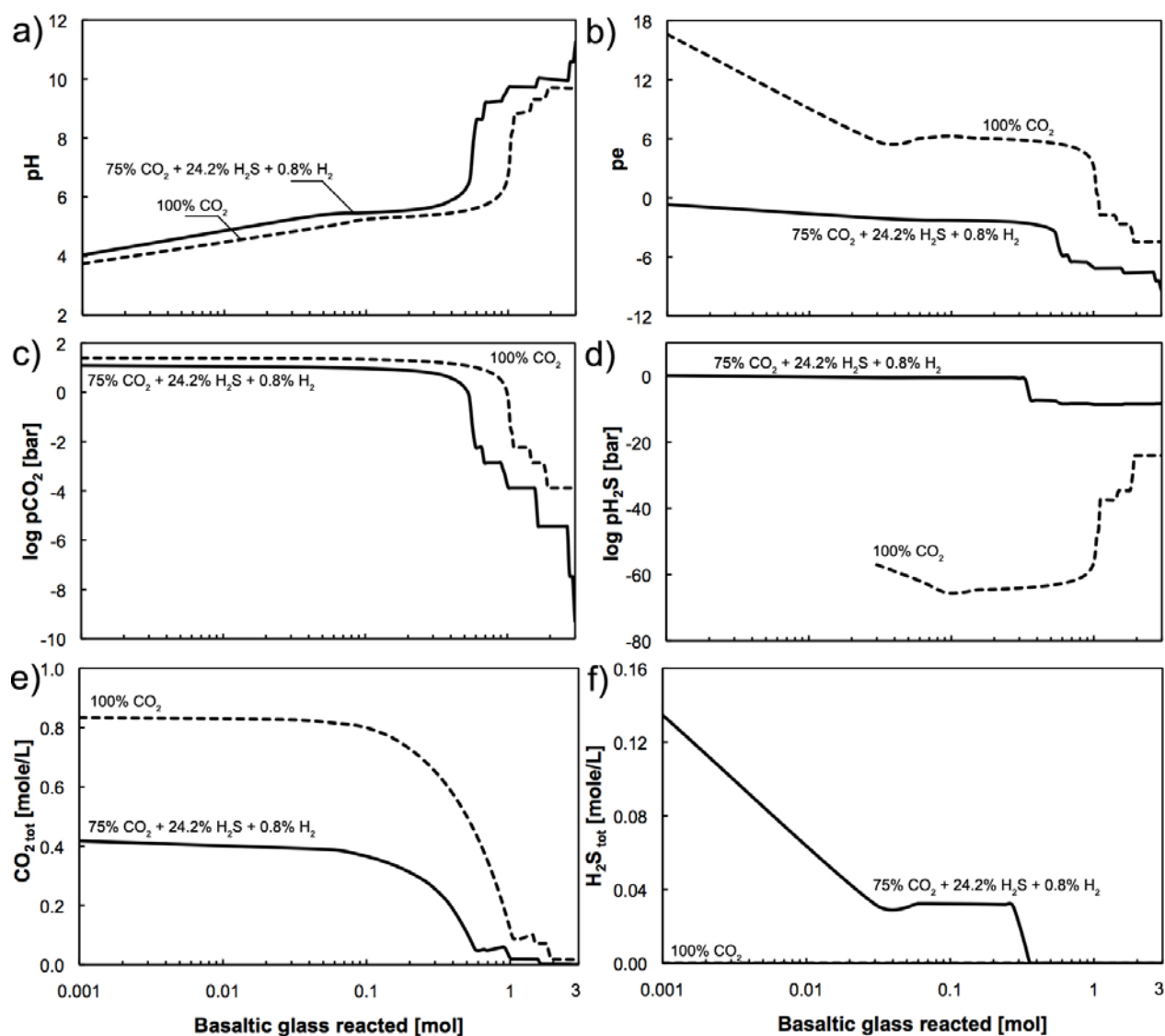


Figure 1. Calculated chemical evolution of the fluid phase during reaction of water saturated with pure CO₂ and a CO₂-H₂S-H₂ gas mixture at 25 bars total pressure and 25 °C with basaltic glass a) pH, b) pe, c) partial pressure of CO_{2(aq)}, d) partial pressure of H₂S_(aq), e) Total dissolved CO₂ and f) Total dissolved H₂S.

1 water equilibrated with pure CO₂ and 75% CO₂ + 24.2% H₂S + 0.8% H₂, respectively. The equilibrium gas partial pressure CO₂ and H₂S is relatively low for the HN-1 water equilibrated with the 75% CO₂ + 24.2% H₂S + 0.8% H₂ gas mixture, owing to the low solubility of H₂. The addition of the H₂, however, reduces the fluid phase, preventing most H₂S oxidation.

The saturation indices for calcite, dolomite, Ca-chabazite, mesolite, Ca-stilbite, Ca-Mg-Fe-smectite, in HN-1 water after its equilibration with the injection gases showed dramatic shift from being saturated to heavily undersaturated. These are secondary phases that are present in the host rocks at the study site. The primary minerals of basalt and basaltic glass were undersaturated before and after injection.

3.1 Reaction path modelling

One liter of these gas-saturated injection fluids were used in further PHREEQC calculations to assess their interaction with Stapafell basaltic glass (e.g. Oelkers and Gislason,

2001; Gislason and Oelkers, 2003; Gysi and Stefansson, 2011; Stockmann et al., 2011). Selected secondary minerals found associated with low temperature (<100°C) CO₂-H₂S-water-basalt interaction (Benning et al., 2000; Cahill et al., 2000; Rogers et al., 2006; Gysi and Stefansson 2011; Stefansson et al., 2011) were allowed to precipitate, if saturated in the aqueous phase. For example, quartz was not allowed to precipitate, although more stable than calcedony. The results of these calculations can be seen in Figures 1-5.

In the pure CO₂ injection the dissolution of 1 to 1.8 moles of basaltic glass was needed to raise the pH to 8–9, the pH typical of basaltic groundwaters (Alfredsson et al., 2012). The redox state (pe) in Figure 1, was calculated based on the oxygen concentration for the injected fluid phase. As the basaltic glass dissolved in this fluid, the dissolved FeII/FeIII redox couple was used to fix pe. The first carbonate minerals calculated to form were Ca-Mg-Fe-carbonate and dolomite at pH less than 7–8. Ankerite

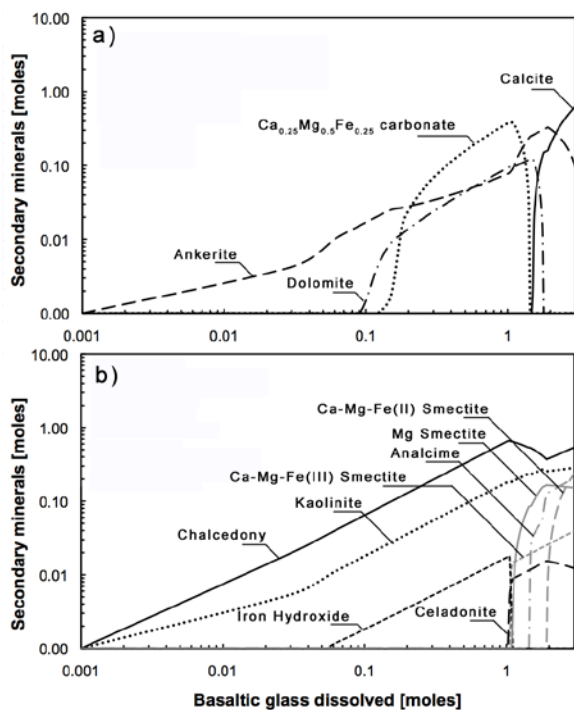


Figure 2. Calculated chemical evolution of the fluid phase and solids during reaction of water saturated with pure CO₂ at 25 bars total pressure and 25° C with basaltic glass a) mass of precipitated carbonates and b) mass of other precipitated secondary minerals.

(CaFe(CO₃)₂) is calculated to precipitate between pH 8 and 9, and finally calcite at pH >9. Chalcedony and kaolinite precipitated throughout the model calculations. Iron hydroxide precipitated at pH 3.7 to 7. The main clay minerals formed were Mg-smectite, Ca-Mg-Fe-smectite, and celadonite at pH above 6.

The 75% CO₂ + 24.2% H₂S + 0.8% H₂ gas mixture injection model showed the similar trends; results are shown in Fig. 1 and Fig. 3. The evolution of this fluid exhibits several significant differences from that of the pure CO₂ injection. First, because of the presence of H₂ and H₂S this fluid is more reducing. Second, less than 0.7 moles of basaltic glass were needed to raise pH to that typical of basaltic groundwaters. The hydrogen sulfide precipitated as elemental sulfur early in the model calculation but as greigite and later mackinawite with increasing basaltic glass dissolution. The sulfur was fully sequestered after less than 0.5 moles of basaltic glass had dissolved as shown in Figure 1f. In this calculation, CO₂ was mostly sequestered as dolomite and to a lesser degree as Ca-Mg-Fe-carbonate at low pH, changing into ankerite at around pH 9 and finally calcite above pH 9. Chalcedony and kaolinite precipitated throughout the simulations. Mg-smectite and celadonite precipitated above pH 6. At pH >8 Ca-Mg-Fe-smectite, and the zeolites analcime and scolecite formed.

These models are in good agreement with previous studies of CO₂-basalt interactions, both in nature and in experiments (Rogers et al., 2006; Schaef et al., 2010; Gysi and Stefánsson, 2011). Schaef et al. (2010) showed that the

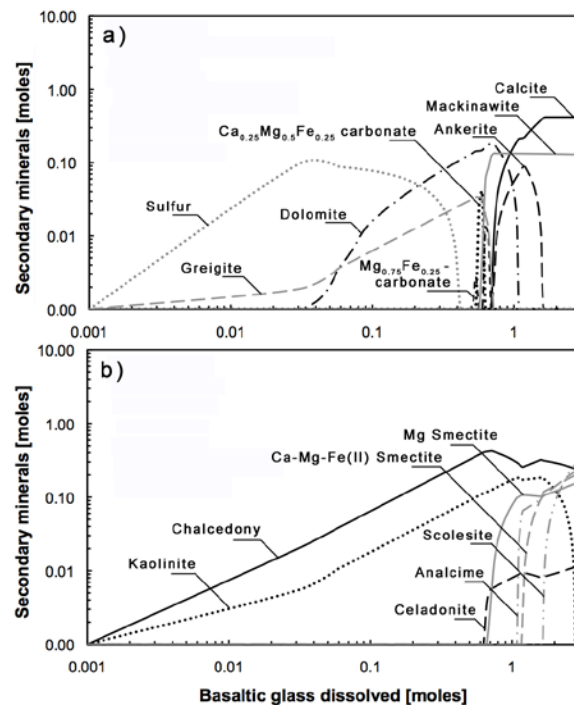


Figure 3. Calculated chemical evolution of the fluid phase and solids during reaction of water saturated with 75% CO₂ + 24.2% H₂S + 0.8% H₂ at 25 bars total pressure and 25° C with basaltic glass a) mass of precipitated carbonates and sulfur-bearing minerals and b) mass of other precipitated secondary minerals.

addition of H₂S to basalt carbonation experiments, resulted in co-precipitation of carbonate- and iron-sulphide coatings. In some cases pyrite precipitation inhibited carbonate mineral formation. This is in agreement with the model calculations described above and shown in Figures 1 and 3. Stefánsson et al. (2011) modelled H₂S sequestration into basalt at geothermal conditions. The main secondary mineral formations calculated to precipitate were sulphide minerals and perhaps elemental sulfur formation at temperatures below 150°C.

The volume of primary and secondary solids in the two model simulations is shown in Figs 4. and 5. These calculations were performed assuming the rock porosity was 8%. The dissolution of basaltic glass and precipitation of secondary minerals provokes a volume increase with time. The volume of the solids begins to exceed that of the initial rock after ~1 mole of basaltic glass has dissolved. This result suggests that pore clogging may be a factor, but only at some distance from the injection well.

4. CONCLUSION

Geochemical model calculations show that basalts are strongly undersaturated in CO₂ charged injection waters promoting their dissolution. Carbonate minerals readily become supersaturated as the basalt dissolves into these fluids. Geochemical model calculations suggest that adding H₂S gas to the injected gas mixture, results in rapid mineralization of both CO₂ and H₂S.

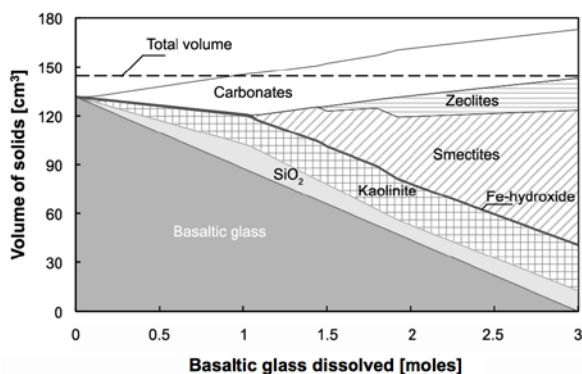


Figure 4. Changes in the total volume of solids during the simulation of water saturated with pure CO₂ at 25 bars pressure and 25° C. The calculation assumes an initial 8% rock porosity.

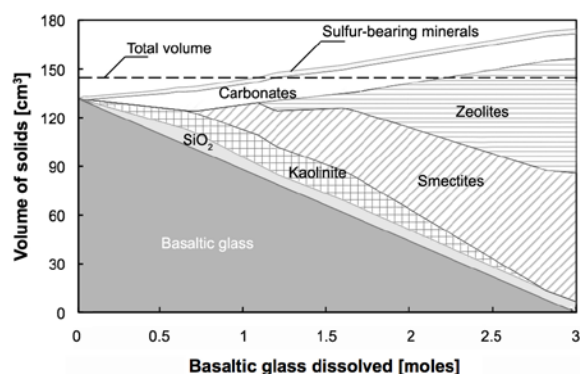


Figure 5. Changes in the total volume of solids during the simulation of water saturated with 75% CO₂ + 24.2% H₂S + 0.8% H₂ at 25 bars pressure and 25° C. The calculation assumes an initial 8% rock porosity.

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REFERENCES

- Alfredsson, H.A., Hardarson, B.S., Franzson, H., and Gislason, S.R.: CarbFix, CO₂ sequestration in basaltic rock at the Hellisheidi site in SW Iceland: Stratigraphy and chemical composition of the rocks at the injection site. *Mineralogical Magazine* 72, 1-5 (2008).
- Alfredsson, H.A., Wolff-Boenisch, D., and Stefánsson, A.: CO₂ sequestration in basaltic rocks in Iceland: Development of a piston-type downhole sampler for CO₂ rich fluids and tracers. *Energy Procedia* 4, 3510-3517 (2011).
- Alfredsson, H.A., Oelkers, E.H., Hardarson, B.S., Franzson, H., Gunnlaugsson, E., Gislason, S.R.: The geology and water chemistry of the Hellisheidi, SW-Iceland carbon storage site. *International Journal of Greenhouse Gas Control* (2012 – in press).
- Aradóttir, E.S., Sigurdardóttir, H., Sigfússon, B., Gunnlaugsson, E.: CarbFix: a CCS pilot project imitating and accelerating natural CO₂ sequestration. *Greenhouse Gases: Science and Technology*, 1, p. 105–118 (2011).
- Aradóttir, E.S., Sonnenthal, E., Björnsson, G., Jonsson, H.: Multidimensional reactive transport modeling of CO₂ mineral sequestration in basalts at the Hellisheidi geothermal field, Iceland. *Int. J. Greenhouse Gas Control* 9, p. 24-40 (2012).
- Bachu, S., Gunter, W.D., Perkins, E.H.: Aquifer disposal of CO₂: hydrodynamic and mineral trapping. *Energy Convers. Mgmt.* 35, p. 269–279 (1994).
- Benning, L.G., Rick, T.W., and Barnes, H.L.: Reaction pathways in the Fe–S system below 100°C. *Chemical Geology* 167, p. 25–51 (2000).

Benson, S.M., Cole, D.R.: CO₂ sequestration in deep sedimentary formations. *Elements* 4, p. 325–331 (2008).

Broecker, W.S., Kunzig, R., 2008. Fixing Climate: What Past Climate Changes Reveal About the Current Threat—An How to Counter It. *Hill and Wang*, New York (2008).

Cahill, C.L., Benning, L.G., Barnes, H.L., Parise, J.B.: In situ time-resolved X-ray diffraction of iron sulfides during hydrothermal pyrite growth. *Chemical Geology* 167, p. 53–63 (2000).

Franzson, H., Gudfinnsson, G.H., Helgadóttir, H.M.: Porosity, density and chemical composition relationships in altered Icelandic hyaloclastites. In: *Water-Rock Interaction XIII* – Birkle, P. and Torres-Alvarado, I. S. (eds). CRC Press Inc., ISBN 978-0-415-60426-0 (2010).

Frolova, J., Ladygin, V., Franzson, H., Sigurdsson, O., Stefánsson, V., Shustrov, V.: Petrophysical Properties of Fresh to Mildly Altered Hyaloclastite Tuffs. *Proceedings World Geothermal Congress*, Antalya, Turkey, 24-29 April (2005).

Garcia, B., Beaumont, V., Perfetti, E., Rouchon, V., Blanchet, D., Oger, P., Dromart, G., Huc, A.Y., and Haeseler, F.: Experiments and geochemical modelling of CO₂ sequestration by olivine: potential, quantification. *Appl. Geochem.* 25, p. 1383–1396 (2010).

Gislason, S.R. and Eugster H.P.: Meteoric water–basalt interactions. I: a laboratory study. *Geochim. Cosmochim. Acta* 51, p. 2827–2840 (1987a).

Gislason, S.R. and Eugster H.P.: Meteoric water–basalt interactions. II: a field study in N.E. Iceland. *Geochim. Cosmochim. Acta* 51, p. 2841–2855 (1987b).

Gislason, S.R., Veblen, D.R., and Livi, K.J.T.: Experimental meteoric water–basalt interactions: Characterization and interpretation of alteration products. *Geochim. Cosmochim. Acta* 57, p. 1459–1471 (1993).

- Gislason, S.R., Snorrason, Á., Kristmannsdóttir, H.K., Sveinbjörnsdóttir, Á.E., Torsander, P., Ólafsson, J., Castet, S., Dupré, B.: Effects of volcanic eruptions on the CO₂ content of the atmosphere and the oceans: the 1996 eruption and flood within the Vatnajökull Glacier, Iceland. *Chemical Geology* 190, p. 181–205 (2002).
- Gislason, S.R., and Oelkers, E.H.: Mechanism, rates and consequences of basaltic glass dissolution: II. An experimental study of the dissolution rates of basaltic glass as a function of pH and temperature. *Geochimica et Cosmochimica Acta* 67, p. 3817–3832 (2003).
- Gislason, S.R., Wolff-Boenisch, D., Stefansson, A., Oelkers, E. H. Gunnlaugsson, E., Sigurdardóttir, H., Sigfusson, B., Broecker, W.S., Matter, J.S., Stute, M., Axelsson, G., Fridriksson, T.: Mineral sequestration of carbon dioxide in basalt: A pre-injection overview of the CarbFix project. *International Journal of Greenhouse Gas Control* 4, p. 537–545 (2010).
- Goldberg, D.S., Takahashi, T., Slagle, A.L.: Carbon dioxide sequestration in deep sea basalt. *Proceedings of the National Academy of Sciences of the United States of America* 105, p. 9920–9925 (2008).
- Gysi, A.P., and Stefánsson, A.: CO₂-water-basalt interaction. Numerical simulation of low temperature CO₂ sequestration into basalts, *Geochimica et Cosmochimica Acta* 75, p. 4728–4751 (2011).
- Holloway, S.: Storage of fossil fuel-derived carbon dioxide beneath the surface of the earth. *Ann. Rev. Energy Environ.* 26, 145–166 (2001).
- Jakobsson, S.P., and Moore, J.G.: Hydrothermal minerals and alteration rates at Surtsey volcano, Iceland. *Geological Society of America Bulletin* 97, p. 648–659 (1986).
- Kelemen P.B., and Matter J.: In situ carbonation of peridotite for CO₂ storage. *Proceedings of the National Academy of Sciences of the United States of America* 105, p. 17295–17300 (2008).
- Lackner, K.S., Wendt, C.H., Butt, D.P., Joyce, E.L., Sharp, D.H.: Carbon dioxide disposal in carbonate minerals. *Energy* 20, p. 1153–1170 (1995).
- Matter, J.M., Broecker, W.S., Gislason, S.R., Gunnlaugsson, E., Oelkers, E.H., Stute, M., Sigurdardóttir, H., Stefansson, A., Alfreðsson, H.A., Aradóttir, E.S., Axelsson, G., Sigfusson, B., Wolff-Boenisch, D.: The CarbFix Pilot Project – Storing Carbon Dioxide in Basalt. *Energy Procedia* 4, p. 5579–5585 (2011).
- McGrail, B.P., Schaefer, H.T., Ho, A.M., Chien, Yi-Ju, Dooley, J.J., Davidson, C.L.: Potential for carbon dioxide sequestration in flood basalts. *J. Geophys. Res.* 111. doi:10.1029/2005JB004169 B12201 (2006).
- Metz, B., Davidson, O., de Coninck, H., Loos, M., Meyer, L. (Eds.): IPCC Special Report on Carbon Dioxide Capture and Storage. *Cambridge University Press*, New York (2005).
- Neuhoff, P.S., Fridriksson, T., Arnórsson, S., Bird, D.K.: Porosity evolution and mineral paragenesis during low-grade metamorphism of basaltic lavas at Teigarhorn, Eastern Iceland. *Am. J. Sci.* 299, p. 467–501 (1999).
- Oelkers E.H., and Gislason S.R.: The mechanism, rates, and consequences of basaltic glass dissolution: I. An experimental study of the dissolution rates of basaltic glass as a function of aqueous Al, Si, and oxalic acid concentration at 25° C and pH = 3 and 11. *Geochimica et Cosmochimica Acta* 65, p. 3671 – 3681 (2001).
- Oelkers E.H., and Cole, D.R.: Carbon dioxide sequestration: A solution to a global problem. *Elements*, 4, p. 305–310 (2008).
- Parkhurst, D.L., and Appelo, C.A.J.: User's guide to PHREEQC (Version 2) - a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: *U.S. Geological Survey Water-Resources Investigations Report* 99-4259, 312 p. (1999).
- Rogers, K., Neuhoff, P., Pedersen, A., Bird, D.: CO₂ metasomatism in a basalt hosted petroleum reservoir, Nuussuaq, West-Greenland. *Lithos* 92, p. 55–85 (2006).
- Schaefer, H.T., McGrail, B.P., Owen, A.T.: Carbonate mineralization of volcanic province basalts. *International Journal of Greenhouse Gas Control* 4, p. 249–261 (2010).
- Stefánsson, A., and Gislason, S.R.: Chemical weathering of basalts, SW Iceland: effect of rock crystallinity and secondary minerals on chemical fluxes to the ocean. *Am. J. Sci.* 301, p. 513–556 (2001).
- Stefánsson, A., Arnórsson, S., Gunnarsson, I., Kaasalainen, H., and Gunnlaugsson, E.: The geochemistry and sequestration of H₂S into the geothermal system at Hellisheidi, Iceland. *Journal of Volcanology and Geothermal Research* 202, p. 179–188 (2011).
- Stockmann, G.J., Wolff-Boenisch, D., Gislason, S.R., Oelkers, E.H.: Do carbonate precipitates affect dissolution kinetics? 1: Basaltic glass. *Chemical Geology* 284, p. 306–316 (2011).
- Stroncik, N.A., Schmincke, H-U.: Evolution of palagonite: Crystallization, chemical changes, and element budget. *Geochemistry, Geophysics, Geosystems* 7, p. 1017 (2001).