

## P3: CarbFix:

ETT

2025-02-16

This practical will take place on your laptops via a web-browser (hopefully). Navigate to moodle in a web browser and click on the link to the CarFix practical. This will open a Binder webpage which will compile into an interface that is identical to the RStudio App. Some of you will be familiar with this app, but if you have never used it before you will need to spend a few minutes familiarising yourself with it and making sure you know how to run R.

The CarbFix project in Iceland was created to develop the technology to store carbon dioxide as stable carbonate minerals directly in the subsurface by reacting gas charged injection waters with basaltic rocks. Carbon storage in basaltic rocks offers numerous advantages including their ability to promote mineral carbonation and their large potential storage volume. Numerous studies have focused on developing the technology to safely store CO<sub>2</sub> in basaltic rocks including laboratory experiments, modelling and field studies. Basaltic rocks are rich in divalent cations such as Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Fe<sup>2+</sup>. The injection of acidic water enriched in CO<sub>2</sub> promotes the release of these cations, potentially leading to the formation of carbonate minerals such as calcite, magnesite, and siderite as the continued dissolution of basalt increases the pH of the aqueous fluid. About 5% of the continents and most of the oceanic floor are comprised of basaltic rocks, including the mid-oceanic ridges. As such the largest basaltic storage potential lies offshore; theoretically all CO<sub>2</sub> from the burning of fossil fuel carbon (estimated to be ca. 5000Gt). The flanks of mid-ocean ridges contain highly fractured and permeable basaltic layers with a pervasive hydrothermal circulation of about 1000Gt seawater/yr. Lab results have demonstrated that basaltic rocks dissolve rapidly in seawater which is rich in CO<sub>2</sub>.

The CarbFix injection site is equipped with a 2000m deep injection well and 8 monitoring wells ranging in depth from 50 to 1300m in depth. The subsurface rocks at the injection site are primarily olivine tholeiite basalts consisting of lava flows and hyaloclastite formations. The hyaloclastites are relatively low permeability glassy rocks formed under ice and melt water during glaciations; the boundaries between hyaloclastites and lava flows, and those between individual lava flows boundaries are preferential fluid flow pathways. Some alteration is observed in the hyaloclastite rocks starting at 120–300m depth. The common alteration minerals at this depth are smectite, calcite, Ca-rich zeolites, and poorly crystalline iron-hydroxides.

Fluid injection was targeted at a lava flow sequence located 400–800m below the surface with the main aquifer located at ca. 530m depth. Loss on ignition measurements on rock samples suggest that over 80% of the primary rocks in the target zone are currently unaltered. Tracer tests were conducted

This is an R markdown document. It is similar to a jupyter notebook that you might be more familiar with. You can both explore the code, and also compile the final document to pdf output. This should provide you with some familiarisation of "R", as well as the science.

Those of you who took petrology at PII may well have heard about CarbFix already.

Fe<sup>2+</sup> is not a typical cation in natural waters. Think about why it is a cation in these particular waters

Do you remember how much carbon is in the ocean-atmosphere system?

Note that there has already been a sequel to CarbFix, CarbFix2, which now has a sequel "Seastone"

both under natural and forced flow conditions from 2008 to 2011 to define the system hydrology. These tests indicated that the flow from the HN-02 injection well to the first monitoring well (HN-04) consists of relatively homogenous porous media intersected by a low volume and fast flow path that channels about 3% of the tracer flow.

CO<sub>2</sub> was injected dissolved in seawater in two phases (phase I and phase II). The injection fluid was spiked with nonreactive but volatile sulfur hexafluoride (SF<sub>6</sub>) and trifluoromethyl sulfur pentafluoride (SF<sub>5</sub>CF<sub>3</sub>) tracers to assess plume migration in the reservoir. The SF<sub>6</sub> was used during phase I and SF<sub>5</sub>CF<sub>3</sub> during phase II.

Because dissolved or mineralized CO<sub>2</sub> cannot be detected by conventional monitoring methods such as seismic imaging, the fate of the injected CO<sub>2</sub> was monitored with a suite of chemical and isotopic tracers. The injected CO<sub>2</sub> was spiked with carbon-14 (14 C) to monitor its transport and reactivity.

**1 TASK: Read in the data from [Matter et al. \(2016\)](#).**

Note that this data was collected from in monitoring well HN04.

**2 TASK: Plot a graph of SF<sub>6</sub> and SF<sub>5</sub>CF<sub>3</sub> versus days after injection.**

**3 QUESTION: Noting that the SF<sub>6</sub> and SF<sub>5</sub>CF<sub>3</sub> are inert tracers, suggest when the injected CO<sub>2</sub> rich fluid was detected at the HN04 monitoring well.**

**4 TASK: Plot a graph of 14C versus days after injection.**

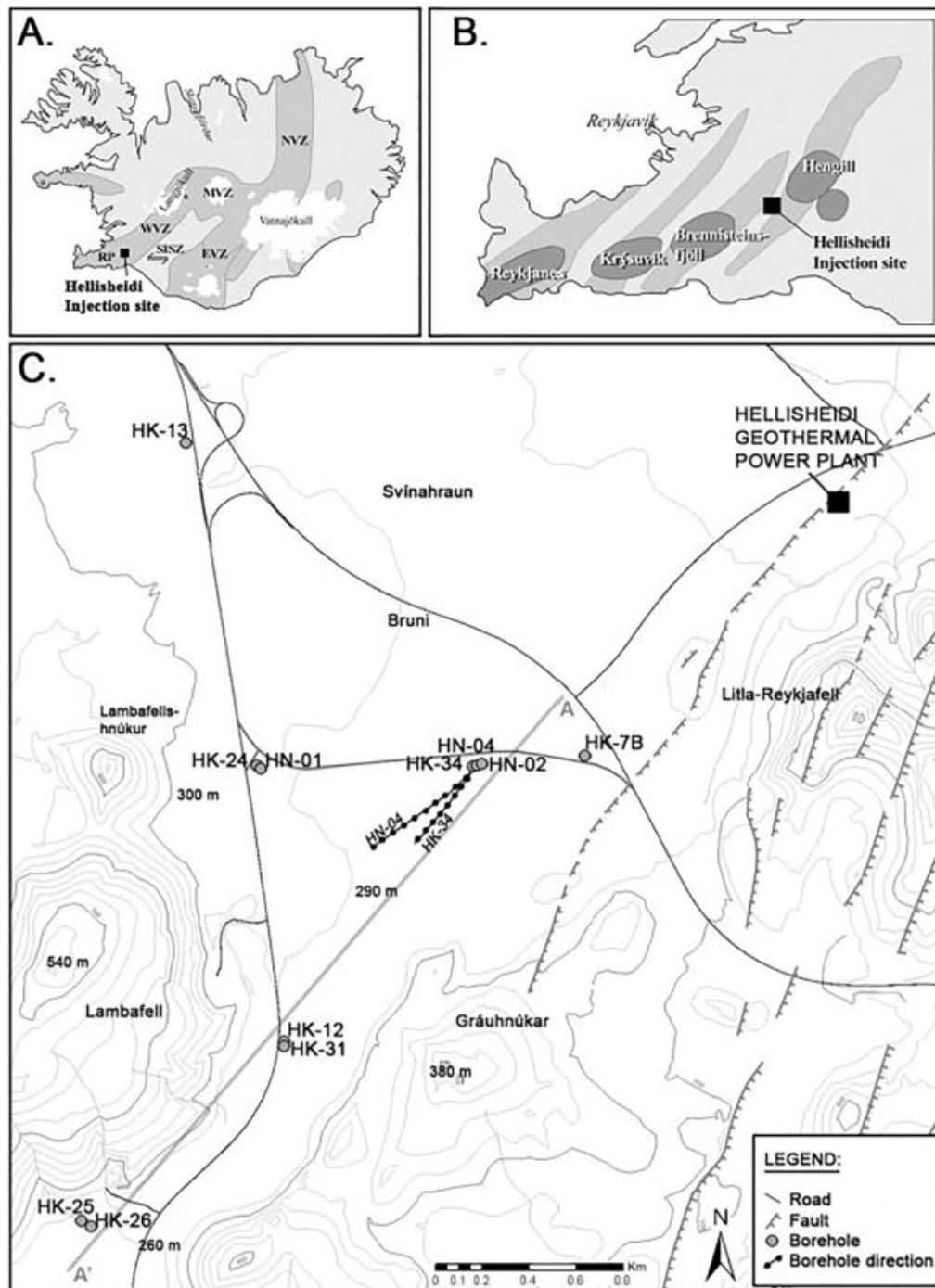


Figure 1: Map of the Carbfix site from @OELKERS2018

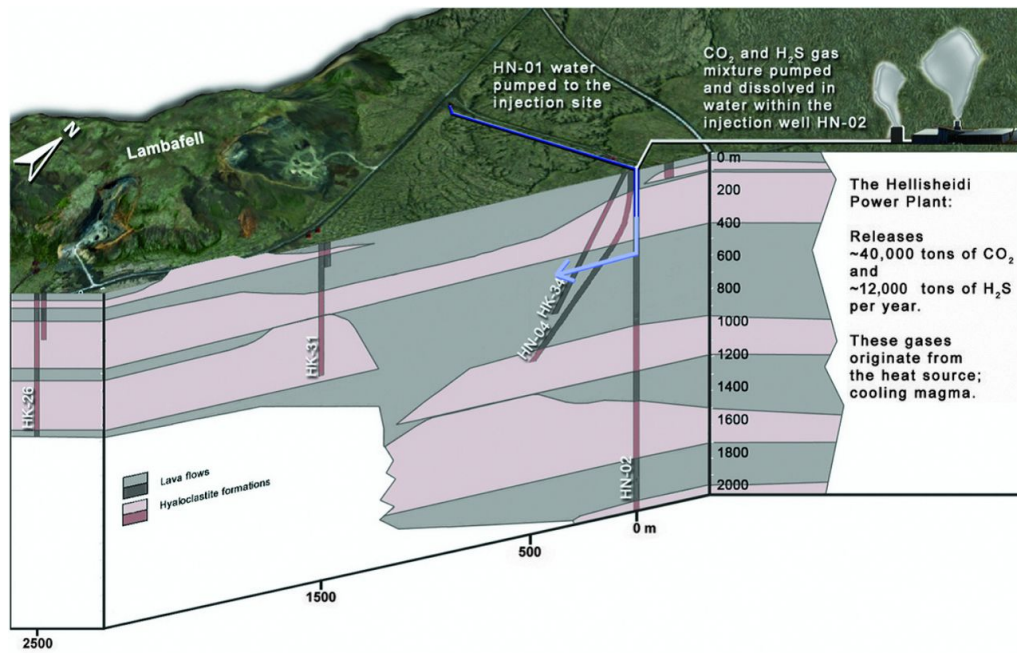


Figure 2: Section of the Carbfix site from @Matter:2016aa

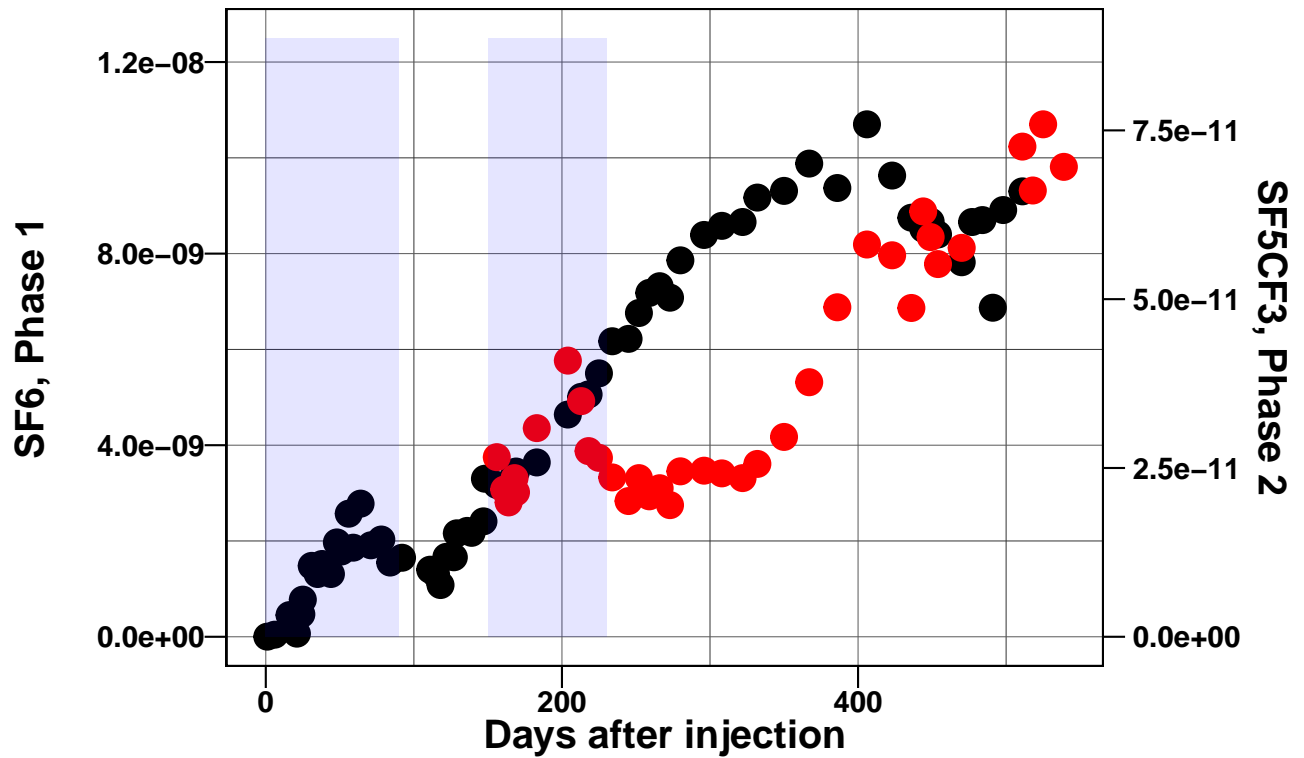


Figure 3: SF<sub>6</sub> vs days after injection. Blue shaded areas correspond to injection periods.

The  $^{14}\text{C}$  concentrations of the injected fluids were 40.0 Bq/liter and 6 Bq/liter, respectively. By comparison, the  $^{14}\text{C}$  concentration in the reservoir before the injections was 0.0006 Bq/liter.

- 5 **QUESTION:** How long does the fluid take to break through at the monitoring well HN04?
- 6 **QUESTION:** What happens to  $^{14}\text{C}$  at the monitoring well during the injection period? Suggest possible explanations.
- 7 **TASK:** Plot a graph of pH versus days after injection.
- 8 **QUESTION:** What happens to the pH at the monitoring well during the injection period? Why?

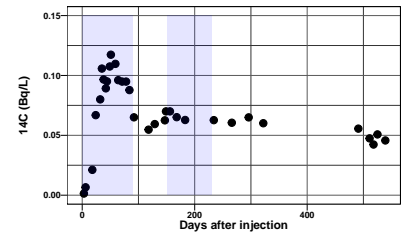


Figure 4:  $^{14}\text{C}$  vs days after injection. Blue shaded areas correspond to injection periods.

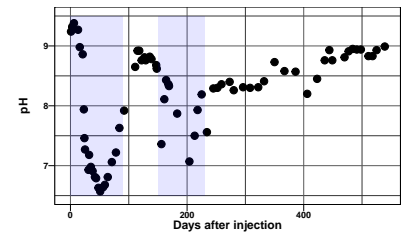


Figure 5: pH vs days after injection. Blue shaded areas correspond to injection periods.

**9 TASK: Plot a graph of DIC versus days after injection.**

**10 QUESTION: What happens to DIC at the monitoring well during the injection period? Suggest possible explanations.**

The fate of the injected CO<sub>2</sub> was quantified using mass balance calculations. The mixing fraction between the injected solution (*IS*) and ambient groundwater (*GW*) was calculated for each extracted water sample (*i*) using:

$$[SF_6]_i = X[SF_6]_{IS} + (1 - X)[SF_6]_{GW} \quad (1)$$

with *X* being the fraction of injected solution in the extracted water sample

**11 TASK: Compute the mixing fraction *X* for each of the samples in the Matter et al. (2016) dataset. Note that the SF<sub>6</sub> and SF<sub>5</sub>CF<sub>3</sub> concentrations in the injected fluids were  $2.33 \times 10^{-8}$  cc at standard temperature and pressure (ccSTP)/cc and  $2.24 \times 10^{-8}$  cc-STP/cc, respectively. Assume that the concentrations of SF<sub>6</sub> and SF<sub>5</sub>CF<sub>3</sub> in ambient groundwater are zero.**

The expected DIC values due to pure mixing between the injected fluid and ambient groundwater can be determined from:

$$DIC_{mix} = X[DIC]_{IS} + (1 - X)DIC_{GW} \quad (2)$$

This is the DIC that would be expected assuming conservative mixing based on the SF<sub>6</sub> data. The alkalinity of the groundwater from monitoring well HN-4 was 1.91 meq/L and the pH was 9.43 at 20C. Remember that alkalinity is not the same as DIC, but DIC can be calculated from the alkalinity given the pH.

**12 TASK Determine the DIC of the ambient groundwater.**

**13 TASK: Compute the  $DIC_{mix}$  assuming the conservative behaviour of SF<sub>6</sub>. Note that the DIC<sub>IS</sub> was 0.82 mol/liter in phase 1. Note that this assumes that DIC has behaved conservatively.**

**14 TASK: Plot the  $DIC_{mix}$  and DIC on the same graph. What do you notice about the difference between  $DIC_{mix}$  and the measured DIC? What do you infer has happened?**

The expected <sup>14</sup>C values due to pure mixing between the injected fluid and ambient groundwater can be determined from:

$$^{14}C_{mix} = X^{14}C_{IS} + (1 - X)^{14}C_{GW} \quad (3)$$

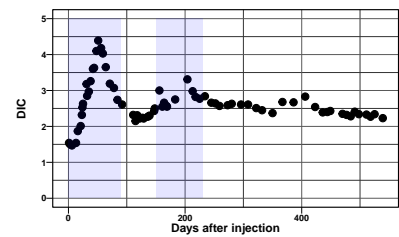


Figure 6: DIC vs days after injection. Blue shaded areas correspond to injection periods.

This kind of simple mass balance equation should be familiar to you and you should expect to know how to formulate and use it.

If you are not clear about how to calculate the DIC, it will make an ideal supervision exercise.....

Note that as calculated here it is greatly exaggerating the effect in the @Matter:2016aa paper. The conclusion is similar, but exaggerated. On reading the @Matter:2016aa paper I've not managed to understand why the calculations are not reproducing their numbers.

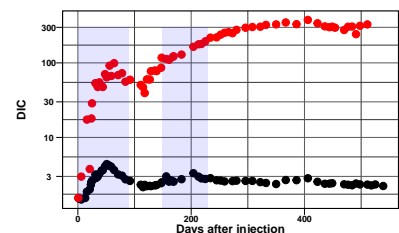


Figure 7: DIC vs days after injection. Red data is modelled. Blue shaded areas correspond to injection periods.

**15 TASK: Compute the  $^{14}\text{C}_{\text{mix}}$  assuming the conservative behaviour of  $\text{SF}_6$ . Note that the  $^{14}\text{C}_{\text{IS}}$  was 40.0 Bq/liter in phase 1. By comparison, the  $^{14}\text{C}$  concentration in the reservoir before the injections ( $^{14}\text{C}_{\text{GW}}$ ) was 0.0006 Bq/liter. Note that this assumes that DIC has behaved conservatively.**

**16 TASK: Plot the  $^{14}\text{C}_{\text{mix}}$  and  $^{14}\text{C}$  on the same graph. What do you notice about the difference between  $^{14}\text{C}_{\text{mix}}$  and the measured  $^{14}\text{C}$ ? What do you infer has happened?**

Differences in DIC and  $^{14}\text{C}$  concentrations between the values measured in the retrieved fluid samples and the expected values assuming only mixing between injectate and ambient groundwater yield the loss of DIC and  $^{14}\text{C}$  due to carbonate precipitation.

**17 TASK: Use the lever rule to estimate the loss of DIC, compared to conservative behaviour defined by mixing between injection waters and ambient groundwater.**

**18 TASK: Plot a graph of the fraction of DIC loss.**

The fast conversion rate of dissolved  $\text{CO}_2$  to calcite minerals in the CarbFix storage reservoir is most likely the result of several key processes:

1. The novel  $\text{CO}_2$  injection system that injected water-dissolved  $\text{CO}_2$  into the subsurface
2. The relatively rapid dissolution rate of basalt, releasing Ca, Mg, and Fe ions required for the  $\text{CO}_2$  mineralization,
3. The mixing of injected water with alkaline formation waters,
4. The dissolution of preexisting secondary carbonates at the onset of the  $\text{CO}_2$  injection, which may have contributed to the neutralization of the injected  $\text{CO}_2$ -rich water via the reaction  $\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} = \text{Ca}^{2+} + 2\text{HCO}_3^-$ .

The efficiency of mineral carbonation, however, can be limited if Mg clay minerals rather than Mg carbonate minerals form in response to the injection of  $\text{CO}_2$  into basalts. Magnesium clay formation is detrimental to carbon storage efforts because these minerals consume divalent Mg that could otherwise be used for carbonate mineral formation, and because Mg-bearing clays could decrease host rock permeability. Mg has three stable isotopes ( $^{24}\text{Mg}$ ,  $^{25}\text{Mg}$  and  $^{26}\text{Mg}$ ) which are thought to be fractionated by the formation of clay minerals [Hindshaw et al. \(2020\)](#).

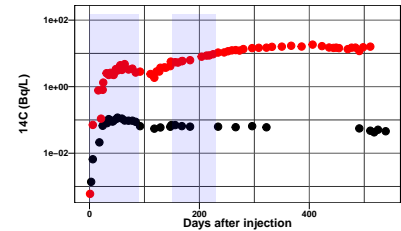


Figure 8: DIC vs days after injection. Blue shaded areas correspond to injection periods.

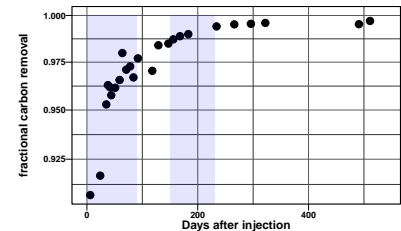


Figure 9: DIC vs days after injection. Blue shaded areas correspond to injection periods.

Will Knapp and ETT have been compiling a database of Mg isotope data that has been published to date.

**19 TASK: Read in a Mg isotope database of all data to date.**

**20 TASK: Make a plot of the evolution of the number of published Mg isotope data over the last decade.**

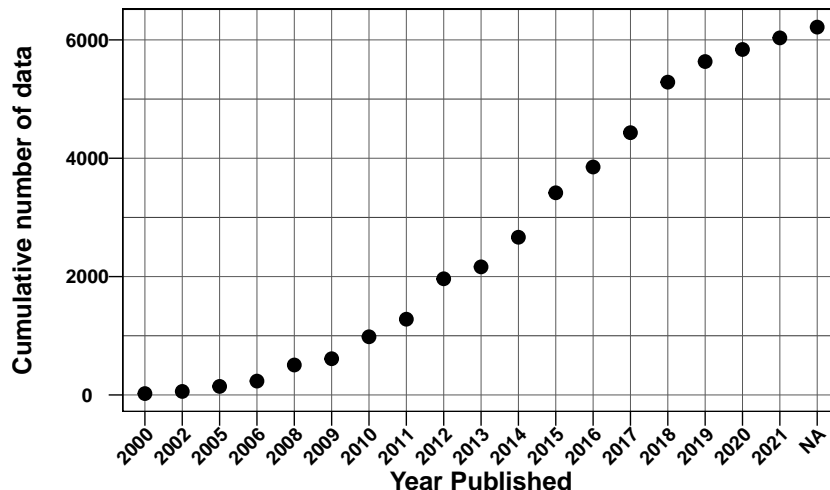


Figure 10: Summary of how much Mg isotope data has been published to date

The data has been categorised for you so that global trends in the data can be teased out.

**21 TASK: Run the following chunk to tidy up these categories.**

**22 TASK: Run the following script that makes a plot summarising the whole database.**

**23 QUESTION: Which of the data categories on the plot suggest that clay might fractionate Mg isotopes?**

If you are interested in this you can read more in [Tipper \(2022\)](#)

**24 QUESTION: What do you note about the range of Silicate rock? (Hint: Look at the box).**

Mg isotope ratios have been measured on the fluids from the monitoring well [Oelkers et al. \(2018\)](#). # TASK: Read in the data from [Oelkers et al. \(2018\)](#)

The "dots" at the end of the boxplot represent outliers. There are a number of different rules for determining if a point is an outlier, but the method that R and ggplot use is the "1.5 rule". Outliers are defined by:

1. less than  $Q1 - 1.5 * IQR$
2. greater than  $Q3 + 1.5 * IQR$

Where Q refers to a quartile. The whiskers are defined as:

1.  $upperwhisker = \min(max(x), Q3 + 1.5 * IQR)$
2.  $lowerwhisker = \max(min(x), Q1 - 1.5 * IQR)$

The box is defined by the interquartile range ( $IQR = Q3 - Q1$ )



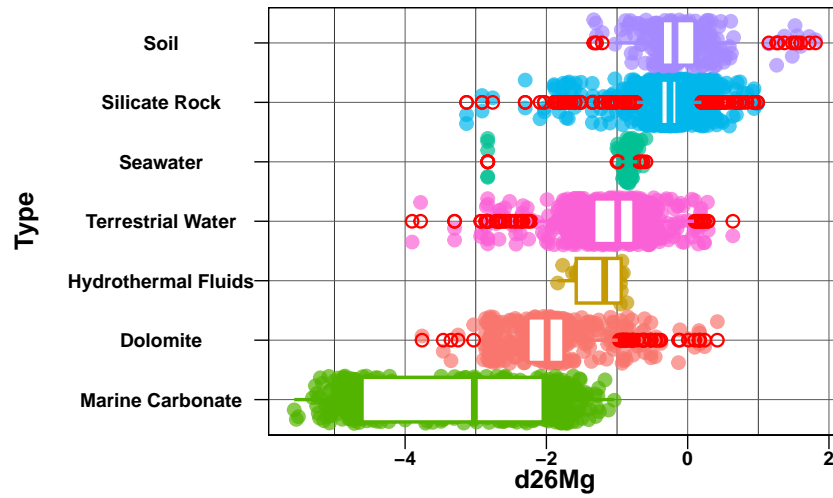


Figure 11: Caltech Mg isotope data published to date. Red data are outliers.

**25 TASK: Make a graph of  $\delta^{26}\text{Mg}$  versus time.**

**QUESTIONS: By comparing the Mg isotope dta from Carbfix, with the global compilation of Mg isotope what do you infer is happening. Consider 1) What controlled the  $\delta^{26}\text{Mg}$  prior to injection. How do the  $\delta^{26}\text{Mg}$  values compare to the composition of basalt and seawater? Do the data reflect the precipitation of carbonate minerals? Do the data reflect the precipitation of clay minerals?**

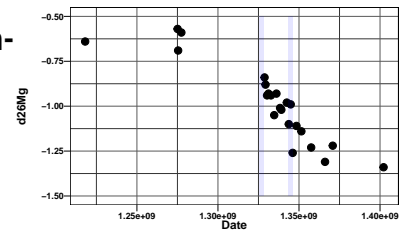


Figure 12: d26Mg vs date after injection (note the longer period of monitoring). Blue shaded areas correspond to injection periods.

Ruth S. Hindshaw, Rebecca Tosca, Nicholas J. Tosca, and Edward T. Tipper. Experimental constraints on mg isotope fractionation during clay formation: Implications for the global biogeochemical cycle of mg. 531:115980, 2020. doi: <https://doi.org/10.1016/j.epsl.2019.115980>. URL <http://www.sciencedirect.com/science/article/pii/S0012821X19306727>.

Juerg M. Matter, Martin Stute, Sandra Ó. Snæbjörnsdóttir, Eric H. Oelkers, Sigurdur R. Gislason, Edda S. Aradóttir, Bergur Sigfusson, Ingvi Gunnarsson, Holmfridur Sigurdardóttir, Einar Gunnlaugsson, Gudni Axelson, Helgi A. Alfredsson, Domenik Wolff-Boenisch, Kiflom Mesfin, Diana Fernandez de la Reguera Taya, Jennifer Hall, Knud Dideriksen, and Wallace S. Broecker. Rapid carbon mineralization for permanent disposal of anthropogenic carbon dioxide emissions. *Science*, 352(6291): 1312–1314, 2022/11/25 2016. doi: 10.1126/science.aad8132. URL <https://doi.org/10.1126/science.aad8132>.

Eric H. Oelkers, Rhiannon Butcher, Philip A.E. Pogge von Strandmann, Jan A. Schuessler, Friedhelm von Blankenburg, Sandra Ó. Snæbjörnsdóttir, Kiflom Mesfin, Edda Sif Aradóttir, Ingvi Gunnarsson, Bergur Sigfússon, Einar Gunnlaugsson, Juerg M. Matter, Martin Stute, and Sigurdur R. Gislason. Using stable mg isotope signatures to assess the fate of magnesium during the in situ mineralisation of co2 and h2s at the carbfix site in sw-iceland. *Geochimica et Cosmochimica Acta*, 2018. ISSN 0016-7037. doi: <https://doi.org/10.1016/j.gca.2018.11.011>. URL <http://www.sciencedirect.com/science/article/pii/S0016703718306410>.

Edward T. Tipper. *Magnesium Isotopes: Tracer for the Global Biogeochemical Cycle of Magnesium Past and Present or Archive of Alteration?* Elements in Geochemical Tracers in Earth System Science. Cambridge University Press, Cambridge, 2022. ISBN 9781108994309. doi: DOI: 10.1017/9781108991698. URL <https://www.cambridge.org/core/elements/magnesium-isotopes/CACF42378EE114210970DB789FFC5FDB>.