

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/303450549>

# Rapid carbon mineralization for permanent disposal of anthropogenic carbon dioxide emissions

Article in Science · May 2016

DOI: 10.1126/science.aad8132

CITATIONS

556

READS

4,322

18 authors, including:



**Juerg Matter**

University of Southampton

165 PUBLICATIONS 6,659 CITATIONS

SEE PROFILE



**Martin Stute**

Lamont - Doherty Earth Observatory Columbia University

207 PUBLICATIONS 11,536 CITATIONS

SEE PROFILE



**Sandra Ó. Snæbjörnsdóttir**

Carbfix

47 PUBLICATIONS 2,038 CITATIONS

SEE PROFILE



**Eric H. Oelkers**

King Abdullah University of Science and Technology

391 PUBLICATIONS 24,587 CITATIONS

SEE PROFILE

## CARBON SEQUESTRATION

# Rapid carbon mineralization for permanent disposal of anthropogenic carbon dioxide emissions

Juerg M. Matter,<sup>1,2\*</sup> Martin Stute,<sup>2</sup> Sandra Ó. Snæbjörnsdóttir,<sup>3</sup> Eric H. Oelkers,<sup>3,4,5</sup> Sigurdur R. Gislason,<sup>3</sup> Edda S. Aradóttir,<sup>6</sup> Bergur Sigfusson,<sup>6,7</sup> Ingvi Gunnarsson,<sup>6</sup> Holmfríður Sigurðardóttir,<sup>6</sup> Einar Gunnlaugsson,<sup>6</sup> Gudni Axelsson,<sup>8</sup> Helgi A. Alfredsson,<sup>3</sup> Domenik Wolff-Boenisch,<sup>3,9</sup> Kiflom Mesfin,<sup>3</sup> Diana Fernandez de la Reguera Taya,<sup>2</sup> Jennifer Hall,<sup>2</sup> Knud Dideriksen,<sup>10</sup> Wallace S. Broecker<sup>2</sup>

Carbon capture and storage (CCS) provides a solution toward decarbonization of the global economy. The success of this solution depends on the ability to safely and permanently store CO<sub>2</sub>. This study demonstrates for the first time the permanent disposal of CO<sub>2</sub> as environmentally benign carbonate minerals in basaltic rocks. We find that over 95% of the CO<sub>2</sub> injected into the CarbFix site in Iceland was mineralized to carbonate minerals in less than 2 years. This result contrasts with the common view that the immobilization of CO<sub>2</sub> as carbonate minerals within geologic reservoirs takes several hundreds to thousands of years. Our results, therefore, demonstrate that the safe long-term storage of anthropogenic CO<sub>2</sub> emissions through mineralization can be far faster than previously postulated.

The success of geologic CO<sub>2</sub> storage depends on its long-term security and public acceptance, in addition to regulatory, policy, and economical factors (1). CO<sub>2</sub> and brine leakage through a confining system above the storage reservoir or through abandoned wells is considered one of the major challenges associated with geologic CO<sub>2</sub> storage (2–4). Leakage rates into the atmosphere of  $\leq 0.1\%$  are required to ensure effective climate change mitigation (5, 6). To avoid CO<sub>2</sub> leakage, caprock integrity needs to be evaluated and monitored (7). Leakage risk is further enhanced by induced seismicity, which may open fluid flow pathways in the caprock (8). Mineral carbonatization (i.e., the conversion of CO<sub>2</sub> to carbonate minerals) via CO<sub>2</sub>-fluid-rock reactions in the reservoir minimizes the risk of leakage and thus facilitates long-term and safe carbon storage and public acceptance (9). The potential for carbonatization is, however, limited in conventional CO<sub>2</sub> storage reservoirs such as deep saline aquifers and depleted oil and gas reservoirs in sedimentary basins due to the lack of calcium-, magnesium-, and iron-rich silicate minerals required to form carbonate minerals (10, 11). An alternative is to inject CO<sub>2</sub> into basaltic rocks,

which contain up to 25% by weight of calcium, magnesium, and iron. Basaltic rocks are highly reactive and are one of the most common rock types on Earth, covering  $\sim 10\%$  of continental surface area and most of the ocean floor (12, 13).

The CarbFix pilot project in Iceland was designed to promote and verify in situ CO<sub>2</sub> mineralization in basaltic rocks for the permanent disposal of anthropogenic CO<sub>2</sub> emissions (14). Two injection tests were performed at the CarbFix injection site near the Hellisheidi geothermal power plant. Phase I: 175 tons of pure CO<sub>2</sub> from January to March 2012, and phase II: 73 tons of a CO<sub>2</sub>-H<sub>2</sub>S gas mixture in June to August 2012, of which 55 tons were CO<sub>2</sub>. H<sub>2</sub>S is not only a major constituent of geothermal gases but also of CO<sub>2</sub>-rich sour gas. Because the cost of carbon capture and storage (CCS) is dominated by the cost of capture and gas separation, the overall cost could be lowered substantially by injecting gas mixtures rather than pure CO<sub>2</sub> (9). Hence, the purpose of the mixed CO<sub>2</sub>/H<sub>2</sub>S injection was to assess the feasibility of injecting impurities in the CO<sub>2</sub> stream.

The CarbFix injection site is situated about 25 km east of Reykjavik and is equipped with a 2000-m-deep injection well (HN02) and eight monitoring wells ranging in depth from 150 to 1300 m (Fig. 1). The target CO<sub>2</sub> storage formation is at between 400 and 800 m depth and consists of basaltic lavas and hyaloclastites with lateral and vertical intrinsic permeabilities of 300 and  $1700 \times 10^{-15} \text{ m}^2$ , respectively (15, 16). It is overlain by low-permeability hyaloclastites. The formation water temperature and pH in the injection interval range from 20° to 33°C and from 8.4 to 9.4, and it is oxygen-depleted (15). Due to the shallow depth of the target storage reservoir and the risk of CO<sub>2</sub> gas leakage through fractures, a novel CO<sub>2</sub> injection system was designed and used, which

dissolves the gases into down-flowing water in the well during its injection (17). To avoid potential degassing, the CO<sub>2</sub> concentration in the injected fluids was kept below its solubility at reservoir conditions (17). Once dissolved in water, CO<sub>2</sub> is no longer buoyant (17), and it immediately starts to react with the Ca-Mg-Fe-rich reservoir rocks.

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 (<sup>14</sup>C) to monitor its transport and reactivity (18). For the pure CO<sub>2</sub> and the CO<sub>2</sub>/H<sub>2</sub>S injections, the <sup>14</sup>C concentrations of the injected fluids were 40.0 Bq/liter (<sup>14</sup>C/<sup>12</sup>C:  $2.16 \times 10^{-11}$ ) and 6 Bq/liter (<sup>14</sup>C/<sup>12</sup>C:  $6.5 \times 10^{-12}$ ), respectively. By comparison, the <sup>14</sup>C concentration in the reservoir before the injections was 0.0006 Bq/liter (<sup>14</sup>C/<sup>12</sup>C:  $1.68 \times 10^{-13}$ ). This novel carbon tracking method was previously proposed for geologic CO<sub>2</sub> storage monitoring, but its feasibility has not been tested previously (19, 20). Because <sup>14</sup>CO<sub>2</sub> chemically and physically behaves identically to <sup>12</sup>CO<sub>2</sub> and is only minimally affected by isotope fraction during phase transitions (21), it provides the means to accurately inventory the fate of the injected carbon.

In addition to <sup>14</sup>C, we continuously co-injected 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. The SF<sub>6</sub> and SF<sub>5</sub>CF<sub>3</sub> concentrations in the injected fluids were  $2.33 \times 10^{-8} \text{ cc}$  at standard temperature and pressure (ccSTP)/cc and  $2.24 \times 10^{-8} \text{ ccSTP/cc}$ , respectively.

The CO<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub>S mixtures, together with the tracers, were injected into the target storage formation fully dissolved in water pumped from a nearby well. Typical injection rates during phase I injection were 70 g/s for CO<sub>2</sub> and 1800 g/s for H<sub>2</sub>O, respectively (17). Injection rates during phase II varied between 10 and 50 g/s for CO<sub>2</sub> and 417 and 2082 g/s for H<sub>2</sub>O. The dissolved inorganic carbon (DIC) concentration and pH of the injectates were 0.82 mol/liter and 3.85 (at 20°C) for phase I and 0.43 mol/liter and 4.03 for phase II. Fluid samples for SF<sub>6</sub>, SF<sub>5</sub>CF<sub>3</sub>, <sup>14</sup>C, DIC, and pH analyses were collected without degassing using a specially designed downhole sampler from the injection well HN02 (22) or with a submersible pump from the first monitoring well, HN04, located about 70 m downstream from HN02 at 400 m depth below the surface before, during, and after injection (tables S1 to S3).

The arrival of the injectate from phase I at monitoring well HN04 was confirmed by an increase in SF<sub>6</sub> concentration, and a sharp decrease in pH and DIC concentration (Fig. 2, A and B, and table S3). Based on the SF<sub>6</sub> data, the initial breakthrough in HN04 occurred 56 days after injection. Subsequently, the SF<sub>6</sub> concentration slightly decreased before a further increase in concentration occurred, with peak concentration 406 days after initiation of the injection. SF<sub>5</sub>CF<sub>3</sub> behaves similarly (Fig. 2A); its initial arrival was detected 58 days after initiation of the phase II injection,

<sup>1</sup>Department of Ocean and Earth Science, University of Southampton, Southampton, UK. <sup>2</sup>Lamont-Doherty Earth Observatory, Columbia University, Palisades, NY, USA.

<sup>3</sup>Institute of Earth Sciences, University of Iceland, Iceland.

<sup>4</sup>CNRS/UMR 5563, Université Paul Sabatier, Toulouse, France.

<sup>5</sup>Department of Earth Science, University College London, UK. <sup>6</sup>Reykjavik Energy, Reykjavik, Iceland. <sup>7</sup>European Commission, Joint Research Center, Institute for Energy and Transport, Petten, Netherlands. <sup>8</sup>Iceland GeoSurvey, Reykjavik, Iceland. <sup>9</sup>Department of Applied Geology, Curtin University, Perth, Western Australia. <sup>10</sup>Nano-Science Center, Department of Chemistry, University of Copenhagen, Copenhagen, Denmark.

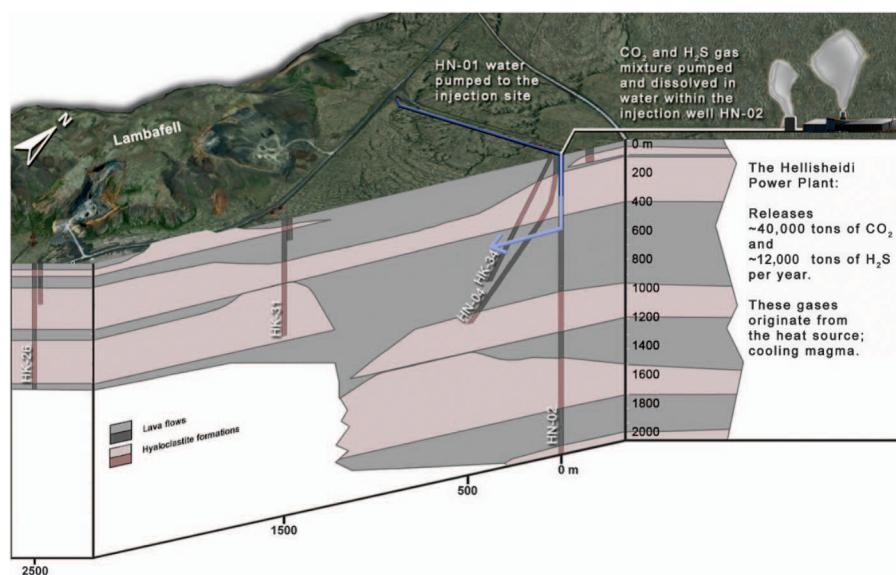
\*Corresponding author. Email: j.matter@southampton.ac.uk

followed by decreasing concentrations until 350 days after the injection started. Subsequently, the  $\text{SF}_5\text{CF}_3$  concentration increased, consistent with the  $\text{SF}_6$  tracer breakthrough curve. The double peaks in these tracer breakthrough curves are also in agreement with results from previous tracer tests showing that the storage formation consists of relatively homogenous porous media intersected by a low-volume and fast flow path that channels about 3% of the tracer flow between HN02 and HN04 (23).

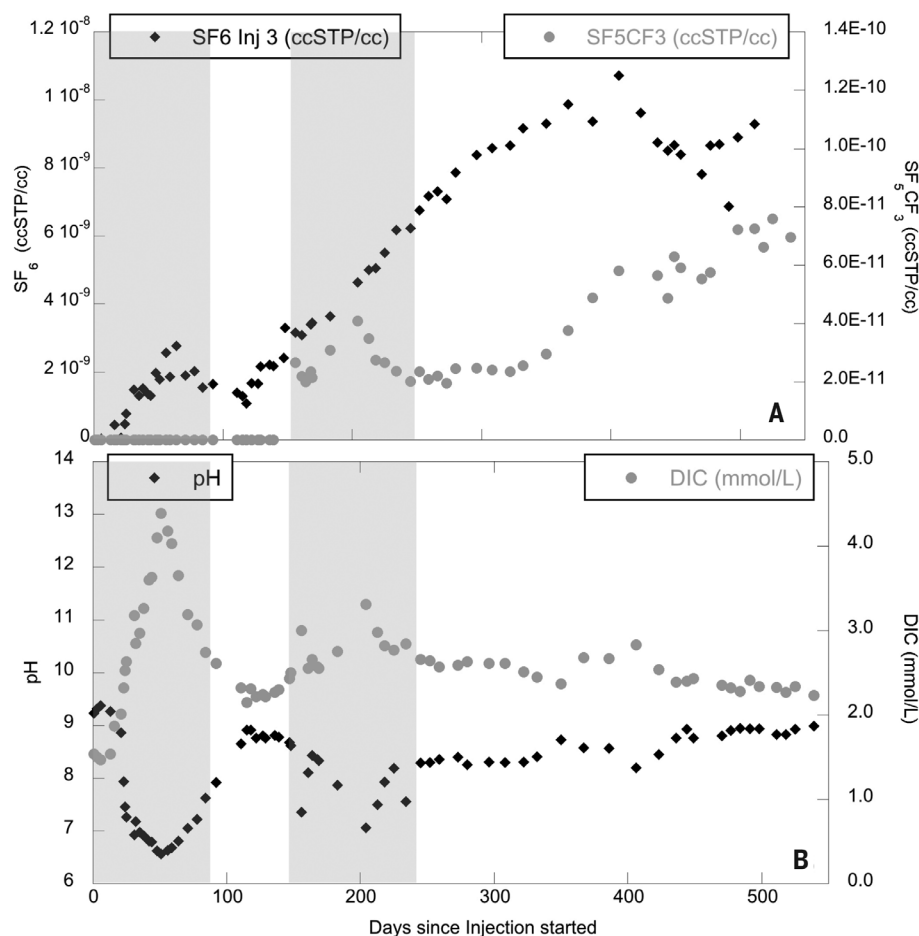
The time series of DIC, pH, and  $^{14}\text{C}$  in HN04 are initially coincident with the  $\text{SF}_6$  record, showing peak concentrations in  $^{14}\text{C}$  and DIC and a decrease in pH around 56 days after injection (Figs. 2B and 3). The small drop in pH and increase in DIC around 200 days after injection is caused by the phase II injection, as confirmed by the  $\text{SF}_5\text{CF}_3$  time series (Fig. 2A). The similar initial pattern in the tracer breakthrough curves and the DIC concentration suggests identical transport behavior of carbon and tracers in the reservoir. However,  $^{14}\text{C}$  and DIC concentrations subsequently decreased and stayed more or less constant for the remaining monitoring period, with the exception of a small increase in concentration induced by the phase II injection (Figs. 2B and 3, A and B).

The fate of the injected  $\text{CO}_2$  was quantified using mass balance calculations (18). The resulting calculated DIC and  $^{14}\text{C}$  concentrations are much higher than those measured in the collected water samples, suggesting a loss of DIC and  $^{14}\text{C}$  along the subsurface flow path toward the monitoring well (Fig. 3, A and B). The most plausible mechanism for this difference is carbonate precipitation. The differences between calculated and measured DIC and  $^{14}\text{C}$  indicate that >95% of the injected  $\text{CO}_2$  was mineralized through water- $\text{CO}_2$ -basalt reactions between the injection (HN02) and monitoring (HN04) wells within 2 years (Fig. 3, A and B). The initial peak concentrations in DIC and  $^{14}\text{C}$  detected around 56 days after injection suggest that travel time along the low-volume fast-flowing flow path was too short for significant  $\text{CO}_2$  mineralization to occur. Most of the injected  $\text{CO}_2$  was probably mineralized within the porous matrix of the basalt that allows for longer fluid residence times and thus extended reaction time. This conclusion is confirmed by (i) calculated fluid saturation states showing that the collected monitoring fluids are at saturation or supersaturation with respect to calcite at all times except during the initial low-volume flow path contribution; (ii) x-ray diffraction and scanning electron microscopy with energy-dispersive x-ray spectroscopy analysis of secondary mineral precipitates collected from the submersible pump in monitoring well HN04 after it was hauled to the surface, showing these precipitates to be calcite (18) (figs. S1 to S3); and (iii) the similarity in the  $^{14}\text{C}$  concentration of the injected  $\text{CO}_2$  and the precipitated collected calcite ( $7.48 \pm 0.8$  and  $7.82 \pm 0.05$  fraction modern).

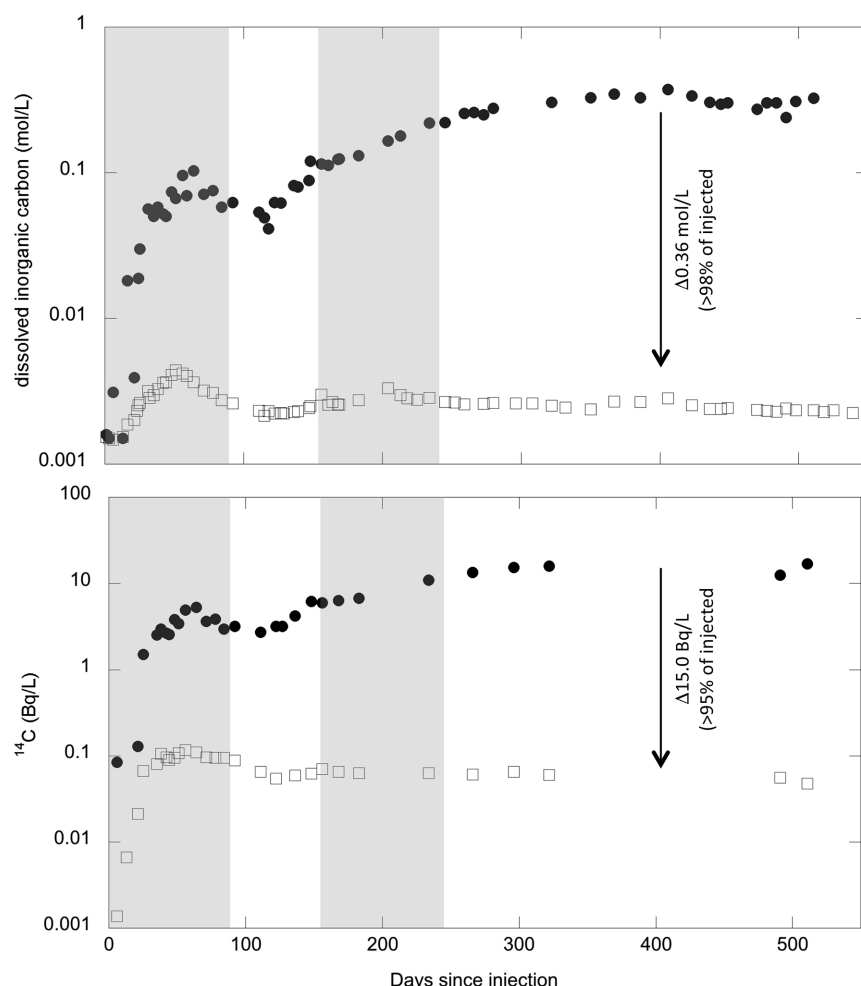
Although monitoring continues, the time scale of the tracer and DIC data discussed is limited to 550 days, because most of the injected  $\text{CO}_2$  was mineralized by this time (Figs. 2 and 3). This 550-day



**Fig. 1. Geological cross-section of the CarbFix injection site.**  $\text{CO}_2$  and  $\text{H}_2\text{S}$  are injected fully dissolved in water in injection well HN02 at a depth between 400 and 540 m. For this study, fluid samples were collected in the injection well HN02 and the monitoring well HN04 [modified from (15)].



**Fig. 2. Change of tracer concentrations, DIC, and pH in the target  $\text{CO}_2$  storage formation fluid.** Time series of (A)  $\text{SF}_6$  and  $\text{SF}_5\text{CF}_3$  tracer concentrations (ccSTP/cc) and (B) pH and DIC in monitoring well HN04 for the pure  $\text{CO}_2$  and the  $\text{CO}_2$  and  $\text{H}_2\text{S}$  injections. The shaded area indicates the phase I and II injection period.



**Fig. 3. Comparison of calculated and measured DIC and  $^{14}\text{C}$  concentrations in the target  $\text{CO}_2$  storage formation fluid.** (A) Time series of expected (solid circles) versus measured (open squares) DIC (mol/liter) in monitoring well HN04, indicating >98% conversion of injected  $\text{CO}_2$  to carbonate minerals, and (B) time series of expected (solid circles) versus measured (open squares)  $^{14}\text{C}_{\text{DIC}}$  (Bq/liter) in monitoring well HN04, showing >95% of injected  $\text{CO}_2$  to be converted to carbonate minerals. The shaded area indicates the phase I and II injection periods.

limit also coincides with the breakdown of the submersible pump in HN04 monitoring well, which resulted in a 3-month gap in the subsequent monitoring data. The pump was clogged and coated with calcite (18).

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: (i) the novel  $\text{CO}_2$  injection system that injected water-dissolved  $\text{CO}_2$  into the subsurface; (ii) the relatively rapid dissolution rate of basalt, releasing Ca, Mg, and Fe ions required for the  $\text{CO}_2$  mineralization; (iii) the mixing of injected water with alkaline formation waters; and (iv) 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 dissolution of preexisting calcite is supported by the  $^{14}\text{C}/^{12}\text{C}$  ratio of the collected fluid

samples, which suggest a 50% dilution of the carbon in the fluid, most likely via calcite dissolution just after it arrives in the basaltic reservoir. Nevertheless, the mass balance calculations clearly demonstrate that these preexisting carbonates re-precipitated during the mineralization of the injected  $\text{CO}_2$ .

The results of this study demonstrate that nearly complete in situ  $\text{CO}_2$  mineralization in basaltic rocks can occur in less than 2 years. Once stored within carbonate minerals, the leakage risk is eliminated and any monitoring program of the storage site can be significantly reduced, thus enhancing storage security and potentially public acceptance. Natural aqueous fluids in basalts and those at the CarbFix site tend to be at or close to equilibrium with respect to calcite, limiting its redissolution (16). The scaling up of this basaltic carbon storage method requires substantial quantities of water and porous basaltic rocks (9). Both are widely available on the continental margins, such

as off the coast of the Pacific Northwest of the United States (12).

## REFERENCES AND NOTES

1. B. Metz, O. Davidson, H. de Coninck, M. Loos, L. A. Meyer, Eds., *IPCC Special Report on Carbon Dioxide Capture and Storage* (Cambridge Univ. Press, New York, 2005).
2. A. Esposito, S. Benson, in *Proceedings of the Society of Petroleum Engineers 2010 Western North American Regional Meeting*, Anaheim, CA, 27 to 29 May 2010 (Society of Petroleum Engineers, 2010), SPE-133604.
3. B. Ellis et al., *Sci. Technol.* **1**, 248–260 (2011).
4. J. M. Bielicki, M. F. Pollak, J. P. Fitts, C. A. Peters, E. J. Wilson, *Int. J. Greenhouse Gas Control* **20**, 272–284 (2014).
5. P. M. Haugan, F. Joos, *Geophys. Res. Lett.* **31**, L18202 (2004).
6. B. van der Zwaan, L. Smekens, *Environ. Model. Assess.* **14**, 135–148 (2009).
7. H. S. Eggleston et al., Eds., *IPCC Guidelines for National Greenhouse Gas Inventories – A Primer* (National Greenhouse Gas Inventories Programme, Institute for Global Environmental Strategies, Japan, 2008).
8. M. D. Zoback, S. M. Gorelick, *Proc. Natl. Acad. Sci. U.S.A.* **109**, 10164–10168 (2012).
9. S. R. Gislason, E. H. Oelkers, *Science* **344**, 373–374 (2014).
10. J. M. Matter, P. B. Kelemen, *Nat. Geosci.* **2**, 837–841 (2009).
11. S. M. V. Gilfillan et al., *Nature* **458**, 614–618 (2009).
12. D. S. Goldberg, T. Takahashi, A. L. Slagle, *Proc. Natl. Acad. Sci. U.S.A.* **105**, 9920–9925 (2008).
13. B. P. McGrail et al., *J. Geophys. Res.* **111**, B12201 (2006).
14. S. R. Gislason et al., *Int. J. Greenhouse Gas Control* **4**, 537–545 (2010).
15. H. A. Alfredsson et al., *Int. J. Greenhouse Gas Control* **12**, 399–418 (2013).
16. E. S. Aradóttir, E. L. Sonnenthal, G. Björnsson, H. Jónsson, *Int. J. Greenhouse Gas Control* **9**, 24–40 (2012).
17. B. Sigfusson et al., *Int. J. Greenhouse Gas Control* **37**, 213–219 (2015).
18. Materials and methods are available as supplementary materials on Science Online.
19. P. P. Bachelor et al., *J. Radioanal. Nucl. Chem.* **277**, 85–89 (2008).
20. K. S. Lackner, S. Brennan, *Clim. Change* **96**, 357–378 (2009).
21. I. D. Clark, P. Fritz, *Environmental Isotopes in Hydrogeology* (Lewis Publishers, Boca Raton, FL, 1997).
22. H. A. Alfredsson, K. Mesfin, D. Wolff-Böenisch, *Greenhouse Gas Sci. Technol.* **6**, 167–177 (2016).
23. M. Rezvani Khalilabad, G. Axelsson, S. Gislason, *Mineral. Mag.* **72**, 121–125 (2008).

## ACKNOWLEDGMENTS

We acknowledge funding from Reykjavik Energy; the U.S. Department of Energy under award number DE-FE0004847 to J.M.M. and M.S.; the European Commission through the projects CarbFix (EC coordinated action 283148), Min-GRO (MC-RTN-35488), Delta-Min (PITN-GA-2008-215360), and  $\text{CO}_2$ -REACT (EC Project 317235) to S.R.G., E.H.O., and Reykjavik Energy; Nordic fund 11029-NORDICCS; and the Icelandic GEORG Geothermal Research fund (09-02-001) to S.R.G. and Reykjavik Energy. We thank T. Kristinnsson and E. Ö. Þrastarson for helping with sample collection in the field. All data used in this study are included in the supplementary materials.

## SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/352/6291/1312/suppl/DC1  
Materials and Methods  
Supplementary Text  
Figs. S1 to S3  
Tables S1 and S2  
References (24–34)

10.1126/science.aad8132





## Rapid carbon mineralization for permanent disposal of anthropogenic carbon dioxide emissions

Juerg M. Matter, Martin Stute, Sandra Ó. Snæbjörnsdottir, Eric H. Oelkers, Sigurdur R. Gislason, Edda S. Aradóttir, Bergur Sigfusson, Ingvi Gunnarsson, Holmfrídur Sigurdardóttir, Einar Gunnlaugsson, Gudni Axelsson, Helgi A. Alfredsson, Domenik Wolff-Boenisch, Kiflom Mesfin, Diana Fernandez de la Reguera Taya, Jennifer Hall, Knud Dideriksen and Wallace S. Broecker (June 9, 2016)  
*Science* **352** (6291), 1312-1314. [doi: 10.1126/science.aad8132]

### Editor's Summary

#### Inject, baby, inject!

Atmospheric CO<sub>2</sub> can be sequestered by injecting it into basaltic rocks, providing a potentially valuable way to undo some of the damage done by fossil fuel burning. Matter *et al.* injected CO<sub>2</sub> into wells in Iceland that pass through basaltic lavas and hyaloclastites at depths between 400 and 800 m. Most of the injected CO<sub>2</sub> was mineralized in less than 2 years. Carbonate minerals are stable, so this approach should avoid the risk of carbon leakage.

*Science*, this issue p. 1312

---

This copy is for your personal, non-commercial use only.

---

#### Article Tools

Visit the online version of this article to access the personalization and article tools:

<http://science.sciencemag.org/content/352/6291/1312>

#### Permissions

Obtain information about reproducing this article:

<http://www.sciencemag.org/about/permissions.dtl>

*Science* (print ISSN 0036-8075; online ISSN 1095-9203) is published weekly, except the last week in December, by the American Association for the Advancement of Science, 1200 New York Avenue NW, Washington, DC 20005. Copyright 2016 by the American Association for the Advancement of Science; all rights reserved. The title *Science* is a registered trademark of AAAS.