CARBON SEQUESTRATION

Rapid carbon mineralization for permanent disposal of anthropogenic carbon dioxide emissions

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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_2. This study demonstrates for the first time the permanent disposal of CO_2 as environmentally benign carbonate minerals in basaltic rocks. We find that over 95% of the CO_2 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_2 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_2 emissions through mineralization can be far faster than previously postulated.

The success of geologic CO_2 storage depends on its long-term security and public acceptance, in addition to regulatory, policy, and economical factors (1). CO_2 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_2 storage (2–4). Leakage rates into the atmosphere of ≤0.1% are required to ensure effective climate change mitigation (5, 6). To avoid CO_2 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_2 to carbonate minerals) via CO_2-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_2 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_2 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 ~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_2 mineralization in basaltic rocks for the permanent disposal of anthropogenic CO_2 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_2 from January to March 2012, and phase II: 73 tons of a CO_2-H_2S gas mixture in June to August 2012, of which 55 tons were CO_2. H_2S is not only a major constituent of geothermal gases but also of CO_2-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_2 (9). Hence, the purpose of the mixed CO_2/H_2S injection was to assess the feasibility of injecting impurities in the CO_2 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_2 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 × 10^{-15} 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_2 gas leakage through fractures, a novel CO_2 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_2 concentration in the injected fluids was kept below its solubility at reservoir conditions (17). Once dissolved in water, CO_2 is no longer buoyant (17), and it immediately starts to react with the Ca-Mg-Fe-rich reservoir rocks.

Because dissolved or mineralized CO_2 cannot be detected by conventional monitoring methods such as seismic imaging, the fate of the injected CO_2 was monitored with a suite of chemical and isotopic tracers. The injected CO_2 was spiked with carbon-14 (^{14}C) to monitor its transport and reactivity (18). For the pure CO_2 and the CO_2/H_2S injections, the ^{14}C concentrations of the injected fluids were 40.0 Bq/liter (^{14}C/^{12}C: 2.16 × 10^{-11}) and 6 Bq/liter (^{14}C/^{12}C: 6.5 × 10^{-12}), respectively. By comparison, the ^{14}C concentration in the reservoir before the injections was 0.0006 Bq/liter (^{14}C/^{12}C: 1.68 × 10^{-13}). This novel carbon tracking method was previously proposed for geologic CO_2 storage monitoring, but its feasibility has not been tested previously (19, 20). Because $^{14}CO_2$ chemically and physically behaves identically to $^{12}CO_2$ 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 ^{14}C, we continuously co-injected nonreactive but volatile sulfur hexafluoride (SF_6) and trifluoromethyl sulfur pentafluoride (SF_5CF_3) tracers to assess plume migration in the reservoir. The SF_6 was used during phase I and SF_5CF_3 during phase II. The SF_6 and SF_5CF_3 concentrations in the injected fluids were 2.33 × 10^{-8} cc at standard temperature and pressure (ccSTP)/cc and 2.24 × 10^{-8} ccSTP/cc, respectively.

The CO_2 and CO_2/H_2S 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_2 and 1800 g/s for H_2O, respectively (17). Injection rates during phase II varied between 10 and 50 g/s for CO_2 and 417 and 2082 g/s for H_2O. 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_6, SF_5CF_3, ^{14}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_6 concentration, and a sharp decrease in pH and DIC concentration (Fig. 2, A and B, and table S3). Based on the SF_6 data, the initial breakthrough in HN04 occurred 56 days after injection. Subsequently, the SF_6 concentration slightly decreased before a further increase in concentration occurred, with peak concentration 406 days after initiation of the injection. SF_5CF_3 behaves similarly (Fig. 2A); its initial arrival was detected 58 days after initiation of the phase II injection,

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followed by decreasing concentrations until 350 days after the injection started. Subsequently, the SF_5CF_3 concentration increased, consistent with the 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}C in HN04 are initially coincident with the SF_6 record, showing peak concentrations in ^{14}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 SF_5CF_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}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 CO_2 was quantified using mass balance calculations (18). The resulting calculated DIC and ^{14}C concentrations are much higher than those measured in the collected water samples, suggesting a loss of DIC and ^{14}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}C indicate that >95% of the injected CO_2 was mineralized through water-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}C detected around 56 days after injection suggest that travel time along the low-volume fast-flowing flow path was too short for significant CO_2 mineralization to occur. Most of the injected 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}C concentration of the injected CO_2 and the precipitated collected calcite (7.48 ± 0.8 and 7.82 ± 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 CO_2 was mineralized by this time (Figs. 2 and 3). This 550-day
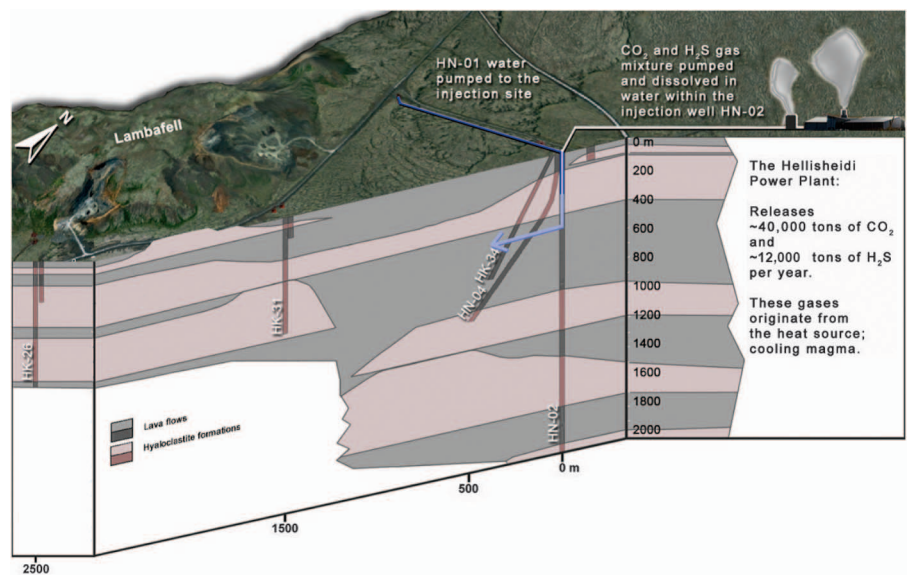

Fig. 1. Geological cross-section of the CarbFix injection site. CO_2 and H_2S are injected fully dissolved in water in injection well HN02 at a depth between 400 and 540 m. For this study, fluid samples were collected in the injection well HN02 and the monitoring well HN04 [modified from (15)].
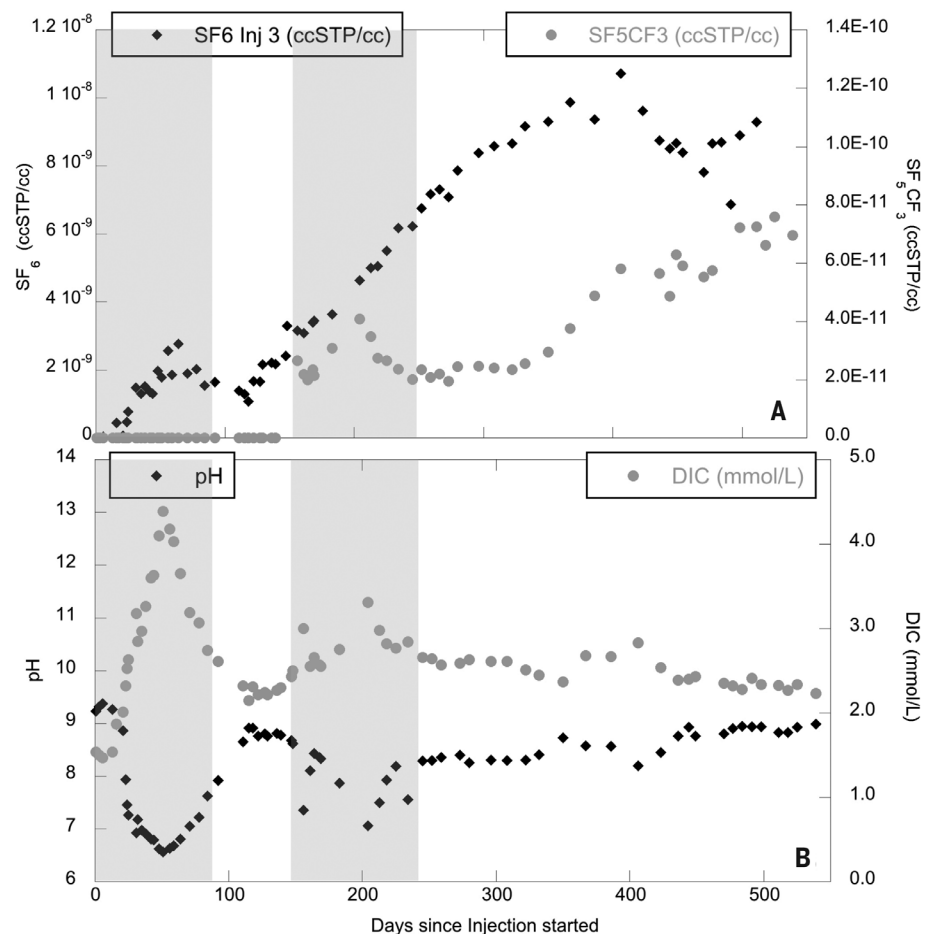

Fig. 2. Change of tracer concentrations, DIC, and pH in the target CO_2 storage formation fluid. Time series of (**A**) SF_6 and SF_5CF_3 tracer concentrations (ccSTP/cc) and (**B**) pH and DIC in monitoring well HN04 for the pure CO_2 and the CO_2 and H_2S injections. The shaded area indicates the phase I and II injection period.
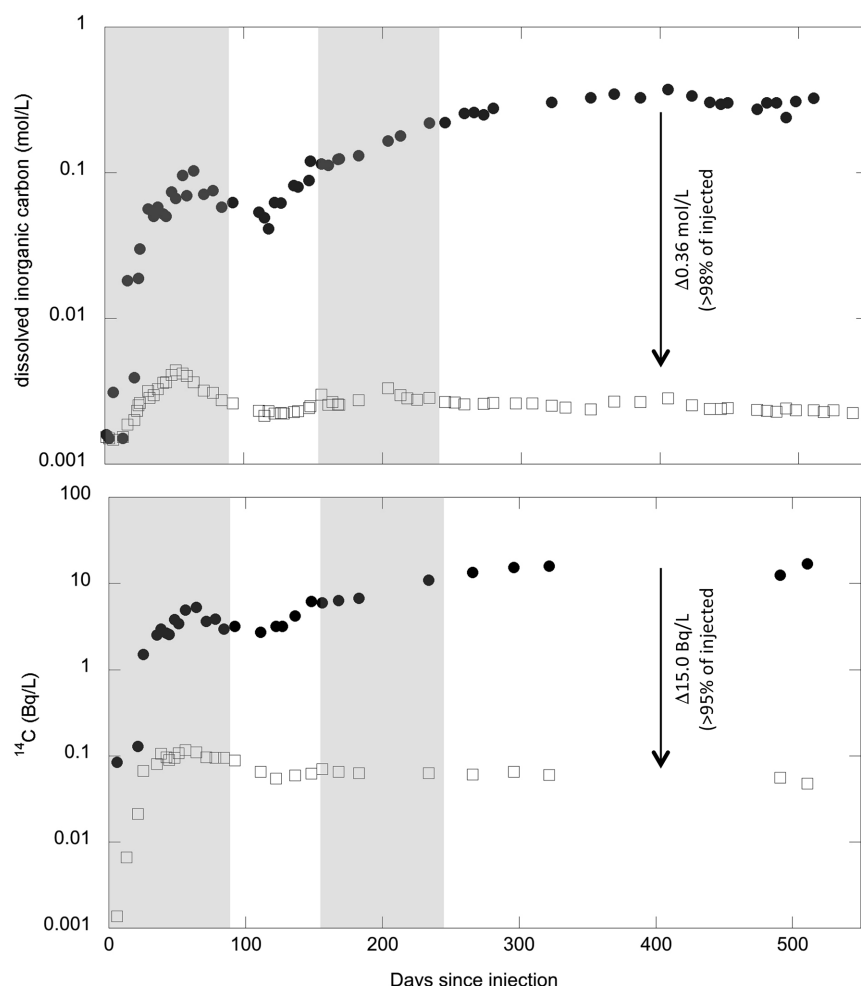
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Fig. 3. Comparison of calculated and measured DIC and ^{14}C concentrations in the target CO_2 storage formation fluid. (**A**) Time series of expected (solid circles) versus measured (open squares) DIC (mol/liter) in monitoring well HN04, indicating >98% conversion of injected CO_2 to carbonate minerals, and (**B**) time series of expected (solid circles) versus measured (open squares) $^{14}C_{DIC}$ (Bq/liter) in monitoring well HN04, showing >95% of injected 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 CO_2 to calcite minerals in the CarbFix storage reservoir is most likely the result of several key processes: (i) the novel CO_2 injection system that injected water-dissolved CO_2 into the subsurface; (ii) the relatively rapid dissolution rate of basalt, releasing Ca, Mg, and Fe ions required for the 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 CO_2 injection, which may have contributed to the neutralization of the injected CO_2-rich water via the reaction $CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2\ HCO_3^-$.

The dissolution of preexisting calcite is supported by the $^{14}C/^{12}C$ 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 CO_2.

The results of this study demonstrate that nearly complete in situ 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*).

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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*)

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Editor's Summary

Inject, baby, inject!

Atmospheric CO_2 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_2 into wells in Iceland that pass through basaltic lavas and hyaloclastites at depths between 400 and 800 m. Most of the injected CO_2 was mineralized in less than 2 years. Carbonate minerals are stable, so this approach should avoid the risk of carbon leakage.

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