

# Lessons in carbon storage from geological analogues

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Geological carbon storage involving injection of CO<sub>2</sub> into geological formations is seen as a critical strategy to manage anthropogenic carbon emissions while society develops carbon-free energy sources. Mitigating the climatic impacts requires the stored carbon to be retained for at least 10 k.y., and there are considerable uncertainties in modeling the fate of the carbon over a time period much longer than we have observed the behavior of CO<sub>2</sub> in geological formations. Key questions are (1) how quickly will the buoyant CO<sub>2</sub> dissolve in formation brines (good), (2) how quickly will the CO<sub>2</sub> brines react with silicate minerals and precipitate solid carbonate phases (good), (3) will CO<sub>2</sub> or CO<sub>2</sub>-charged brines corrode cap-rocks and escape upward (bad), and (4) will CO<sub>2</sub> penetrate up fault zones (bad)?

Studies of naturally occurring CO<sub>2</sub> accumulations may provide answers to the questions regarding its long-term fate. In places, natural CO<sub>2</sub> is actively venting at the surface (for example, from numerous volcanic sources), but elsewhere CO<sub>2</sub> has been retained in geological formations for tens or even hundreds of millions of years (e.g., in the Colorado Plateau, western United States; Gilfillan et al., 2009). Two papers in this issue of *Geology* exploit natural CO<sub>2</sub> accumulations to make inferences on its likely long-term behavior.

Burnside et al., (2013, p. 471 in this issue of *Geology*) estimate rates of leakage from a natural CO<sub>2</sub>-charged aquifer at Green River, Utah, one of the Colorado Plateau CO<sub>2</sub> fields, where CO<sub>2</sub> has been escaping along fault zones for several hundred thousand years, and more recently through uncapped, abandoned petroleum exploration wells. They estimate past rates of CO<sub>2</sub> outgassing by using the U-Th system to date travertine deposits formed by carbonate precipitation where CO<sub>2</sub>-degassing waters reach the surface. Then they measure the volumes of the travertines, and use a degassing model to estimate the volume of CO<sub>2</sub> released as calcite is precipitated. The calculations do not include CO<sub>2</sub> escaping directly in the gas phase, but all CO<sub>2</sub> transported near the surface is thought to be dissolved in the formation brines at present. Burnside et al. estimate that ~20 Mt of CO<sub>2</sub> has escaped from the faults over the past 100 k.y., a rate of ~200 t/yr. It is estimated that CO<sub>2</sub> leaks from Crystal Geyser, the uncapped petroleum exploration well drilled adjacent to the Little Grand Wash fault in 1935, at 11 ± 3.3 kt/yr (Gouveia et al., 2005; Gouveia and Friedmann, 2006). The first obvious conclusion is: don't drill holes into geological stores of CO<sub>2</sub> and leave them uncapped! The more interesting results of this study concern the partition of CO<sub>2</sub> (as it escapes up a fault system) between dissolution in formation brines with subsequent removal by groundwater flow and precipitation of carbonate minerals, and direct escape to the surface.

The second paper on natural analogues to CO<sub>2</sub> storage (Heinemann et al., 2013, p. 411 in this issue of *Geology*) bears on one aspect of the long-term fate of stored CO<sub>2</sub>, the rate at which CO<sub>2</sub> reacts with silicate minerals to cause precipitation in carbonate minerals. They estimated the amount of secondary dolomite [CaMg(CO<sub>3</sub>)<sub>2</sub>] precipitated in a 50 m.y. old, CO<sub>2</sub>-rich gas accumulation in the "Fizzy Discovery" in the southern North Sea. Here, hydrocarbon gas contains ~50 mol% CO<sub>2</sub> and the gas occupies ~68% of the pore space, the rest being occupied by brine. Dolomite precipitation in such a reservoir would be triggered by reaction of CO<sub>2</sub>-charged brine with silicate minerals (clay minerals, alkali feldspar, muscovite, and altered lithic clasts). Dissolution of the silicate minerals supplies the cations (Ca and Mg) for precipitation of dolomite. The reactions would proceed because the equilibrium pH of brines with silicate

minerals is higher than that of brines in equilibrium with carbonate minerals. Heinemann et al. had to distinguish between dolomite present in the reservoir before the CO<sub>2</sub>-rich gas was introduced, and dolomite produced by reaction. They used an ingenious leaching method to progressively strip layers from the dolomite while measuring their carbon and oxygen isotopic composition to show marked isotopic zoning in the dolomites. Then they used the original isotopic composition of the dolomite as sampled in a well in the CO<sub>2</sub>-free part of the field, and that of the injected CO<sub>2</sub> to calculate the mass of CO<sub>2</sub>-precipitated dolomite. They estimate that only 11 ± 8% of the CO<sub>2</sub> has been sequestered as dolomite over the 50 m.y. history of the field, and that such mineral trapping is likely unimportant.

This work raises two important questions. The first relates to the controls on the carbonate-producing reactions. The CO<sub>2</sub> in the "Fizzy field" is only 50% of the gas phase. In such a system, pure CO<sub>2</sub> (or brine saturated in CO<sub>2</sub>) will precipitate carbonate minerals while reacting with silicates until either the silicate minerals are exhausted, or until the activity (i.e., concentration) of CO<sub>2</sub> in the aqueous phase is reduced so that the brine, silicate minerals, and carbonate minerals are all in equilibrium. Given the 50 m.y. history of the field, it is likely that equilibrium is approached. Did the reactions in the "Fizzy field" terminate because suitable silicate minerals were exhausted, or because a reduction in CO<sub>2</sub> activity brought the silicates and dolomite close to equilibrium? Insufficient information is available on the compositions of the silicate minerals and the thermodynamics of fluid-mineral equilibria to properly answer these questions.

The second question relates to the three-dimensional hydrological structure of the reservoir. Reaction between static CO<sub>2</sub> accumulations and reservoir minerals is limited by the availability of reactants, but where CO<sub>2</sub> or CO<sub>2</sub>-charged brines flow through reservoir rocks they may be exposed to much higher surface areas of potentially reactive minerals. Sampling of the "Fizzy field" is far too limited to integrate potential fluid-rock reactions over the whole volume of the field, and we do not know how the CO<sub>2</sub>-rich gas phase migrated into the field, or how CO<sub>2</sub>-charged brines may have circulated away. Sites such as Green River, Utah, may provide more information on the potential fate of stored CO<sub>2</sub>.

The Green River site, with its recently active faults, is unlikely to be chosen as a CO<sub>2</sub> storage site, but has been chosen for study precisely because it is leaking. Most CO<sub>2</sub> accumulations in the Colorado Plateau are not leaking, and are therefore much more difficult to study. If CO<sub>2</sub> did leak up fault systems, however, the hydrology of the leakage could be similar to that at Green River, where CO<sub>2</sub> is thought to leak from 2-3 km depth up the fault systems, variously dissolving in formation brines in the complex stratigraphy of aquifers and aquitards in the Paradox Basin. CO<sub>2</sub>-saturated brines are up to 1-2% denser than their CO<sub>2</sub>-free counterparts, and are therefore much less likely to leak than free, supercritical or gas-phase CO<sub>2</sub>, which is much less dense. In addition, CO<sub>2</sub>-saturated brines flowing through suitably reactive reservoir mineralogies will precipitate carbonate through silicate mineral-fluid reactions, or as a result of CO<sub>2</sub> degassing during decompression. The Green River site provides constraints on the mitigation of both CO<sub>2</sub> escape processes.

We should therefore consider the geology and hydrology of the Green River site. The Navajo Formation, a permeable aquifer at depths of a few hundred meters, is the immediate source of CO<sub>2</sub> and CO<sub>2</sub>-charged brines erupting at the surface in the CO<sub>2</sub> geysers at Green River. The artesian nature of the basin drives vertical migration of the CO<sub>2</sub>-saturated brines

through the faults, and the regional hydrology drives flow rates of a few meters per year toward the southeast or south in the Navajo sandstones. Kampman et al. (2009) modeled the along-flow geochemical gradients in the erupted fluids to show that sharp drops in pH reflected the addition of CO<sub>2</sub> at the two major fault systems, and gradients in fluid chemistry downstream allowed calculation of the fluid-mineral reactions and their rates. These reactions were primarily the consumption of CO<sub>2</sub>, plagioclase, and alkali feldspars, gypsum, and dolomite, and precipitation of calcite, clay minerals, and quartz. Critically, the reaction rates decreased downstream of the CO<sub>2</sub> injection sites, because the magnitude of thermodynamic disequilibrium between the CO<sub>2</sub>-charged brines and silicate minerals decreased.

So how much CO<sub>2</sub> dissolves at the Green River fault systems? Flow rates of 2.5 m/yr in the ~140-m-thick, 20% porosity Navajo sandstone over a lateral distance of 2 km (the width of the CO<sub>2</sub> bleached zone in the exhumed Entrada sandstone at Green River; Wigley et al., 2012) would transport ~4000 t/yr away from the fault zones, 20× the rate that Burnside et al. estimate has been leaking over the past 100 k.y. There are at least two deeper aquifers potentially comparable to the Navajo sandstone (the Wingate and White Rim sandstones). If the fraction of CO<sub>2</sub> dissolved in each is comparable to that in the Navajo sandstone, the fraction of CO<sub>2</sub> reaching the surface would be 0.05<sup>3</sup> or 0.01% of the CO<sub>2</sub> injected into the fault system. Clearly, a large mass of CO<sub>2</sub> is available in the system, since the borehole feeding Crystal Geyser at Green River has been leaking at a rate of 11 kt/yr for 80 yr, ~50× the average natural leakage rate.

We can make a comparable calculation of the net rate of CO<sub>2</sub> sequestration into calcite from the calculations of Kampman et al., (2009). These imply that ~9% of the CO<sub>2</sub> dissolved (400 t/yr) is precipitated in calcite. This is only a small part of the total amount dissolved, although more than is naturally escaping at the surface. This is, however, the integrated mass over a limited portion of the ultimate flow path.

Natural systems are not simple steady-state processes, and these calculations ignore a number of potential complexities. Kampman et al. (2012), used the U-Th ages calculated by Burnside (2010) combined with trace element and carbon, oxygen, and strontium isotope ratios in the travertine veins, to show that the CO<sub>2</sub> degassing was episodic over the past ~135 k.y., with four main pulses in CO<sub>2</sub> leakage coeval with interglacial warming. They hypothesize that changes in groundwater recharge rates, and in the continental stresses related to unloading of the continental ice sheet and associated draining of nearby Lake Bonneville, triggered dilation of fractures in the fault damage zone, thus facilitating enhanced escape of CO<sub>2</sub>. At these times, free CO<sub>2</sub> in the gas phase may have escaped to the surface, and the travertines may not have recorded all emitted CO<sub>2</sub>.

The analogue studies thus teach an important lesson: we can constrain the nature and rates of the processes governing the fate of CO<sub>2</sub> in geological storage reservoirs. Interpreting these observations fully, however, requires understanding the hydrology of the settings, invariably complex where multiphase flows are involved. The most important finding is that free-phase CO<sub>2</sub> dissolves rapidly in formation brines, as supported by studies in which measurements of noble gas concentrations and isotope ratios (e.g., CO<sub>2</sub>/<sup>3</sup>He ratios) indicate that large CO<sub>2</sub> accumulations have lost up to 90% or more of the CO<sub>2</sub> by dissolution into formation

brines. Gilfillan et al. (2009) argued that dissolution is important and fluid-mineral reactions unimportant, as modification of the CO<sub>2</sub>/<sup>3</sup>He and carbon isotopic composition of the CO<sub>2</sub>-gas in many of the ancient CO<sub>2</sub> reservoirs is dominated by isotopic fractionation driven by CO<sub>2</sub> dissolution. However, the stagnant nature of the formation water in these fields precludes the instantaneous isotopic equilibrium between fluid and gas, especially far from their interface, required to preserve information on CO<sub>2</sub> removal from the brine phase, and information on carbonate deposition is unlikely to be preserved in the isotopic composition of the gas cap. In a young CO<sub>2</sub> accumulation (~50 k.y.) undergoing contemporary CO<sub>2</sub> recharge and comparatively rapid fluid flow, the gas phase records both significant dissolution and the production of large quantities of alkalinity by fluid-mineral interactions, which would favor the trapping of CO<sub>2</sub> in carbonate minerals (Dubacq et al., 2012).

The study of natural analogues for CO<sub>2</sub> storage clearly can make important contributions to the debate about the security of geological storage, but interpreting the information may not be straightforward. The studies cited here are just making a start, while illustrating the richness of available information.

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