Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO_2 Capture Project

Geologic Storage of Carbon Dioxide with Monitoring and Verification

Volume 2

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Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO_2 Capture Project

Geologic Storage of Carbon Dioxide with Monitoring and Verification

Edited by

Sally M. Benson
Lawrence Berkeley Laboratory
Berkeley, CA,USA

and Associate Editors

Curt Oldenburg[1], Mike Hoversten[1] and Scott Imbus[2]
[1]Lawrence Berkeley National Laboratory
Berkeley, CA, USA
[2]Chevron Texaco Energy Technology Company
Bellaive, TX, USA

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P.O. Box 211, 1000 AE Amsterdam
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Chapter 4

NATURAL LEAKING CO_2-CHARGED SYSTEMS AS ANALOGS FOR FAILED GEOLOGIC STORAGE RESERVOIRS

Zoe K. Shipton[1], James P. Evans[2], Ben Dockrill[3], Jason Heath[2], Anthony Williams[2],
David Kirchner[4] and Peter T. Kolesar[2]

[1]Centre for Geosciences, Division of Earth Science, University of Glasgow, Glasgow G12 8QQ, UK
[2]Department of Geology, Utah State University, Logan, UT 84322-4505, USA
[3]Department of Geology, Trinity College, Dublin 4, Ireland
[4]Department of Earth and Atmospheric Sciences, Saint Louis University, St. Louis, MO 63013, USA

ABSTRACT

Analysis of leaky CO_2 reservoirs in the northern Paradox Basin, Utah has allowed us to develop a model for the shallow subsurface CO_2 flow system. The results provide information on how CO_2 migrates and reacts with groundwater and reservoir rocks in the subsurface, and what the effects on surface environments are when CO_2 leaks to the surface. A series of shallow fluvial and eolian sandstone groundwater reservoirs are charged with CO_2 derived mostly from clay–carbonate reactions in Paleozoic source rocks within the basin (depths greater than 1.5 km). The CO_2-charged groundwater builds up in a north-plunging anticlinal trap with fault sealing on its southern margin. Top seal is provided by shale-rich formations, but fractures related to the fault damage zone provide conduits through the top seal. This geometry has resulted in a series of stacked reservoirs, and ultimately in escape of the natural CO_2 into the atmosphere. The CO_2 escapes through a series of springs and geysers along the faults, and through wellbores that have penetrated the reservoir. At the surface, rapid degassing of CO_2-charged groundwater results in the formation of travertine mounds around active springs. The presence of deeply incised ancient mounds attests to the long lifespan of this leaky system. There is no evidence of adverse effects of this leakage on wildlife or humans, and the springs provide (somewhat saline) water for plants in this high desert environment. Studies on the effect of long-term leakage both in the subsurface and at the point of leakage to the surface provide data on factors that affect the safety and feasibility of future CO_2 injection projects and should guide the design and implementation of geologic storage projects.

INTRODUCTION

For geological CO_2 storage to be effective, we need to be able to monitor the flow of CO_2 in the subsurface, and to ensure that little or no CO_2 leaks to the Earth's atmosphere over periods of thousands of years [1]. We consider a geological CO_2 storage "system" to consist of four main components: (1) a relatively porous and permeable reservoir lithology acting as a storage "tank", (2) a low-permeability and capillary-entry-pressure sealing lithology that is a barrier to flow out of the reservoir (cap rock and/or fault seal), (3) in the case that the seal fails, the likely migration pathways through the overburden and possible secondary reservoirs where gas may be trapped, and (4) the vadose zone and Earth's surface. Potential negative consequences of CO_2 leakage and seepage from the storage reservoir may potentially be felt if it infiltrates aquifers, and if it interacts with plants, animals, and humans. For accurate risk assessment we need to understand each step of migration from "tank" to surface, to quantify the rates and volumes of gas released to the atmosphere in the case of a leak, to determine the environmental impact of escaped gas on the surface biota, and to design mitigation strategies for the effects of any leakage. Analyses of natural leaky CO_2-rich systems are ideal for determining how CO_2 migrates and reacts with groundwater and reservoir rocks in the subsurface, and what the effects are when it leaks to the surface. These studies provide data on the factors that affect the feasibility and safety of future CO_2 injection projects and should guide their design and implementation.

The Paradox Basin, in the Colorado Plateau region of the United States, contains a number of natural CO_2 reservoirs, which provide analogs for understanding the integrity of stored gas systems [2]. Many of these fields have stored CO_2 for long periods of time, but others leak gas into the atmosphere, primarily along faults. In this paper we review studies of the hydrology, stratigraphy, structural geology, and geochemistry of a naturally degassing CO_2 reservoir in Utah. The CO_2 discharges along the Little Grand Wash and Salt Wash faults, creating a series of CO_2-charged springs and geysers, travertine deposits (both active and ancient), and carbonate-filled veins. A number of abandoned hydrocarbon boreholes also act as active conduits for CO_2 to the surface. This multidisciplinary study summarized here examines the controls and processes active in such leaky systems, and the effect of leakage in surface environments.

GEOLOGICAL SETTING

The Little Grand Wash and Salt Wash normal faults are situated in the northern Paradox Basin (Figure 1). This basin is defined by the extent of organic-rich Pennsylvanian and Permian limestones, shales and evaporites, which cover a large area of southern Utah and western Colorado. A basin-wide system of salt anticlines and faults initiated during Pennsylvanian/Permian uplift of the Uncompaghre plateau to the northeast, and were reactivated during several episodes of deformation ranging from the Triassic to Quaternary [8,9]. Many of the CO_2 reservoirs have accumulated within these salt anticlines, including the leaky reservoir in this study.

The Paradox Basin is filled with a series of clastic and carbonate sedimentary rocks analogous to those in North Sea oil and gas fields, and a number of good reservoir and seal systems exist in the basin. The regionally important Permian White Rim Sandstone reservoir is capped by the shale-rich Triassic Moenkopi and Chinle Formations. The overlying fluvial and eolian redbed reservoir units of the Lower Jurassic Navajo, Kayenta and Wingate Sandstones are capped by the marine limestones of the Carmel Formation, or the shale-rich Dewey Bridge Member of the Entrada Formation. The Middle Jurassic Entrada and Curtis Formations are the youngest good reservoir units in the basin, and are capped by interbedded fluvial and eolian siltstones and sandstones and gypsum seams of the Middle Jurassic Summerville Formation. The remaining overlying sequence does not contain any large reservoir units, but does contain several sand-rich units. The Upper Jurassic Morrison Formation consists of stacked fluvial channels of the Salt Wash Sandstone member, overlain by the bentonite-rich lacustrine shales of the Brushy Basin member. The Lower Cretaceous Cedar Mountain Formation black lacustrine shale is overlain by the Upper Cretaceous Dakota Sandstone conglomeratic channel sandstones. The youngest formation exposed in the field area is the Upper Cretaceous Mancos Formation, a dark organic-rich marine shale.

The east–west trending Little Grand and Salt Wash faults cut an open, north plunging anticline (Figures 1 and 2). The 61 km long, 70–80° south-dipping, Little Grand Wash fault is a complex fault zone comprised of several anastomosing normal faults defining structural terraces with varying dips (Figure 2a). Total vertical separation at the center of the fault is 180–210 m, most of which is accommodated by the southern fault strand. The Salt Wash faults (sometimes termed the Tenmile Graben) are a set of 290° striking dip-slip normal faults that form a graben over 15 km long (Figure 2b). Well data from abandoned oil wells and water wells have been used to constrain the subsurface geometry of the north-plunging anticline and faults.

PRESENT-DAY LEAKAGE

Active Springs and Wellbore Leakage

CO_2-charged groundwater effuses from a number of natural springs and leaky wellbores along the faults. Almost all of these effusions occur to the north (footwall) of both faults (Figure 2). The wellbores are mostly abandoned oil exploration drill holes and a few water wells. The most dramatic of these leaks is the Crystal Geyser on the eastern bank of the Green River in the footwall of the Little Grand Wash fault zone (Figure 3a). This cold-water geyser has erupted at 4–12 h intervals since the Glen Ruby #1-X well was drilled to the base of the Triassic section (TD 801 m) in 1935. The well was spudded into a 21.5 m thick

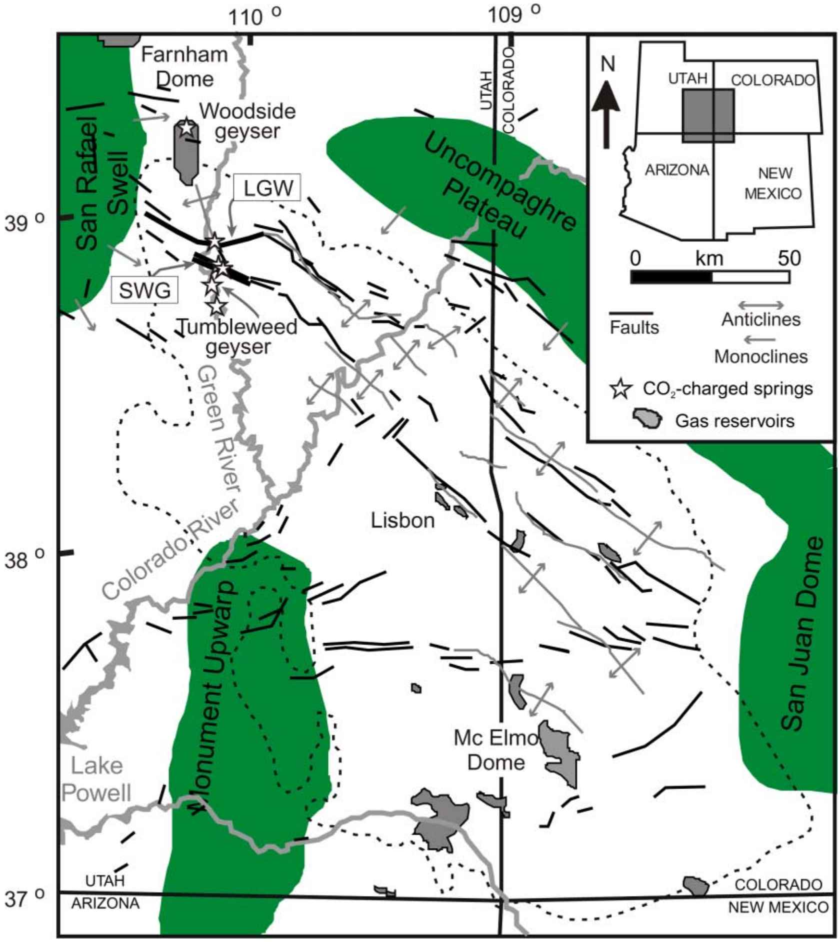

Figure 1: Regional geologic setting of the study area, after Nuccio and Condon [3] and Cappa and Rice [4]. Dotted line marks the extent of the Paradox Basin. LGW, Little Grand Wash fault; SWG, Salt Wash Graben.

travertine mound [10], so the spring system must therefore have been active for a considerable length of time prior to the well being drilled. This is corroborated by reports of "satin spar" at this location in 1869 by the Powell expedition along the Green River [11]. Three other springs within 10 m of the wellhead effuse periodically throughout each geyser eruption. These pools could represent the location of pre-well CO_2-charged springs or could be due to escape of the CO_2-charged waters from the well bore at shallow levels.

Smaller intermittent CO_2 fluxes occur in the Green River, where a line of small bubbles can be observed along the trace of the fault. Approximately 1 km east of the Crystal Geyser and ~ 100 m north of the fault zone, dry gas seeps audibly from the ground. Although there is no surface water at this location, the soil is commonly wet even in the dry season. These observations suggest that a diffuse flux of CO_2 may exist in the vicinity of point-source leaks (springs and wellbore seeps). In the absence of detailed flux monitoring it is

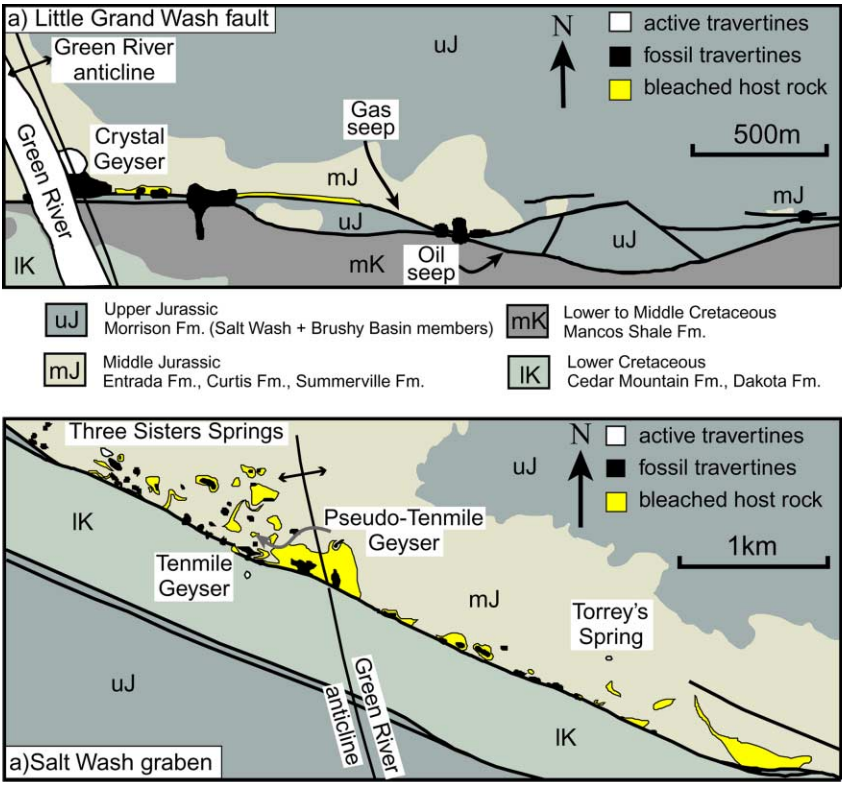

Figure 2: Local geological map of the distribution of active springs, travertine and reduction zones along (a) the Little Grand Wash and (b) the Salt Wash faults (after Dockrill et al. [5]; Williams [6] and Doelling [7]). Note that geologic formations have been grouped to simplify the map.

impossible to estimate the relative contribution of each type of CO_2 leak to the overall flux out of the reservoir (i.e. point sources vs. diffuse seeps under the Green River and possible degassing through soil).

Five CO_2 springs or small geysers occur along the northern Salt Wash fault (Figure 2). The westernmost Three Sisters springs flow continuously, but there is relatively little carbonate deposition at the site (Figure 3b). These springs lie in a 3–4 ha topographic low with saltpan crusts. Water can be found within 10 cm of the surface throughout the region, and we suggest that the surface seeps are a smaller manifestation of a broader gas leakage system. The Tenmile Geyser erupts infrequently with 1–1.5 m high eruptions, is located 200 m south of the northern fault and is the only visible point-source of CO_2 effusion that occurs within the graben (Figure 3c). It is centered on an abandoned well, which may penetrate the fault into the footwall reservoir (unfortunately no drilling records are available for this well). Pseudo-Tenmile geyser, a mineral-charged spring that vents a constant stream of CO_2 bubbles, sits on a low mound 100 m north of the fault. Torrey's Spring is in the footwall of the northern Salt Wash fault (Figure 3d) and is associated with an abandoned drill hole. This spring flows and bubbles continuously and has developed a small carbonate mound ~ 15 m in diameter.

Several other CO_2-charged springs occur in the northern Paradox Basin, all of which are associated with wellbore leakage from abandoned water wells (Figure 1). The once spectacular Woodside Geyser,

Figure 3: Sites of active leakage along the Little Grand Wash and Salt Wash faults. (a) View of Crystal Geyser facing north, trace of fault marked with a dashed line. The orange active travertine deposit is approximately 70 m wide by 80 m long. Note the dull gray inactive travertine exposed in riverbed and on west bank of river. (b) Sampling water from one of the Three Sisters springs. (c) Tenmile Geyser with remains of well casing. (d) Torrey's spring. Note the more restricted size of these mounds, and the lack of well-developed terraces.

approximately 40 km north of the study area, now only erupts sporadically to a height of a few meters from an abandoned oil well. The Tumbleweed and Chaffin Ranch geysers to the south of the faults in this study erupt occasionally from water wells. These other springs fall along the line of the regional north-plunging anticline axis, as do the geysers and springs along the faults, suggesting that the flow of CO_2 or CO_2-charged groundwater is focused along the anticline axis.

Travertine deposits are developed to various degrees around all the active springs. The most well-developed mound is at Crystal Geyser, which consists of down-stepping lobes, which radiate outward from the central wellhead, covered in rimstone terraces (Figure 4a). The other natural springs have smaller, less well-developed travertine mounds (Figure 3b–d). The wellbore leakage sites are surrounded by cemented Quaternary material and thin, friable, poorly developed travertine drapes. We suggest that the degree of travertine development reflects the length of time the spring has been active.

Water Composition

Water samples were collected from seven locations according to the detailed field sampling and measurement methods that Heath et al. [12] developed for sampling high-CO_2 groundwaters. All water samples had in situ temperatures less than 18 °C, confirming that CO_2 degassing is the only driving mechanism for the geysers (rather than high heat flow). The low effusion temperature of the spring waters suggests a shallow source, assuming the waters did not cool during ascent. The δD and $\delta^{18}O$ for the sampled groundwater do not show an $\delta^{18}O$-isotopic shift away from the local meteoric water line, implying that they

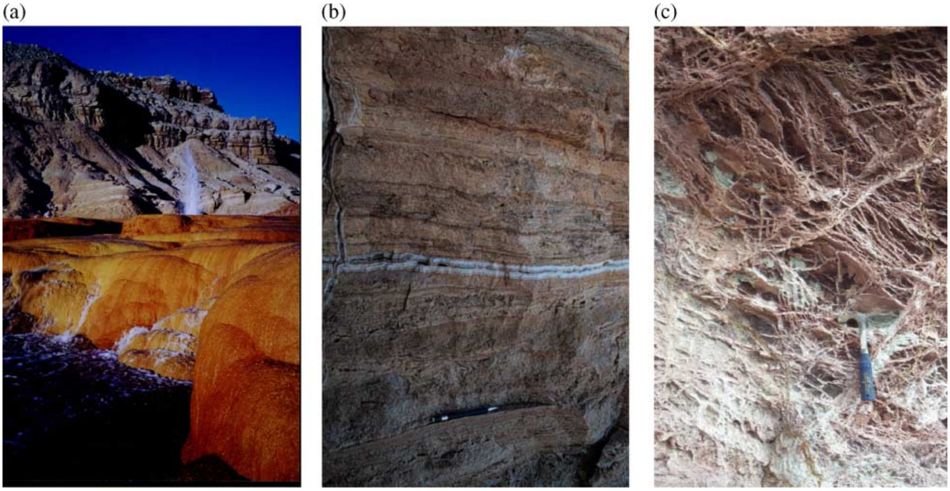

Figure 4: (a) The foreground of this photo shows the surface texture on the active Crystal Geyser terrace, while a typical geyser eruption is occurring in the background. Height of water column in this photo ~ 10 m. (b) Eroded ancient porous terrace travertine cut by a white banded vein with radiating crystals pointing inward from vein walls. (c) Highly altered Summerville Formation below an inactive travertine mound with a dense box-work of white-banded veins.

are meteoric and have not exceeded temperatures of > 100 °C. Given local geothermal gradients [3], the water for the springs along these faults is therefore likely to have come from the Wingate and Navajo Sandstone at around 300–500 m depth [13,14].

The waters are saline and slightly acid, with 13,848–21,228 mg total dissolved solids (TDS) per liter and pH values from 6.07 to 6.55. The $\delta^{13}C$ values of total dissolved carbon from three springs or geysers range from 0.0 to 1.2‰. The waters are supersaturated with respect to calcite, aragonite, dolomite, and hematite, and are undersaturated with respect to anhydrite, gypsum, halite, and quartz, consistent with the carbonate minerals found at the locations of the emanating waters. The carbonate precipitation may be a result of degassing effects that bring the waters to supersaturation with respect to the carbonate phases when the waters reach the surface. All of the waters are closely grouped in the sodium chloride chemical facies (Figure 5) suggesting a similar chemical evolution history of all the waters in the study area. Springs on the southern side of the Salt Wash graben, however, have lower bicarbonate contents, lower salinities and are more alkaline. We suggest that these springs tap a local flow regime and not the regional CO_2-charged groundwater system. Shipton et al. [14] showed that the salinity of the Crystal Geyser water decreases during and after an eruption suggesting that as gas and water are discharged through the water column, fresher water drains into the wellbore.

Gas Composition

Gas samples were collected from seven sites according to the detailed field sampling and measurement methods of Heath et al. [12,13] using both diffusion samplers and glass bottle samplers. The sample sites include three abandoned drill holes and four natural bubbling springs. The gases emanating from all the springs are 95.66–99.41% CO_2 by volume with minor amounts of Ar, O_2, and N_2. A small amount of atmospheric gases are probably entrained during geyser eruptions and the vigorous bubbling of the emanating waters. The $\delta^{13}C$ values of the CO_2 gas phase range from − 6.42 to − 6.76‰ (SD 0.13‰). This indicates that the CO_2 gases may all come from the same source and that the travel path may not greatly alter the carbon isotopic values, even though the gases are emanating from three distinct areas nearly 10 km apart. Thus, the same type of gas may be ubiquitous in the northern part of the Paradox Basin.

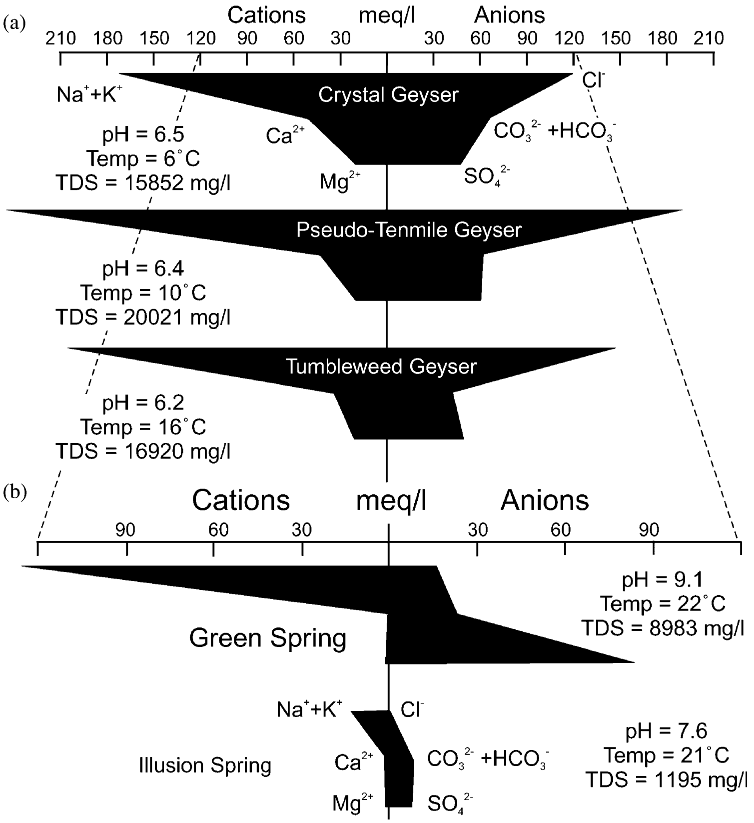

Figure 5: Stiff diagrams showing chemical compositions of the waters from various springs in milliequivalents per liter (after Heath et al. [13]). (a) Springs associated with CO_2 leakage and which erupt in geyser-like eruptions. For all of these springs pHs are slightly acidic, all have low temperatures and fairly high total dissolved solids. All the waters are chemically similar, with Na^+ and Cl^- as the major ions and fall in the same chemical facies. All waters have high levels of bicarbonate indicating high CO_2. (b) Springs on the south strand of the Salt Wash fault, note the change in scale. The pHs of the south strand springs are higher and their total dissolved solids are much lower.

INACTIVE SPRINGS

A series of partial to complete remnants of ancient travertine mounds runs parallel to the Little Grand Wash and Salt Wash fault traces (Figure 2). All the ancient travertine along both faults is situated either on, or to the north of, the fault zones. The ancient travertines are up to 4 m thick and occur up to 30 m above the present level of the actively forming deposits, forming a resistant cap on top of a series of buttes, reflecting the progressive down-cutting of the Green River.

Cross-sectional exposures through well-developed ancient travertine mounds demonstrate the processes that are likely to be active below the surface of the modern mounds [5]. The base of all the ancient travertine mounds consists of carbonate-cemented sediment suggesting that colluvium surrounding the leak site was cemented by the erupting spring waters. The main body of the travertine mounds consists of interbedded layers of sub-horizontal layered carbonate and cemented colluvium. The carbonate layers have a distinctive terraced texture that is similar to the rimstone textures of the active travertines (Figure 4b), so we suggest this unit represents the aggrading surface of a fossil travertine deposit. The host rock underlying the ancient travertine deposits is cut by carbonate veins and is altered along sporadic beds. In sand-dominated lithologies, the veins are 4–15 cm thick and usually have a reduction halo 1–5 cm wide. In mud-dominated lithologies a box-work of thin veins (5–20 mm thick) can almost obliterate the host-rock fabric (Figure 4c). Thick white-banded veins (5–80 cm) cut through the entire thickness of the mounds. These veins are interpreted to precipitate predominantly in a sub-aqueous environment from rapidly degassing CO_2-rich waters and therefore represent the primary migration pathways of fluids through the deposit.

Carbon and oxygen isotopic compositions of travertines provide insight into the origin of the water and CO_2 and the precipitation conditions of the carbonate over a longer timespan than do the analyses for the modern water and gas. The $\delta^{13}C$ and $\delta^{18}O$ values of the layered carbonate facies from both active and inactive travertine overlap (Figure 6), implying that they were precipitated from parental fluids that have remained isotopically consistent over time. Veins within the fault zone and on the south side of the faults have much lighter $\delta^{13}C$ values than the travertine mounds indicating that the non-travertine-related veins were generated from different sources and fractionation processes (Figure 6). The CO_2-charged water appears therefore to have not crossed the fault zone. The $\delta^{18}O$ values for the white-banded veins and non-travertine veins are similar indicating that precipitation of all the carbonate veins occurred at comparable low temperatures from meteoric waters.

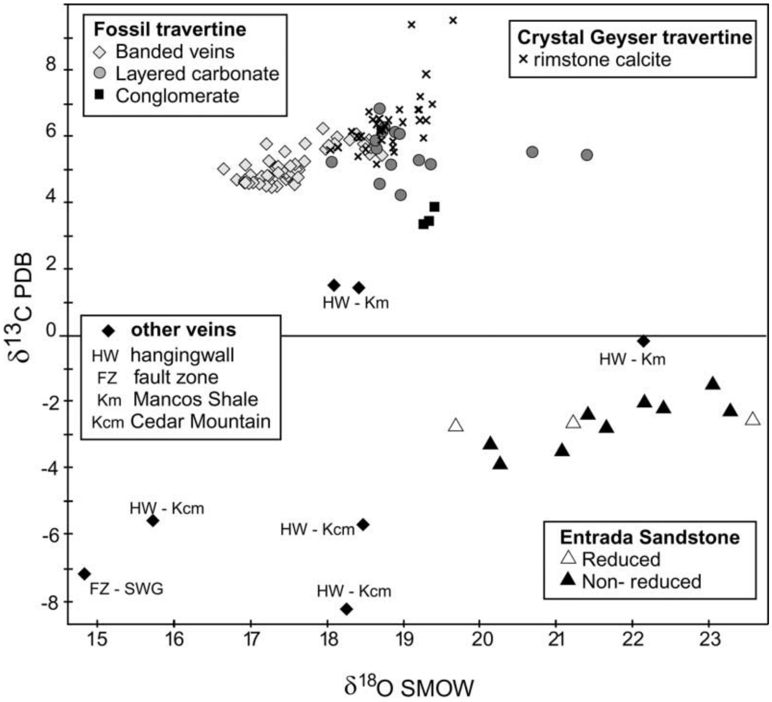

Figure 6: Carbon and oxygen isotope data from fossil travertine and active Crystal Geyser travertine (after Dockrill et al. [5]). Samples for veins from the Salt Wash fault zone (FZ-SWG), and north of the Little Grand Wash fault (HW-Km) and Salt Wash Graben (HW-Kcm) are also plotted. The stable isotope signatures of these veins are very different from the travertine-related veins, and are interpreted to be precipitated from different source waters. Data for red unreduced Entrada Sandstone and reduced Entrada Sandstone are also shown.

IRON OXIDE REDUCTION AND HYDROCARBON STAINING

Areas of the Entrada and Curtis Formation red beds near the Little Grand Wash and Salt Wash faults have been altered to pale yellow or white. This is due to extra-formational reducing fluids stripping out Fe^{2+}- and Mn^{2+}-bearing minerals causing an apparent bleaching of the unit (see Refs. [8,15]). These reducing fluids could include hydrocarbons, organic acids, methane, or hydrogen sulphide [15,16]. The iron oxide reduction is focused in structural highs (i.e. where the anticlinal crest is cut by both faults) and at leak points (i.e. below travertine deposits) along both faults. The reduced zones are interpreted to represent the migration pathways of buoyant fluids through this faulted system. The reduced sandstones are isotopically consistent with the non-reduced red sandstones and are isotopically distinct from any precipitates related to the overlying travertine mounds (Figure 6). This indicates that the presently erupting carbonate-rich fluids are not responsible for the reduction zones and that one or more earlier reducing fluids must have migrated through this faulted system to cause the reduction zones. It is interesting to note that similar altered rocks are seen on a large-scale across the Paradox Basin [15,17].

A fresh oil seep is located to the east of the active seeps along the Little Grand Wash fault and the Salt Wash Member sandstones close to this oil seep contain patches of bitumen staining. This seep has been active since at least the 1940s [18] and the freshness of the oil indicates that there is active flow of petroleum to the surface. Carbon isotopes of the oil from the seep with respect to saturated and aromatic hydrocarbons are -28.47 and $-29.26‰$, respectively [19]. These values are much more depleted than the $\delta^{13}C$ of the CO_2 gas. Without a detailed paradiagenetic study it is not clear whether the flow of hydrocarbons is related to the flow of CO_2, but the close spatial association of the CO_2 leaks, the oil seep and the reduced sandstone suggests that similar pathways are used by hydrocarbons, the present day CO_2 flow, and possibly a separate phase of reducing fluids.

DISCUSSION

Source of the CO_2

Unusual volumes of CO_2 appear to have been generated in the Paradox basin and the likely sources are discussed in Refs. [13,14] on the basis of the isotopic signature of the gas and carbonates. Measured helium R/R_a values of ~ 0.3 [14] are well out of the range for mantle helium signatures of 7–21 and are similar to crystal values [20]. It should be noted, however, that transport properties of He and CO_2 are distinct and that He and CO_2 might be expected to fractionate during migration. Although hydrocarbon source rocks occur in the Paradox Formation [3], the thermal degradation of organic matter during diagenesis and catagenesis results in values of $\delta^{13}C_{CO_2}(g)$ from -8 to $-12‰$ (Ref. [21]), lower than those measured from the springs (-6.42 to $-6.76‰$). Production of CO_2 from the degradation of organic matter through sulfate reducing or methanogenic bacteria produces more depleted values of $\delta^{13}C_{HCO_3}$ than are seen in our analyses [22].

Clay–carbonate diagenetic reactions at temperatures of about 100–200 °C during deep burial of impure carbonate sedimentary rocks can generate large amounts of CO_2 gas [23,24]. By assuming isotopic equilibrium between the source carbonates and the gases, Heath et al. [13] showed that the clay–carbonate reactions involving rocks with $\delta^{13}C_{CaCO_3}$ values of $+1$ to $-3‰$ (close to the average $\delta^{13}C$ marine carbonates) could have produced the CO_2. Occurrences of metamorphic CO_2 have been identified elsewhere in the Paradox Basin (e.g. Figure 1). The average $\delta^{13}C_{CO_2}$ isotopic value of $-6.60‰$ from the effusing gases is $\sim 2‰$ more negative than would usually be expected from the thermal decomposition of marine carbonates. To establish if the gases do derive from metamorphic sources, travel pathways from the source to the area must be identified such as faults and the structural grain of the basin.

Most of these CO_2 sources come from relatively deep in the basin (depths of 1–1.5 km in upper Paleozoic or Triassic rocks) and it is likely that faults provide pathways for flow of CO_2 through normally sealing lithologies such as the Paradox Salt. This scenario requires the generation of a gas phase that can migrate away from the gas source to accumulate in shallow aquifers. One scenario involves the generation of a free-phase of CO_2 when gas-charged groundwater rises above ~ 2 km depth. The free-phase CO_2 can migrate by diffusive and advective flow much faster as a separate supercritical or gas phase, depending on depth. We suggest that the rapid uplift and erosion of the Colorado Plateau has brought CO_2 source waters to shallow depths which has facilitated generation, migration, and accumulation of CO_2 in shallow reservoirs.

Shallow Flow Pathways

Our observations of fault structure and aqueous and carbonate geochemistry enable us to construct a conceptual model of the regional groundwater flow in the upper 1.5 km of the basin (Figure 7).

Potentiometric surface data from groundwater wells show that regional groundwater flows from the northwest to the southeast [25]. Water temperature and stable isotope data for springs along both faults show

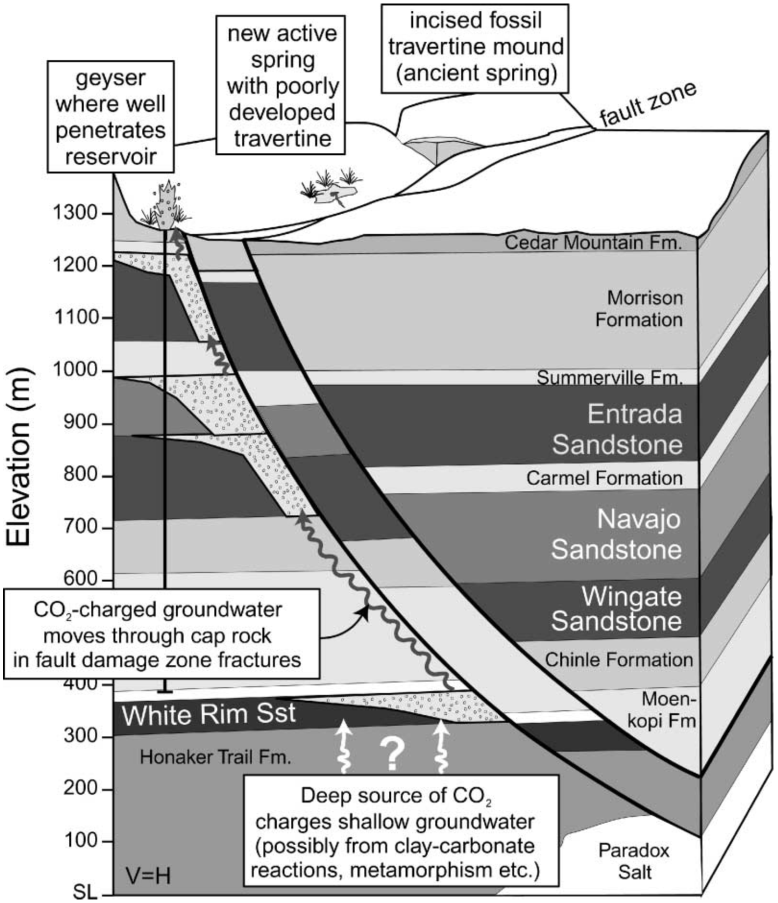

Figure 7: Schematic north–south cross-section through the Little Grand Wash fault (after Williams [6]), used to illustrate the conceptual reservoir model developed in this study. The subsurface geology, specifically unit thicknesses, is constrained by wells. CO_2-charged groundwater (small circles) is pooled in a north plunging anticlinal trap against the south-dipping fault. Although the fault zone geometry is much more complex than is indicated by this cross-section, water-chemistry data and stable isotopes from veins on the south side of the fault show that little or no cross-fault CO_2 migration is occurring. From HCO_3 concentration in different wells, the CO_2 gas may have infiltrated into many of the sandstone formations such as the Entrada, Navajo, Kayenta, and Wingate (schematic CO_2-filled reservoirs are not shown to scale). Fractures related to the faulting allow infiltration of the CO_2-charged groundwater through the otherwise sealing cap rock (arrows). Springs and geysers mark points where CO_2-charged groundwater escapes along natural fractures, or through wellbores that penetrate the reservoirs.

that the CO_2 is charging a reservoir approximately 300–500 m below the surface. Conversely, relatively short flow paths in a local flow system are indicated by the geochemistry of springs on the south strand of the Salt Wash fault. All of the modern and ancient CO_2 leakage points lie on the structural high where the north-plunging anticline is cut by the faults. Therefore, the faults are acting as flow barriers to southeast directed CO_2-charged groundwater flow, and CO_2-charged groundwater is accumulating against the faults within the folded reservoir. Within the framework of this model for the geometry of the shallow CO_2 storage system, the observations and data collected at the leaky faults can give us insight into each of the four components of the CO_2 system.

CO_2 reservoir

In our model, shallow groundwater reservoirs are charged from below by CO_2 generated at depth. These shallow reservoirs are the high-porosity eolian or fluvial Jurassic sandstones. The extent of reaction between the reservoir rocks and the CO_2-charged fluid is unclear, but the continued effusion of the springs and geysers at the same locality through time shows that the high porosity must be maintained, and that the porosity is not being clogged by the products of diagenetic reactions.

Cap rock and fault seal

The topseal for upward movement of fluid from the shallow aquifer reservoirs is provided by shale-rich Jurassic units. A lateral seal is provided by the fault rocks. The difference between the stable isotope signatures of veins in the hanging wall and footwall of the faults shows that the faults have acted as effective barriers for cross-fault flow at depth. The nature of the fault rocks at depth is partly dependent on the type of rocks that are juxtaposed across the faults and the amount of displacement that those fault rocks have undergone. The faults in this area offset a series of clean sandstones and shale-rich rocks and therefore could be expected to produce a clay-rich fault gouge which would be expected to act as a barrier to cross-fault flow as discussed by Yielding et al. [26]. It must be emphasized that predicting fault seal from throw distributions is prone to error, and a small variation in fault-zone thickness or properties can create an apparent “hole” where fluid can leak through the fault.

In contrast to the fault rocks, the shale-rich units that provide the topseal are leaking. Lithologically similar cap rocks have retained their integrity in CO_2 reservoirs elsewhere in the Paradox Basin (e.g. McElmo Dome, Lisbon Dome, Figure 1); therefore an explanation must be sought for why the cap rocks have failed at this location. Prior to drilling of the well, the leakage was focused in the immediate footwall to the faults. We suggest that fractures that formed in the cap rock as part of the damage zone to the faults are providing a conduit for leakage. It is also possible that an increase in CO_2 volume at shallow depths leads to hydrofracturing, therefore enhancing fracture permeability. The fractures through the cap rock must have stayed open for substantial amounts of time (i.e. they are not self-sealing). The strength and mechanical behavior of the cap rock units and the hydrodynamic behavior of CO_2-rich fluid at shallow depths are poorly understood. Without such data, a reliable prediction could not presently be made of the integrity of cap rocks in similar structural settings.

Migration pathways

In our conceptual shallow reservoir model, the CO_2-rich waters are sourced from the Wingate and Navajo Formations. Chemical analyses of groundwater from oil and gas exploratory and development wells, water wells and springs within ~100 km of the field area indicate that high dissolved CO_2 concentrations are common in many formations from the Devonian Elbert Formation to the Jurassic Entrada Sandstone as well as the Navajo, Kayenta and Wingate Sandstones [27]. This distribution of CO_2 content suggests that there is a sequence of stacked CO_2-charged aquifers above the primary CO_2 source. This is a critical issue for CO_2 storage since leakage and migration of CO_2 into formations overlying the intended storage formation may provide secondary trapping sites, reducing the overall flux to the surface.

The drilling of the oil and gas wells has provided pathways for rapid transport of gas-charged groundwater through the cap rock. The only leakage south of the sealing fault occurs through a well that may have penetrated the fault and into the footwall reservoir (Tenmile Geyser). Conversely, the two wells that penetrate the Little Grand Wash fault in the Triassic section (sealing lithologies) do not leak. Most of the wellbore leakage is from abandoned oil and gas exploration wells, and no record exists of the type of cement or casing that was used in these wells. Injection wells drilled for future storage projects are likely to be specially engineered to avoid leakage in this manner. However, any oil- and gas-rich area, which may present an attractive target for CO_2 disposal is likely to contain a large number of abandoned wells.

Effect of Leakage on the Surface

Leakage of CO_2 to the surface has occurred in this system for at least some portion of the Holocene, and thus any effects on the local biological system should be evident. Our initial observations show that there is little or no impact of the CO_2 emissions on the local ecosystems, although more work needs to be done to quantify these observations. The region lies in a high, cold desert, so the natural populations of organisms are limited. We observed no changes in plant mortality around any of the leakage sites. Indeed, slightly enhanced growth of salt tolerant plants occurs at several sites due to the increase of water at the surface (Figures 3 and 4). The water is very high in TDS, S^{2-}, and Cl^-, thereby limiting the type of plant that can tolerate the areas near the springs. Although we might expect to see local effects from the higher salinity groundwater that effuses from the Crystal Geyser, Mayo et al. [28] showed that it does not have a significant effect on the downstream salinity of the Green River. The CO_2 effusion has resulted in no reported casualties (from analysis of historical records and oral histories acquired by historian D. Martindale, Utah State University, personal communication), even though the area is visited by locals and tourists.

Much of the leaking CO_2 is vented to the atmosphere, but some is trapped by the formation of the carbonate travertine mounds. From the groundwater composition, we can estimate the amount of calcite that would precipitate out given the amount of CO_2 that remains in solution (i.e. run a reaction from the supersaturated initial condition to equilibrium). The Crystal Geyser averages 50–100 m^3 of water per eruption, and we estimate that 0.90 g of calcite are precipitated per liter of H_2O, and 3.60 g CO_2/L H_2O are released to the atmosphere. If we assume that the reaction is run to completion, we find that about 10% of the carbon flux is trapped in the travertine. This estimate is a maximum, however, as it assumes that the reaction that precipitates the calcite achieves equilibrium, does not consider the changing water chemistry as it flows over the ground surface, and does not account for the free gas phase present in the system. Thus, our analysis shows that for this natural leaking system, very little of the escaped carbon is presently trapped at the surface. The trapping efficiency could be increased by adding reactive cations (Ca^{2+}, Mg^{2+}, Sr^{2+}) and raising pH, but for a large-scale leak, such an effort may not be effective. It appears that in the Little Grand Wash–Salt Wash fault system, the rate of CO_2 transport to the surface, in both the natural and industrially developed parts of the system, is faster than the rate of mineral precipitation. Thus, in the present study, surface mineralization due to leaking CO_2 does not seal the system.

CONCLUSIONS

We have integrated a variety of geologic data sets and methodologies to examine the sources, travel paths, and fate of CO_2 from a subsurface reservoir to the Earth's surface. The geological and structural analysis shows that the three-dimensional structure of the system consists of an open, north-plunging anticline cut by northwest-trending normal faults. These faults cut a Mesozoic section of clastic rocks that range from high-porosity and permeability eolian and fluvial sandstones, which are the dominant aquifers of the area, and low-permeability shales that appear to form effective top seals to a series of stacked CO_2-charged reservoirs. Although the faults provide a barrier to cross fault flow, the footwall reservoir has leaked for >150 years through the fault-related fractures in the damage zone. Typically in these types of rocks, analyses of fault seal capacity would predict that these faults would be barriers for cross-fault flow. In contrast, fractures in the damage zone associated with the faults appear to provide a conduit for CO_2 leakage through the cap rock units. The sealing characteristics of faults are therefore a key to understanding the storage capacity in these settings. More recent leakage is focused around abandoned oil wells and water wells.

Long-term leakage appears to have had an insignificant effect on surface biota, and no adverse effect on the salinity of the Green River. Despite the fact that the Crystal geyser is visited by tourists and locals, there are no reported casualties from the high CO_2 concentrations. However, water in the aquifers above the CO_2 source tends to have high values of TDS and chemistries that classify them as "contaminated" water.

RECOMMENDATIONS

1. *Leaky faults and fracture systems*. Experience with ongoing geologic CO_2 storage projects has highlighted that each storage site has a very specific set of circumstances requiring detailed structural characterization. Faults and fracture systems pose a leakage risk to any proposed geologic storage site. The risk of encountering sub-seismic scale faults and fractures means that detailed structural characterization and an understanding of cap rock integrity is an essential component of any future CO_2 disposal project.
2. *Wellbore leakage*. The leakage around the wellbores has been continuous since 1935, though we suspect that natural leakage has occurred for much longer. Much anecdotal information regarding damage done to the Ruby well and crude attempts at plugging the well indicate that free CO_2 gas is a robust component in a water gas system to depths of less than 500 m. Although injection and monitoring designed for a storage system would be specially engineered, it is clear that older wells pose a potential for long-term leakage that must be examined.
3. *Surface trapping*. We show that groundwater flow can result in transport of CO_2 for some distance before precipitation results. In the present study, a relatively large amount of CO_2 is vented to the atmosphere relative to the estimated amount precipitated in a mineral phase at the surface. The kinetics of carbonate reactions must be well understood before a "self-sealing" scenario can be proposed for shallow leakage.
4. *Cap rock integrity*. Careful analysis of seal integrity is critical in designing a geologic storage program because fractures and faults can provide pathways for gas migration. The few outcrops of the shale-rich "seal" in the present study all contain abundant veins and fractures, indicating that much more work is needed to understand this part of the system. There are few geomechanical and geochemical data sets that constrain the ability of shale and siltstone cap rocks to prevent the transport of CO_2.
5. *Future studies of CO_2 leakage*. In addition to the dramatic localized fluxes of CO_2 at the geysers and springs near the Green River, there may also be diffuse CO_2 fluxes over a broader area surrounding the fault zone. This could occur if either the cap rock integrity has been compromised by distributed fracturing, or if the CO_2 is spreading out within the vadose zone from localized fractures. The only way to address these questions is to fully characterize the flux of CO_2 from all springs, dry seeps and elevated "background" soil CO_2 with a campaign of monitoring fluxes and concentrations. This could be done locally above the leaky reservoirs identified in this study, and across the Colorado Plateau above other known CO_2 reservoirs. In addition to increasing our understanding of CO_2 flow in the shallow subsurface and vadose zone environments, a monitoring program in this area would be useful for testing instruments and methods, and for assessing hazards associated with elevated CO_2 concentrations.

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