Natural Leaking CO_2-charged Systems as Analogs for Geologic Sequestration Sites

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Abstract

We examine the geology, hydrology and geochemistry of a naturally charged CO_2 system in southeastern Utah in order to determine how CO_2 gas flows through host rock and water and the fluxes of gas through an analog sequestration system. Natural CO_2 springs lie along two steeply dipping normal faults that cut Mesozoic shales and sandstones. Several springs occur on abandoned drill holes. Geochemical studies of the gas and water indicate that the gas is sourced from at least 1 km depth, and travels nearly vertically along fault zones and abandoned boreholes to the surface. Surface expressions of the leaks include springs, tufa deposits, and large veins that formed near the earth's surface. Modeling of the water chemistry of the Crystal Geyser system indicates that ~ 60% of the CO_2 is released to the atmosphere; only 6 % is trapped in a mineral phase. Geologic and geochemical evidence suggests that the area has been leaking for at least several thousand years.

The results of this study show that CO_2 gas migrates rapidly from depth, and that once established, CO_2 flow paths are able to stay open. It does not appear that mineralization was rapid enough or thermodynamically favorable to allow the system to seal by precipitation of carbonate minerals.

Introduction

The development of pilot projects to test the feasibility of geologic sequestration of CO_2 in the subsurface requires that we understand a geologic and hydrogeochemical system that has received little attention to date. There are few studies of the interaction of CO_2 with rocks and water at likely sequestration depths, little is know about the possible fate of CO_2 in a leaking system, and few studies have examined the nature of CO_2 phase changes at conditions likely to be encountered in a storage system.

We examine a naturally charged CO_2-rich system in southeastern Utah, in which active and ancient leakage of CO_2 has occurred along a series of faults. This system consists of a relatively porous and permeable reservoir rock, 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), a migration pathways through the overburden and possible secondary reservoirs where gas may be trapped, and the vadose zone and Earth's surface. Potential negative consequences of CO_2 leakage and seepage from the sequestration 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 reservoir to the surface, and quantify the rates and volumes of gas released to the atmosphere in the case of a leak, determine the environmental impact of escaped gas on the surface biota, design mitigation strategies for the effects of any leakage, and design monitoring equipment that can detect 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. In addition, naturally leaking CO_2 systems do not require permitting or costly engineering systems to test different components and processes of the system.

This contribution briefly summarizes our multidisciplinary work performed on a leaking CO_2 system, and focuses on the amount, longevity, and nature of leakage. Summaries of our work can be found in Shipton et al., in press a, b. Details of the hydrochemistry are in Heath (2004) and Heath et al., submitted a, b; structural analysis of the faults is in Williams (2004) and a regional structural analysis and detailed study of the isotopes of the carbonate deposits is in Dockrill et al. (in prep a, b).

Geological setting

The Paradox Basin, in the Colorado Plateau region of the United States, contains a large number of natural CO_2 reservoirs, which provide analogs for understanding the integrity of stored gas systems. 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 summarize 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 (Figure 1) create 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.

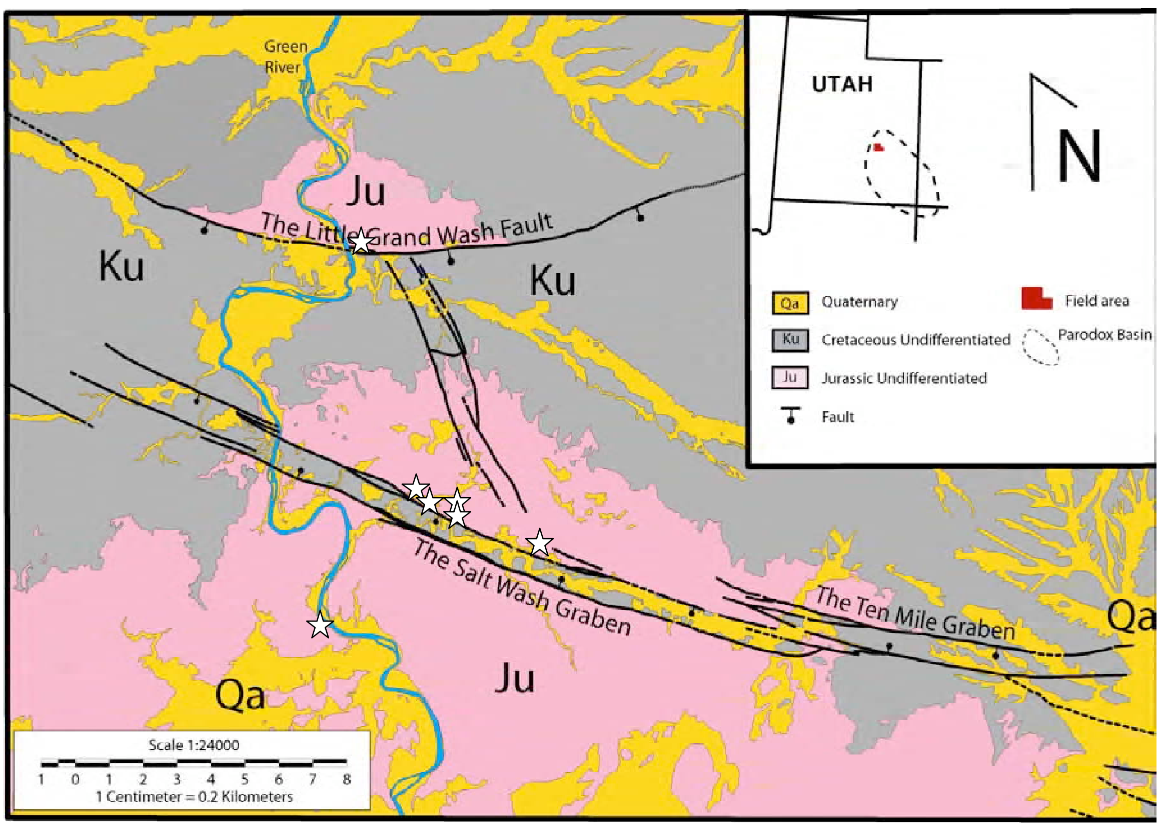

Figure 1. Generalized geologic map of the Little Grand Wash and Salt Wash faults. Ju – Jurassic rocks: Ku – Cretaceous rocks, Qa – Quaternary deposits.

The Little Grand Wash and Salt Wash normal faults lie along the northern Paradox Basin (Figure 1). This basin is defined by the extent of organic-rich Pennsylvanian and Permian limestone, shale and evaporite, 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. Many of the CO_2 reservoirs have accumulated within these salt anticlines, including the leaky reservoir in this study. The faults cut the Mesozoic section of the Colorado Plateau which consists of shale-rich Triassic Moenkopi and Chinle Formation reservoir units of the Lower Jurassic sandstones which are overlain shale-sandstone sequences, capped by a thick Upper Cretaceous Mancos Shale.

The east-west trending Little Grand and Salt Wash faults cut an open, north plunging anticline (Figure 1). The 61 km long, 70º to 80º souths dipping, Little Grand Wash fault is a complex fault zone comprised of several normal faults defining structural terraces with varying dips. Total vertical separation at the center of the fault is 180 to 210 m, most of which is accommodated by the southern fault strand. The Salt Wash faults (sometimes termed the Tenmile

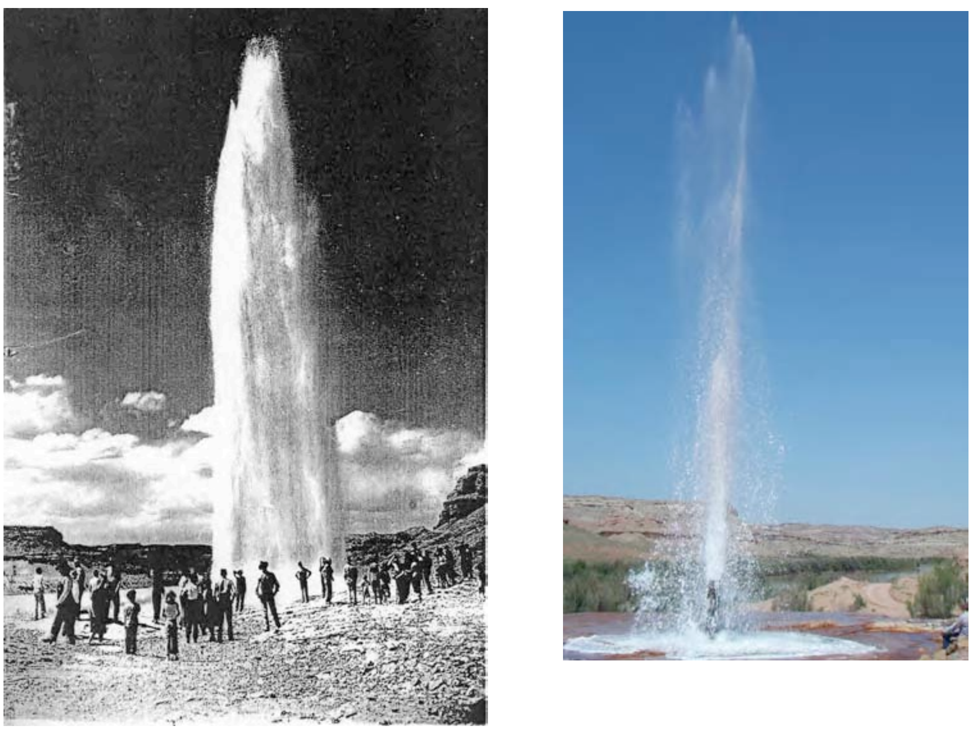

Figure 2. Two views of eruption of the Crystal Geyser. Left figure circa 1950; right photo from 2001. Degassing of the system over time is suggested by the changing height of the geyser.

Graben) are a set of 290° striking dip-slip normal faults that form a graben over 15 km long. Well data from abandoned oil wells and water wells have been used to constrain the subsurface geometry of the north-plunging anticline and faults.

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. 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 2). This cold-water geyser has erupted at 4 to 12 hour 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 travertine mound, 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. 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.

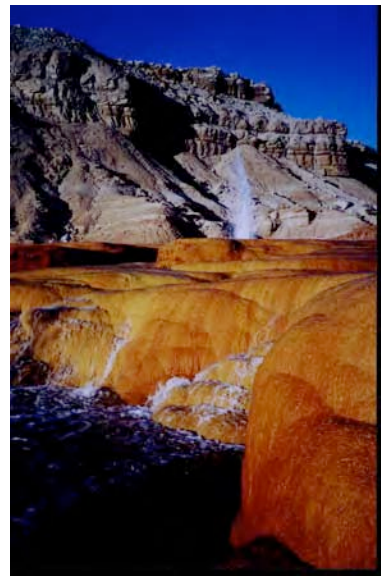

Figure 3. Left figure shows a natural spring along the Salt Wash fault. Right figure of the Crystal Geyser showing the travertine, CO_2-rich waters, and gas erupting.

Five CO_2 springs or small geysers occur along the northern Salt Wash fault (Figure 3). The westernmost Three Sisters springs flow continuously, but there is relatively little carbonate deposition at the site. These springs lie in a 3 to 4 hectare 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 to 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. It is centered on an abandoned well, which may penetrate the fault into the footwall reservoir (no drilling records are available for this well). One geyser with 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 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, 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 and tufa 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. The other natural springs have smaller, less well-developed travertine mounds (Figure 3). The wellbore leakage sites are surrounded by cemented Quaternary material and thin, friable, poorly developed travertine drapes (Figure 3).

Water and gas composition

Water samples collected from seven locations all had in situ temperatures less than 18°C, confirming that CO_2 degassing is the 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 a $\delta^{18}O$ isotopic shift away from the local meteoric water line, implying that they are meteoric. Given local geothermal gradients, the water for the springs along these faults is therefore likely to have come from the Wingate and Navajo Sandstones at around 300 to 500 m depth. The waters are saline and slightly acid, with 13,848 to 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. The carbonate precipitation is a result of degassing that brings 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 suggesting a similar chemical evolution history of all the waters in the study area.

Gas samples collected from seven sites using diffusion samplers and glass bottle samplers included three abandoned drill holes and four natural bubbling springs. The gases emanating from all the springs are 95.66% to 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. No methane or H_2S is found, which argues against a biogenic source of the CO_2. The $\delta^{13}C$ values of the CO_2 gas phase range from -6.42 to -6.76‰ (± 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.

Source of the CO_2

Unusual volumes of CO_2 are generated in the Paradox basin and the likely sources are discussed in Heath et al. (submitted) and Shipton et al. (in press a) on the basis of the isotopic signature of gas and carbonates. Helium R/Ra values of ~0.3 are well out of the range for mantle helium signatures of 7 to 21 and are similar to crustal values [20]. Heath (2004, submitted) suggests that the CO_2 is sourced from clay-carbonate diagenetic reactions at temperatures of about 100 to 200°C during deep burial of impure carbonate sedimentary rocks can generate large amounts of CO_2 gas. By assuming isotopic equilibrium between the source carbonates and the gases, Heath et al. (submitted) shows that the clay-carbonate reactions involving rocks with $\delta^{13}C$ $CaCO_3$ values of +1 to -3‰ (close to the average $\delta^{13}C$ of marine carbonates) could have produced CO_2.

Most of these CO_2 sources come from present depths of 1 to 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 upper portions of the Paradox salt and the Triassic shale. If the CO_2 is sourced from these depths, it likely is at or near the critical point where CO_2 becomes a supercritical fluid. We suggest that the deep well, and the faults, allow buoyant CO_2 to rise, depressurizing to produce a gas phase that migrates away from the source to accumulate in shallow aquifers. Episodic eruptions of the Crystal Geyser and some of the other springs suggests that the hydrostatic pressure prevents CO_2 flow to the surface until the pCO_2 exceeds the hydrostatic pressure; eruptions cease when the gas pressure drops below the hydrostat.

Shallow flow pathways

We have constructed a conceptual model of the regional groundwater flow in the upper 1.5 km of the basin (Figure 4). Potentiometric surface data from groundwater wells show that regional groundwater flows from the northwest to the southeast. Water temperature and stable isotope data for springs along both faults show that the CO_2 is charging a reservoir approximately 300 to 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.

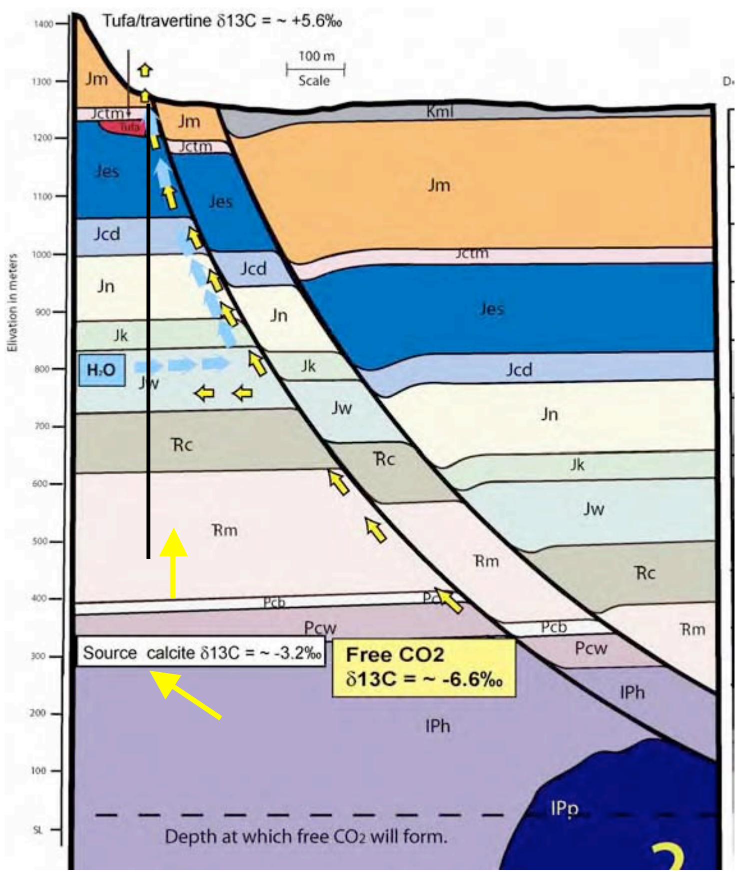

Figure 4. Cross section of the Little Grand Wash fault system with proposed gas and water pathways indicated. Units labeled Jw, Jk and Jn are the principal aquifers of the area, and are charged from below by a free CO_2 gas. This gas likely originates at some depth, and flows along the fault zone and through the borehole to the surface. Carbon isotope values of the different phases are show.

The shale-rich units that provide the topseal are leaking in our study area, but 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 CO2 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 is poorly understood. Without such data, a reliable prediction could not presently be made of the integrity of cap rocks in similar structural settings.

Similar leakage of natural gas from engineered underground natural gas storage facilities (refs) are analogs to the Little Grand Wash – Salt Wash system, and shows that buoyant gases may exploit fractures and faults to create rapid migration pathways. In our study area, naturally occurring fractures and faults, and old drillholes, are the paths, and thus a designed underground CO_2 storage facility must have a careful inventory of old drill holes as well as the thorough study of fractures and faults of the region.

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. The water is very high in TDS, S2-, 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, the discharged water does not have a significant effect on the downstream salinity of the Green River (Mayo et al., 1991). 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 Univ., personal comm..), even though locals and tourists visit the area.

Leakage rates and fluxes

We can place minimum estimates on the ratio of CO_2 vented to the atmosphere by examining the water chemistry and using simple chemical equilibrium relationships. Past measurements of the water fluxes for the Crystal Geyser averages 50 - 100 m^3 of water per eruption. We use the water chemistry analyses (Heath, 2004) as a starting point for the composition of the water, and using a water chemistry-modeling program (PHREEQ), we allow the water to go to equilibrium. The final composition of the water thus allows us to calculate the amount of carbon that remains in the water, the amount that is precipitated, and the amount that vents to the atmosphere. The calculations do not consider kinetics, and thus are likely a minimum estimate for the amount of CO_2 vented, since the reactions do not occur instantaneously.

For the starting chemistry of the water, we use the values of of $8.93x10^{-3}$ mol Ca^{2+}/kg water, a total carbon content of 0.1311 moles, and a partial pressure of CO_2 of $10^{0.16}$ atm. In the resulting reaction, $8.92x10^{-3}$ mole calcite/kg water precipitates, $8.16x10^{-3}$ moles of CO_2 gas exsolves from the solution when it is allowed to equilibrate to with the atmospheric pressure (PCO_2 of $10^{-3.5}$ atm). The solution after equilibrium will have $1x10^{-5}$ moles Ca, and 0.04052 moles total CO_2. From these amounts, we can determine a "mineralization trapping efficiency" in which the amount of carbon precipitated in the calcite is 6.8% of the total C: 62.2% exsolves in the CO2 gas, and 30.9% remains in solution. Some (or perhaps all) of the carbon in solution likely degasses from the solution over time.

Our analysis shows that for this natural leaking system, very little of the escaped carbon is presently trapped at the surface. While the tufa, travertine, and vein deposits appear impressive in the field, they likely represent a small fraction of the total carbon released from the subsurface. 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. 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

Our work on the natural CO_2 system of the Little Grand Wash and Salt Wash faults, southeastern Utah, shows that subsurface CO_2 reservoirs may leak through low-permeability cap rocks or along old boreholes. We show that such migration may occur rapidly, over distances > 1km, and over long periods of time. We show that the CO_2 is likely sourced at or near the depths at which CO_2 is a fluid, exsolves and migrates into overlying aquifers, and discharges at the surface. This discharge results in a large fraction of the CO_2 being vented to the atmosphere and an effusion of saline water at the surface. Other engineered pressurized gas-charged systems have failed catastrophically (Katzung et al., 1996) and these results suggest that there is little time between reservoir pressure drops and escape to the surface. Our results show that a geologic sequestration site must have a thorough inventory of old boreholes; a complete geological and geochemical survey of the area, and a risk analysis for the site.

Acknowledgements

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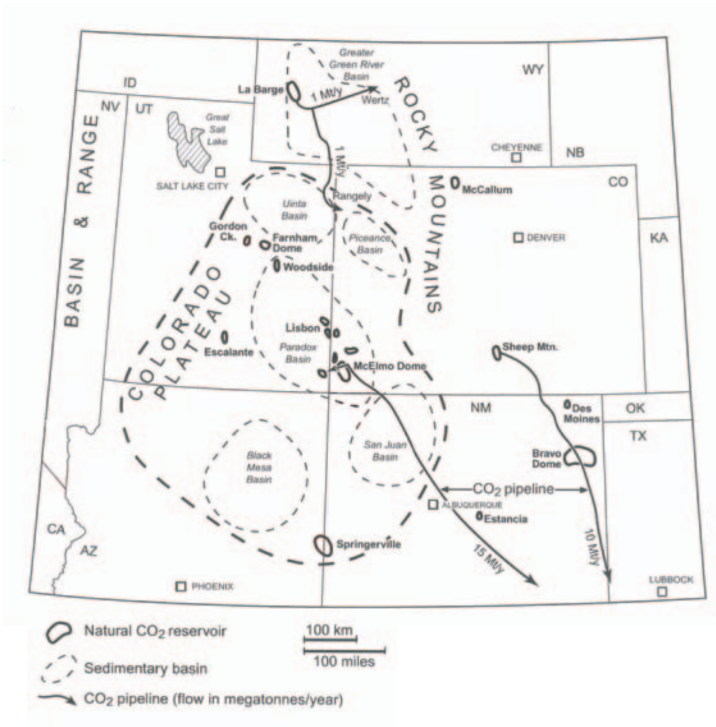

Figure A1. Regional setting of the Little Grand Wash area in the Colorado Plateau. Numerous accumulations of CO2 are stored in reservoirs, anda significant CO2 infrastructure exists across the region.

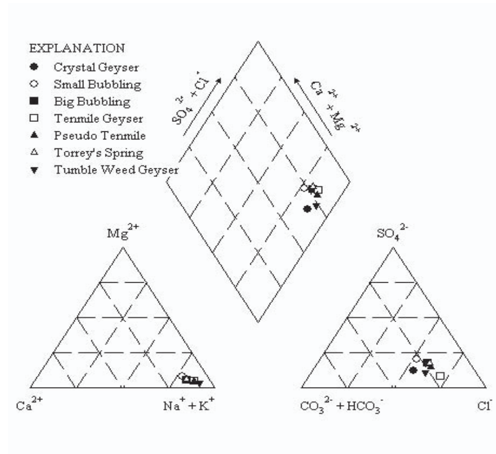

Figure A3. Water chemistry plots show waters are sodium chlorite and bicarbonate waters.

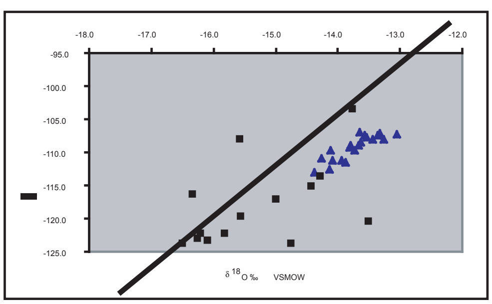

Figure A3. Stable isotopic analyses of water from the springs and geysers are parallel to the global meteoric water line, and indicate a meteoric source.