

Plumbing the Depths: Testing Natural Tracers of Subsurface CO₂ Origin and Migration, Utah

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ABSTRACT

The effective geological storage of fluid CO₂ in porous subsurface rock will require the ability to track, and identify the origin of, any CO₂ seepage measured at the near surface. In a study relevant to postplacement seepage, we examine natural CO₂ springs around Green River on the Colorado Plateau, United States, in an attempt to determine the CO₂ origins. We use a combination of natural geochemical and isotopic tracers to fingerprint the origin of CO₂ and water erupting at the surface. Stable oxygen and hydrogen isotope data enable the estimation that 80–90% of the spring water is derived from shallow groundwater, with the remainder originating from a deep saline aquifer. Carbon dioxide and water volumes imply the ascent of CO₂ as a separate fluid or gas, not just in solution in the pore water. Stable carbon isotopes of CO₂ are unable to discriminate between possible sources. However, the CO₂ contains trace amounts of noble gas isotopes, which can be used to demonstrate that approximately 0–20% of CO₂ erupted at the surface originates from the mantle, with the remainder originating from the crust. Within the study area, diverse noble gas signatures at different springs are observed, implying that no homogeneous free-phase accumulation at shallow depths exists as has been previously proposed. Natural tracers are, in this case, capable of resolving CO₂ origins and migration pathways. From this study, we conclude that the errors and uncertainty in tracing anthropogenically stored CO₂ will be reduced dramatically if a baseline survey is conducted to unambiguously characterize aquifer water chemistry, CO₂, and noble gas content, before the addition of anthropogenic CO₂ to the subsurface.

INTRODUCTION

An important aspect of engineered CO₂ storage is the ability to monitor the storage site and to trace the CO₂ after injection. In several proposed regulatory systems, such as those for Australia and the United Kingdom, the storage site can be defined as both the aquifer into which the CO₂ is injected and also the overburden sediments above the reservoir. The overburden then becomes part of the storage site, and its performance needs to be evaluated. Migration of CO₂ through overburden is poorly understood (Benson and Hepple, 2005), and parameters influencing leakage rates in overburden are poorly quantified (Wildenborg et al., 2005). If seepage or leakage is detected after CO₂ injection, then there will be a need to establish the liability for remediation, and hence a need to establish unambiguous ownership of that CO₂. Resolving disputed ownership is likely to be particularly relevant where several CO₂ owners injected into the same saline aquifer, either simultaneously or intermittently. One possibility is the use of naturally occurring gas tracers or the isotope ratios of trace gases. If natural tracers cannot be used, then artificial gas tracers may have to be added to the CO₂ at the time of injection. This will marginally increase the cost of storage, and hence industries may wish to avoid the expense. Nimz and Hudson (2005) successfully demonstrated the potential for use of the noble gas Xe along with natural CO₂ from McElmo Dome during enhanced oil recovery (EOR) operations in west Texas. In this study, we use naturally occurring noble gas tracers and isotopic ratios to attempt to answer two questions about a natural CO₂ occurrence: (1) what is the origin of the CO₂ and (2) how is it transported in the subsurface? A crucial factor in determining leakage rates through overburden is whether the CO₂ forms a free phase or is entirely in solution in the pore waters. This study is a test of stable isotope and gas tracer technology applied to the practical problem of tracing CO₂ movement, rates, and identifying diverse CO₂ origins in the subsurface.

This case study uses a suite of natural CO₂ springs, where water and gas have migrated through an overburden and been analyzed at the surface. This study can also be used to gain insight into a future situation where CO₂ is detected on the surface near to a storage site, and the origin is contested. Here we demonstrate that where multiple sources may exist and become mixed during ascent, CO₂ itself carries insufficient information to characterize its origin. In contrast, natural noble gas tracers can be used to discriminate CO₂ sourced from within the shallow aquifer, CO₂ sourced from a deeper aquifer (putative storage reservoir), and CO₂ sourced from the mantle. The ranges of uncertainty remain wide and point to the value of gathering and recording baseline information from reservoir and overburden fluid geochemistry before any engineered injection com-

mences. The Green River springs do not form an exact analog for a leaking engineered storage site because we find no evidence for a CO₂-filled reservoir at depth. Stable isotope and noble gas tracers do help to disentangle water and gas origins. The Green River springs do provide a location where natural CO₂ from two sources, derived from depths similar to engineered storage, is migrating up through overburden aquifers, faults, and fractures to form a mixed effusion on the land surface.

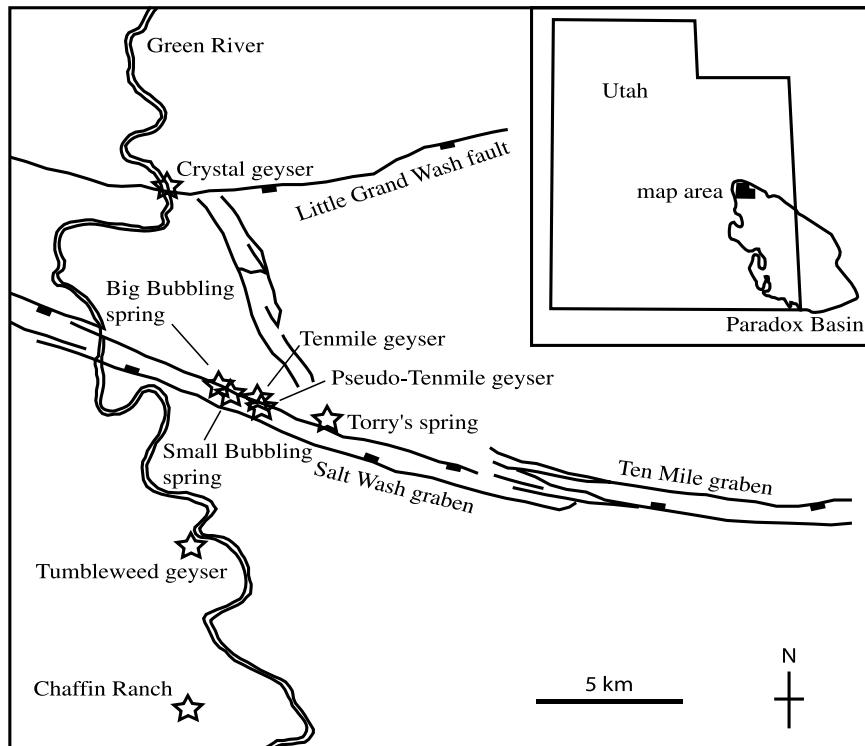
GEOLOGICAL SETTING

Natural trace gases have been studied in a group of CO₂-rich springs located some 10 km (6 mi) south of the town of Green River in Utah, here referred to as the Green River springs. These are CO₂-charged springs associated with the Little Grand Wash and Salt Wash faults lying at the northern end of the Paradox Basin (Figure 1). The faults control the present-day flow of gas and groundwater to the surface (Shipton et al., 2004; Heath et al., 2009). Both faults are part of a series of steeply dipping (70–80°), west-northwest-trending normal faults that are found in the region (Figure 1). The vertical separation on the Little Grand Wash fault near the Green River is 180–210 m (590–689 ft) (Shipton et al., 2004). The timing of movement along the faults is poorly constrained, although Shipton et al. (2004) argued for early Tertiary and Quaternary slip movement.

The Paradox Basin primarily contains sediments of Pennsylvanian and Permian age (Nuccio and Condon, 1996). The basin is commonly defined according to the areal extent of the Pennsylvanian Paradox Formation, which includes abundant evaporites. The Green River springs lie at the northwest of the basin, which is terminated in this direction by the uplifted San Rafael swell. The Paradox Basin is covered by up to 5000 ft (1500 m) of Jurassic and Triassic continental sediments. Paleocene and younger sediments have been removed by erosion (Nuccio and Condon, 1996).

Associated with the Little Grand Wash fault zone are springs of CO₂-rich water and free gas, an active CO₂ charged geyser, and both active and fossil travertine deposits. The most notable of these is the cold-water CO₂-charged Crystal geyser, which erupts to heights of up to 25 m (82 ft) at 4–12-hr intervals. The geyser began erupting in 1935 when the Glen Ruby #1-X well was drilled to a depth of 800 m (2625 ft) in search of oil; prior to this, springs existed but no geyser was present. This and the other CO₂-rich springs associated with the fault zone are described in more detail by Shipton et al. (2004). These springs have been proposed as analogs for large-scale leakage from a fractured reservoir and are currently subject to extensive research. The geological background of these sites is described in more detail by Heath et al. (2009). Carbon dioxide and other gases in

FIGURE 1. Map of the Green River area showing the location of the natural CO₂ seeps and geysers sampled (modified from Williams, 2005). Extent of the Paradox Basin redrawn from data in Hansley (1995).



the springs have been proposed to originate from a combination of sources: mantle degassing, clay-carbonate reactions, thermal metamorphism of carbonates, or atmospheric and soil gas recharge combined with diagenetic reactions, including maturation of organic material (see the review by Wycherley et al., 1999).

Rush et al. (1982) described the hydrogeology of the Green River area. They defined two aquifers (Figure 2). The upper Navajo aquifer, recognized by Naftz et al. (1997), is of Mesozoic age and includes the Wingate, Navajo, and Entrada sandstones. The lower aquifer is in contact with the Paradox salt and is here referred to as the Paleozoic aquifer. Over a much larger regional scale, actually two aquifers of Paleozoic strata are seen, but only the lower of these is present in the Green River area. The well from which the present-day Crystal geyser is sourced penetrates through the Navajo aquifer and into the sub-Navajo aquiclude (Shipton et al., 2005, their figure 7).

Here, we use noble gas tracers to determine the origin and transport mechanisms of CO₂ within the Green River springs as a test of the applicability of the gas tracer method for the monitoring of anthropogenic CO₂ storage. Noble gases are conservative tracers and are therefore unaffected by any chemical processes acting on subsurface fluids. Noble gases are introduced into the crust from both mantle and atmospheric reservoirs. Addition of mantle fluids incorporates mantle-derived noble gases, ³He in particular, resulting in elevated ³He/⁴He ratios. Atmosphere-derived noble gas isotopes such as ²⁰Ne, ³⁶Ar, and ⁸⁴Kr are introduced into the crust dissolved in

the groundwater and are therefore characteristically fractionated according to their relative solubilities in water. Once in the crust, the noble gas signature of a fluid can be altered by radiogenic production, which will increase the proportion of radiogenic noble gas isotopes such as ⁴He, ²¹Ne, and ⁴⁰Ar, and by physical processes such as boiling. With careful measurement, these distinct sources can be distinguished from each other to allow the extent of crustal, mantle, and atmospheric contributions to the crustal fluid to be constrained (Ballentine et al., 2002).

Published noble gas chemistry of the Green River springs is limited. Recent helium isotope analysis on CO₂ from Crystal geyser and Big Bubbling spring measured ³He/⁴He ratios of 0.302 and 0.310 R_a , respectively (Heath, 2004; Heath et al., 2009). Shipton et al. (2004) used these data and $\delta^{13}\text{C}$ measurements to infer that the CO₂ is derived from the thermal breakdown of marine carbonates. They suggest that this is most likely to be the result of contact metamorphism of marine carbonates caused by the Tertiary intrusions in the region of the La Sal and Henry mountains. In contrast, Baer and Rigby (1978) proposed that the CO₂ was generated within the Navajo Sandstone by the dissolution of rock fragments.

Shipton et al. (2004, 2005) and Heath et al. (2009) considered that the CO₂ was present in the subsurface as a free phase and formed accumulations analogous to oil or natural gas fields within sandstones below the Green River springs. Baer and Rigby (1978) seem to have presumed that the CO₂ was in solution in the Navajo aquifer; i.e., that no free-phase CO₂ exists. Previous authors have not considered the issue of CO₂ migration

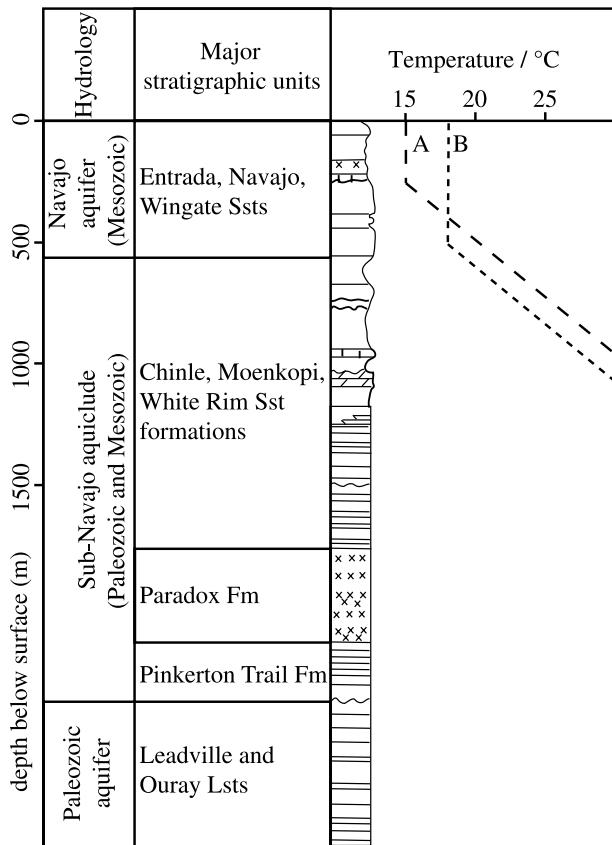


FIGURE 2. Summary stratigraphy of the Green River area; only major formations are shown. Modified from Rush et al. (1982) and Hintze (1993). Note that the Paradox salt is shown in its original stratigraphic position and may now be substantially higher up the stratigraphy because of diapirism, especially in the vicinity of the Little Grand Wash fault. The depth scale is only approximate, especially below 1000-m (3281-ft) depth. The hydrologic units are from Rush et al. (1982). The thermal profiles are extremes based on estimates of surface temperature and geothermal gradient. Sst = Sandstone; Fm = Formation; Lst = Limestone.

in detail, although Shipton et al. (2004, 2005) and Heath et al. (2009) presumably thought that the free-phase CO₂ would migrate in an analogous way to oil or gas. The alternative is transport in solution in the pore waters.

METHODS

Sampling and Analyses

Gas samples from the Green River springs were collected for this study in the summer of 2004; sampling localities are shown on Figure 1. Gases were collected using a copper tube technique similar to the method used at McElmo Dome outlined by Gilfillan et al. (2008). All of the seeps were actively releasing gases within

pools of water at the time of sampling. A plastic funnel connected to a length of high-pressure hosing was positioned over the bubbling gas and submerged into the water. The water provides a seal from the atmosphere, preventing air contamination of the samples. The high-pressure hose was directly connected to two copper tubes, allowing duplicate samples to be collected. Gas was allowed to flow freely into the copper tubes for a minimum of 10 min. The clamps were then shut sequentially working back from the clamp farthest from the seep.

Isotopic ratios (³He/⁴He, ²⁰Ne/²²Ne, ²¹Ne/²²Ne, ⁴⁰Ar/³⁶Ar) and elemental abundances (⁴He, ²⁰Ne, ⁴⁰Ar, ⁸⁴Kr) were determined on the University of Manchester's MAP-215 mass spectrometer, using the techniques outlined by Gilfillan (2006) and Gilfillan et al. (2008). All gas concentrations are corrected to standard temperature and pressure (STP). The δ¹³C analysis for dissolved gas was undertaken at University of Toronto using procedures detailed by Sherwood Lollar et al. (1997) and Ballantine and Sherwood Lollar (2002). Results are expressed relative to the international Vienna PeeDee belemnite (V-PDB) standard. Helium isotope ratios (³He/⁴He) are expressed relative to the ratio in air ($R_a = R_{\text{measured}}/R_{\text{air}}$ where $R_{\text{air}} = 1.399 \times 10^{-6}$). All other ratios are absolute values. Pore-water analyses for the Paradox Basin were taken from the literature.

RESULTS: COMPOSITION OF ERUPTED GAS AND WATER

Noble gas contents of the Green River gases are given in Table 1. The CO₂, which is the predominant component (e.g., Heath et al., 2009), exhibits a small range in δ¹³C from -6.47 to -8.50‰ (Table 1). Isotopic ratios of the noble gases are in Table 2. A marked variation within the composition of the trace noble gases is observed.

DISCUSSION

Carbon Dioxide Solubility in the Subsurface

To assess the mechanism of CO₂ migration (solution versus free-phase), the solubility of CO₂ must be known for the appropriate physical and chemical conditions relevant to the Green River area. Specifically, CO₂ solubility will vary with burial depth as temperature, pressure, and salinity vary. Hence, a model for this solubility change is constructed. The solubility of CO₂ in water has been determined experimentally in numerous studies, with good agreement between the different sources. In the temperature and pressure range of

TABLE 1. Location, carbon stable isotope ratio, and noble gas isotope concentrations for the Green River springs.

| Spring | Location (Lat/Long) | $\delta^{13}\text{C}$ (CO ₂) (‰ V-PDB) | ^4He ($\times 10^{-4}$) (cm ³ STP/cm ³) | ^{20}Ne ($\times 10^{-8}$) (cm ³ STP/cm ³) | ^{40}Ar ($\times 10^{-5}$) (cm ³ STP/cm ³) | ^{84}Kr ($\times 10^{-9}$) (cm ³ STP/cm ³) |
|----------------------|---------------------|--|---|--|--|--|
| Tumbleweed | 38.7617, -110.1331 | -6.47 (10) | 0.467 (5) | 5.36 (6) | 4.10 (3) | 0.474 (3) |
| Torrey's | 38.8594, -110.0728 | -5.90 (20) | 1.08 (2) | 0.889 (17) | 4.17 (4) | 2.71 (18) |
| Crystal geyser: main | 38.9390, -110.1355 | -7.00 (10) | 0.0761 (10) | 1.24 (2) | 5.92 (5) | 2.32 (14) |
| Crystal geyser: side | 39.9390, -110.1351 | -6.68 (10) | 0.158 (1) | 0.277 (4) | 5.89 (5) | 0.671 (4) |
| Chaffin Ranch | 38.7641, -110.1274 | -8.20 (30) | 1.04 (2) | 0.277 (10) | 2.44 (2) | 1.99 (12) |
| Small Bubbling | 38.8733, -110.1166 | nd | 0.114 (2) | 0.969 (35) | 2.47 (2) | 0.840 (5) |
| Big Bubbling | 38.8717, -110.1115 | -8.50 (30) | 0.0657 (9) | 0.104 (2) | 1.07 (1) | 0.308 (2) |
| Pseudo-Tenmile | 38.8664, -110.1004 | nd | 0.0582 (8) | 0.203 (4) | 1.08 (1) | 0.591 (4) |
| Tenmile | 38.8634, -110.1012 | -8.00 (10) | 5.37 (5) | 8.55 (8) | 4.26 (4) | 1.71 (10) |

V-PDB = Vienna PeeDee belemnite; STP = standard temperature and pressure.

interest, CO₂ solubility decreases with increasing temperature and salinity but increases with increasing pressure. To calculate the solubility of CO₂ at the Crystal geyser site, construction of a geothermal model is necessary. Clearly, a significant vertical movement of water within the top part of the rock column is observed, bringing heat as well as CO₂ to the surface. The temperature of the geyser water at the surface has been measured as 15.5–17.8°C (Baer and Rigby, 1978), although this would be reduced during ascent by the exsolution of CO₂ from the water and the expansion of the CO₂ bubbles (Pruess, 2005). If we assume that the local average surface temperature is 7–10°C (Ramsey, 2002) and the geothermal gradient is 21.2°C/km (Heath et al., 2009), then the minimum depth from which the waters might be sourced is 260–500 m (853–1640 ft) (Heath et al., 2009). This interval includes the Navajo aquifer, which has been generally assumed to be the source of the geyser waters (Baer and Rigby, 1978; Waltham, 2001). In our model of CO₂ salinity, we hence assume a constant pore-water temperature (15 or 18°C) from the surface to where

this intersects the geothermal gradient (Figure 2). We use the regional geothermal gradient below this depth. Pressure is assumed to be hydrostatic.

The solubility of CO₂ at the surface is estimated from a compilation of CO₂ solubility measured at 1 atm pressure (Stephens and Stephens, 1963). By fitting a curve through the data, the solubility of CO₂ at 18°C is estimated to be 0.073 mol%. The solubility of CO₂ at 15 and 18°C and variable pressure was estimated using measurements of solubility at 18 to 20°C (Stephens and Stephens, 1963). A plot of solubility versus log pressure is approximately a straight line, and the equation of the best-fit line is used to estimate solubility. For depths below 500 m (1640 ft), CO₂ solubility is taken from Kohl and Nielson (1997) in Metz et al. (2005).

Because of the interplay of increasing temperature and pressure deeper into the subsurface, the solubility of CO₂ in pure water has a minimum at the surface and a maximum between 650- and 800-m (2132- and 2625-ft) depth depending on the thermal profile (Figure 3). Below this depth, solubility decreases slowly. The solubility

TABLE 2. Noble gas isotope ratios for the Green River springs.

| Spring | $^3\text{He}/^4\text{He}/R_a$ | $^{20}\text{Ne}/^{22}\text{Ne}$ | $^{21}\text{Ne}/^{22}\text{Ne}$ | $^{40}\text{Ar}/^{36}\text{Ar}$ | $^{38}\text{Ar}/^{36}\text{Ar}$ | CO ₂ / ^3He ($\times 10^{11}$) |
|----------------------|-------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|--|
| Tumbleweed | 0.224 (4) | 9.72 (6) | 0.0293 (2) | 402 (2) | 0.1894 (9) | 0.661(15) |
| Torrey's | 0.227 (4) | 9.59 (11) | 0.0321 (4) | 893 (5) | 0.1891 (9) | 0.291(7) |
| Crystal geyser: main | 0.266 (6) | 9.93 (6) | 0.0282 (2) | 387 (2) | 0.1959 (10) | 3.50 (8) |
| Crystal geyser: side | 0.265 (4) | 9.47 (16) | 0.0293 (5) | 680 (4) | 0.1875 (9) | 1.67 (4) |
| Chaffin Ranch | 0.232 (4) | 9.43 (10) | 0.0314 (5) | 872 (5) | 0.1874 (9) | 0.296 (7) |
| Small Bubbling | 0.256 (5) | 9.71 (6) | 0.0278 (2) | 322 (2) | 0.1887 (9) | 2.35 (6) |
| Big Bubbling | 0.242 (5) | 9.52 (9) | 0.0300 (4) | 761 (4) | 0.1884 (9) | 4.47 (11) |
| Pseudo-Tenmile | 0.386 (5) | 9.78 (9) | 0.0293 (3) | 546 (3) | 0.1865 (9) | 3.15 (8) |
| Tenmile | 0.228 (4) | 9.45 (5) | 0.0300 (2) | 524 (3) | 0.1923 (10) | 0.0585 (13) |

of CO₂ decreases with increasing salinity. Salinity is assumed to be constant within the major aquifers, 11,000–14,000 ppm for Crystal geyser and the Navajo aquifer (Baer and Rigby, 1978; Waltham, 2001), and 100,000 ppm for brines associated with the Paradox salt (Hanshaw and Hill, 1969). The Navajo aquifer water will have CO₂ solubility depressed by less than 5% compared to fresh water (Enick and Klara, 1990, cited in Metz et al., 2005). By contrast, the Paradox brines will have a CO₂ solubility of only about 60% compared to fresh water. Figure 3 shows the effects of salinity on CO₂ solubility below Crystal geyser, assuming that the Paradox brines penetrate as far as the top of the sub-Navajo aquiclude (Figure 2).

Pore-water Movement Below the Green River Springs

In this section, we first try to identify sources of the spring waters at the Green River site. Noble gas and carbon isotopic ratios are then used in an attempt to distinguish the sources of CO₂ erupting from the Green River springs. The sources and volumes of the pore waters must be known if the mechanism of transport of the CO₂ in the subsurface is to be assessed.

Using oxygen and hydrogen stable isotope chemistry to constrain the origin of the water erupted by the Green River springs is possible. Oxygen has three common isotopes, of which the vast majority is ¹⁶O. The ratio of ¹⁸O to ¹⁶O is measured and reported relative to the standard mean ocean water (SMOW) in parts per thousand ($\delta^{18}\text{O}$ as ‰ V-SMOW). Present-day ocean water has a value of around –1‰ V-SMOW, whereas basinal brines have small positive values. Hydrogen has two stable isotopes, hydrogen and deuterium, the ratio of which is also reported relative to V-SMOW (δD in ‰). A combination of these two measurements is a powerful tool used in studies of pore waters within sedimentary rocks (Faure, 1986).

Figure 4 shows stable oxygen and hydrogen isotopic analyses of pore water from the Paradox Basin from the Green River area and the Greater Aneth oil field, southeast Utah. The oil field lies some 150 km (93 mi) to the southeast of Green River and is the closest known source of subsurface isotopic water analyses. Although ideally, we would have isotopic analyses of the subsurface waters in the Green River area prior to the introduction of the CO₂, these do not exist. Here, we will assume that the analyses from the Greater Aneth area can be applied to the Green River area. The composition of the Paleozoic strata is similar, and the bulk pore-water chemistry is thought to be controlled by the dissolution of evaporites within the Paradox Formation, which are certainly present in both locations. Hence, although regional data must be used, which introduces some uncertainty in the

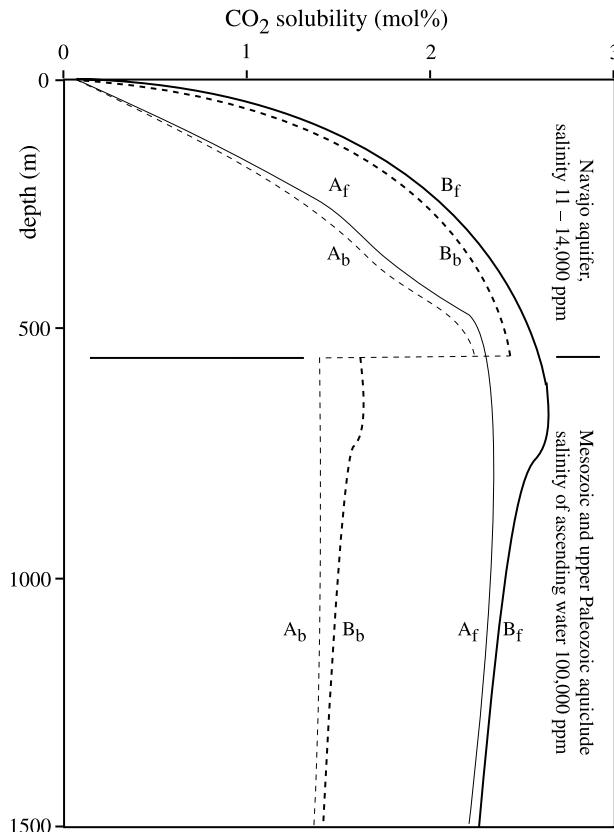
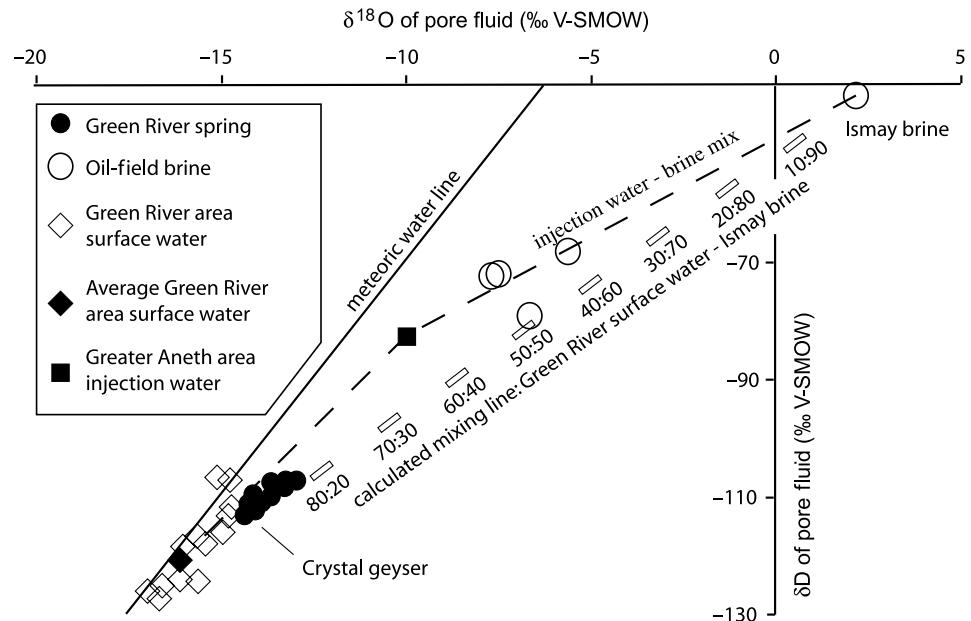


FIGURE 3. Solubility of CO₂ in fresh water (curves A_f and B_f) and brine (curves A_b and B_b) for thermal profiles A and B on Figure 2. The salinity of the water ascending through the Mesozoic and upper Paleozoic aquiclude is assumed to be the same as the underlying lower Paleozoic aquifer (salinity from Rush et al., 1982). The Navajo aquifer is assumed to have the same salinity as the water erupted from Crystal geyser (salinity from Baer and Rigby, 1978).

proportions in which the different sources contribute, the use of these data does not introduce uncertainty in the sources of the spring water itself.

Heath et al. (2009) interpreted the Green River springs' isotopic data as derived from a local meteoric water line; i.e., the sampled waters are pure meteoric water, with no basinal brine component. A more detailed examination of the data enables us to reinterpret the analyses as lying upon a mixing line between the Ismay brine (Spangler, 1992) and the Green River area surface water (Mayo et al., 2003). The Ismay brine, the isotopically heaviest water sample from the Greater Aneth area, was sampled from the Desert Creek member, Paradox Formation, of Pennsylvanian (Upper Carboniferous) age. The Ismay brine is thought to be the only deep-water sample that is uncontaminated with surface water reinjected into the subsurface for pressure support during hydrocarbon production (Naftz and Spangler, 1994). The remaining brine samples are

FIGURE 4. Stable O and H isotope ratio crossplot for pore waters within the Paradox Basin. The Green River springs lie on a mixing line between surface water and the Ismay deep saline brine. The Green River springs data are tabulated by Heath (2004) and presented by Heath et al. (2009). The surface waters for the Green River area are from Mayo et al. (2003), the deep brine analyses are from Spangler (1992), and the Greater Aneth area injection water is from Naftz and Spangler (1994). The global meteoric water line is from Clark and Fritz (1997). SMOW = standard mean ocean water.



approximately 50:50 mixtures of injected surface water and original subsurface brine. The Green River springs lie close to the mixing line. A simple proportion indicates that the Green River springs comprise between 10 and 20% of Paradox brine, the remainder of the water being surface water carried to depth within the Navajo aquifer. However, although the slope of the mixing line seems relatively well determined, the actual composition of the Green River brine could lie almost anywhere on this line. In the absence of a local analysis, we will assume that the Ismay brine is representative of the brine within the Paleozoic aquifer below the Green River springs. This introduces uncertainty into the proportions of brine and aquifer water within the Green River springs, which is difficult to quantify.

The estimate of the 10–20% deep aquifer brine within the Green River springs is compatible with the known hydrology of the area. The Navajo aquifer is fed with meteoric water from the San Rafael swell, some 40–50 km to the northwest (Heath et al., 2009) and is of low salinity (200–5000 ppm average total dissolved solids [TDS]; Rush et al., 1982, p. 45). Crystal geyser itself lies at the meteoric-rich end of the Green River springs data, so the effusive water is only 10% Paradox brine. Note that the Crystal geyser water has a salinity of only 11,000–14,000 ppm (Baer and Rigby, 1978), which compares to a range of 11,000 to 21,000 ppm recorded for the Green River springs as a whole (Heath et al., 2009). This is as expected if the Crystal geyser water is 10% Paradox brine, which has an average salinity of about 100,000 ppm in the Green River area (Rush et al., 1982, p. 45). The most probable scenario is hence that the Green River springs are derived by mixing 80–90% shallow meteoric water with 10–20% deep saline water.

What Drives the Water Flow from the Springs?

Previous authors have assumed that the eruption of Crystal geyser is powered by the pressure of trapped CO₂ gas because the water is too cool for a thermal drive (e.g., Waltham, 2001; Shipton et al., 2004, 2005). This is reasonable because the solubility of CO₂ decreases substantially as the pore waters ascend from about 500-m (1640-ft) depth to the surface (Figure 3). However, the other springs may be driven simply by the artesian hydrologic head of the elevated aquifer recharge zones. Rush et al. (1982) stated that differences in hydrologic head will drive water from the Paleozoic aquifer into the Navajo aquifer and will also drive water from the Navajo aquifer to the surface.

Carbon Dioxide Origin: Models

For CO₂ storage, in some countries, demonstrating that CO₂ from different owners can be detected and discriminated if a leak occurs will be necessary. A pilot study by Nimz and Hudson (2005) shows that natural noble gases can be successful in fingerprinting the origin of CO₂. In the Mabee field of Texas, the CO₂ used for EOR was shown, surprisingly, not to originate from Bravo Dome (as the field operators had thought) but from McElmo Dome, another natural accumulation on the Colorado Plateau. In the case of leakage from an engineered storage site, the ability to identify the source of the CO₂ could be crucial in assigning liability. The present study addresses the general question: is it possible to determine the origin of CO₂ by analysis of noble gases in surface emissions using the Green River site as a test case?

The gases emitted by the Green River springs are predominantly CO₂ but include nitrogen and trace noble gases (Heath et al., 2009) (Table 1). Heath et al. (2009) also detected between 0.06 and 0.89 mol% oxygen but suspected that this was the result of atmospheric entrainment during eruption. Hydrogen sulfide has not been detected by chemical analysis, but H₂S can be smelled by observers in the vicinity of Crystal geyser during an eruption, indicating a concentration in excess of 0.5 ppb. The trace gases within the Green River springs' gases, and their isotopic compositions, can be used to determine the origins of the gases.

Previous workers have concentrated on identifying a single source for the CO₂ from four candidate origins: (1) igneous activity carrying CO₂ ultimately derived from the mantle; (2) diagenetic clay-carbonate reactions within the crust; (3) hydrocarbon maturation and other reactions involving buried organic matter; and (4) thermal decarbonation of carbonate rocks during metamorphism (e.g., Shipton et al., 2004, 2005; Heath et al., 2009). When considering origins of the noble gases, the function of atmospheric and soil gases may also be important. These gases are dissolved in meteoric water at the earth's surface and are carried into aquifers and hence into the crust in solution. Additionally, acidic groundwater can dissolve limestone or carbonates within sandstones, hence absorbing fossil CO₂.

Summarizing previous work on the origin and transport of CO₂ in the Green River springs into two end-member models is possible. Shipton et al. (2004, 2005) and Heath et al. (2009) presumed that the Green River springs are fed from a deep subsurface source of CO₂ that is analogous to the large, commercially exploited accumulations located around the Colorado Plateau, e.g., St. John's Dome. In contrast, Baer and Rigby (1978) considered that the CO₂ was derived by reactions within the Navajo aquifer, i.e., at relatively shallow depths of burial. In this latter scenario, no accumulation of free-phase CO₂ below the Green River springs is observed. All the CO₂ is present in solution in the aquifer pore water, and exsolution only occurs as the water is brought to the ground surface. Below, we attempt to determine which of the models best explain the distribution of measured tracers in the spring waters.

Carbon Dioxide Origin: Gas Tracers Using C and O Isotopes

Stable isotope ratios of carbon are potential indicators of the source of the CO₂. Carbon has two naturally occurring stable isotopes, ¹²C and ¹³C, of which ¹²C is the most abundant. The ratio of these can be measured and expressed relative to a standard in parts per thousand ($\delta^{13}\text{C}$ in ‰ V-PDB). The isotopic composition of carbon generated by geological processes is known, for

example, processes such as the maturation of kerogen during oil generation (Faure, 1986). Carbon dioxide from the Green River springs collected for this study has a narrow range of $\delta^{13}\text{C}$ from -6.5 to -8.5‰ V-PDB (Table 1), whereas those of Heath et al. (2009) have an even tighter distribution from -6.4 to -6.8‰ V-PDB. This small discrepancy between the two data sets may be caused by the differing collection methods used for sampling the gases.

The Colorado Plateau is surrounded by large natural subsurface CO₂ accumulations, which are analogs of oil or natural-gas fields. A recent noble gas study has shown that most of these are derived from the mantle via igneous processes (Gilliland et al., 2008). Hence, the Green River CO₂ could be of mantle origin, sourced from a large accumulation at depth. The $\delta^{13}\text{C}$ of CO₂ emitted from the Green River springs is within the compositional range of mantle-derived carbon (-3 to -8‰ PDB, Wycherley et al., 1999) but is also mostly within the range of bulk crustal carbon (-5 to -7‰ V-PDB). Carbon isotopes therefore do not provide simple evidence of either a mantle or crustal origin for the CO₂.

In the absence of organic reactions, the isotopic composition of dissolved CO₂ will be controlled by the composition of carbonates within the host rock. Marine limestones within the Paradox Formation have $\delta^{13}\text{C}$ close to 0‰ V-PDB (Garden et al., 2001), whereas authigenic carbonates from the Navajo Sandstone have $\delta^{13}\text{C}$ of about 0 to -6‰ V-PDB (Beitler et al., 2005). Using the fractionation factor of Emrich et al. (1970), in Faure (1986), this corresponds to a dissolved bicarbonate $\delta^{13}\text{C}$ of -2 to -8‰ V-PDB in the Navajo aquifer and $\delta^{13}\text{C}$ of about -3‰ V-PDB in the Paleozoic aquifer. The uncertainty in the carbon isotope ratio for the Paleozoic aquifer is probably similar to that of the Navajo aquifer, suggesting that $-3 \pm 3\text{‰}$ V-PDB is a realistic estimate. When CO₂-rich pore waters ascend, they are subject to a high degree of degassing during uplift to the surface because of the dramatic decrease in CO₂ solubility (Figure 3). Then the exsolved gas will be of similar isotopic composition to the dissolved bicarbonate, although probably slightly more negative because of fractionation effects. Hence, the dissolved bicarbonate within either the Navajo aquifer or the Paleozoic aquifer is a potential source of the Green River springs' gases, and these two sources cannot be distinguished using carbon isotope ratios.

Using Helium Isotopes to Track CO₂ Origins

Potentially useful tracers of the origin of CO₂ are ³He and ⁴He. The concentration of ³He is expressed relative to the concentration of CO₂ and is assumed to be conserved during any migration of the gases. The ³He is primordial in origin, as opposed to ⁴He, which is produced by the radioactive decay of elements such as U, Th,

and K. Because the latter elements are mostly concentrated in the crust and are rare in the mantle, ³He is typically associated with the mantle and ⁴He with the crust. Helium is present within the atmosphere at only low concentrations (5×10^{-6} volume/volume at STP; Ballentine et al., 2002). Aquifer water will hence have high CO₂/³He ratios compared to mid-ocean-ridge basalts (MORB) (taken to be representative of the mantle) because of soil processes and the dissolution of high CO₂ minerals such as calcite that will only contribute CO₂ and not ³He.

Figure 5 shows CO₂/³He ratios plotted against the CO₂ concentration for all of the Green River springs, along with the CO₂/³He range of MORB and data from deep natural CO₂ accumulations around the Colorado Plateau (Gilfillan et al., 2008). All of the samples except that of Tenmile geyser have CO₂/³He ratios above the MORB range. This indicates that the CO₂ from most of the springs is dominated by a component derived from the crust (see O'Nions and Oxburgh, 1988, for crustal CO₂/³He values). The lower CO₂/³He ratios of Tenmile geyser, Chaffin Ranch, and Torrey's spring (Figure 1) suggest a significant but variable mantle component.

Green River Springs: He and CO₂ Origins

The proportion of CO₂ derived from the crust and mantle can be calculated using the measured ³He/⁴He ratios of the springs (Table 2). These show a small variation from 0.224 to 0.265 R_a, with the exception of Pseudo-Tenmile geyser, which has a higher value of 0.386 R_a, possibly because of air contamination (air has an R_a value of 1 by definition). This spring has a very slow gas discharge rate, possibly allowing atmospheric air to become dissolved in the spring water and form a component of the sampled gas. The only previous published ³He/⁴He ratios from the Green River springs (Heath et al., 2009) both exceed 0.3 R_a, which we again interpret as the result of contamination by air. Heath et al. (2009) did report oxygen within their gas samples (0.06–0.89 mol%). Free oxygen does not normally occur in subsurface waters and is hence consistent with air contamination. Note that Heath et al. (2009) sampled two of the three springs with the lowest absolute abundance of He (according to our data), which would magnify any contamination problems. The remaining low He-abundance spring is Pseudo-Tenmile geyser, where our own sample is also thought to be contaminated with air, as outlined above.

To calculate crustal and mantle inputs to the CO₂, the input from air must be first quantified. This is calculated using the measured ⁴⁰Ar/³⁶Ar ratio of the springs' gases (derived from equation 35 of Ballentine et al., 2002):

$$[{}^{40}\text{Ar}]_{\text{air}} = [{}^{40}\text{Ar}]_{\text{meas}} \times ({}^{40}\text{Ar}/{}^{36}\text{Ar})_{\text{air}} / ({}^{40}\text{Ar}/{}^{36}\text{Ar})_{\text{meas}} \quad (1)$$

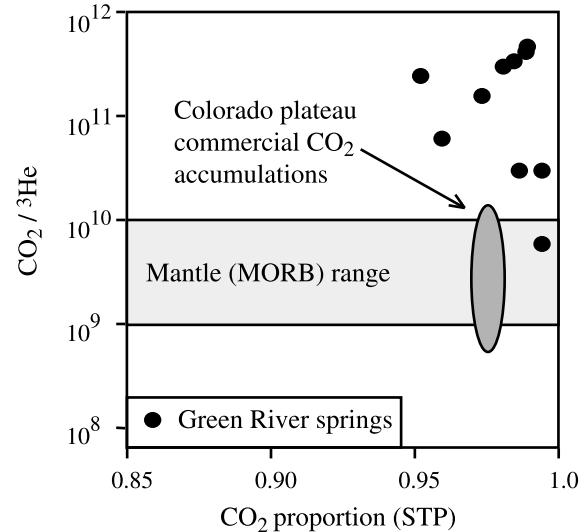


FIGURE 5. The CO₂/³He ratios plotted versus CO₂ abundance. All but one of the Green River seeps have CO₂/³He ratios above the MORB range, indicating that the CO₂ is predominantly derived from a crustal source. Measurement errors are smaller than printed symbols. The shaded region highlights the range of CO₂/³He values measured in pure magmatic samples (mid-ocean-ridge basalts [MORB]; Ballentine et al., 2002). Also plotted (as a vertical ellipse) is the data from the deep CO₂ reservoirs of McCallum Dome, Sheep Mountain, Bravo Dome, McElmo Dome, Doe Canyon, and St. John's Dome (Gilfillan et al., 2008). STP = standard temperature and pressure.

The proportion of air-derived Ar is high (33–91%) because of the high total Ar content of air compared to the crust and mantle. Figure 6 shows how the air component controls the ⁴⁰Ar/³⁶Ar and ⁴He/²⁰Ne isotope ratios caused by the high air concentrations in the air of Ar and Ne. From the air-derived ⁴⁰Ar, the air contribution to the total erupted CO₂ can be calculated because the ratio CO₂/⁴⁰Ar for air is known. The air contribution is small (0.1–1.4 vol.% CO₂; Table 3). It is significant that the anomalous Crystal geyser has the highest air contribution, perhaps because of air entrainment during the spectacular eruptions. Correcting measured ³He/⁴He ratios for the air component is now possible (to leave just the crust and mantle ratios), but the correction is very small and certainly less than the precision of the data. This is confirmed by the measured ⁴He/²⁰Ne ratios, where air-dominated He would have a value close to air (0.288; Ballentine et al., 2002), whereas measured values are much higher (313 to 13,002).

All ³He/⁴He ratios measured for the Green River gases are significantly higher than a ³He/⁴He_{crust} ratio (defines the value for the equations) of 0.02 R_a but lower than the subcontinental ³He/⁴He_{mantle} ratio of 6 R_a (Fitton et al., 1991). Using these end-member values,

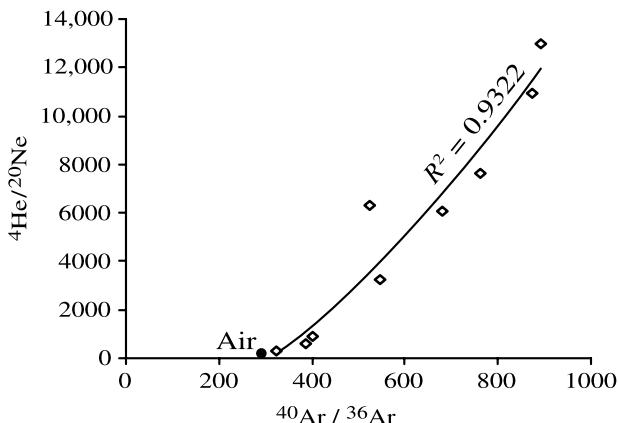


FIGURE 6. Air-influenced isotopic ratios of Green River springs' gases. The influence of air (shown as a circle) is high for isotope ratios where one isotope is derived from air (${}^{36}\text{Ar}$, ${}^{20}\text{Ne}$). Air is dissolved in meteoric recharge and is introduced into the subsurface by descending aquifer flow.

the origin of the He isotopes can be calculated (from equation 38 of Ballentine et al., 2002). The ${}^x\text{He}_{\text{origin}}$ denotes a proportion within a unitary volume of gas.

$${}^4\text{He}_{\text{crust}} = \frac{{}^4\text{He}_{\text{measured}} \times ({}^3\text{He}/{}^4\text{He}_{\text{mantle}} - {}^3\text{He}/{}^4\text{He}_{\text{measured}})}{({}^3\text{He}/{}^4\text{He}_{\text{mantle}} - {}^3\text{He}/{}^4\text{He}_{\text{crust}})} \quad (2)$$

The crustal contribution to ${}^4\text{He}$ ranges from 94 to 97%, the remainder from the mantle. The crustal contribution to ${}^3\text{He}$ can also be calculated:

$${}^3\text{He}_{\text{crust}} = {}^4\text{He}_{\text{crust}} \times {}^3\text{He}/{}^4\text{He}_{\text{crust}} \quad (3)$$

where ${}^4\text{He}_{\text{crust}}$ can be derived from equation 2.

In all the Green River springs, only 5–8% of the total ${}^3\text{He}$ comes from the crust; the remainder are from the mantle. These figures can be used to calculate the proportion of the CO_2 from the mantle and crust, knowing the atmosphere contribution as above. An unknown is the crustal $\text{CO}_2/{}^3\text{He}$ ratio, which is variable (e.g., O'Nions and Oxburgh, 1988). A simple mass balance approach allows the crustal $\text{CO}_2/{}^3\text{He}$ ratio to be calculated for the springs' gases, from which both the crust and mantle contributions follow. We assume that gases other than CO_2 have negligible overall volume.

$$\begin{aligned} {}^3\text{He}_{\text{mantle}} \times \text{CO}_2/{}^3\text{He}_{\text{mantle}} + {}^3\text{He}_{\text{crust}} \times \text{CO}_2/{}^3\text{He}_{\text{crust}} \\ + \text{CO}_2 \text{ air} = 1 \end{aligned} \quad (4)$$

For the $\text{CO}_2/{}^3\text{He}$ ratio of gases derived from the mantle, the conventional range is 1×10^9 to 1×10^{10}

(Ballentine et al., 2002). Because Tenmile geyser has a ratio within this range, we can presume that the mantle gas must have a ratio below this. Hence, we have used a range of 1×10^9 to 6×10^9 for the mantle gas $\text{CO}_2/{}^3\text{He}$ ratio. The results of the calculation are shown in Table 3. The crustal contribution of CO_2 is generally between 80 and 99% of the total CO_2 , with the exception of Tenmile geyser, which has a higher contribution from the mantle (16–99%). From these results, stating whether the crustal component is derived from deep crustal reactions or from aquifer water that has interacted with crustal minerals is not possible. The calculated $\text{CO}_2/{}^3\text{He}$ ratios for the crust are from 6×10^{10} to 6×10^{12} , which are within the range considered by O'Nions and Oxburgh (1988) to be typical of the crust.

Neon Isotopes as Tracers of CO_2

A potentially useful natural tracer of CO_2 gas origin is Ne. Following Ballentine (1997), Ne can be resolved into contributions from mantle, air, and crust. These end members have distinct isotopic compositions and are now well defined (Ballentine et al., 2001, 2002). In all of the Green River springs, the only significant source of Ne is the atmosphere; contributions from both crust and mantle are irresolvably small (Figure 7). Several of the Ne isotopic ratios measured at the Green River springs are outside the range of the air-crust-mantle system. We attribute this to mass fractionation, observed previously by both Kennedy et al. (1990) and Zhou et al. (2005). This fractionation can be explained by a noble gas concentration gradient in the groundwater during degassing as it approaches the surface, which causes diffusive partial re-equilibration of the noble gas isotopes.

TABLE 3. Calculated origin of CO_2 .

| Spring | CO_2 Origin (%) | | | Crust $\text{CO}_2/{}^3\text{He}$ |
|--------------------------------|--------------------------|--------|------------|---|
| | Crust | Mantle | Atmosphere | |
| Crust Mantle Atmosphere | | | | |
| Tumbleweed | 92 | 6.7 | 1.2 | 7.3E+11 |
| Torrey's | 84 | 16 | 0.5 | 2.9E+11 |
| Crystal geyser: main | 97 | 1.3 | 1.4 | 4.8E+12 |
| Crystal geyser: side | 97 | 2.7 | 0.7 | 2.3E+12 |
| Chaffin Ranch | 84 | 15 | 0.2 | 3.0E+11 |
| Small Bubbling | 98 | 1.9 | 0.6 | 3.2E+12 |
| Big Bubbling | 99 | 1.0 | 0.1 | 5.6E+12 |
| Pseudo-Tenmile geyser | 98 | 1.5 | 0.1 | 6.4E+12 |
| Tenmile geyser | 21 | 78 | 0.7 | 1.4E+10 |

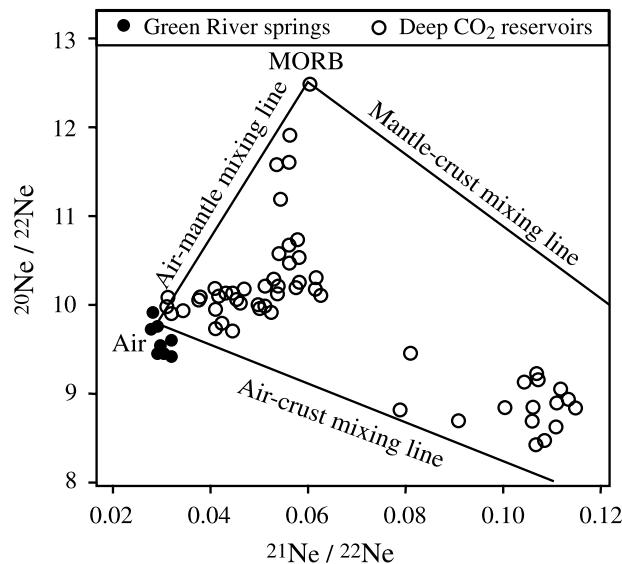


FIGURE 7. Neon isotope ratio crossplot comparing Green River springs' gases to deep CO₂ accumulations of the Colorado Plateau (Gilfillan, 2006). The deep CO₂ has Ne derived from all of air, crust, and mantle, but the Ne within the Green River springs gases is of atmospheric origin. This is not air contamination during sampling but air dissolved in groundwater of meteoric origin within the Navajo aquifer. MORB = mid-ocean-ridge basalts.

As previously outlined, the atmospheric contributions to the CO₂ sampled are negligible. Therefore, the air-dominated Ne isotope ratios show that the Ne must be derived from aquifer water that contains dissolved atmospheric Ne, i.e., meteoric water. However, the data cannot be interpreted as simply showing that all of the CO₂ was derived from meteoric water. This is because Ne concentrations in air are high compared to those in the Green River gases, so a small proportion of air in the Navajo aquifer would swamp the Ne from other sources, i.e., from the crust or mantle. However, the abundance of Ne and its isotope signatures does serve to differentiate the Green River gases from the large mantle-sourced accumulations around the Colorado Plateau, which contain minimal atmospheric Ne. In Figure 7, these mantle-sourced CO₂ accumulations form mixing lines between mantle (MORB), crust, and air, with an inferred local deep crust value at $^{21}\text{Ne}/^{22}\text{Ne} = 0.06$.

CARBON DIOXIDE MOVEMENT AND TRANSPORT IN THE SUBSURFACE

Regardless of the origin of CO₂, it must migrate through water-saturated rocks to reach the surface. Only

two mechanisms exist by which CO₂ can migrate in the subsurface: (1) in solution in advecting pore water or (2) as a free phase analogous to migrating hydrocarbons or natural gas. This migration route will influence the total ratio of CO₂/water and the $^3\text{He}/\text{CO}_2$ ratio measured at the surface. Therefore, understanding if CO₂ migrates entirely in aqueous solution or if some or all of the CO₂ has migrated as free gas is important. Previous workers have postulated both the existence of an accumulation of free-phase CO₂ below the Green River springs, within the Navajo aquifer (Shipton et al., 2004, 2005; Heath et al., 2009), and that the CO₂ is in solution. Constraining transport mechanisms beneath Green River springs by considering the relative volumes of water and CO₂ erupted is possible using the solubility of CO₂ discussed above.

We use Crystal geyser to calculate CO₂ transport because semiquantitative estimates are available of its discharge. The rate of CO₂ effusion at Crystal geyser has been measured as 12,000 t/yr (Gouveia et al., 2005). The rate of water flux from Crystal geyser was measured in the early 1970s and was reported by Baer and Rigby (1978) as $117 (\pm 4) \text{ m}^3$ every 4.25 hr, although the method of measurement is not stated. This corresponds to $240,000 \text{ m}^3/\text{yr}$ ($8,475,520 \text{ ft}^3/\text{yr}$). However, the modern flux is different, possibly after a dynamite charge was dropped down the hole (Walther, 2001)! When the CO₂ flux was determined in 2004, the geyser erupted only five times in 48 hr; i.e., only once every 9 hr. Assuming that the volume of the eruptions is unchanged because the measurements were made, a better estimate of the present-day water flux may hence be 100,000 t/yr. This is probably a maximum estimate of the volume of water discharged because anecdotal evidence suggests that eruptions were longer and more vigorous in the past (Walther, 2001). Combining the estimates of water and CO₂ fluxes enables a concentration of CO₂ to be calculated as 4.4 mol%. This is almost twice the maximum theoretical solubility of CO₂ at the base of the Navajo aquifer. The excess of CO₂ strongly suggests that at least some of the CO₂ ascending from the Navajo aquifer must be present as a separate phase and not in solution.

Unfortunately, considerable uncertainty in the estimation of the volumes of discharged CO₂ and water is observed. For the estimate of CO₂ volume, measurements were only taken at ground level, the height of the CO₂ plume was inferred. This could have introduced a considerable error into the estimate. The problem of changes in erupted water volumes through time also exists. Given the uncertainties involved, stating categorically that the CO₂ erupted at Crystal geyser has to be present as a free phase even within the deeper parts of the Navajo aquifer is perhaps not correct, but it seems very likely that at least some of the CO₂ must be present as a free phase. The fact that the gas is erupting as a free phase at the surface is readily apparent.

Carbon Dioxide Transport into the Navajo Aquifer

If free-phase CO₂ within the Navajo aquifer below the Green River springs is present, then it must be introduced into the aquifer in this form from the stratigraphy below. This is because no known processes can form sufficient CO₂ to saturate pore waters and form a free phase at the low temperatures of the Navajo aquifer except perhaps for biological processes. Stable carbon isotope ratios of the CO₂ (Table 1) show quite conclusively that the CO₂ within the springs is not of biological origin. The lack of an in-situ CO₂ source within the Navajo aquifer is confirmed by chemical analysis of waters from the aquifer away from the Green River springs area. These show low salinities (200–6000 ppm average TDS; Rush et al., 1982) that equate to average CO₂ concentrations of less than 0.1 mol%.

We know from the stable isotopes of erupted water (above) that the pore waters feeding Crystal geyser are derived in the proportions 10:90 from the Paleozoic and Navajo aquifers. Therefore, the composition of the fluids that flow between the aquifers can be estimated as about 44 mol% CO₂. This massively exceeds the solubility of CO₂ for the appropriate physical conditions (Figure 3) such that the CO₂ must be moving as a free phase. Also, we can conclude that the concentration of CO₂ in the water derived from the Paleozoic aquifer exceeds that in the Navajo aquifer by more than 2 orders of magnitude. Even allowing that 90% of the spring water is derived from the Navajo aquifer, we can estimate that 50 times more CO₂ is derived from the Paleozoic than the Navajo aquifer. A further deduction is that the chemistry of the Green River springs' gases at the surface is dominated by the chemistry of the CO₂ from the Paleozoic aquifer, except for those elements that are preferentially concentrated in the groundwater, such as ²⁰Ne and ³⁶Ar (Figure 6).

REGIONAL SYNTHESIS AND IMPLICATIONS FOR THE SEEPAGE OF STORED CO₂

The Green River springs are not the only location of naturally occurring CO₂ in the region. Several CO₂ fields exist; i.e., natural accumulations that are sufficiently large to be commercially exploitable. Some of these (e.g., St. John's Dome, Midway) are associated with surface gas seeps, springs, and travertines. There has been extensive geochemical work on the origin of the CO₂, with recent geochemical work proving a mantle origin (Gilfillan et al., 2008). We presumed that the CO₂ is transported into the crust by igneous processes; i.e., dissolved in magma. Note that the commercial CO₂ accumulations

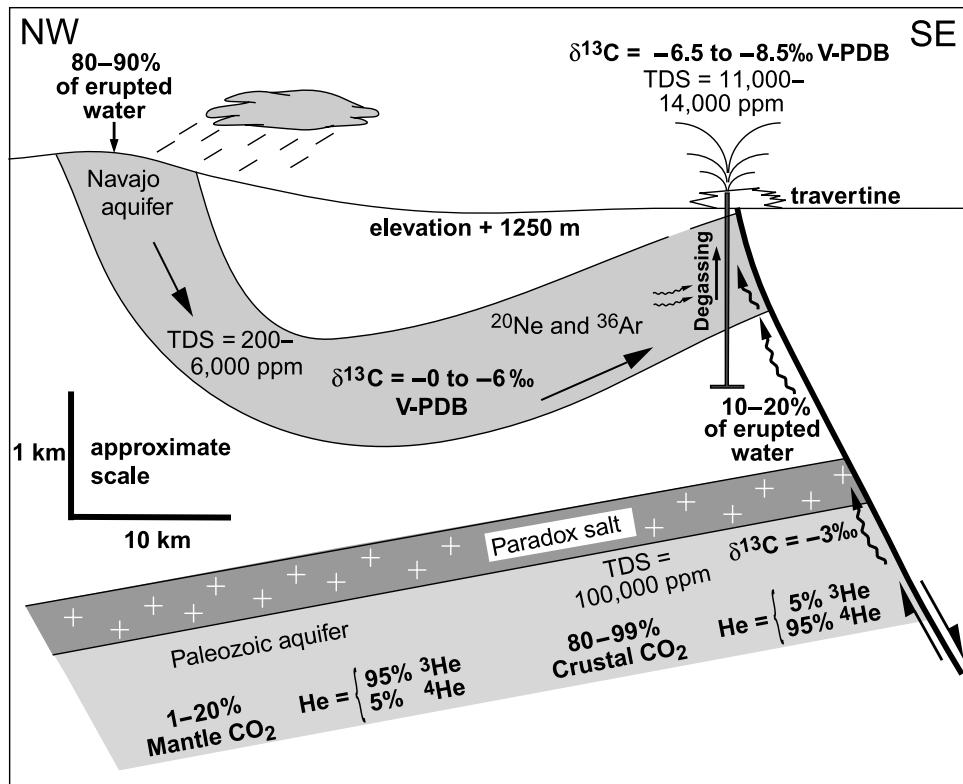
are mostly outside the Paradox Basin. Indeed, most are not strictly on the Colorado Plateau; instead they occur close to the plateau margins. In this context, the Green River springs are unique in that the gas chemistry implies that most of the CO₂ within the deep Paleozoic aquifer is of crustal origin. We also note that the volume of CO₂ emitted by the Green River springs is relatively small; compare the associated travertines that cover only hundreds of square meters at Green River springs with those at St. John's Dome, which cover several square kilometers. Furthermore, the compositions of the Green River gases are quite variable from spring to spring. We conclude that the Green River springs are not caused by the leakage of a large CO₂ accumulation because large accumulations are associated with travertine deposits that are orders of magnitude more extensive and are generally well mixed such that uniform surface spring compositions would be expected.

We propose the following model for the origin of the Crystal geyser CO₂-rich gases (Figure 8). Mantle and crustal CO₂ are present within the Paleozoic aquifer as a free phase as well as in solution. The mantle CO₂ was introduced into the crust through volcanic activity. The crustal CO₂ must be derived either from clay-carbonate reactions or from the thermal metamorphism of carbonates. In either case, the reactions would have stopped when the area began to be uplifted some 37 Ma or perhaps when more rapid uplift occurred some 5 Ma (Nuccio and Condon, 1996). No evidence for a large gas accumulation within the Paleozoic aquifer is observed; in fact, methane is commercially extracted from the same horizon only some 500 m (1640 ft) away from Crystal geyser, suggesting that the CO₂ is perhaps present only within a small volume of the aquifer. Neither is there evidence for a free-phase CO₂ accumulation below the Paleozoic aquifer, where the only potential aquifers are Cambrian dolomitic limestones that lie above the local crystalline basement (Hintze, 1988).

We believe that the free-phase CO₂ migrates buoyantly from the Paleozoic aquifer to the Navajo aquifer, alongside relatively small volumes of brines. These brines are derived from the Paradox Formation, with a dissolved solids content of about 100,000 ppm. The CO₂ then migrates virtually unchanged from the Navajo aquifer along faults to the surface. The contribution to the erupted gas from the Navajo aquifer is minimal except for the addition of air-derived noble gas isotopes such as ²⁰Ne, which are degassed from the meteoric aquifer water. Contrastingly, the brines from the Paleozoic aquifer readily mix in the Navajo aquifer with low-salinity meteoric water in a ratio of 10 or 20% brine to meteoric water to produce water with salinities of 11–14,000 ppm. This water then erupts at the surface.

At the surface, trace noble gases are present in differing concentrations and isotopic ratios within different springs, even those that are close spatially (Tables 1, 2).

FIGURE 8. Summary cartoon of fluid fluxes below the Green River springs. Water is derived predominantly by modern meteoric recharge into the Navajo aquifer, carrying ²⁰Ne and ³⁶Ar but little CO₂. The remaining 10–20% of the water ascends from the Paleozoic aquifer, accompanied by CO₂ as a free phase. No free-phase accumulation of CO₂ is shown within the Navajo aquifer because no evidence of such an accumulation is observed. TDS = total dissolved solids. Note that 90% of surface CO₂ ascends as a free phase from the Paleozoic aquifer; only 10% of surface CO₂ is derived from shallower depths, where CO₂ exsolves from groundwaters in the Navajo aquifer. Note that δ¹³C isotope ratios of CO₂ are reported as isotope ratios relative to Vienna PeeDee belemnite (V-PDB); see text.



Both the calculated origin of the gases (crustal and mantle) and the CO₂/³He of the crustal source are highly variable (Table 3). Hence, these gases forming a free-gas accumulation within the Navajo aquifer, where mixing and homogenization would be expected, is improbable. The free-phase CO₂ may well be restricted to relatively poorly connected fractures within the fault damage zones through which migration is occurring.

Application to Engineered Storage

Man-made storage sites will require monitoring to assess their performance, specifically their integrity and any leakage. If leakage occurs, a problem is to identify stored CO₂ against a background of naturally occurring CO₂ present within the subsurface, oceans, and atmosphere. In some cases, the carbon isotopic ratio (δ¹³C) of the CO₂ from combustion is distinct from background CO₂ and may be a sufficient tracer (e.g., Raistrick et al., 2006). However, this cannot be assumed because the δ¹³C value of the background CO₂ depends upon its origin; for example, natural CO₂ derived by the thermal decarboxylation of kerogen will be indistinguishable from CO₂ from combustion. The isotopic composition of the natural CO₂ background could only be established by direct measurement as part of a baseline geochemical survey. If multiple owners of CO₂ inject into different parts of the same aquifer, or if CO₂ can migrate laterally, then the discrimination of diverse suites of injected CO₂

is likely to be impossible using only C stable isotopes. In such a case, the addition of artificial marker compounds, at parts per million or parts per billion concentrations, would provide unambiguous fingerprinting (e.g., Nimz and Hudson, 2005). These markers would have to be designed such that they migrate with the CO₂.

Noble gas tracers have provided substantial constraints on the origins of CO₂ that erupted at the Green River springs; certainly much more information is available than simply from the stable isotope ratios of the CO₂ itself. Because of the lack of measured baseline data on noble gas and CO₂ contents in the shallow Navajo aquifer and the deep Paleozoic aquifer, noble gases do not, in this case, provide an unequivocal solution to the origin and transport mechanisms of the Green River springs CO₂. With better baseline geochemical data, more would be possible, and the ranges of uncertainty would decrease.

CONCLUSIONS

- 1) Natural cold springs of CO₂-rich water, south of Green River in Utah, provide a setting that can be used as a test of stable isotopes and noble gases as tracers of CO₂ migration through overburden. Using a combination of water chemistry, stable C isotopes, and noble gas ratios, we have produced a model for the origin and migration of the gases, although

- ambiguities remain. In this case, C isotope ratios alone provide minimal information.
- 2) Water in the Green River CO₂ springs is sourced from the underlying Navajo aquifer, as has been commonly assumed. This water is supplied mostly by meteoric recharge some 40–50 km (25–31 mi) away from the spring sites. However, oxygen- and hydrogen-stable isotope ratios of the water show that 10–20% of the discharged water is derived from the underlying Paleozoic aquifer. This is in contact with the Paradox salt and has a salinity of about 100,000 ppm TDS. This salt is the source of the salinity of the spring waters.
 - 3) The erupted CO₂ is mostly derived from crustal sources, with a 1–20% contribution from the mantle. A single spring has 16–99% mantle CO₂. The CO₂ is already mixed within the deeply buried Paleozoic aquifer. This crustal origin for the erupted CO₂ is in contrast to the large, commercially exploited, CO₂ accumulations that surround the Colorado Plateau, which are purely of mantle origin. The Green River springs are not derived from a large accumulation within the Navajo or Paleozoic aquifer, and the Green River springs' gases have markedly distinct noble gas compositions (Ne isotopes, He isotopes, CO₂/³He ratios) from the large accumulations. The Green River springs' gases are variable in composition, arguing against a homogeneous reservoir of free-phase CO₂ within the Navajo aquifer. Migration of free CO₂ gas is inferred because the measured surface volumes contain too much CO₂ to dissolve in the volume of water erupted. Free gas may be confined to fractures associated with the faults and hence not able to mix freely and homogenize.
 - 4) A comprehensive baseline survey should be required in any storage scenario because that will make the identification of future leaks much more certain. The detection of leaks in engineered storage scenarios will only be easy if the stored CO₂ has a distinctive C-isotopic composition that is distinct from the natural background CO₂. A baseline survey will be required to establish if stable C isotopes will be sufficient to track CO₂ movement or whether more advanced techniques are required.
 - 5) Improved discrimination of CO₂ will require the artificial addition of tracers, such as isotopically labeled CO₂ or CH₄. This is especially relevant if aquifers, such as those underlying Green River springs, were sites of commingled CO₂ storage or leakage originating from multiple owners.

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