Plumbing the depths – testing natural tracers of subsurface CO₂ origin and migration, Utah, USA.

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Abstract

The effective geological storage of liquid 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 post-emplacement seepage, we examine natural CO₂ springs around Green River, on the Colorado Plateau USA, 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 estimation that 80 – 90 % of the springwater is derived from shallow groundwater, with the
remainder originating from a deep saline aquifer. CO₂ and water volumes imply ascent of CO₂ as a discrete phase, not just in solution in the porewater. Stable carbon isotopes of CO₂ are unable to discriminate between possible sources. However the CO₂ contains trace amounts of noble gas isotope, 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 there are diverse noble gas signatures at different springs, implying that there is no homogeneous free-phase accumulation at shallow depths 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 characterise aquifer water chemistry, CO₂ and noble gas content before addition of anthropogenic CO₂ to the subsurface.

Keywords: carbon, oxygen, isotope, He, Ne, overburden, CO₂ storage, CO₂ sequestration, Crystal Geyser, noble gas

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 UK, 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 CO$_2$ 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 CO$_2$ injection, then there will be a need to establish the liability for remediation, and hence a need to establish unambiguous ownership of that CO$_2$. Resolving disputed ownership is likely to be particularly relevant where several CO$_2$ owners have 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 CO$_2$ 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 CO$_2$ from McElmo Dome, during EOR operation 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 CO$_2$ occurrence: 1) what is the origin of the CO$_2$, and 2) how is it transported in the subsurface. A crucial factor in determining leakage rates through overburden is whether the CO$_2$ forms a free phase, or is entirely in solution in the porewaters. 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 overburden, and been analysed 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 characterise 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 geochemistries being before any engineered injection commences. The Green River Springs do not form an exact analogue for a leaking engineered storage site, as 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 CO$_2$-rich springs located some 10km south of the town of Green River in Utah, USA, here referred to as the Green River springs. These are CO$_2$-charged springs associated with the Little Grand Wash and Salt Wash faults lying at the northern end of the Paradox Basin (Fig. 1). The faults control the present day flow of gas and groundwater to the surface (Shipton et al., 2004; Heath et al., 2006). Both faults are part of a series of steeply dipping (70-80º) WNW trending normal faults that are found in the region (Fig. 1). These are sub-seismic in size, with throws of 10-40m. The timing of movement along the faults is poorly constrained, although Shipton et al. (2004) argue for Early Tertiary and Quaternary slip movement.

The Paradox Basin primarily contains sediment of Pennsylvanian and Permian age (Nuccio and Condon, 1996). The basin is usually defined according to the areal extent of the Pennsylvanian Paradox Formation, which includes abundant evaporites. The Green River springs lie at the north-west 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 CO$_2$-rich water and free gas, an active CO$_2$ charged geyser, and both active and fossil travertine deposits. The most notable of these is the cold-water CO$_2$-charged Crystal Geyser, which erupts to heights of up to 25m at 4 - 12 hour intervals. The geyser began erupting in 1935 when the Glen Ruby #1-X well was drilled to a depth of 800m in search of oil – prior to this there were springs but no geyser. This and the other CO$_2$-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. (2006). CO$_2$ and other gases in 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 review by Wycherley et al., 1999).

Rush et al. (1982) describe the hydrogeology of the Green River area. They define two aquifers (Fig. 2). The upper “Navajo Aquifer”, defined 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, there are actually two aquifers of paleozoic strata, 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 Fig. 7).

Here, we use noble gas tracers to determine the origin and transport mechanisms of CO$_2$ within the Green River springs, as a test of the applicability of the gas tracer method for the monitoring of anthropogenic CO$_2$ 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, $^3$He in particular, resulting in elevated $^3$He/$^4$He ratios. Atmosphere derived noble gas isotopes such as $^{20}$Ne, $^{36}$Ar and $^{84}$Kr 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 $^4$He, $^{21}$Ne and $^{40}$Ar, 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 CO$_2$ from the Crystal geyser and Big Bubbling Spring measured $^3$He/$^4$He ratios of 0.302 and 0.310 R$_a$
respectively (Heath, 2004; Heath et al., 2006). Shipton et al. (2004) used this data and $\delta^{13}C$ measurements to infer that the CO$_2$ is derived from 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 CO$_2$ was generated within the Navajo sandstone by the dissolution of rock fragments.

Shipton et al. (2004, 05) and Heath et al. (2006) considered that the CO$_2$ 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 CO$_2$ was in solution in the Navajo aquifer, i.e. that there was no free-phase CO$_2$. Previous authors have not considered the issue of CO$_2$ migration in detail, though Shipton et al. (2004, 05) and Heath et al. (2006) presumably thought that the free-phase CO$_2$ would migrate in an analogous way to oil or gas. The alternative is transport in solution in the porewaters.

**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 Fig. 1. Gases were collected using a copper tube technique similar to the method used
at McElmo Dome outlined in Gilfillan et al. (2007). 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 minutes. The clamps were then shut sequentially working back from the clamp furthest from the seep.

Isotopic ratios ($^3\text{He}/^4\text{He}$, $^{20}\text{Ne}/^{22}\text{Ne}$, $^{21}\text{Ne}/^{22}\text{Ne}$, $^{40}\text{Ar}/^{36}\text{Ar}$) and elemental abundances ($^4\text{He}$, $^{20}\text{Ne}$, $^{40}\text{Ar}$, $^{84}\text{Kr}$) were determined on the University of Manchester’s MAP-215 mass spectrometer, using the techniques outlined in Gilfillan et al. (2007) and Gilfillan (2006). All gas concentrations are corrected to standard temperature and pressure (STP). $\delta^{13}\text{C}$ analysis for dissolved gas was undertaken at University of Toronto using procedures detailed in Ballentine and Sherwood Lollar (2002) and Sherwood Lollar et al., (1997). Results are expressed relative to the international V-PDB standard. Helium isotope ratios ($^3\text{He}/^4\text{He}$) 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. Porewater analyses for the Paradox Basin were taken from the literature.

**Results - Composition of erupted gas and water**
Noble gases contents of the Green River gases are given in Table 1. The CO₂, which is the predominant component (e.g. Heath et al., 2006), exhibits a small range in δ¹³C from -6.47 to -8.50‰ (Table 1). Isotopic ratios of the noble gases are in Table 2. There is marked variation within the composition of the trace noble gases.

**Discussion**

**CO₂ solubility in the subsurface**

In order 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 interest, CO₂ solubility decreases with increasing temperature and salinity, but increases with increasing pressure. In order to calculate the solubility of CO₂ at the Crystal Geyser site, it is first necessary to construct a geothermal model. Clearly, there is significant vertical movement of water within the top part of the rock column, bringing heat as well as CO₂ to the surface. The temperature of the geyser water at the surface has been measured as 15.5 to 17.8 °C (Baer and Rigby, 1978) though 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., 2006), then the minimum depth from which the waters might be sourced is 260 – 500m (Heath et al., 2006). 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 porewater temperature (15 or 18 °C) from the surface to where this intersects the geothermal gradient (Fig. 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 atmosphere 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 500m, 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 at between 650 and 800m depth depending on the thermal profile (Fig. 3). Below this depth, solubility decreases slowly. Solubility of CO$_2$ 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 CO$_2$ solubility depressed by less then 5% compared to fresh water (Enick and Klara, 1990, cited in Metz et al., 2005). By contrast, the Paradox brines will have a CO$_2$ solubility of only c. 60% compared to fresh water. Figure 3 shows the effects of salinity on CO$_2$ solubility below Crystal Geyser, assuming that the Paradox brines penetrate as far as the top of the sub-Navajo aquiclude (Fig. 2).

_Porewater movement below the Green River springs_

In this section, we firstly 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 source(s) of CO$_2$ erupting from the Green River springs. The source and volumes of the porewaters must be known if the mechanism of transport of the CO$_2$ in the subsurface is to be assessed.

It is possible to use oxygen and hydrogen stable isotope chemistry to constrain the origin of the water erupted by the Green River springs. Oxygen has three common isotopes, of which the vast majority is $^{16}$O.
The ratio of $^{18}$O to $^{16}$O is measured and reported relative to Standard Mean Ocean Water in parts per thousand ($\delta^{18}$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 ($\delta$D in ‰). A combination of these two measurements is a powerful tool used in studies of porewaters within sedimentary rocks (Faure, 1986).

Figure 4 shows stable oxygen and hydrogen isotopic analyses of porewater from the Paradox Basin from the Green River area and the Greater Aneth oil field, SE Utah. The oil field lies some 150 km to the SE of Green River, and is the closest known source of subsurface isotopic water analyses. While ideally, we would have isotopic analyses of the subsurface waters in the Green River area prior to the introduction of the CO$_2$, 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 are similar, and the bulk porewater chemistry is thought to be controlled by the dissolution of evaporites within the Paradox Formation, that are certainly present in both locations. Hence, whilst regional data must be used which introduces some uncertainty in the proportions in which the different sources contribute, use of this data does not introduce uncertainty in the sources of the spring water itself.
Heath et al. (2006) 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. More detailed examination of the data enables us to re-interpret 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. It is thought to be the only deep water sample that is uncontaminated with surface water re-injected into the subsurface for pressure support during hydrocarbon production (Naftz and Spangler, 1994). The remaining brine samples are approximately 50:50 mixtures of injected surface water and original subsurface brine. The Green River springs lie close to the mixing line. Simple proportion indicates that the Green River springs comprise between 10 and 20% Paradox brine, the remainder of the water being surface water carried to depth within the Navajo aquifer. However, while 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 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 NW (Heath et al., 2006) and is of low salinity (200 – 5000 ppm average TDS; Rush et al., 1982, p.45). Crystal Geyser itself lies at the meteoric-rich end of the Green River springs data, so that the effusive water is only 10% Paradox brine. It is noteworthy 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., in press). This is as expected if Crystal Geyser water is 10% Paradox brine, which has an average salinity of c. 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 of 80 - 90% shallow meteoric water with 10 - 20% deep saline water.

*What drives the water flow from the springs themselves?*

Previous authors have assumed that the eruption of Crystal Geyser is powered by the pressure of trapped CO\textsubscript{2} gas, as the water is too cool for a thermal drive (e.g. Waltham 2001; Shipton et al., 2004; 2005). This is reasonable, as the solubility of CO\textsubscript{2} decreases substantially as the porewaters ascend from c. 500m depth to the surface (Fig. 3). However, the other springs may be driven simply by the artesian hydrological head of the elevated aquifer recharge zones. Rush et al. (1982) state 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.

\textit{CO}_2 \textit{Origin - models}

For \textit{CO}_2 storage, in some countries it will be necessary to demonstrate that \textit{CO}_2 from different owners can be detected and discriminated if a leak occurs. A pilot study by Nimz and Hudson (2005) shows that natural noble gases can be successful in fingerprinting the origin of \textit{CO}_2. In the Mabee field of Texas, the \textit{CO}_2 used for EOR was shown, surprisingly, not to originate from Bravo Dome (as the field operators had thought), but from the 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 \textit{CO}_2 could be crucial in assigning liability. The present study addresses the general question: is it possible to determine the origin of \textit{CO}_2 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 \textit{CO}_2 but include nitrogen and trace noble gases (Heath et al. 2006 and Table 1). Heath et al. (2006) also detected between 0.06 and 0.89 mol % oxygen, but suspected that this was the result of atmospheric entrainment during eruption. Hydrogen sulphide has not been detected by chemical analysis but \textit{H}_2\textit{S} 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 CO$_2$ from four candidate origins: i) igneous activity carrying CO$_2$ ultimately derived from the mantle; ii) diagenetic clay-carbonate reactions within the crust; iii) hydrocarbon maturation and other reactions involving buried organic matter; iv) thermal decarbonation of carbonate rocks during metamorphism (e.g. Shipton et al., 2004, 2005; Heath et al., 2006). When considering origins of the noble gases, the role 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’ CO$_2$.

It is possible to summarise previous work on the origin and transport of the CO$_2$ in the Green River springs into two end-member models. Shipton et al. (2004, 2005) and Heath et al. (2006) presumed that the Green River springs are fed from a deep sub-surface source of CO$_2$ that is analogous to the large, commercially-exploited accumulations located around the Colorado Plateau, e.g. St John’s Dome. The CO$_2$ would be present as a free phase, either as a gas or a supercritical fluid, and such an accumulation would be present within the shallow Navajo aquifer. In contrast, Baer and Rigby (1978) considered that the CO$_2$ was derived by
reactions within the Navajo Aquifer, i.e. at relatively shallow depths of burial. In this latter scenario, there is no accumulation of free-phase CO₂ below the Green River Springs, but all the CO₂ is present in solution in the aquifer porewater, and exsolution only occurs as the waters is brought to the ground surface. Below, we attempt to determine which of the models best explains the distribution of measured tracers in the spring waters.

**CO₂ 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 (δ¹³C 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 δ¹³C from –6.5 to –8.5 ‰ V-PDB (Table 1), while those of Heath et al. (2006) have an even tighter distribution from –6.4 to –6.8 ‰ V-PDB. This small discrepancy between the two data sets may be due to the differing collection methods used for sampling the gases.

The Colorado Plateau is surrounded by large natural subsurface CO₂ accumulations, that are analogues of oil or natural gas fields. Recent isotopic work has shown that most of these are derived from the mantle
via igneous processes (Gilfillan et al., 2007). Hence, the Green River CO$_2$ could be of mantle origin, sourced from a large accumulation at depth. The $\delta^{13}$C of CO$_2$ 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 largely 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 CO$_2$.

In the absence of organic reactions, the isotopic composition of dissolved CO$_2$ will be controlled by the composition of carbonates within the host rock. Marine limestones within the Paradox Formation have $\delta^{13}$C close to 0‰ V-PDB (Garden et al., 2001), while authigenic carbonates from the Navajo Sandstone have $\delta^{13}$C of c. 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 $\delta^{13}$C of –2 to –8‰ V-PDB in the Navajo Aquifer, and $\delta^{13}$C of c. -3‰ V-PDB in the Paleozoic Aquifer. The uncertainly in the carbon isotope ratio for the Paleozoic aquifer is probably similar to that of the Navajo aquifer, suggesting that -3 ± 3‰ V-PDB is a realistic estimate. When CO$_2$-rich porewaters ascend, they are subject to a high degree of degassing during uplift to the surface due to the dramatic decrease in CO$_2$ solubility (Fig. 3). Then the exsolved gas will be of similar isotopic composition to the dissolved bicarbonate, though probably slightly more negative due to fractionation effects. Hence the dissolved bicarbonate within either the Navajo Aquifer or the Paleozoic Aquifer are potential
sources of the Green River springs’ gases, and these two sources cannot be distinguished using carbon isotope ratios.

*Helium isotopes to track CO₂ origins*

Potentially useful tracers of the origin of CO₂ are $^3$He and $^4$He. The concentration of $^3$He is expressed relative to the concentration of CO₂, and is assumed to be conserved during any migration of the gases. $^3$He is primordial in origin, as opposed to $^4$He which is produced by the radioactive decay of elements such as U and Th. As the latter elements are mostly concentrated in the crust, and are rare in the mantle, $^3$He is typically associated with the mantle and $^4$He with the crust. Helium is present within the atmosphere at only low concentrations ($5 \times 10^{-6}$ volume/volume at STP; Ballentine et al., 2002). Aquifer water will hence have high CO₂/$^3$He ratios compared to Mid-Ocean Ridge Basalts (MORB - taken to be representative of the mantle) due to soil processes, and the dissolution of high CO₂ minerals such as calcite that will only contribute CO₂ and not $^3$He.

Figure 5 shows CO₂/$^3$He ratios plotted against CO₂ concentration for all of the Green River springs, along with the CO₂/$^3$He range of MORB and data from deep natural CO₂ accumulations around the Colorado Plateau (Gilfillan et al., 2007). All of the samples except that of Tenmile geyser have CO₂/$^3$He ratios above the MORB range. This indicates that the CO₂ from the majority of the springs is dominated by a component derived from the crust (see O’Nions and Oxburgh 1988 for crustal CO₂/$^3$He values). The lower CO₂/$^3$He ratios of Tenmile Geyser, Chaffin Ranch
and Torrey’s Spring (Fig. 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 $^{3}$He/$^{4}$He 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 due to 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 $^{3}$He/$^{4}$He ratios from the Green River springs (Heath et al., 2006) both exceed 0.3 R$_a$, which we again interpret as the result of contamination by air. Heath et al. (2006) 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. (2006) 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.

In order to calculate crustal and mantle inputs to the CO₂, the input from air must be first quantified. This is calculated using the measured
$^{40}\text{Ar}/^{36}\text{Ar}$ ratio of the springs’ gases (derived from equation 35 of Ballentine et al., 2002):

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

The proportion of air-derived Ar is high (33 – 91%) due to the high total Ar content of air, compared to the crust and mantle. Figure 6 shows how the air component controls the $^{40}\text{Ar}/^{36}\text{Ar}$ and $^4\text{He}/^{20}\text{Ne}$ isotope ratios, due to the high air concentrations in air of Ar and Ne. From the air-derived $^{40}\text{Ar}$, the air contribution to the total erupted $\text{CO}_2$ can be calculated as the ratio $\text{CO}_2/^{40}\text{Ar}$ for air is known. The air contribution is small (0.1 – 1.4 volume % $\text{CO}_2$; Table 3). It is significant that the anomalous Crystal Geyser has the highest air contribution, perhaps due to air entrainment during the spectacular eruptions. It is now possible to correct measured $^3\text{He}/^4\text{He}$ ratios for the air component (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 $^4\text{He}/^{20}\text{Ne}$ ratios, where air-dominated He would have a value close to air (0.288; Ballentine et al., 2002), while measured values are much higher (313 to 13002).

All $^3\text{He}/^4\text{He}$ ratios measured for the Green River gases are significantly higher than the crustal $^3\text{He}/^4\text{He}$ ratio of 0.02 $R_a$ but lower than the subcontinental mantle ratio of 6 $R_a$ (Fitton et al., 1991). Using these end-member values, the origin of the He isotopes can be calculated.
(from Eqn 38 of Ballentine et al., 2002). $^X$He$_{\text{origin}}$ denotes a proportion within a unitary volume of gas.

$^4$He$_{\text{crust}} = \left( ^3\text{He}/^4\text{He}_{\text{mantle}} - ^3\text{He}/^4\text{He}_{\text{measured}} \right) / \left( ^3\text{He}/^4\text{He}_{\text{mantle}} - ^3\text{He}/^4\text{He}_{\text{crust}} \right)$

(2)

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

$^3$He$_{\text{crust}} = \left( ^3\text{He}_{\text{crust}} x ^3\text{He}/^4\text{He}_{\text{crust}} \right) / \left[ ^3\text{He}_{\text{crust}} x ^3\text{He}/^4\text{He}_{\text{crust}} + (1 - ^4\text{He}_{\text{crust}} x ^3\text{He}/^4\text{He}_{\text{mantle}} \right]$  

(3)

In all the Green River Springs, only 5 - 8% of the total $^3$He comes from the crust, the remainder 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 CO$_2/^3$He ratio, which is variable (e.g. O’Nions and Oxburgh, 1988). A simple mass balance approach allows the crustal CO$_2/^3$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.

$^3$He$_{\text{mantle}} x \text{CO}_2/^3$He$_{\text{mantle}} + ^3$He$_{\text{crust}} x \text{CO}_2/^3$He$_{\text{crust}} + \text{CO}_2 \text{ air} = 1$  

(4)
For the $\text{CO}_2/\text{He}^3$ ratio of gases derived from the mantle, the conventional range is $1 \times 10^9$ to $1 \times 10^{10}$ (Ballentine et al. 2002). As 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 $1 \times 10^9$ to $6 \times 10^9$ for the mantle gas $\text{CO}_2/\text{He}^3$ ratio. The results of the calculation are shown in Table 3. The crustal contribution of $\text{CO}_2$ is generally between 80 and 99% of the total $\text{CO}_2$, with the exception of Tenmile Geyser which has a higher contribution from the mantle (16 – 99%). From these results, it is not possible to state whether the crustal component is derived from deep crustal reactions, or from aquifer water that has interacted with crustal minerals. The calculated $\text{CO}_2/\text{He}^3$ ratios for the crust are from $6 \times 10^{10}$ to $6 \times 10^{12}$, which are within the range considered by O’Nions and Oxburgh (1988) to be typical of the crust.

**Neon isotopes as tracers of $\text{CO}_2$**

A potentially useful natural tracer of $\text{CO}_2$ 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., 2002; Ballentine et al., 2001). 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 outwith 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.

As previously outlined the atmospheric contributions to the CO$_2$ sampled is 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 CO$_2$ 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 do serve to differentiate the Green River gases from the large mantle-sourced accumulations around the Colorado Plateau, which contain minimal atmospheric Ne. On Figure 7, these mantle-sourced CO$_2$ accumulations form mixing lines between mantle (MORB), crust and air, with an inferred local deep crust value at $^{21}$Ne/$^{22}$Ne = 0.06.

**CO$_2$ movement and transport in the subsurface**

Regardless of the origin of CO$_2$, it must migrate through water saturated rocks to reach the surface. There are only two mechanisms by which CO$_2$ can migrate in the subsurface: in solution in advecting porewater; or as a free phase analogous to migrating hydrocarbons or natural gas.
This migration route will influence the total ratio of CO$_2$:water, and the $^3$He:CO$_2$ ratio measured at the surface. Therefore it is important to understand if CO$_2$ migrates entirely in aqueous solution, or if some or all of the CO$_2$ has migrated as free gas. Previous workers have postulated both the existence of an accumulation of free-phase CO$_2$ below the Green River Springs, within the Navajo Aquifer (Shipton et al., 2004, 2005; Heath et al., 2006), and that the CO$_2$ is in solution. It is possible to constrain transport mechanisms beneath Green River Springs by considering the relative volumes of water and CO$_2$ erupted, using the solubility of CO$_2$ discussed above.

We use Crystal Geyser to calculate CO$_2$ transport, as there are semi-quantitative estimates available of its discharge. The rate of CO$_2$ effusion at Crystal Geyser has been measured as 12,000 t / a (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 (±4) m$^3$ every 4.25 hours, though the method of measurement is not stated. This corresponds to 240,000 m$^3$ / a. However the modern flux is different, possibly after the land owner dynamited the Geyser in a dispute about public access (Waltham, 2001). When the CO$_2$ flux was determined in 2004, the Geyser erupted only 5 times in 48 hours, i.e. only once every 9 hours. Assuming that the volume of the eruptions is unchanged since the measurements were made, a better estimate of the present-day water flux may hence be 100,000 tonnes / a. This is probably a maximum estimate of the volume of water discharged, as
anecdotal evidence suggests that eruptions were longer and more vigorous in the past (Waltham, 2001). Combining the estimates of water and CO$_2$ fluxes enables a concentration of CO$_2$ to be calculated as 4.4 mol %. This is almost twice the maximum theoretical solubility of CO$_2$ at the base of the Navajo aquifer. The excess of CO$_2$ strongly suggests that at least some of the CO$_2$ ascending from the Navajo Aquifer must be present as a separate phase, not in solution.

Unfortunately, there is considerable uncertainty in the estimation of the volumes of discharged CO$_2$ and water. For the estimate of CO$_2$ volume, measurements were only taken at ground level, the height of the CO$_2$-plume was inferred. This could have introduced a considerable error into the estimate. There is also the problem of changes in erupted water volumes through time. Given the uncertainties involved, it is perhaps not correct to state categorically that the CO$_2$ erupted at Crystal Geyser has to be present as a free phase even within the deeper parts of the Navajo Aquifer, but it seems very likely that at least some of the CO$_2$ must be present as a free phase. The fact that the gas is erupting as a free phase at the surface is readily apparent.

**CO$_2$ transport into the Navajo Aquifer**

If there is free-phase CO$_2$ within the Navajo aquifer below the Green River springs, then it must be introduced into the aquifer in this form from the stratigraphy below. This is because there are no known
processes that can form sufficient CO$_2$ to saturate porewaters and form a free phase at the low temperatures of the Navajo aquifer, except perhaps for biological processes. Stable carbon isotope ratios of the CO$_2$ (Table 1) show quite conclusively that the CO$_2$ within the springs is not of biological origin. The lack of a in-situ CO$_2$ 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 (average 200-6000 ppm total dissolved solids; Rush et al., 1982) that equate to average CO$_2$ concentrations of less than 0.1 mol %.

We know from the stable isotopes of erupted water (above) that the porewaters 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 c. 44 mol % CO$_2$. This massively exceeds the solubility of CO$_2$ for the appropriate physical conditions (Fig. 3) such that the CO$_2$ must be moving as a free phase. Also, it can be concluded that concentration of CO$_2$ 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, it can be estimated that 50 times more CO$_2$ 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 CO$_2$ from the Paleozoic aquifer, except for those elements that are preferentially concentrated in the groundwater, such as $^{20}$Ne and $^{36}$Ar (Fig. 6).
Regional synthesis and implications for the seepage of stored CO$_2$

The Green River springs are not the only location of naturally–occurring CO$_2$ in the region. There are several CO$_2$ fields, i.e. natural accumulations that are sufficiently large to be commercially exploitable. Some of these (e.g. St Johns Dome, Midway) are associated with surface gas seeps, springs and travertines. There has been extensive geochemical work on the origin of the CO$_2$, with recent geochemical work proving a mantle origin (Gilfillan et al., 2007). It is presumed that the CO$_2$ is transported into the crust by igneous processes, i.e. dissolved in magma. Note that the commercial CO$_2$ accumulations are mostly outwith the Paradox Basin. Indeed, most are not strictly on the Colorado Plateau, rather they occur close to the Plateau margins. In this context, the Green River Springs are unique, in that the gas chemistry implies that the majority of the CO$_2$ within the deep Paleozoic aquifer is of crustal origin. We also note that the volume of CO$_2$ 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 kilometres. Furthermore, the composition 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 CO$_2$ accumulation, as 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 CO$_2$–rich gases (Fig. 8). Mantle and crustal CO$_2$ are present within the Paleozoic Aquifer, as a free phase as well as in solution. The mantle CO$_2$ was introduced into the crust through volcanic activity. The crustal CO$_2$ 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 ago or perhaps when more rapid uplift occurred some 5 Ma ago (Nuccio and Condon, 1996). There is no evidence for a large gas accumulation within the Paleozoic Aquifer, in fact methane is commercially extracted from the same horizon only some 500 m away from Crystal Geyser, suggesting that the CO$_2$ is perhaps present only within a small volume of the aquifer. Neither is there evidence for a free-phase CO$_2$ 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 CO$_2$ 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 c. 100,000 ppm. The CO$_2$ 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 $^{20}$Ne 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 and 2). Both the calculated origin of the gases (crustal and mantle) and the CO$_2$/He of the crustal source are highly variable (Table 3). It is hence improbable that these gases form a free gas accumulation within the Navajo Aquifer, where mixing and homogenisation would be expected. The free-phase CO$_2$ 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 CO$_2$ against a background of naturally occurring CO$_2$ present within the sub-surface, oceans and atmosphere. In some cases, the carbon isotopic ratio ($\delta^{13}$C) of the CO$_2$ from combustion is distinct from ‘background’ CO$_2$ and may be a
sufficient tracer (e.g. Raistrick, 2006). However, this cannot be assumed, as the $\delta^{13}$C value of the ‘background’ CO$_2$ depends upon its origin, for example natural CO$_2$ derived by the thermal decarboxylation of kerogen will be indistinguishable from CO$_2$ from combustion. The isotopic composition of the natural CO$_2$ background could only be established by direct measurement as part of a baseline geochemical survey. If multiple owners of CO$_2$ inject into different parts of the same aquifer, or if CO$_2$ can migrate laterally, then the discrimination of diverse suites of injected CO$_2$ is likely to be impossible using only C stable isotopes. In such a case, the addition of artificial marker compounds, at ppm or ppb concentrations, would provide unambiguous fingerprinting (e.g. Nimz and Hudson 2005). These markers would have to be designed such that they migrate with the CO$_2$.

Noble gas tracers have provided substantial constraints on the origins of CO$_2$ erupted at Green River Springs, certainly much more information is available than simply from the stable isotope ratios of the CO$_2$ itself. Because of the lack of measured baseline data on noble gas and CO$_2$ 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 CO$_2$. With better baseline geochemical data, more would be possible and the ranges of uncertainty would decrease.
Conclusions

1) Natural cold springs of CO$_2$-rich water, south of Green River in Utah, provide a setting which can be used as test of stable isotopes and noble gases as tracers of CO$_2$ 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) The CO$_2$-charged Green River springs are sourced from the underlying Navajo Aquifer, as has been commonly assumed. This water is supplied largely by meteoric recharge some 40 - 50 km away from the spring sites. However, oxygen and hydrogen stable isotope ratios of the water show that 10% to 20% of the discharged water is derived from the underlying Palaeozoic Aquifer. This is in contact with the Paradox salt, and has a salinity of c. 100,000 ppm TDS. This salt is the source of the salinity of the spring waters.

3) The erupted CO$_2$ is largely derived from crustal sources, with a 1 - 20 % contribution from the mantle. A single spring that has 16 – 99% mantle CO$_2$. The CO$_2$ is already mixed within the deeply buried Paleozoic Aquifer. This origin for the erupted CO$_2$ is in contrast to the large, commercially exploited, CO$_2$ 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, CO$_2$/$^3$He ratios) from the large accumulations. The Green River Springs’ gases are variable in composition, arguing against a homogeneous reservoir of free phase CO$_2$ within the Navajo Aquifer. Migration of free CO$_2$ gas is inferred, because the measured surface volumes contain too much CO$_2$ 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 homogenise.

4) A comprehensive baseline survey should be required in any storage scenario, as 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 CO$_2$ has a distinctive C-isotopic composition that is distinct from the natural, background CO$_2$. A baseline survey will be required to establish if stable C isotopes will be sufficient to track CO$_2$ movement, or whether more advanced techniques are required.

5) Improved discrimination of CO$_2$ will require artificial addition of tracers, such as isotopically labelled CO$_2$ or CH$_4$. This is especially relevant if aquifers, such as those underlying Green River Springs, were sites of co-mingled CO$_2$ storage or leakage originating from multiple owners.
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Fig. 1. Map of the Green River area showing the location of the natural CO$_2$ seeps and geysers sampled (after Williams, 2005). Extent of Paradox Basin from Hansley (1995).
Fig. 2. Summary stratigraphy of the Green River area, only major formations are shown. From Hintze (1993) and Rush et al. (1982). Note that the Paradox salt is shown in its original stratigraphic position, and may now be substantially higher up the stratigraphy due to diapirism, especially in the vicinity of the Little Grand Wash Fault. The depth scale is approximate only, especially below c. 1000m depth. The hydrologic units are from Rush et al. (1982). The thermal profiles are extremes based upon estimates of surface temperature and geothermal gradient.
Fig. 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 Fig. 2. 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).
Fig 4. Stable O and H isotope ratio cross-plot for porewaters within the Paradox Basin. The Green River springs lie on a mixing line between surface water and Ismay deep saline brine. The Green River springs data are tabulated in Heath (2004) and presented in Heath et al. (2006). The surface waters for the Green River area are from Mayo et al. (2003), the deep brine analyses from Spangler (1992), the Greater Aneth area injection water from Naftz and Spanlger (1994). The global meteoric water line is from Clark and Fritz (1997).
Fig. 5. CO$_2$/$^3$He ratios plotted versus CO$_2$ abundance. All but one of the Green River seeps have CO$_2$/$^3$He ratios above the MORB range indicating that the CO$_2$ is predominantly derived from a crustal source. Measurement errors are smaller than printed symbols. The shaded region highlights the range of CO$_2$/$^3$He values measured in pure magmatic samples (MORB, Ballentine et al., 2002). Also plotted (as a vertical ellipse) is the data from the deep CO$_2$ reservoirs of McCallum Dome, Sheep Mountain, Bravo Dome, McElmo Dome, Doe Canyon and St John’s Dome (Gilfillan et al.,
Fig. 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 (36Ar, 20Ne). Air is dissolved in meteoric recharge, and is introduced into the subsurface by descending aquifer flow.
Fig. 7. Neon isotope ratio cross plot comparing Green River Springs' gases to deep CO₂ accumulations of the Colorado Plateau (Gilfillan et al., 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.
Fig. 8. Summary cartoon of fluid fluxes below the Green River Springs. Water is derived predominantly by modern meteoric recharge into the Navajo aquifer, carrying $^{20}$Ne and $^{36}$Ar but little CO$_2$. The remaining 10 - 20% of the water ascends from the Paleozoic aquifer, accompanied by CO$_2$ as a free phase. No free-phase accumulation of CO$_2$ is shown within the Navajo aquifer, as there is no evidence that such an accumulation exists.
<table>
<thead>
<tr>
<th>Spring</th>
<th>Location (Lat/Long)</th>
<th>$\delta^{13}$C(CO$_2$) ‰ V-PDB</th>
<th>$^4$He (x $10^{-4}$) (cm$^3$STP/cm$^3$)</th>
<th>$^{20}$Ne (x $10^{-6}$) (cm$^3$STP/cm$^3$)</th>
<th>$^{40}$Ar (x $10^{-5}$) (cm$^3$STP/cm$^3$)</th>
<th>$^{84}$Kr (x $10^{-9}$) (cm$^3$STP/cm$^3$)</th>
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<tbody>
<tr>
<td>Tumbleweed</td>
<td>38.7617, -110.1331</td>
<td>-6.47 (0.10)</td>
<td>0.467 (0.005)</td>
<td>5.36 (0.06)</td>
<td>4.10 (0.003)</td>
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<td>Torrey’s</td>
<td>38.8594, -110.0728</td>
<td>-5.90 (0.20)</td>
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<td>4.17 (0.004)</td>
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<td>Crystal: Side</td>
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<td>Pseudo-Tenmile</td>
<td>38.8664, -110.1004</td>
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<td>0.0582 (0.0008)</td>
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<td>1.08 (0.001)</td>
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<td>4.26 (0.004)</td>
<td>1.71 (0.010)</td>
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Figures in brackets are standard error
Wilkinson et al., Table 2. Noble gas isotope ratios for the Green River Springs

<table>
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<td>Tumbleweed</td>
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<tr>
<td>Crystal: Main</td>
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### Wilkinson et al. Table 3 – Calculated origin of CO₂

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<th>CO₂ origin %</th>
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<td>Tumbleweed</td>
<td>92</td>
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<td>1.2</td>
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<td>16</td>
<td>0.5</td>
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<td>Crystal Geyser: Main</td>
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<td>1.3</td>
<td>1.4</td>
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<td>0.7</td>
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