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The noble gas geochemistry of natural CO₂ gas reservoirs from the

Colorado Plateau and Rocky Mountain provinces, USA

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ABSTRACT

Identification of the source of CO₂ in natural reservoirs and development of physical models to account for the migration and interaction of this CO₂ with the groundwater is essential for developing a quantitative understanding of the long term storage potential of CO₂ in the subsurface. We present the results of 57 noble gas determinations in CO₂ rich fields (>82%) from three natural reservoirs to the east of the Colorado Plateau uplift province, USA (Bravo Dome, NM., Sheep Mountain, CO. and McCallum Dome, CO.), and from two reservoirs from within the uplift area (St Johns Dome, AZ., and McElmo Dome, CO.). We demonstrate that all fields have CO₂/³He ratios consistent with a dominantly magmatic source. The most recent volcanics in the province date from 8 – 10 ka and are associated with the McElmo Dome field. The oldest magmatic activity dates from 42 - 70 Ma and is associated with the McElmo Dome field, located in the tectonically stable centre of the Colorado Plateau: CO₂ can be stored within the subsurface on a millennia timescale.

The manner and extent of contact of the CO₂ phase with the groundwater system is a critical parameter in using these systems as natural analogues for geological storage of anthropogenic CO₂. We show that coherent fractionation of groundwater ²⁰Ne/³⁶Ar with crustal radiogenic noble gases (⁴He, ²¹Ne, ⁴⁰Ar) is explained by a two stage re-dissolution model: Stage 1: Magmatic CO₂ injection into the groundwater system strips dissolved air-derived noble gases (ASW) and accumulated crustal/radiogenic noble gas by CO₂/water phase partitioning. The CO₂ containing the groundwater stripped gases provides the first reservoir fluid charge. Subsequent charges of CO₂ provide no more ASW or crustal noble gases, and serve only to dilute the original ASW and crustal noble gas rich CO₂. Reservoir scale preservation of concentration gradients in ASW-derived noble gases thus provide CO₂ filling direction. This is seen in the Bravo Dome and St Johns Dome fields. Stage 2: The noble gases re-dissolve into any available gas stripped groundwater. This is modeled as a Rayleigh distillation process and enables us to quantify for each sample: 1) the volume of groundwater originally 'stripped' on reservoir filling; and 2) the volume of groundwater involved in subsequent interaction. The original water volume that is gas stripped varies from as low as 0.0005 cm^3 groundwater/cm³ gas (STP) in one Bravo Dome sample, to 2.56 cm^3 groundwater/cm³ gas (STP) in a St Johns Dome sample. Subsequent gas/groundwater

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equilibration varies within all fields, each showing a remarkably similar range, from zero to $\sim 100 \text{ cm}^3$ water/cm³ gas (at reservoir pressure and temperature).

1. INTRODUCTION

Carbon dioxide (CO_2) has been identified as the most important compound currently affecting the stability of the Earth's climate and represents 62.5% of globally generated greenhouse gases (International Panel on Climate Change, 1996; 2001; 2007). Geologic storage of anthropogenic CO_2 in depleted oil and gas reservoirs is one of the key options for short-term control of CO_2 emissions. However, CO_2 is a reactive gas that has significantly more influence upon the host rocks and their formation waters than petroleum fluids (Baines and Worden, 2004). In order for this technology to be safely implemented the long term consequence of injecting CO_2 into the subsurface must be quantified.

Natural subsurface CO₂ accumulations have existed on geological timescales and provide key analogues that inform us about the feasibility of long term storage of anthropogenic CO₂ (e.g. Baines and Worden, 2004; Haszeldine et al., 2005). Despite the amount of information available from these sites, in many natural CO₂ reservoirs the source of the CO₂ and basin scale processes that act on them are poorly understood. This is partially due to the multiple origins of CO₂ in natural gases. These include methanogenesis, oil field biodegradation, kerogen decarboxyilation, hydrocarbon oxidation, decarbonation of marine carbonates and degassing of magmatic bodies (Jenden et al., 1993; Wycherley et al., 1999). δ¹³C(CO₂) can be used to distinguish between some of these different sources. However, the $\delta^{13}C(CO_2)$ of natural gas fields containing high CO₂ concentrations (>70% CO₂) almost always lies in the overlapping range between magmatic degassing and carbonate breakdown, and these different sources cannot be readily distinguished. In addition, because of the high CO2 solubility in water and CO₂ reactivity, the extent of interaction of the CO₂ phase with the groundwater is a critical parameter in quantifying CO₂ sinks. The groundwater systems associated with CO₂ gas deposits are often similar to those of oil and gas field brines and there are few techniques available to quantify regional groundwater movement through age/residence time determination or the groundwater volumes that have interacted with the trapped reservoir phase.

Noble gas isotopic and abundance measurements can be used to constrain CO₂ origins and subsurface interaction with the groundwater system. This is because noble gases from the terrestrial atmosphere, dissolved in groundwater, can be distinguished isotopically from those from the mantle that contain a primordial signature, and those produced by the radiogenic decay of U, Th and K within the crust. When combined with the distinct elemental abundance patterns of the different sources, it is possible to resolve the relative noble gas input from each source to any crustal fluid. This allows the extent of crustal, mantle and atmospheric contributions to the fluid to be constrained (e.g. Ballentine et al., 2002). Additionally, noble gases can be used to constrain natural gas associated water residence times (Zhou and et al., 2005) and quantify the degree of interaction a crustal fluid has had with the groundwater system (Ballentine et al., 1991; Pinti and Marty, 1995; Ballentine et al., 2005).

Whilst primordial noble gas isotopes have been studied in CO_2 -rich well gases since 1961 (e.g. Zartman et al., 1961; Phinney et al., 1978; Caffee et al., 1999; Ballentine et al., 2005; Holland and Ballentine 2006), no systematic study using a full noble gas data set to investigate CO_2 origin and quantify its interaction with the groundwater system subsurface has yet been undertaken. Here we present a He, Ne, Ar, Kr and Xe isotopic study of the CO_2 from five separate producing gas fields located throughout the Colorado Plateau and Rocky Mountain provinces. In this paper we show how measured $CO_2/^3$ He ratios enable us to determine the CO_2 source in each system. We then use the noble gases to identify the subsurface processes acting on the CO_2 and develop a quantitative model of gas and groundwater interaction.

2. THE COLORADO PLATEAU AND ROCKY MOUNTAIN NATURAL CO2 RESERVOIRS

The Colorado Plateau is a massive, high-standing tectonic block located in the south western US, centred on the Four Corners of the states of Colorado, New Mexico, Utah and Arizona (Fig. 1). It is abruptly flanked to the east by the majestic Rocky Mountains, the result of at least 2 km of uplift during the Laramide Orogeny and later Cenozoic uplifts (Baars, 2000). The bulk of magmatic activity on the Colorado Plateau occurred in the Late Cenozoic, along the transitional south western margin (primary between 5-15 Ma) and the northwest southeast trending Rio Grande Rift (0 - 5 Ma) (Fitton et al., 1991). This has coincided with the most-recent and best constrained uplift event at the Plateau's southwest margin between 6 Ma and

1 Ma (Parsons and McCarthy, 1995). The province contains at least nine producing or abandoned gas fields that contain up to 2800 billion m^3 of natural CO₂ (Allis et al., 2001). At the present time the authors are aware of five fields that are commercially producing CO₂, primarily for Enhanced Oil Recovery (EOR) and industrial use, and one field which is currently under development. The majority of the fields are fault bounded anticlines which have four way anticlinal closure or a fault seal along one of the field margins (Shipton et al., 2004).

We focus on the following reservoirs: McCallum Dome, (Jackson Co, CO); Sheep Mountain, (Huerfano County, CO); Bravo Dome, (Harding County, NM); McElmo Dome and the related field Doe Canyon, (Montezuma County, CO) and St Johns Dome (Apache County, AZ) (Fig. 1.). All of these sites contain extremely high CO₂ concentrations, averaging 95-99% CO₂, 1-4% N₂, 0.1-1% He and other trace gases (Allis et al., 2001). We provide detail of the individual geological setting and in particular the relationship of all of these fields to nearby volcanic features associated with the Colorado Plateau uplift event in the Appendix.

3. SAMPLE COLLECTION AND ANALYTICAL TECHNIQUES

Samples from the gas fields were collected directly from producing wellheads that tap the natural gas reservoirs. Sample localities were chosen on site to provide a wide range of depth and spatial distribution across the fields. Samples were collected via the conventional ³/₄-inch National Pipe Thread (NPT) sample port of the well head using two field-sampling techniques.

At McElmo Dome the gas was allowed to flow through a 60 cm length of 10 mm diameter, internally polished refrigeration grade copper tubing before being sealed at either end at close to atmospheric pressure following the technique described by Ballentine and Sherwood Lollar (2002). At St. John's Dome, McCallum Dome, Sheep Mountain and Bravo Dome samples were collected in Swagelok[®] 300 ml stainless steel sampling cylinders fitted at both ends with two high-pressure valves. All cylinders were baked at 150 °C under vacuum before being shipped to the field. The cylinders were attached directly to the sampling port of the wellhead prior to the gas undergoing any form of commercial processing. A 20 cm length of high pressure hosing was attached to the other end of the cylinder as an exhaust to prevent turbulent back mixing. The cylinders were flushed through with gas from the wellhead for 5 minutes before the outer valve was shut and the cylinder equilibrated at wellhead pressure, which ranged from 1400 – 3500 Pa. The cylinder valve closest to the well head was then shut and the gas vented by opening the outer cylinder valve. This valve was closed before complete positive pressure was lost. This purge procedure was repeated 5 more times before all valves were closed sequentially from the outer valve to the valve closest to the sampling port.

Noble gas abundance and isotopes for all samples except those from Bravo Dome (documented in Ballentine et al., (2005)) were determined at the University of Manchester using an all metal purification line and a MAP 215 mass spectrometer. Sub-samples for stable isotope determination are reported elsewhere. Aliquots of the samples were expanded into a calibrated volume of 69.37 cm³ containing a Baratron[®] at known temperature. This volume only was expanded onto a Ti sponge furnace, preheated to 1173 K, and then cooled to room temperature over 15 minutes. Subsequently, the sample was equilibrated with a Zr-Al SAES[®] getter heated to 523 K, to remove most of the active gases, and then equilibrated with charcoal held at 77.3 K to trap the Ar, Kr and Xe, leaving only He and Ne free in the vacuum line. The He and Ne was then expanded into an additional calibrated storage volume of 718 cm³ fitted with a 1 cm³ pipette. The volume of CO₂ administered for analysis varied from 3 cm³ to 38 cm³ (STP) depending on the concentration of noble gases within the sample.

For He analysis a 1 cm³ aliquot from the storage volume was expanded into the UHV mass spectrometer extraction line, where the sample was further cleaned on a SAES[®] GP50 getter at 523 K and a SAES[®] GP50 getter at 293 K before admission to the mass spectrometer for analysis. A second aliquot (~35 cm³) was taken from the storage volume, purified on both the GP50 and NP10 getters, and the Ne separated from He on a cryogenic activated charcoal trap at 38 K. The Ne was subsequently expanded onto a charcoal trap at 77.3 K to remove any residual ⁴⁰Ar and reduce interference on the ²⁰Ne measurements, and inlet into the mass spectrometer for analysis. Following evacuation of the mass spectrometer and the storage volume after Ne analysis the charcoal trap containing the Ar, Kr and Xe was heated to ~253 K and the gas expanded into the storage volume. A 35 cm³ aliquot was expanded onto the GP50 and NP10 getters for further purification and then expanded into the mass spectrometer for Ar and Kr determination. The remaining gas in the storage bottle was expanded onto an activated charcoal trap held at 163 K, quantitatively trapping the Xe, some Kr and allowing the Ar to be pumped away. On warming the charcoal trap to ~253 K, the Xe was released and then inlet into the mass spectrometer for determination.

Mass spectrometer sensitivity and mass discrimination were calibrated by comparison to standards prepared from known volumes of dry air. Full procedural blanks were measured before, during and after the analysis program. Blanks were indistinguishable from atmosphere isotopic compositions. Blank levels were negligible compared to original sample size for all isotopes except ²⁰Ne, which was typically <1%, with the exception of two of the Sheep Mountain samples (2-10-O and 3-23-D), and those of McElmo Dome. Blank correction in the McElmo Dome samples varied from 0.27% to a maximum of 8.5% in two cases. During isotope and abundance analysis, appropriate mass peaks were monitored to correct for interferences caused by the doubly charged ions of ⁴⁰Ar²⁺ and ⁴⁴CO₂²⁺⁺. These were found to be negligible in all cases. Quoted errors are at the 1 σ level of confidence and

include statistical analytical error, air standard reproducibility, the expansion volume uncertainty and mass spectrometer sensitivity stability.

4. RESULTS

A total of fifty seven deep well gas samples from the five gas reservoirs were collected. Table 1 documents the sample location, well depth and the results of noble gas isotopic composition measurements (³He/⁴He, ²⁰Ne/²²Ne, ²¹Ne/²²Ne and ⁴⁰Ar/³⁶Ar). Table 2 outlines the major component abundance (CO₂, N₂, and CH₄) and noble gas abundance measurements (⁴He, ²⁰Ne, ⁴⁰Ar, ⁸⁴Kr). For several Bravo Dome, Sheep Mountain and four McElmo Dome samples ¹³⁰Xe and ¹³⁰Xe/¹³⁶Xe was also determined.

4.1. Major gas species

 CO_2 concentrations in all fields typically range from 92-99% with the exception of two samples from the St. John's Dome field and the single sample from Doe Canyon (near McElmo Dome). The remaining gas is dominated by N₂, CH₄, trace C₂H₆ and noble gases. Within both St Johns Dome and McElmo Dome fields, the only fields with individual sample gas composition measurements available, there is a positive correlation between the N₂ concentration and He concentration (Fig. 2). In the St. John's Dome this correlates to an increase in depth and proximity to the gas/groundwater contact within the field. The correlation of N₂ with He is similar to trends observed in the Hugoton-Panhandle giant gas field ascribed to accumulation of metamorphic N₂ and crustal ⁴He in the regional groundwater and subsequent focussing though degassing (Ballentine and Sherwood Lollar, 2002).

4.2. $CO_2/^{3}$ He ratios and CO_2 origins

Figure 3 shows $CO_2/^3$ He ratios plotted against CO_2 concentration for all of the CO_2 gas fields. All of the samples from the gas fields have $CO_2/^3$ He ratios within or below the MORB range of 1 x 10⁹ to 1 x 10¹⁰ (Marty and Jambon, 1987). This is quite distinct from the higher $CO_2/^3$ He values predicted for near ³He-free carbonates (Sherwood Lollar et al., 1997; Ballentine et al., 2001). The origin of the CO_2 in all fields, with the exception of the well studied Bravo Dome, has previously been thought to be derived from the thermal breakdown of carbonates. Our new results conclusively show that a significant proportion of the CO_2 , if not all, is magmatic in origin. Whilst we believe the CO_2 to be predominantly mantle derived, and indeed all of the fields are proximal to Late Cenozoic volcanism (Appendix), most CO₂ accumulations are multi-sourced (Baines and Worden, 2004). We cannot therefore rule out the addition of some crustal derived CO₂ to the reservoirs, particularly the single sample from McCallum Dome and several of the McElmo Dome samples which exhibit the highest well gas $CO_2/^3$ He ratios. The $CO_2/^3$ He ratios that are significantly lower than the MORB range in the St. John's Dome and Doe Canyon fields can only be ascribed to CO_2 loss or fractionation relative to ³He subsequent to magmatic degassing (Sherwood Lollar et al., 1997).

4.3. Noble gases

4.3.1. Helium

Measured ⁴He/²⁰Ne ratios in all fields are significantly above the air ratio of 0.032, showing that atmospheric He contributions to all samples are negligible. ³He/⁴He ratios therefore represent a mixture of crustal-radiogenic and mantle-derived helium (Fig. 4.).

The highest 3 He/ 4 He values are from the Bravo Dome field which shows a coherent variation from 3.78 to 0.764 R_a (where R_a is the atmospheric ratio) and increasing 4 He from west to east across the field towards the gas/groundwater contact (Ballentine et al., 2005). A similar pattern is seen in the McCallum field (0.354 to 0.448 R_a) where the North McCallum field shows a clear increase in 4 He concentration and a correlated reduction in the 3 He/ 4 He ratio. This pattern contrasts with St. John's Dome (0.394 to 0.455 R_a). 3 He/ 4 He ratios increase across the St Johns field toward the gas/groundwater contact, the increase in 3 He/ 4 He corresponds with a significant increase in 4 He concentration. 3 He/ 4 He ratios from within the Sheep Mountain (0.916 up to 1.06 R_a) and McElmo Dome (0.125 to 0.173 R_a) field show no spatial coherence indicating that either the crustal and mantle He components are well mixed before input into the gas field or have been homogenized within the reservoir subsequent to filling. The single sample from Doe Canyon has a significantly lower and more crustal radiogenic ratio of 0.065 R_a and correspondingly higher 4 He.

4.3.2. Neon

Within Bravo and St. Johns Dome there is a clear and coherent correlation between increasing ²⁰Ne concentrations and increased proximity to the Gas/Water contact. A similar trend can be seen in the bulk of the McCallum and Bravo Dome fields although it is masked

by several outlying data points. No such trend exists within the Sheep Mountain dataset implying that the Ne systematics are more complex than those of the other fields.

Figure 5 documents the ²⁰Ne/²²Ne and ²¹Ne/²²Ne measured from all samples in the study. Three distinct trends can be identified using the Ne isotope data. The Bravo Dome field is the only system to exhibit mixing between a pre-mixed crust/air component and the mantle component. Sheep Mountain, St. John's and McCallum Domes illustrate a contrasting relationship between a pre-mixed crust/mantle component and air. McElmo Dome clearly contains the greatest contribution of crustal radiogenic components, which is reflected by the high ²¹Ne/²²Ne ratios observed within the field but, unlike the other fields, shows no coherent mixing trend.

Uniquely amongst the noble gases, the contribution of atmospheric, mantle and crustal Ne components can be unambiguously resolved from the Ne isotopes alone (Ballentine, 1997). This is because the air, mantle and crustal end-member isotopic compositions are different and well defined (20 Ne/ 22 Ne_{air} = 9.80, 21 Ne/ 22 Ne_{air} = 0.029, 20 Ne/ 22 Ne_{mntl} = 12.5, 21 Ne/ 22 Ne_{mntl} = 0.06, 20 Ne/ 22 Ne_{crust} = 0.30, 21 Ne/ 22 Ne_{crust} = 0.52 (Ballentine et al., 2002; Ballentine et al., 2005)). The range of calculated average ⁴He/ 21 Ne_{crust} values of 2.89 x 10⁷ to 5.08 x 10⁷ within all of the fields are higher than both the measured average crust value of 1.71 x 10⁷ and theoretical estimates of between 2.02 – 2.64 x 10⁷ (Ballentine and Burnard, 2002). This is consistent with release from a shallow, low temperature regime (Ballentine et al., 1994; Ballentine and Sherwood Lollar 2002).

4.3.3. Argon

In all of the reservoirs bar Sheep Mountain ⁴⁰Ar correlates directly with ⁴He and ²⁰Ne. A similar relationship exists between ³⁶Ar and ²⁰Ne within all the reservoirs and is particularly strong within Bravo, McCallum and St. Johns Dome. As with ²⁰Ne, ³⁶Ar increases with proximity to the Gas/Groundwater contact.

Measured ⁴⁰Ar/³⁶Ar ratios from all of the reservoirs are considerably above the air value of 295.5, as a result of a resolvable excess of ⁴⁰Ar (⁴⁰Ar*) (Fig. 4). Helium isotopes indicate both mantle and crustal contributions to the noble gases, the ⁴⁰Ar* is therefore a mixture of mantle and crustal-derived ⁴⁰Ar. In the case of Bravo Dome, ⁴⁰Ar*/⁴He correlates with ³He/⁴He isotope variation with a correlation coefficient of 0.993 (Ballentine et al., 2005). Extrapolating

to ${}^{3}\text{He}/{}^{4}\text{He}_{crust} = 1 \times 10^{-8}$ (Ballentine and Burnard 2002) resolves ${}^{4}\text{He}/{}^{40}\text{Ar}_{crust} = 22.0$. This is significantly above average crustal production of ${}^{4}\text{He}/{}^{40}\text{Ar}_{crust} = 5$ and is consistent with the resolved ${}^{4}\text{He}/{}^{21}\text{Ne}_{crust}$ discussed above, indicating a thermal regime controlling the release of crustal radiogenic light noble gases in preference to heavier noble gases (Ballentine et al., 1994; Ballentine and Sherwood Lollar 2002). The mantle derived ${}^{4}\text{He}/{}^{40}\text{Ar}$ relationships at Bravo Dome are discussed elsewhere (Ballentine et al., 2005; Holland and Ballentine 2006). Within the other reservoirs, without significant ${}^{3}\text{He}/{}^{4}\text{He}$ variation, contributions to ${}^{40}\text{Ar}{}^{*}$ from both the mantle and crust cannot be simply resolved and the ${}^{40}\text{Ar}{}^{*}$ must be considered as a mix of the crustal and mantle components (${}^{40}\text{Ar}_{crust+mantle}$).

³⁸Ar/³⁶Ar values in all measured samples are indistinguishable from the atmospheric ratio. While the Bravo Dome samples are not reported here, a recent analysis of a second suite of samples are similarly indistinguishable from the air value suggesting that at the level of analytical precision no kinetic fractionation of Ar isotopes due to commercial production (e.g. Zhou et al., 2005) or significant radiogenic ³⁶Ar or ³⁸Ar contributions are resolvable.

4.3.4. Krypton, Xenon groundwater noble gas components

⁸⁴Kr in all fields correlate with ³⁶Ar and also with ²⁰Ne within Bravo, McCallum and St. Johns Domes. In both St. Johns and Bravo Domes there is a clear and coherent increase in ⁸⁴Kr on moving towards the gas/groundwater contact confirming that the majority of the ⁸⁴Kr is derived from the dissolved air component within the groundwater. ¹³⁰Xe within Bravo Dome exhibits a similar increase as observed in ²⁰Ne, ³⁶Ar and ⁸⁴Kr on moving eastwards towards the gas/water contact.

²⁰Ne and ³⁶Ar within crustal fluids are dominantly derived from the atmosphere dissolved in groundwater at recharge (Ballentine et al., 2002). Nevertheless, in these mantle-derived CO₂ fluids mantle and crustal ²⁰Ne and to a lesser extent ³⁶Ar may be present. Using the Ne isotope resolution technique outlined by Ballentine (1997) the atmospheric contribution to ²⁰Ne for each sample can be resolved. Within Bravo Dome a plot of I/²²Ne vs ²⁰Ne/²²Ne vs ²¹Ne/²²Ne, where I is any noble gas isotope, defines a plane and enables the end member contribution to each noble gas isotope to be calculated and allows us to uniquely determine the ³⁶Ar_(atm) for each Bravo Dome sample. For this reason we use Bravo Dome as our reference system. Within the other fields the more limited spread of data does not make this

possible. Using the Ne isotopes we calculate the maximum ²⁰Ne mantle contribution to these fields is ~10%. This is small compared to the range of observed ²⁰Ne/³⁶Ar and we make the simplifying assumption that ²⁰Ne and ³⁶Ar is entirely groundwater-derived. Observed (mantle-corrected in the case of Bravo Dome) ²⁰Ne/³⁶Ar ratios are compiled in Table 3.

Bravo Dome ²⁰Ne/³⁶Ar_(atm) values range between 0.152 and 0.430 and compare with a reference air saturated water (ASW) value of 0.152. ASW is defined here as groundwater equilibrated with air at 10°C at an altitude of 2000 m and containing a 10% Ne excess air component. McElmo Dome samples show ²⁰Ne/³⁶Ar that ranges from below ASW at 0.061, to 0.389, similar to the upper limit of Bravo Dome. McCallum Dome ²⁰Ne/³⁶Ar ratios range from 0.312 up to 0.462, again similar to the Bravo Dome upper limit, while St Johns Dome samples range from 0.136 to 0.219, close to ASW. In contrast all Sheep Mountain samples are strongly fractionated relative to ASW. The majority of Sheep Mountain samples have ²⁰Ne/³⁶Ar ratios in the range of 0.530 to 1.31. However, four samples show ²⁰Ne/³⁶Ar values ranging from 2.01 to 3.08. Similar extreme values have been observed before in natural gases with ²⁰Ne/³⁶Ar_(atm) values up to 1.4 in CO₂-N₂ rich gases in the Indus Basin (Battani et al., 2000) and up to ²⁰Ne/³⁶Ar_(atm) of 4.9 in dry biogenic methane gases in the Macuspana basin, Mexico (Prinzhofer et al., 2000). The mechanisms that can account for the fractionation of ²⁰Ne/³⁶Ar in the gas phase from ASW are discussed in section 5.1.

Similar to ³⁶Ar, ⁸⁴Kr and ¹³⁰Xe in Bravo Dome samples can also be corrected for nonatmosphere (mantle) contributions using the Ne isotope system to define the ⁸⁴Kr/³⁶Ar_{mntl} and ¹³⁰Xe/³⁶Ar_{mntl} ratios (0.051 and 0.001045, respectively). ⁸⁴Kr and ¹³⁰Xe in all other gas fields are assumed to be dominantly atmospheric in origin. ⁸⁴Kr/³⁶Ar vs ²⁰Ne/³⁶Ar and ⁸⁴Kr/³⁶Ar vs ¹³⁰Xe/³⁶Ar is shown in Fig. 6a and 6b respectively. Mantle corrected ⁸⁴Kr/³⁶Ar ratios in Bravo Dome range from 0.013 to 0.026 compared with the ASW value of 0.045. A wider range in ⁸⁴Kr/³⁶Ar is observed in St. John's Dome, McElmo Dome and McCallum Dome with ⁸⁴Kr/³⁶Ar ratios varying from 0.021 to 0.072 over a relatively narrow ²⁰Ne/³⁶Ar range. In contrast, with the exception of a few samples, the majority of Sheep Mountain samples show only a small range in ⁸⁴Kr/³⁶Ar ratios similar to the air value (0.020) (Fig. 6a). Within the McElmo Dome and Sheep Mountain fields there is a clear correlation between increasing ⁸⁴Kr/³⁶Ar and increasing ¹³⁰Xe/³⁶Ar (Fig. 6b). Mantle corrected ¹³⁰Xe/³⁶Ar ratios from Bravo Dome exhibit a similarly narrow range to that observed in the ⁸⁴Kr/³⁶Ar (Fig. 6b).

4.3.5 Fractionation of groundwater and crustal-derived noble gases

The fractionation observed in the ²⁰Ne/³⁶Ar ratios within Bravo Dome and McCallum Dome correlates to some fractionation of the ⁴He/⁴⁰Ar_(crust+mantle), and to a lesser degree the ⁴He/²¹Ne_(crust+mantle) ratios. Within Bravo Dome ⁴He/⁴⁰Ar_(crust+mantle) ratios range from 1.64 to 6.79, a fourfold increase, whereas the ${}^{4}\text{He}/{}^{21}\text{Ne}_{(crust+mantle)}$ ratios double, from 8.90 x 10⁷ to 2.46 x 10⁷. ${}^{4}\text{He}/{}^{40}\text{Ar}_{(crust+mantle)}$ values from McCallum Dome more than double from an initial value of 2.66 to 5.90, with ${}^{4}\text{He}/{}^{21}\text{Ne}_{(crust+mantle)}$ ratios only increasing from 2.24 x 10⁷ to 3.83 x 10^7 . As the degree of ${}^{4}\text{He}/{}^{21}\text{Ne}_{(crust+mantle)}$ fractionation is less than that of ${}^{4}\text{He}/{}^{40}\text{Ar}_{(crust+mantle)}$ these fractionation trends are consistent with a solubility controlled gas/groundwater phase partition process (e.g. Ballentine et al. 1991). Coherent fractionation of the groundwaterderived and crustal radiogenic noble gases indicates that these differently sourced noble gases are premixed prior to the fractionation event, probably in the groundwater. In contrast, the extreme fractionation of the ²⁰Ne/³⁶Ar_(atm) ratios in the Sheep Mountain field does not correlate with any fractionation of the ⁴He/⁴⁰Ar_(crust+mantle) or ⁴He/²¹Ne_(crust+mantle) ratios. Whilst ²⁰Ne/³⁶Ar fractionation in St. Johns Dome is small (0.125 to 0.170) there is nevertheless a clear correlation between the increase in ²⁰Ne/³⁶Ar and an increase in both ⁴He/⁴⁰Ar and ⁴He/²¹Ne on moving towards the Gas/Groundwater contact. Observed McElmo Dome ²⁰Ne/³⁶Ar values are the only ones to significantly fall below the nominal ASW value of 0.152, by as much as 30%. Whilst there are also several ²⁰Ne/³⁶Ar values which are significantly above the ASW value of 0.152 no clear relationship between this fractionation and either ⁴He/²¹Ne or ⁴He/⁴⁰Ar exists within the field. This could be because the fractionation processes which have been acting in the other reservoirs did not occur in this field or the groundwater system has been perturbed destroying any pre-existing correlations.

5. QUANTIFYING GAS/WATER VOLUMES

In the simplest case, equilibration of a large gas/water volume ratio in the subsurface will cause near quantitative degassing of the groundwater and result in a gas phase that has the groundwater, ASW, noble gas isotopic and elemental composition. As the subsurface gas/water volume ratio decreases the least soluble gases will tend to be enriched in the gas

phase until $V_{gas}/V_{water} \rightarrow 0$ when the limit of the enrichment is controlled by the relative solubility of the respective gases. For example, the maximum enrichment of the Ne relative to Ar in the gas phase though phase equilibrium degassing is K_{Ne}/K_{Ar} where K_{Ne} and K_{Ar} are the respective Henry's constants for Ne and Ar (e.g. Ballentine et al., 1991; 2002). K_{Ne} and K_{Ar} are given for average field conditions in Table 4 and predict a maximum enrichment of Ne relative to Ar from ASW values by a factor of ~2.

The ²⁰Ne/³⁶Ar in both Bravo and McElmo Dome CO₂ gases extend from groundwater elemental ratios to fractionated values that cannot be accounted for by simple equilibration between the CO₂ and groundwater phases. The preservation in some samples of ASW elemental ratios in these fields and the near ASW ratios in the St Johns Dome samples suggests that some degree of 'gas stripping' of the groundwater noble gas composition may be a common feature of these systems. Coherent fractionation of the crustal radiogenic noble gases, where fractionation has occurred, points to systems that are well mixed prior to the fractionating process. The fractionating process is therefore subsequent to the ASW gas stripping.

In contrast there is no overlap of the ${}^{20}\text{Ne}/{}^{36}\text{Ar}$ in the Sheep Mountain samples with the groundwater value, this system shows extreme ${}^{20}\text{Ne}/{}^{36}\text{Ar}$ fractionation and no coherence with the crustal radiogenic gases. While we make the simplifying assumption that the process of ${}^{20}\text{Ne}/{}^{36}\text{Ar}$ fractionation in the Sheep mountain CO₂ field is the same as that in the other gas fields, it is clear that Sheep Mountain is more complex: interaction between the CO₂ and a phase containing crustal radiogenic gases has occurred subsequent to the ${}^{20}\text{Ne}/{}^{36}\text{Ar}$ fractionating event. It is nevertheless, only by considering all systems that we can start to identify the common processes, and in particular the role of groundwater, in these critical analogues for CO₂ storage.

5.1. Fractionation of ²⁰Ne/³⁶Ar (and ⁸⁴Kr/³⁶Ar, ¹³⁰Xe/³⁶Ar)

We now consider the different processes that have the potential to fractionate 20 Ne/ 36 Ar (and 84 Kr/ 36 Ar, 130 Xe/ 36 Ar) beyond the limit imposed by simple gas/water phase equilibrium. As Ar, relative to Ne, is more soluble in oil than water, equilibration of the groundwater with an oil phase could increase the 20 Ne/ 36 Ar in the water phase (Bosch and Mazor 1988). Subsequent groundwater/CO₂ phase equilibration could then produce higher 20 Ne/ 36 Ar in the CO₂ gas

phase. However, with the exception of Sheep Mountain which is located near to a recent hydrocarbon gas discovery (Worrall, 2004) and McCallum Dome which is part of an actively producing oil field, there is no evidence of significant oil phase components in any of the reservoirs (Appendix). In the Indus Basin, where the high 20 Ne/ 36 Ar ratios have been attributed to oil involvement, there is a correlation between 20 Ne/ 36 Ar and 1/ 36 Ar ratios (Battani et al., 2000). There is no such correlation in the CO₂ gas fields of this study.

Similarly, ⁸⁴Kr/³⁶Ar and ¹³⁰Xe/³⁶Ar in excess of groundwater values (Fig. 6) may be caused by the release of atmosphere-derived Xe and Kr that is adsorbed and trapped in organic-rich sediments. ¹³⁰Xe/³⁶Ar enrichment factors up to ~200 relative to water in equilibrium with air have been observed (Fanale and Cannon, 1971; Kennedy et al., 1990; Torgersen and Kennedy, 1999; Kennedy et al., 2002; Torgersen et al., 2004). Direct evidence that Kr and Xe excesses survive sedimentary consolidation and low degrees of thermal alteration is documented in Kr and Xe excesses observed in gas released by the biogenic breakdown of coal (Zhou et al., 2005). However, whilst we cannot rule out this mechanism altogether, we discount organic-sediment derived Kr and Xe for the same reason that we discount oil-involvement in all reservoirs (except McCallum Dome and Sheep Mountain) as there is no organic-rich source rock.

The second mechanism we consider is non-equilibrium diffusion. Atmosphere-derived Ne, Kr and Xe excesses have been reported in secondary silica phases, volcanic glasses, tektites, and in MORB and OIB basalts (Matsubara and Matsuda, 1995; Matsuda et al., 1989; Pinti et al., 1999). Torgersen et al., (2004) have proposed that variable enrichments of noble gases can be accounted for by incomplete emptying followed by partial filling of lithic grains and half spaces, similar to the mechanism proposed by Pinti et al., 1999 for air diffusion into fresh pumice. Pinti et al., (*op cit*) further demonstrate that both elemental and isotopic compositions show clear mass dependent fractionation both between the elemental ratios and isotopic compositions of Ne and Ar. While the significant mantle and crustal Ne contributions makes subtle isotopic fractionation in Ne hard to identify, we observe no significant mass related fractionation in either the ³⁸Ar/³⁶Ar ratios or elemental abundance patterns and discount this as a significant fractionation mechanism for these reservoirs. We further note that in other gas reservoirs where mass dependent fractionation of the groundwater gases

has been observed in the ²⁰Ne/²²Ne and ³⁸Ar/³⁶Ar isotopic ratios, the dominant elemental fractionation is solubility controlled (Zhou et al., 2005).

In principle multiple stages of exsolution and dissolution can increase the solubility fractionation limit (Zartman et al., 1961). In this case a gas phase exsolved from the water with a low Gas/Water volume ratio will have an elevated ²⁰Ne/³⁶Ar ratio. This could be redissolved into a smaller volume of water by a change in physical conditions such as a pressure increase, a decrease in temperature and salinity, or mixing with unsaturated (with respect to the gas phase) water. This creates a local increase in both the groundwater noble gas concentration and the magnitude of noble gas fractionation in solution. Subsequent formation of a gas phase in equilibrium with the now modified groundwater could show a fractionation significantly in excess of that predicted by the single stage equilibrium model. To achieve this, the pressure/temperature conditions must fluctuate and the resulting fractionated gas phase volume is very small compared to the fluid/water volume required to produce any significant fractionation (Ballentine et al., 2002) and we discount this as a viable gas field scale mechanism.

We now consider a partial re-dissolution model (Fig. 9). This is a two stage process. Stage one is the complete degassing of the groundwater noble gases into the gas phase. Stage two is partial re-equilibration (closed system) or Rayleigh fractionation (open system) caused by re-dissolution of the noble gases from the gas phase into a noble gas stripped groundwater (possibly caused regionally by stage 1).

5.1.1. Bravo Dome

Average reservoir conditions and Henry's constants are given in Table 4. Neither closed system batch fractionation nor open system Rayleigh degassing models of gas exsolving from an ASW groundwater phase can account for the observed maximum fractionation (Fig. 7). The high 20 Ne/ 36 Ar_(atm) and low 84 Kr/ 36 Ar_(atm) values can however, be explained by the redissolution model. Since CO₂ is a significantly better solvent than water (King et al., 1992), noble gases will preferentially partition into the CO₂ in the subsurface. In the case of the Bravo Dome field we argue that gas stripping of the groundwater system associated with the gas field occurs through the injection and movement of magmatic CO₂ through the groundwater during an initial reservoir filling stage. The 20 Ne concentration in the gas phase,

orders of magnitude lower than that predicted by groundwater degassing (Fig. 8), corroborates this concept. The CO_2 must have migrated as a separate phase and would have had the capacity to quantitatively partition any gases from the groundwater phase into the CO_2 , effectively 'stripping' the groundwater of its dissolved gas content. This would produce a CO_2 reservoir with an ASW-like composition that would also have contained any radiogenic-crustal noble gases that the stripped groundwater had accumulated. At this stage the groundwater is saturated with respect to CO_2 , but is completely depleted with respect to the atmosphere-derived noble gases (Fig. 9).

Subsequent charges of magmatic CO_2 would then pass through the gas stripped groundwater but serve only to dilute the ASW-derived and crustal-radiogenic noble gases in the CO_2 trapping structure. Bravo Dome preserves a clear ²⁰Ne concentration gradient, increasing from west to east in the field. We argue this both corroborates the model and requires the reservoir filling direction, which may still be ongoing (Baines and Worden, 2004), to be from the west.

The noble gases in the gas phase can then re-equilibrate with any degassed groundwater. This re-equilibration will occur under either open system or closed system conditions depending on the available volume of water for re-equilibration and factors such as whether there is significant water movement or not. For open system conditions, the re-dissolution process will follow a Rayleigh fractionation path. Under closed system conditions, the fractionation trend will be the exact reverse of that calculated for batch fractionation of a gas phase exsolving from water. Using the Bravo Dome reservoir conditions, we show in Figure 7 that the open system Rayleigh fractionation re-dissolution model accounts for all of the mantle corrected 20 Ne/ 36 Ar_(atm) and 84 Kr/ 36 Ar_(atm) ratios that are observed in the field, with the exception of one sample (BD11). This occurs with coherent fractionation of the radiogenic noble gases that we argue are stripped from the groundwater at the same time as the ASW noble gases.

Using the open system re-dissolution model outlined above, the fractionation of the measured gas phase ²⁰Ne/³⁶Ar ratios from the groundwater value defines the proportion of ³⁶Ar lost from the gas phase into solution. It is then straightforward to calculate the initial concentration of ³⁶Ar, ³⁶Ar, ³⁶Ar_{init}, within the gas phase prior to the fractionating (re-dissolution) process (Table

3)(e.g. Zhou et al., 2005). From the concentration of ³⁶Ar in ASW we then calculate for each sample the volume of water required to have been gas 'stripped' to supply the ³⁶Ar_{init} and present this as the Stage 1 Water/Gas volume ratio. For the Bravo Dome system, Stage 1 Water/Gas volume ratio ranges from 0.0005 to 0.071 cm³ of water per cm³ gas (STP) (Table 3). Under reservoir conditions 1 cm³ of groundwater can hold 4.66 cm³ of CO₂ (STP) in solution (Spycher and Preuss, 2005). This results in a Water/Gas ratio of 0.215 and is far higher than the largest estimated Stage 1 V_{Water}/V_{Gas} Bravo Dome value. This is consistent with the CO₂ gas charging the reservoir as a separate and distinct phase, and therefore with the gas 'stripping' conceptual model proposed (Fig. 9).

It is trivial to then calculate the volume of water, under reservoir conditions (Table 4), that the gas phase noble gases must re-dissolve into in order to fractionate the ²⁰Ne/³⁶Ar values from ASW (0.152) to that observed. For the Bravo Dome system this varies from zero to 104 cm³ water per cm³ gas (RTP) (RTP = Reservoir Temperature and Pressure) (Table 3), which corresponds to zero to 1.51 cm³ water per cm³ gas (STP). The volume of degassed water required to fractionate the ²⁰Ne/³⁶Ar from ASW to observed values is far larger than the volume of water 'stripped' to supply the gases, by up to a factor of 50. Little, if any, CO₂ will dissolve in this water while it remains CO₂ saturated. For the first time we quantify on a sample by sample basis the volume of water the gas in this CO₂ storage analogue has interacted with both i) on reservoir filling; and ii) subsequent to reservoir filling.

5.1.2. Sheep Mountain

We have already noted from the lack of correlation of radiogenic noble gases with the ASWderived ²⁰Ne/³⁶Ar that the reservoir fluid history at Sheep Mountain is more complex than in the other fields studied. It is interesting to note that the groundwater salinity in this field is significantly lower than that of the other fields too (Table 4), possibly indicating an influence from younger less saline fluids. Nevertheless, In Figure 10a we show that the ²⁰Ne/³⁶Ar ratios in the Sheep Mountain gases can also be accounted for by the re-dissolution of a gas phase with an initial gas composition of ASW, consistent with the model described for Bravo Dome. The model predicted ⁸⁴Kr/³⁶Ar values are below those observed (Fig. 10a). This could be explained by a higher initial groundwater excess air component or a sedimentary excess-air ⁸⁴Kr, possibly sourced from hydrocarbons associated with the nearby Oakdale natural gas field (Worrall, 2004). The lack of any spatial ²⁰Ne concentration trend within the field suggests that any filling history has not been preserved.

For comparison we use the extent of fractionation of ²⁰Ne/³⁶Ar from ASW values to determine the original ³⁶Ar_{init} abundances prior to the re-dissolution stage and calculate the volume of groundwater 'stripped' for each sample (Table 3). These values range from 0.025 cm³ to 2.32 cm³ water per cm³ gas (STP)(Table 4), significantly higher than the Bravo Dome values. The volume of water required to fractionate the ²⁰Ne/³⁶Ar from ASW to observed values under reservoir conditions (Table 4) assuming an open system range from 48.6 to 114 cm³ water per cm³ gas (RTP), with the four most extreme fractionated gas requiring 144 to 175 cm³ water per cm³ gas (RTP)(Table 3). Excluding the four extreme samples, the reservoir condition Gas/Water volume ratio range for the reservoir re-equilibration is similar to that of Bravo Dome.

5.1.3. McCallum Dome

²⁰Ne/³⁶Ar values within this field can also be explained by the re-dissolution of noble gases into a previously stripped groundwater (Fig. 10b). Similar to Sheep Mountain, the observed ⁸⁴Kr/³⁶Ar ratios are however, higher than the re-dissolution model predicts. This could be explained by an addition of approximately 70% excess Kr (Fig. 10b). Like Sheep Mountain, McCallum Dome is proximal to local hydrocarbon production and we speculate that the excess Kr may be related to sedimentary Kr released on the decomposition of the source kerogen (Torgersen and Kennedy, 1999). Using the fractionation of ²⁰Ne/³⁶Ar from ASW, the volume of stripped groundwater required to account for the ³⁶Ar_{init} abundance prior to redissolution ranges from 0.21 to 0.60 cm³ water per cm³ gas (STP), similar to the upper values at Sheep Mountain (Table 3). The volume of water required to fractionate the ²⁰Ne/³⁶Ar from ASW to observed values under reservoir conditions (Table 5) assuming an open system range from 49 to 86 cm³ water per cm³ gas (RTP), similar to the volumes calculated for Bravo Dome and Sheep Mountain.

5.1.4. St. John's Dome

The observed ²⁰Ne/³⁶Ar ratios in the St. John's Dome samples are close to the calculated ASW value of 0.152. This implies that limited re-equilibration of noble gases has occurred since the groundwater was stripped of its ASW composition. ⁸⁴Kr/³⁶Ar ratios from the St.

John's field are also close to the ASW value of 0.045. Using the re-dissolution model and average reservoir conditions (Table 4), the volume of groundwater stripped on reservoir filling varies from 0.15 to 2.5 cm³ water per cm³ gas (STP), while re-equilibration requires zero to 31 cm³ water per cm³ gas (RTP) (Table 3). In a similar fashion to Bravo Dome, St. Johns Dome preserves a marked ²⁰Ne concentration gradient, increasing from the centre of the trapping structure next to the Coyote Wash fault to the margin of the structure in the north (appendix). We argue that this is the result of the dilution of ASW noble gases by magmatic CO₂ injection within the centre of the reservoir implying that the reservoir was filled by CO₂ migrating into the reservoir via the Coyote Wash fault.

5.1.5 McElmo Dome

As mentioned previously McElmo Dome ²⁰Ne/³⁶Ar values are the only ones to significantly fall below the nominal ASW value of 0.152, by as much as 30%. ⁸⁴Kr/³⁶Ar values also exhibit a greater variation than observed in other fields ranging from 0.02 to a maximum ratio of 0.072. While the latter could be accounted for by an excess ⁸⁴Kr component, this would not account for the low ²⁰Ne/³⁶Ar, suggesting some degree of perturbation of the groundwater system prior to stripping. With this caveat, we nevertheless calculate ³⁶Ar_{init} assuming an unperturbed ASW. The volume of ASW required to account for the ³⁶Ar_{init} varies from 0.011 cm³ to 0.49 cm³ water per cm³ gas (STP) (Table 3). The re-dissolution groundwater volumes range from zero to 91 cm³ water per cm³ gas (RTP) and are within the range of all other fields.

6.0 SUMMARY

Geological CO₂ sequestration requires the safe storage of CO₂ on a timescale in the region of a 1 ka to 10 ka (Haszeldine et al., 2005). The long-term consequences of increasing the gross volume of CO₂ in the crust must be identified in order for geologic CO₂ sequestration to be proven as a safe and viable method to reduce emissions of this greenhouse gas. Identification of the source of CO₂ in natural reservoirs and development of physical models to account for the migration and interaction of this CO₂ with the groundwater is essential for developing a quantitative understanding of the long term storage potential of CO₂ in the subsurface. The Bravo Dome, Sheep Mountain, St Johns Dome and McCallum Dome CO₂ fields in the Colorado Plateau and Rocky Mountain provinces, USA provide a key set of analogues. The $CO_2/^3$ He values of all of the well gas samples show that the CO_2 in each of the separate reservoirs has a significant, if not dominant magmatic component. The magmatic activity related to all of the fields dates from late Tertiary through to the late Quaternary (Appendix). The most recent magmatic events related to the natural gas fields studied occurred in the Raton-Clayton volcanic field close to Bravo Dome between 10 ka and 8 ka (Broadhead, 1998). The next youngest is associated with St. John's Dome; the last phase of volcanic activity from the nearby Springerville Volcanic field dates from 0.3 to 2.1 Ma (Rauzi, 1999). Magmatic activity associated with both the Sheep Mountain and McCallum Dome fields is older, dating from the Late Tertiary (Maughan, 1988; Woodward, 1983). The oldest intrusive igneous rocks in the study are those associated with McElmo Dome, from the nearby Ute Mountain and La Plata Mountain laccoliths which have been dated at 40 - 72 Ma (Stevens et al., 2004). These ages have been determined on surface intrusive igneous rocks. It is probable that deep igneous activity will have continued for a significant period after these surface rocks were formed. However, the dates provide a crude estimation of the CO₂ residence time in the reservoir and imply millions of year timescales for CO₂ residence in these fields.

We have shown that a common two stage groundwater gas stripping and re-dissolution model (Fig. 9), can explain the first order trends observed in the air derived noble gas isotopes in all CO_2 reservoirs studied. This model allows us to quantify on a sample by sample basis the volume of water originally 'gas stripped' during reservoir filling and the volume of groundwater the gas in the reservoir has subsequently interacted with. In detail, perturbation of the original groundwater or sedimentary contributions to Kr may explain where there is a mismatch in some fields between model and observation. The original field Gas/Groundwater ratio clearly controls the degree to which magmatic signatures are resolvable from accumulated crustal gases and dissolved air within the groundwater. This value is highly variable from one system to another. Where the original field Gas/Groundwater ratio varies systematically across a single field, this is most likely caused by dilution caused by subsequent charges of CO_2 that do not contain any ASW-derived noble gases and therefore preserves a record of reservoir filling direction. Different initial Gas/Groundwater ratios may play a fundamental role in determining the relative abundance of CO_2 to other species and its isotopic composition prior to reservoir filling, but is beyond the scope of this work. While the degree of gas/water

interaction subsequent to reservoir filling is variable across individual fields, the maximum volume of water that samples have interacted with is, under reservoir conditions, remarkably similar in all fields.

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Appendix

A1. Bravo Dome

The Bravo Dome field (originally named the Bueyeros field) is located south of Cortez in Harding County, northeast New Mexico (Fig. 1; A1). The field is a large (2000 km²) northwest trending anticlinal nose situated on the spur of the Sierra Grande arch (Baines and Worden, 2004). The region is bounded by the Tucumari basin to the south and the Dalhart Basin to the north (Baars, 2000; Johnson, 1983).

Bravo Dome produces almost pure (99%) CO₂ from the Tubb formation at depths of 600 to 700 m with an average thickness of 30 m (Broadhead, 1993; Broadhead, 1998; Stevens et al., 2001). This is an arkosic sandstone of Permian age and was formed by sand-dominated alluvial, fluvial and aeolian deposition. CO_2 is trapped by a combination of stratigraphic pinch-out, fold closure and possibly hydrodynamic forces. The reservoir is sealed by the impervious Cimarron Anhydrite which is a mix of shallow marine evaporates and arkosic muds (Baines and Worden, 2004; Broadhead, 1993; Broadhead, 1998). Average porosity and permeability are 20% and 42 mD respectively (Allis et al., 2001). Total reserves are estimated to be 450 billion m³ (Allis et al., 2001). The CO_2 is believed to have migrated from vents associated with the nearby Rio Grande rift volcanic activity. Known volcanic activity in the region dates from 10,000 to 8,000 years ago suggesting that the field filled recently (Broadhead, 1998 and Cassidy, 2005). CO_2 migration into the field may still be ongoing, as indicated by a significant pressure increase (29 kPa) in an isolated shut in well over the last decade (Baines and Worden, 2004).

A2. Sheep Mountain

The Sheep Mountain gas field is located at the northern end of the Raton Basin, 45 km northwest of the town of Walsenberg, south central Colorado (Fig. 1; A2). The surrounding region, Huerfano Park, is bounded on the west by the Sangre de Cristo Mountains and on the east by the Wet Mountains. The Raton Basin stretches some 175 miles to the south, from southern Colorado and northern New Mexico. The sedimentary sequence in the region ranges from Pennsylvanian through to Tertiary in age, and lies under and east of the Paldura thrust sheet (Woodward, 1983). Folding and overthrusting induced by this thrust created the Malachite syncline and the little Sheep Mountain anticline. This northwest trending anticlinal fold is bounded on the northeast side by a minor thrust fault and forms the structural trap of the field (Fig. A3). The reservoir produces almost pure CO_2 (~97%) from the Cretaceous Dakota and Jurassic Entrada sandstones at depths of 1400 m to 1800 m. Porosity within the reservoir varies from 16 - 20%, roughly twice the typical porosity of the Dakota and Entrada of 6-

10% (Worrall, 2004). This is believed to be because the sandstones within the folded thrust sheet are not subjected to silicification reactions related to groundwater recharge. This is because the Dakota and Entrada sandstones contained within the Sheep Mountain thrust sheet do not outcrop on the west side of the Raton basin, where groundwater recharge primarily occurs (Worrall, 2004). The field is relatively small (20 km²) and contains 70 billion m³ of CO₂ (Stevens et al., 2001).

The local igneous rocks are related to normal faulting of the province which accompanied upwarping in late Tertiary time. During this period large volumes of volcanic rock were extruded from vents along the Sierra Grande arch, within the Raton Basin and on the eastern margin of the basin. Major intrusives accompanied this volcanic activity, producing extensive sills and laccoliths (Woodward, 1983). The distinctive peaks of Little Sheep Mountain, Sheep Mountain and Dike Mountain are the result of laccoliths intruded during this period. The Sheep Mountain – Little Sheep Mountain laccolith trends north-northwest covering an area of approximately 13 km². The rocks are light grey, phaneritic to aphinitic, intermediate-acidic igneous rocks and are named as a monzonite porphyry (Johnston, 1959; Roth, 1983; Woodward, 1983). Prior to this work the CO₂ source was thought to be due to the thermal breakdown of carbonates as a result of the nearby intrusives (Caffee et al., 1999).

A3. McCallum Dome

McCallum dome is a comparatively small field situated in the North Park basin, northern Colorado (Fig 1). The field is comprised of two large anticlines, North McCallum Dome which is some 6 km northeast of the town of Walden and the faulted en-echelon South McCallum Dome that lies some 2 km to the southeast of the North Dome (Carpen, 1957a; Carpen, 1957b). The CO₂ is trapped in late Laramide related anticlines and faulted anticlines, as a result of a combination of structural and stratigraphic traps (onlap pinch-outs) (Maughan, 1988). The field produces CO₂ from the Lower Cretaceous Dakota and Lakota sandstones and has produced from the stratigraphically lower Morrison sands in the past (Carpen, 1957a). The reservoirs are relatively deep ranging from 1500 to 1900 m. Hydrocarbons are also produced from the field, sourced from the Perrie B shale reservoir which is typically 1 km above the Dakota/Lakota CO₂ reservoir. Small quantities of oil have been documented in the Lakota reservoir above the Gas/Water contact. The most prolific producer is the Dakota Sandstone which has an average thickness of 7-12 m, an average porosity of 15.7% and permeability of 70 mD (300 mD max). The Lakota sandstone is a coarser grained rock, and hence has a higher average porosity of 18.5% and an average permeability of 100 mD (450 mD max.) (Maughan, 1988). The field was first discovered in 1925 and has steadily produced small quantities of CO₂ since 1927. Cumulative production to 1999 is believed to be 19.5 billion m³ (Allis et al., 2001). Currently four wells are in operation with the field producing around 1.076 billion m³ per year of CO₂ for industrial use

Tertiary volcanic and terrigenous clastics lie unconformably on top of the Cretaceous sediments in the vicinity of the field. These were produced at the start of the Oligocene as a result of the main episode of the Laramide Orogeny. Evidence for high heat flow in the area dates from the Late Tertiary and is expressed by local hydrothermal mineralization. The province is believed to still have an elevated geothermal gradient as indicated by the presence of active thermal springs (Maughan, 1988). Prior to this work, thermal breakdown of carbonates as a result of this high heat flow regime had been highlighted as the most probable source of the CO_2 (Biggs, 1957; Maughan, 1988).

A4. McElmo Dome

McElmo Dome is a large (800 km²) anticline situated at the south eastern end of the Paradox Basin in the Four Corners area of southwest Colorado (Fig. 1). The field is 35 km southeast of Cortez and just north of Ute Mountain. A small related field, Doe Canyon, lies some 5 km to the northwest. As the field is located in the centre of the Colorado Plateau, the surrounding surface geology is dominated by flat-lying sedimentary stratigraphy. The field is the world's largest known supply of commercial CO_2 (Stevens et al., 2001). CO_2 is contained in a supercritical state within the Carboniferous (Mississippian) Leadville limestone which is some 100 m thick. The reservoir structure is complex, consisting of interbedded porous permeable dolomite and tight limestones and ranges in depth from 1,800 to 2,600 m (Fig. A3). CO_2 is trapped by a combination of structural closure, permeability barriers within the Leadville Formation, CO_2 -groundwater contact and a 400 m thick salt cap rock of the Paradox Formation. Porosity within the field varies from 3.5% to 25%, averaging 11% and permeability averages 23 mD (Stevens et al., 2001). The CO_2 -groundwater contact tilts west at an approximate gradient of 10 m/km, which is believed to be the result of local hydrodynamic conditions within the Leadville Formation resulting in the field being filled to spill point (Gerling, 1983).

The igneous history of the surrounding area is dominated by intrusive rocks, including the Ute Mountain and La Plata Mountain laccoliths which lie a few km south and east of the field respectively. Both intrusions date from 40 - 72 Ma. Prior to this work, carbon isotope measurements have been used to suggest that the CO_2 in the McElmo Dome field is derived from the thermal breakdown of the Leadville limestone associated with heating caused by the nearby Ute Mountain intrusion (Cappa and Rice, 1995).

A5. St. John's Dome

St. John's Dome is a large (1,800 km²), asymmetrical faulted anticline situated on the southern tip of the Colorado Plateau on the Arizona/New Mexico border. The field lies on the edge of the Holbrook

Basin, in the transition zone between the Colorado Plateau, Basin and Range and Rio Grande Rift tectonic provinces (Fig. 1, A4). This is part of the Mogollen slope which is comprised of Precambrian crystalline basement, Paleozoic through to Cenozoic age sediments and Cenozoic volcanics (Rauzi, 1999). CO_2 in the field is trapped in the Permian Supai Formation which is a predominantly finegrained alluvial sandstone intercalated with siltstone, anhydrite and dolomite. The reservoir is dissected by a major reverse fault, named the Coyote Wash fault, and smaller plays which may have influenced the sourcing and trapping of the CO_2 (Rauzi, 1999). Cap rocks in the field are impermeable anhydrites which vertically separate the CO_2 into multiple zones. The reservoir is relatively shallow at 200 - 700 m and produces CO_2 from a gas state. Average reservoir porosity is 10% and permeability varies widely averaging 10 mD (Stevens et al., 2001). Estimated reserves are believed to be in the region of 445 billion m³ (Stevens et al., 2001).

The Springerville Volcanic Field (SVF) lies approximately 50 km southwest of the St. John's field. The SVF field covers nearly 3,000 km², with a volume of 300 km² of lava from some 400 volcanic centres. This is one of many late Pliocene to Holocene, predominantly basaltic, volcanic fields which surrounds the southern margin of the Colorado Plateau (Baars, 2000). The field is characterized by two main types of mafic lavas: an older (5 - 6 Ma) Olivine pyretic basalt with an enriched lithospheric source and a younger (0.3 - 2.1 Ma) alkali basalt which reflects mixing between an enriched mantle source and an ocean-island type source (Rauzi, 1999). No igneous or volcanics were cored during exploration of the field and, prior to this work, the source of St. John's Field CO₂ had not been investigated in detail (Rauzi, 1999).

Fig. 1. Map of the Colorado Plateau illustrating the sites of major Cenozoic igneous provinces, location of the natural CO₂ reservoirs sampled and other CO₂ reservoirs within the region. (Modified from Allis et al., 2001).

Fig. 2. Plot of N₂ against ⁴He concentration for the McElmo Dome, Doe Canyon and St. John's Dome fields, showing a positive correlation between N₂ and ⁴He. This relationship is attributed to the gas phase (CO₂) stripping old groundwater containing accumulated ⁴He and N₂ (Ballentine and Sherwood Lollar 2002).

Fig. 3. Plot of $CO_2/{}^{3}$ He against CO_2 concentration for all of the reservoirs studied. All error bars are smaller than printed symbols. The shaded region highlights the range of $CO_2/{}^{3}$ He values measured in pure magmatic samples (MORB). All of the samples from the deep gas fields plot within or below this range, indicating the presence of a significant quantity of magmatic 3 He, implying a mantle origin for the CO_2 within these fields (Sherwood Lollar et al., 1999; Ballentine et al., 2001).

Fig. 4. Plot of ³He/⁴He (R/R_a) against ⁴⁰Ar/³⁶Ar for all samples. The clear correlation between ³He/⁴He and ⁴⁰Ar/³⁶Ar within Bravo Dome contrasts with the lack of variation measured in both Sheep Mountain and McElmo Dome and the anti correlation observed in McCallum.

Fig. 5. Plot of ²⁰Ne/²²Ne ratio against ²¹Ne/²²Ne for all samples. Bravo Dome exhibits mixing between a pre-mixed crust/air component and the mantle. St. Johns, Sheep Mountain and McCallum highlight mixing between a pre-mixed crust/mantle component and air. The distinct values measured from McElmo Dome show that this field contains the highest proportional contribution from crustal/radiogenic sources.

Fig. 6a. Plot of ²⁰Ne/³⁶Ar against ⁸⁴Kr/³⁶Ar for all reservoirs studied. The majority of the ²⁰Ne/³⁶Ar values lie close to the calculated ASW ratios. Sheep Mountain field shows extreme fractionation in ²⁰Ne/³⁶Ar.

Fig. 6b. Plot of ⁸⁴Kr/³⁶Ar against ¹³⁰Xe/³⁶Ar for Sheep Mountain, McElmo Dome and Bravo Dome. The Xe and Kr systems are similar in both the McElmo Dome and Sheep Mountain fields. The extreme fractionation of ²⁰Ne/³⁶Ar observed in the Sheep Mountain field is not reflected in the other elemental ratios. Bravo Dome values are corrected for mantle contributions using ⁸⁴Kr/³⁶Ar_{mntl} = 0.051 and ¹³⁰Xe/³⁶Ar_{mntl} = 0.001045 (Ballentine et al., 2005).

Fig. 7. Plot of mantle corrected ²⁰Ne/³⁶Ar_(atm) against ⁸⁴Kr/³⁶Ar_(atm) for the Bravo Dome field. Also plotted are the Air and ASW values and the calculated Rayleigh and Batch fractionation curves for a gas phase exsolving from a groundwater that has an initial ASW composition (dashed lines). The tick marks on the dashed lines represent the proportion of Ar remaining in the groundwater phase. Also plotted is the Rayleigh fractionation line which would be produced by a gas phase dissolving into a water phase initially containing no noble gases (solid line). This is the re-dissolution model discussed in the text. The **bold** tick marks on the solid fractionation line represent the proportion of Ar <u>lost</u> from the gas phase. With the exception of the ⁸⁴Kr/³⁶Ar ratio of BD11, the fractionation pattern observed in the air derived ratios can be explained by the re-dissolution model.

Fig. 8. Plot of ²⁰Ne/³⁶Ar_(atm) against ²⁰Ne_(atm) for the samples from the Bravo Dome field. Also plotted are the predicted ²⁰Ne concentration values assuming Rayleigh Fractionation of a gas phase exsolving from the groundwater. The predicted concentrations are several orders of magnitude greater than the observed concentrations, implying that the atmospheric noble gases within the reservoir have been significantly diluted, most probably by injection of magmatic CO_2 .

Fig. 9. Cartoon illustrating the two stage degassed groundwater and re-dissolution model. **Stage 1**: Magmatic CO₂ injection into the groundwater system causes the groundwater to become fully saturated in CO₂ with excess gas forming a free CO₂ gas phase. The free gas phase migrates upwards; stripping dissolved air-derived noble gases and accumulated crustal/radiogenic noble gases through CO₂/water phase partitioning. This produces a groundwater phase that is fully saturated in CO₂ and completely degassed with respect to ASW and crustal noble gases (and N₂). The CO₂ gas containing the groundwater stripped gases, on encountering a trapping structure, provides the first reservoir fluid charge. Subsequent charges of CO₂ provide no more ASW and crustal noble gases, and serve to dilute the original ASW and crustal noble gase rich CO₂. Reservoir scale preservation of concentration gradients in ASW-derived noble gases thus provide CO₂ filling direction (cf Bravo Dome, St Johns). **Stage 2**: When recharge of the gas cap stops, the noble gases will begin to re-dissolve into the gas stripped groundwater. This will result in a fractionation of the ASW-derived noble gases (Fig. 9). The magnitude of this fractionation will depend on the volume of water in contact with the gas phase and whether it is an open or closed system. Only limited CO₂ re-dissolution will occur caused for example, by a change in reservoir conditions or carbonate precipitation resulting in a reduction of the groundwater CO₂ saturation level.

Fig. 10a. Plot of ²⁰Ne/³⁶Ar against ⁸⁴Kr/³⁶Ar for the Sheep Mountain field. Also plotted are the calculated Rayleigh fractionation curve for a gas phase evolving from an ASW groundwater (dashed line) and the Rayleigh fractionation curve for gas with an ASW composition re-dissolving into degassed water containing no noble gases

(solid line). This second model accounts for the observed ²⁰Ne/³⁶Ar. However the observed ⁸⁴Kr/³⁶Ar values are up to 4 times higher than predicted, possibly as a result excess sedimentary Kr and un-resolvable mantle contributions to ⁸⁴Kr. In both figures ASW and air values are also plotted.

Fig. 10b. Plot of ²⁰Ne/³⁶Ar against ⁸⁴Kr/³⁶Ar for the McCallum field. ²⁰Ne/³⁶Ar ratios can be explained by a similar model of re-dissolution of noble gases into a previously stripped groundwater as outlined for Bravo Dome and Sheep Mountain. ⁸⁴Kr/³⁶Ar ratios are significantly above those predicted by the model which we attribute to approximately 70% excess Kr associated with the source kerogen within the field. On both figures tick marks on the dashed line represent the proportion of Ar in the gas phase, whilst those on the solid re-dissolution line indicates the proportion of Ar lost to the groundwater.

	Location	Donth	Producing						
Field & Well	Sec-Twp-Rge	(m)	Formation	³He/⁴He	²⁰ Ne/ ²² Ne	²¹ Ne/ ²² Ne	40 Ar/36 Ar	³⁸ Ar/ ³⁶ Ar	¹³⁰ Xe/ ¹³⁶ Xe
	Or Lat-Long	(11)	Tormation						
McCallum	(North McCallum)								
No. 3 (8-3)	8/9N/78W	1618	Lakota	0.354 (7)	10.10 (9)	0.0627 (8)	7049 (51)	0.186 (2)	nm
No. 5	3/9N/79W	1520	Lakota	0.409 (7)	10.17 (8)	0.0615 (5)	3893 (34)	0.193 (11)nm
No. 36	8/9N/79W		Dakota/Lakota	0.448 (8)	9.98 (6)	0.0500 (3)	2412 (17)	0.204 (4)	nm
No. 13	2/9N/79W	1625	Lakota/Morrison	0.393 (7)	10.02 (11)	0.0464 (4)	3434 (28)	0.195 (3)	nm
No. 79	4/9N/79W	1766	Dakota/Lakota	0.406 (6)	10.06 (6)	0.0454 (8)	3819 (41)	0.196 (3)	nm
Sheep Mtn									
8-2-P	2/9-28S/70W	1558	Dakota	0.981 (10)	10.14 (6)	0.0411 (4)	13839 (42)	0.184 (3)	0.422 (2)
2-10-0	15/9-27S/70W	1003	Entrada	0.984 (12)	10.08 (5)	0.0377 (2)	10745 (45)	0.185 (2)	0.421 (2)
9-26	26/9-27S/70W	1736	Dakota	0.934 (14)	10.19 (8)	0.0460 (3)	16486 (73)	0.185 (4)	0.417 (1)
2-9-H	9/9-27S/70W	930	Dakota	0.945 (19)	10.11 (6)	0.0311 (3)	4378 (23)	0.183 (6)	0.444 (4)
3-15-B	15/9-27S/70W	949	Dakota	0.937 (16)	10.11 (6)	0.0376 (3)	8746 (24)	0.187 (2)	0.430 (3)
4-13		1590	Dakota	0.942 (18)	10.20 (6)	0.0405 (3)	17314 (98)	0.186 (4)	0.416 (2)
4-26-E	26/9-27S/70W	1544	Entrada	1.024 (18)	10.29 (11)	0.0614 (3)	20783 (70)	0.185 (4)	0.412 (2)
3-23-D	22/9-27S/70W	1547	Dakota	0.988 (14)	10.15 (4)	0.0535 (3)	16812 (36)	0.185 (2)	0.418 (3)
7-35-L	2/9-28S/70W	1585	Dakota	0.916 (14)	10.23 (3)	0.0511 (3)	17594 (35)	0.186 (2)	0.414 (2)
2-35-C	26/9-27S/70W	1571	Dakota	0.963 (19)	10.29 (8)	0.0528 (3)	16574 (52)	0.183 (3)	0.426 (2)
1-15-C	15/9-27S/70W	1131	Entrada	0.967 (16)	9.94 (6)	0.0311 (3)	5194 (31)	0.185 (5)	nm
3-4-0	9/9-27S/70W	1201	Dakota	0.937 (14)	9.93 (9)	0.0342 (3)	4539 (11)	0.188 (2)	0.416 (3)
4-14-M	22/9-27S/70W	2015	Dakota	0.892 (15)	9.97 (6)	0.0404 (3)	17895 (175)	0.186 (8)	0.440 (1)
5-15-0	22/9-27S/70W	1427	Dakota	1.056 (15)	9.89 (6)	0.0319 (3)	8720 (26)	0.184 (3)	0.422 (2)
4-4-P	9/9-27S/70W	1058	Dakota	0.970 (14)	10.15 (8)	0.0440 (3)	16017 (40)	0.186 (3)	0.417 (2)
5-9-A	9/9-27S/70W	1023	Dakota	1.006 (18)	10.15 (3)	0.0428 (3)	17814 (41)	0.188 (3)	0.419 (1)
1-1-J	2/9-28S/70W	1656	Dakota	0.908 (16)	9.84 (3)	0.0407 (3)	12036 (24)	nm	nm
1-22-H	22/9-28S/70W	1528	Entrada	0.981 (17)	10.03 (2)	0.0401 (3)	10863 (70)	nm	nm
Bravo Dome									
BD01	23/19N/34E	653	Tubb	1.670 (8)	10.66 (3)	0.0562 (3)	10700 (314)	nm	nm
BD02	32/21N/35E	643	Tubb	0.764 (4)	9.96 (3)	0.0501 (3)	4654 (41)	nm	0.432 (1)
BD03	36/22N/34E	620	Tubb	0.896 (4)	10.01 (1)	0.0515 (1)	5342 (71)	nm	nm
BD04	8/20N/34E	670	Tubb	1.611 (8)	10.59 (4)	0.0541 (4)	9886 (185)	nm	0.419 (1)
BD05	34/20N/35E	644	Tubb	0.965 (5)	9.93 (1)	0.0526 (2)	5408 (38)	nm	0.430 (1)
BD06	26/22N/32E	648	Tubb	1.503 (8)	10.49 (4)	0.0561 (4)	9197 (161)	nm	nm
BD07	3/19N/33E	718	Tubb	2.104 (11)	11.20 (5)	0.0542 (4)	10923 (308)	nm	0.423 (2)
BD08	9/18N/33E	732	Tubb	1.143 (6)	10.21 (3)	0.0578 (4)	6643 (65)	nm	nm
BD09	17/21N/33E	659		1.724 (9)	10.74 (5)	0.0578 (5)	nm	nm	nm
BD10	7/22N/34E	649		1.104 (6)	10.20 (2)	0.0537(3)	6/19 (81)	nm	nm
BD11	25/19N/30E	640		3.784 (19)	11.88 (5)	0.0565 (4)	21453 (1274)	nm	nm
BD12	27/19N/30E	604		3.627 (18)	40.05 (5)	0.0570 (5)	20888 (1017)	nm	
BD13	22/18N/35E	725		1.318(7)	10.25 (5)	0.0579 (5)	7714 (220)	nm	0.425 (1)
	10/10N/34E	700		1.413(7)	10.54 (12)	0.0563(2)	0490 (020)	nm	
BD120	27/19N/30E	604	ddu'i	3.034 (18)	11.60 (6)	0.0537 (2)	22492 (2474)	nm	nm
	27 7202 400 0250	2420	التعطينالم	0.065 (1)	0 00 (0)	0.0700 (2)	9060 (1E)	0 105 (1)	0 405 (0)
	37,1392,-100.0239	2439	Leadville	0.005(1)	0.02 (0)	0.0700(3)	15441 (20)	0.103(1)	0.423(2)
	37 5052 108 0004	2040	Leadville	0.143(2) 0.149(1)	9.13(12)	0.1044(13) 0.1110(7)	14025 (141)	0.103(1)	0.421(2)
VC-4	37 4520 -108 8583	2445		0.140(1) 0.137(3)	9.03 (3) 8 70 (7)	0.1119(7)	2500 (5)	0.104(3)	0.423 (2) nm
SC-9	37 3034 -108 8733	2349		0.137(3)	8.62 (7)	0.0910(11) 0.1100(13)	16206 (37)	0.100(1) 0.186(1)	0 / 18 (3)
VB_2	37 4472 -108 8075	2386		0.130(3)	8 90 (8)	0.1109(13)	16230 (37)	0.188(1)	0.410(3)
YC-1	37 4520 -108 8583	2500		0.123(1) 0.142(2)	8.90 (6)	0.1112(0) 0.1132(5)	151/18 (27)	0.100(1)	0.423 (2) nm
	37 4871 -108 8807	2533		0.142(2) 0.160(1)	0.34(3)	0.1132(3)	14058 (75)	0.102 (1)	nm
HD-2	37 4572 -108 9008	2304		0.103(1)	8 42 (8)	0.0010(3) 0.1070(11)	20231 (651)	nm	nm
VΔ_2	37 4692 -108 7811	2429	Leadville	0.138 (3)	8 48 (15)	0.1070(11) 0.1084(20)	18407 (60)	nm	nm
VE_1	37 4818 -108 8123	2423		0.130(3) 0.173(3)	8.84 (0)	0.1004(20) 0.1147(13)	18515 (151)	nm	nm
	37 5280 -108 8718	2324		0.173 (3)	8 72 (5)	0.1147(13) 0.1062(7)	18522 (85)	nm	nm
SC-10	37 3034 -108 8733	2455	Leadville	0.139 (2)	9 15 (8)	0.1002(7)	21179 (54)	nm	nm
HC-2	37 4734 -108 8860	2455		0.139(2)	9.13(0)	0.1071(41) 0.1060(34)	21173 (34)	nm	nm
HB-1	37 5087 -108 8802	2435	Leadville	0.148(2)	8 85 (5)	0 1061 (17)	22198 (144)	nm	nm
YD_1	37 4610 . 108 8224	2430		0.145(3)	8 84 (5)	0.1006 (6)	10708 (01)	nm	nm
St John's Dome	57.4013, -100.0224	2700		0.140(3)	0.0+(0)	0.1000 (0)	13700 (81)		
22-1X	34 4265 -109 2664	655	Sunai	0 455 (8)	9 75 (9)	0 0408 (2)	1369 (13)	0 197 (3)	nm
10-22	34 2437 -100 1645	690	Sunai	0.394 (8)	9 71 (11)	0.0446(2)	1492 (15)	0 197 (2)	nm
3-1	34 3771 -109 2563	553	Supai	0 433 (9)	9 80 (3)	0.0420(3)	1687 (16)	0 193 (4)	nm
1 a orroro to los	t aignificant figure	o in broo	koto nm=net m		5.00 (0)	3.5 120 (0)		J. 100 (T)	

Table 1. Sample location, producing formation and noble gas isotope ratios

 1σ errors to last significant figure in brackets, nm=not measured

Field & Well	CO ₂ %	N₂ %	CH₄%	C ₂ H ₆ %	⁴ He (x 10 ⁻⁴) cm ³ (STP)cm ⁻³	²⁰ Ne (x 10 ⁻⁸) cm ³ (STP)cm ⁻³	⁴⁰ Ar (x 10 ⁻⁴) cm ³ (STP)cm ⁻³	⁸⁴ Kr (x 10 ⁻¹⁰ cm ³ (STP)cm ⁻³	¹³⁰ Xe (x 10 ⁻¹²))cm ³ (STP)cm ⁻³
McCallum	Mean gas	composition	from	producers			. ,		<i>,</i> , , , , , , , , , , , , , , , , , ,
No. 3 (8-3)	(92.1)	(0.34)	(5.0)	(0.39)	12.3 (2)	1.17 (2)	2.06 (1)	10.2 (3)	nm
No. 5	-	-	-	-	15.5 (2)	2.71 (3)	3.98 (2)	37.8 (7)	nm
No. 36	-	-	-	-	1.32 (12)	8.10 (8)	0.179 (8)	8.42 (5)	nm
No. 13	-	-	-	-	18.8 (2)	4.36 (5)	4.78 (2)	51.0 (5)	nm
No. 79	-	-	-	-	9.16 (21)	2.53 (3)	3.49 (2)	41.6 (4)	nm
Sheep Mtn	Mean gas	Composition	n from	Allis et al., 2001					
8-2-P	(97.0)	(0.6)	(1.7)	-	3.13 (3)	1.47 (2)	1.69 (1)	3.03 (2)	4.76 (8)
2-10-0	-	-	-	-	2.96 (3)	3.04 (3)	1.62 (1)	3.10 (3)	4.65 (8)
9-26	-	-	-	-	2.95 (3)	0.613 (9)	1.57 (2)	2.60 (1)	4.11 (7)
2-9-H	-	-	-	-	3.07 (3)	9.77 (10)	1.39 (1)	5.54 (1)	8.93 (15)
3-15-B	-	-	-	-	2.90 (3)	1.54 (2)	1.60 (2)	3.98 (7)	6.50 (11)
4-13	-	-	-	-	3.47 (4)	1.11 (2)	2.08 (2)	2.75 (3)	5.63 (10)
4-26-E	-	-	-	-	3.15 (3)	0.442 (4)	1.73 (1)	1.66 (5)	4.47 (8)
3-23-D	-	-	-	-	3.17 (3)	0.579 (9)	1.84 (2)	1.62 (3)	3.27 (6)
7-35-L	-	-	-	-	3.06 (3)	0.749 (12)	1.56 (1)	4.49 (4)	5.22 (9)
2-35-C	-	-	-	-	2.87 (3)	0.573 (8)	1.57 (1)	2.71 (5)	4.79 (8)
1-15-C	-	-	-	-	2.71 (3)	6.77 (10)	1.55 (2)	6.49 (9)	nm
3-4-0	-	-	-	-	2.99 (3)	2.64 (3)	1.57 (1)	8.61 (5)	4.89 (9)
4-14-M	-	-	-	-	3.00 (3)	1.11 (1)	1.63 (2)	1.76 (6)	1.06 (17)
5-15-0	-	-	-	-	2.92 (3)	4.33 (5)	1.51 (1)	3.69 (3)	5.44 (9)
4-4-P	-	-	-	-	2.52 (2)	1.31 (2)	1.60 (2)	2.73 (5)	5.52 (10)
5-9-A	-	-	-	-	2.94 (3)	1.28 (2)	2.06 (1)	3.05 (5)	3.15 (6)
1-1-J	-	-	-	-	2.16 (2)	0.878 (12)	1.66 (1)	5.29 (9)	nm
1-22-H	-	-	-	-	3.22 (3)	0.937 (13)	1.55 (1)	5.72 (1)	nm
Bravo Dome	Mean gas	composition	Trom (0)	Cassidy, 2006	0.044 (12)	0.160 (2)	0 202 (2)	1 01 (2)	n m
	(99.0)	(0.20)	(0)	-	0.944(12)	0.109(2)	0.303(3)	1.01(2)	0.02 (40)
	-	-	-	-	4.15(5)	0.700(7)	0.052(0)	5.04(14)	9.63 (40)
BD03	-	-	-	-	3.31(4)	0.521(5)	0.000 (0)	3.24 (0) 1.03 (3)	2 00 (0)
BD04	-	-	-	-	9.01(2)	0.101(2)	0.200 (3)	1.03 (3)	2.09 (9)
BD05	_	-			1 20 (2)	0.440(4)	0.350 (3)	1.35(0)	0.15 (25) nm
BD00	-	-	-	-	1.20(2)	0.202(2)	0.330 (3)	0.000 (36)	1 96 (10)
BD08	_	_	_	_	1 61 (2)	0.100(2) 0.264(3)	0.396 (4)	2 00 (5)	nm
BD00	_	_	_	_	0.081 (12)	0.204 (0)	nm	2.00 (0)	nm
BD10	_	-	-	-	1.99 (3)	0.308(3)	0.396 (3)	2 02 (5)	nm
BD10 BD11	_	-	-	-	0.391 (5)	0.000(0)	0 241 (4)	0.455(19)	9 94 (9)
BD12	_	-	-	-	0 415 (6)	0.100 (1)	0.242(3)	0 467 (24)	nm
BD13	-	-	-	-	1 53 (2)	0 240 (3)	0.382(4)	1.92 (5)	3 18 (6)
BD14	-	-	-	-	1 15 (2)	0 179 (4)	0.307(3)	1 23 (4)	nm
BD12b	-	-	-	-	0.413 (6)	0.120 (2)	0.240 (4)	0.490 (24)	nm
McElmo Dome					01110 (0)	0=0 (=)	0.2.00(1)	01.00 (= !)	
Doe Canyon	73.3	19.7	3.94	0.0013	501 (34)	8.08 (8)	33.1 (2)	87.7 (2)	8.55 (15)
MC-1	97.8	1.95	0.13	0.0059	9.58 (8)	0.376 (4)	2.26 (1)	5.99 (8)	9.64 (16)
HE-2	98.2	1.54	0.12	0.0065	70.5 (7)	0.307 (30)	12.1 (1)	22.1 (4)	4.53 (8)
YC-4	97.7	2.00	0.14	0.0065	10.2 (10)	0.573 (6)	2.43 (2)	21.4 (1)	nm
SC-9	97.9	1.82	0.12	0.0064	14.8 (14)	0.497 (5)	2.64 (2)	5.19 (17)	8.48 (14)
YB-2	98.1	1.72	0.12	0.0056	6.42 (61)	0.371 (4)	2.27 (2)	5.07 (13)	11.5 (19)
YC-1	97.7	2.00	0.14	0.0065	12.1 (12)	0.423 (5)	2.40 (2)	5.54 (8)	nm
HF-1	nm	nm	Nm	nm	19.3 (26)	0.564 (12)	4.00 (2)	9.54 (7)	nm
HD-2	97.7	1.98	0.15	0.0068	11.7 (12)	0.128 (2)	2.43 (2)	7.18 (7)	nm
YA-2	98.2	1.53	0.12	0.0073	15.0 (15)	0.130 (2)	2.34 (2)	5.80 (10)	nm
YE-1	98.1	1.63	0.13	0.0071	9.75 (8)	0.143 (3)	2.41 (2)	5.80 (16)	nm
HA-1	97.7	2.00	0.15	0.0061	11.0 (11)	0.205 (7)	2.95 (2)	7.29 (12)	nm
SC-10	98.1	1.64	0.11	0.0059	11.6 (11)	0.413 (5)	2.59 (2)	6.51 (5)	nm
HC-2	98.0	1.72	0.14	0.0068	10.7 (10)	0.409 (5)	2.60 (2)	5.57 (7)	nm
HB-1	97.8	1.91	0.16	0.0077	9.94 (10)	0.247 (4)	2.41 (2)	4.00 (7)	nm
YD-1	97.8	1.94	0.16	0.0072	5.68 (6)	0.366 (5)	2.26 (2)	8.25 (8)	nm
St. John's Dome				_					
22-1X	82.9	16.0	0.12	0	134 (13)	34.4 (47)	25.9 (2)	641 (10)	nm
10-22	98.9	1.0	0.012	0	9.42 (9)	2.30 (4)	2.52 (2)	67.6 (2)	nm
3-1	91./	8.0	0.0634	U	70.6 (7)	15.1 (21)	11.7 (1)	290 (9)	nm
10 errors to last	t significar	nt figure in	brackets	, nm=not mea	asured				

Table 2. Gas Composition (%) and noble gas isotope concentrations (cm³STP/cm³)

		-		36 •			
Field & Well McCallum Dome	Observed ²⁰ Ne/ ³⁶ Ar	³⁶ Ar lost to stage 2 water	Measured ³⁵ Ar cm ³ (STP)cm ⁻³ (x 10 ⁻⁸)	^{°°} Ar _{init} cm ³ (STP)cm ⁻³ (x 10 ⁻⁸)	Stage 1 V _{water} /V _{Gas} (STP)	Stage 2 V _{water} /V _{Gas} (STP)	Stage2 V _{water} /V _{Gas} (RTP)
No. 5	0.462	0.888	2.54	22.6	0.2054	1.487	85.61
No. 36	0.305	0.745	8.91	34.9	0.3169	2.595	49.06
No. 13	0.358	0.815	12.2	65.7	0.5960	2.002	63.59
No. 79	0.312	0.757	8.09	33.3	0.3024	2.418	52.65
Sheep Mtn							
8-2-P	1.209	0.933	1.22	18.2	0.1652	0.967	107.93
2-10-O	2.014	0.973	1.51	56.6	0.5130	1.295	144.56
9-26	0.645	0.792	0.950	4.58	0.0415	0.562	62.77
2-9-H	3.076	0.988	3.18	255	2.3173	1.570	175.20
3-15-B	0.843	0.872	1.83	14.3	0.1294	0.734	81.88
4-13	0.927	0.892	1.20	11.1	0.1010	0.796	88.85
4-26-E	0.530	0.704	0.835	2.82	0.0256	0.436	48.61
3-23-D	0.535	0.710	1.08	3.72	0.0338	0.442	49.36
7-35-L	0.922	0.891	0.812	7.45	0.0676	0.792	88.43
2-35-C	0.675	0.809	0.849	4.44	0.0403	0.591	65.96
1-15-C	2.263	0.978	0.299	138	1.2555	1.372	153.09
3-4-0	0.762	0.846	0.346	22.5	0.2040	0.669	74.70
4-14-M	1.216	0.934	0.911	13.8	0.1249	0.971	108.35
5-15-O	2.496	0.982	0.173	95.7	0.8678	1.435	160.11
4-4-P	1.311	0.942	0.998	17.3	0.1566	1.019	113.76
5-9-A	1.104	0.921	1.16	14.7	0.1332	0.907	101.27
1-1-J	0.635	0.787	1.38	6.48	0.0588	0.552	61.66
1-22-H	0.658	0.800	1.42	7.11	0.0645	0.575	64.21
Bravo Dome							
BD01	0.362	0.786	0.212	0.992	0.0090	1.261	87.01
BD02	0.426	0.841	1.25	7.87	0.0714	1.502	103.60
BD03	0.430	0.843	0.881	5.62	0.0510	1.513	104.39
BD04	0.406	0.826	0.222	1.27	0.0115	1.429	98.57
BD05	0.385	0.809	0.873	4.56	0.0414	1.351	93.24
BD06	0.349	0.772	0.299	1.31	0.0119	1.206	83.23
BD07	0.279	0.661	0.191	0.562	0.0051	0.883	60.95
BD08	0.314	0.726	0.505	1.84	0.0167	1.057	72.94
BD09			o			4 000	0.00
BD10	0.395	0.818	0.499	2.73	0.0248	1.389	95.83
BD11	0.152	0.00	0.0549	0.0547	0.0005		0.00
BD12	0.247	0 770	0.406	1 76	0.0160	1 100	0.00
	0.347	0.770	0.400	1.70	0.0100	1.199	02.73
	0.290	0.095	0.290	0.946	0.0000	0.909	00.00
DD 120 MaElma Dama	0.430	0.043	0.0494	0.315	0.0029	1.015	104.39
	0 107	0 427	11 1	71 7	0 6505	0 132	24 91
	0.197	0.427	1 /6	1 1.1	0.0303	0.132	50.42
HF-2	0.354	0.840	8.66	54 1	0.0413	0.434	81 53
VC-4	0.061	0.040	0.00	0.34	0.4912	0.434	0.00
SC-9	0.307	0.000	1.62	7 44	0.0674	0 361	67.82
VB-2	0.253	0.700	1.02	4 42	0.0074	0.262	49.18
VC-1	0.255	0.000	1.58	5 36	0.0486	0.288	54 16
HF-1	0.198	0.430	2.85	5.00	0.0453	0.133	25.01
HD-2	0.106	0.000	1 20	1 20	0.0109	0.100	0.00
YA-2	0.103	0.000	1.20	1.20	0.0115		0.00
YF-1	0 110	0.000	1.30	1.30	0.0118		0.00
HA-1	0.128	0.000	1.59	1.59	0.0145		0.00
SC-10	0.338	0.823	1 22	6.91	0.0627	0 409	76 95
HC-2	0.389	0.870	1.05	8.07	0 0732	0 482	90.56
HB-1	0 228	0.584	1.08	2 61	0.0236	0 207	38.96
YD-1	0.319	0 799	1 15	5.73	0.0520	0.380	71 43
St. John's Dome	0.010	0.100			0.0020		
22-1X	0.182	0.320	189	278	2,5251	0.289	14.89
10-22	0.136	0.000	16.9	16.9	0.1534		0.00
3-1	0.219	0.544	69.2	152	1.3784	0.592	30.53
	-	-				-	

Table 3: Calculated groundwater noble gas concentrations (cm³STPcm⁻³) and ratios

Reservoir	Average Depth (m)	Pressure (MPa)	Bore Hole Temp (K)	TDS (mg/l)	KNe (GPa)	KAr (GPa)	KKr (GPa)	KXe (GPa)
Bravo Dome ^a	820	8.03	314	85000	18.57	8.16	5.49	3.80
McCallum Dome ^c	1630	15.97	333	13300	13.33	6.56	4.86	3.28
McElmo Dome [♭]	2450	24.00	344	20000	13.08	7.06	5.48	3.79
Sheep Mountain ^c	1400	13.71	331	800	12.79	6.10	4.43	3.05
St. Johns Dome ^b	630	6.17	322	4210	13.35	5.78	3.82	2.71

Table 4: Reservoir Conditions Used in Models

^a Broadhead (1993) ^b Stevens et al., (2004) ^c Field Operators

Figure captions for appendix

Fig. A1. Top surface map of the Tubb sandstone at Bravo Dome showing the folded and faulted structure of the field. Also shown is the approximate location of the gas/water contact which is poorly defined to the southwest. Contours are in feet above Mean Sea Level (MSL). Figure modified from Cassidy, (2006).

Fig. A2. Structure map of the top Dakota Formation illustrating the well locations sampled for this study and the complex folded and thrusted reservoir geology. Contours are in feet above MSL. The gas water contact is located at approximately 4000 feet across the reservoir. Figure modified from Roth (1983).

Fig. A3. Top surface map of the Leadville limestone at McElmo Dome showing the faulted complex structure of the field, approximate position of the gas/water contact and the wide distribution of wells sampled in this study. Contours are in feet below mean sea level. (Modified from Stevens, 2004).

Fig. A4. Top surface map of Permian Supai formation at St. John's Dome showing the faulted anticlinal structure of the field and the position of the three wells sampled in this study. Contours are in feet above mean sea level. (Modified from Rauzi, 1999 by Reddy).





Figure 2



Figure 3



Figure 4







Figure 6a



Figure 6b



Figure 7



Figure 8











Figure 10b



Figure A1



Figure A2



Figure A3





