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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. John's 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 to 10 ka and are associated with the Bravo Dome field. The oldest magmatic activity dates from 42 to 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. John's 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 cm³ groundwater/cm³ gas (STP) in one Bravo Dome sample, to 2.56 cm³ groundwater/cm³ gas (STP) in a St. John's Dome sample. Subsequent gas/groundwater equilibration varies within all fields, each showing a similar range, from zero to ~100 cm³ water/cm³ gas (at reservoir pressure and temperature).

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1. INTRODUCTION

Carbon dioxide (CO₂) has been identified as the most important compound currently affecting the stability of the Earth's climate (Intergovernmental Panel on Climate Change, 1996, 2001, 2007). Geologic storage of anthropogenic CO₂ in depleted oil and gas reservoirs is one of the key options for short-term control of CO₂ emissions. However, CO₂ 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 CO₂ 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 decarboxylation, hydrocarbon oxidation, decarbonation of marine carbonates and degassing of magmatic bodies (Jenden et al., 1993; Wycherley et al., 1999). $\delta^{13}\text{C}(\text{CO}_2)$ can be used to distinguish between some of these different sources. However, the $\delta^{13}\text{C}(\text{CO}_2)$ 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 et al., 2006) 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., 1996; Torgeresen and Kennedy, 1999; Ballentine and Sherwood Lollar, 2002; Zhou et al., 2005).

Whilst primordial noble gas isotopes have been studied in CO₂-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 CO₂ 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 CO₂ from five separate producing gas fields located throughout the Colorado Plateau and Rocky Mountain provinces. In this paper we show how measured CO₂/³He ratios enable us to determine the CO₂ source in each system. We then use the noble gases to identify the subsurface processes acting on the CO₂ 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 and 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 and 1 Ma

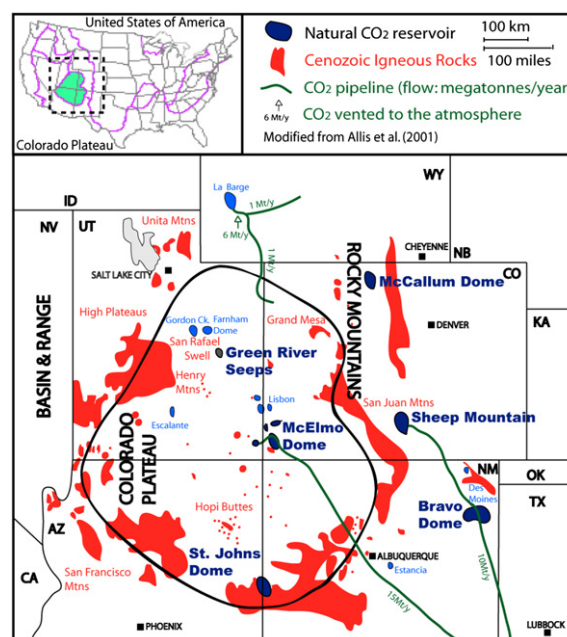


Fig. 1. Map of the Colorado Plateau illustrating the sites of major Cenozoic igneous provinces, location of the natural CO₂ reservoirs sampled and other CO₂ reservoirs within the region.

(Parsons and McCarthy, 1995). The province contains at least nine producing or abandoned gas fields that contain up to 2800 billion m³ 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. John's 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-in. National Pipe Thread (NPT) sample port of the wellhead 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 min before the outer valve was shut and the cylinder equilibrated at wellhead pressure, which ranged from 1400 to 3500 Pa. The cylinder valve closest to the wellhead 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 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. After evacuation of the He from the spectrometer, Ne was expanded onto a charcoal trap at 77.3 K, to remove any residual ⁴⁰Ar and reduce interference on the ²⁰Ne measurements, and then 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 1σ 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

CO₂ concentrations in all fields typically range from 92% to 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. John's 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 through degassing (Ballentine and Sherwood Lollar, 2002).

4.2. CO₂/³He ratios and CO₂ origins

Fig. 3 shows CO₂/³He ratios plotted against CO₂ concentration for all of the CO₂ gas fields. All of the samples from the gas fields have CO₂/³He ratios within or below the MORB range of 1 × 10⁹ to 1 × 10¹⁰ (Marty and Jambon, 1987). This is quite distinct from the higher CO₂/³He values predicted for near ³He-free carbonates (Sherwood Lollar et al., 1997; Ballentine et al., 2001). The origin of the CO₂ in all fields, with the exception of the well studied Bravo Dome, has previously been thought to be the result of thermal breakdown of carbonates. Our new results conclusively show that a significant proportion of the CO₂, if not all, is magmatic in origin. Whilst we believe the CO₂ 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 CO₂/³He ratios. The CO₂/³He ratios that are significantly lower than the MORB range in the St. John's Dome and Doe Canyon fields can only be ascribed to CO₂ 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 ³He/⁴He 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 ⁴He 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 ⁴He concentration and a correlated reduction in the ³He/⁴He ratio. This pattern contrasts with St. John's Dome (0.394 to 0.455 R_a). ³He/⁴He ratios increase across the St. John's field toward the gas/groundwater contact, the increase in ³He/⁴He corresponds with a significant increase in ⁴He concentration. ³He/⁴He 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 ⁴He.

4.3.2. Neon

Within Bravo and St. John's 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 McElmo 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.

Fig. 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 (²⁰Ne/²²Ne_{air} = 9.80, ²¹Ne/²²Ne_{air} = 0.029, ²⁰Ne/²²Ne_{mantl} = 12.5, ²¹Ne/²²Ne_{mantl} = 0.06, ²⁰Ne/²²Ne_{crust} = 0.30, ²¹Ne/²²Ne_{crust} = 0.52 (Ballentine et al., 2002; Ballentine et al., 2005)). The range of calculated average ⁴He/²¹Ne_{crust}

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

Field & well	Location Sec-Twp-Rge or Lat-Long	Depth (m)	Producing formation	³ He/ ⁴ He (<i>R/R_a</i>)	²⁰ Ne/ ²² Ne	²¹ Ne/ ²² Ne	⁴⁰ Ar/ ³⁶ Ar	³⁸ Ar/ ³⁶ Ar	¹³⁰ Xe/ ¹³⁶ Xe
<i>McCallum</i> (North McCallum)									
No. 3 (8-3)	8/9N/78W	1618	Lakota	0.354 (7)	10.10 (9)	0.0627 (8)	7049 (124)	0.186 (3)	nm
No. 5	3/9N/79W	1520	Lakota	0.409 (7)	10.17 (8)	0.0615 (5)	3894 (84)	0.193 (11)	nm
No. 36	8/9N/79W		Dakota/Lakota	0.448 (8)	9.98 (6)	0.0500 (3)	2412 (43)	0.204 (5)	nm
No. 13	2/9N/79W	1625	Lakota/Morrison	0.393 (7)	10.02 (11)	0.0464 (4)	3451 (63)	0.195 (3)	nm
No. 79	4/9N/79W	1766	Dakota/Lakota	0.406 (6)	10.06 (6)	0.0454 (8)	3884 (90)	0.196 (4)	nm
<i>Sheep Mtn</i>									
8-2-P	2/9-28S/70W	1558	Dakota	0.981 (10)	10.14 (6)	0.0411 (4)	13839 (42)	0.187 (5)	0.422 (4)
2-10-O	15/9-27S/70W	1003	Entrada	0.984 (12)	10.08 (5)	0.0377 (2)	10744 (39)	0.186 (3)	0.421 (2)
9-26	26/9-27S/70W	1736	Dakota	0.934 (14)	10.19 (8)	0.0460 (3)	16486 (68)	0.188 (8)	0.417 (1)
2-9-H	9/9-27S/70W	930	Dakota	0.945 (19)	10.11 (6)	0.0311 (3)	4378 (21)	0.186 (11)	0.444 (5)
3-15-B	15/9-27S/70W	949	Dakota	0.937 (16)	10.11 (6)	0.0376 (3)	8746 (19)	0.190 (3)	0.430 (3)
4-13		1590	Dakota	0.942 (18)	10.20 (6)	0.0405 (3)	17293 (92)	0.189 (7)	0.416 (3)
4-26-E	26/9-27S/70W	1544	Entrada	1.024 (18)	10.29 (11)	0.0614 (3)	20785 (49)	0.188 (8)	0.412 (2)
3-23-D	22/9-27S/70W	1547	Dakota	0.988 (14)	10.15 (4)	0.0535 (3)	17026 (48)	0.187 (5)	0.418 (3)
7-35-L	2/9-28S/70W	1585	Dakota	0.916 (14)	10.23 (3)	0.0511 (3)	17591 (34)	0.188 (5)	0.414 (2)
2-35-C	26/9-27S/70W	1571	Dakota	0.963 (19)	10.29 (8)	0.0528 (3)	16567 (49)	0.186 (5)	0.426 (2)
1-15-C	15/9-27S/70W	1131	Entrada	0.967 (16)	9.94 (6)	0.0311 (3)	5194 (31)	0.188 (9)	nm
3-4-O	9/9-27S/70W	1201	Dakota	0.937 (14)	9.93 (9)	0.0342 (3)	4538 (10)	0.190 (3)	0.416 (3)
4-14-M	22/9-27S/70W	2015	Dakota	0.892 (15)	9.97 (6)	0.0404 (3)	17895 (174)	0.189 (16)	0.440 (1)
5-15-O	22/9-27S/70W	1427	Dakota	1.056 (15)	9.89 (6)	0.0319 (3)	8720 (25)	0.187 (6)	0.422 (2)
4-4-P	9/9-27S/70W	1058	Dakota	0.970 (14)	10.15 (8)	0.0440 (3)	16011 (37)	0.189 (6)	0.417 (2)
5-9-A	9/9-27S/70W	1023	Dakota	1.006 (18)	10.15 (3)	0.0428 (3)	17813 (38)	0.190 (5)	0.419 (2)
1-1-J	2/9-28S/70W	1656	Dakota	0.908 (16)	9.84 (3)	0.0407 (3)	12038 (22)	nm	nm
1-22-H	22/9-28S/70W	1528	Entrada	0.981 (17)	10.03 (2)	0.0401 (3)	10864 (69)	nm	nm
<i>Bravo Dome</i>									
BD01	23/19N/34E	653	Tubb	1.670 (8)	10.66 (3)	0.0562 (3)	10723 (393)	nm	nm
BD02	32/21N/35E	643	Tubb	0.764 (4)	9.96 (3)	0.0501 (3)	4660 (59)	nm	0.432 (1)
BD03	36/22N/34E	620	Tubb	0.896 (4)	10.01 (1)	0.0515 (1)	5346 (92)	nm	nm
BD04	8/20N/34E	670	Tubb	1.611 (8)	10.59 (4)	0.0541 (4)	9911 (237)	nm	0.419 (1)
BD05	34/20N/35E	644	Tubb	0.965 (5)	9.93 (1)	0.0526 (2)	5412 (56)	nm	0.430 (1)
BD06	26/22N/32E	648	Tubb	1.503 (8)	10.49 (4)	0.0561 (4)	9213 (206)	nm	nm

BD07	3/19N/33E	718	Tubb	2.104 (11)	11.20 (5)	0.0542 (4)	10955 (387)	nm	0.423 (2)
BD08	9/18N/33E	732	Tubb	1.143 (6)	10.21 (3)	0.0578 (4)	6650 (90)	nm	nm
BD09	17/21N/33E	659	Tubb	1.724 (9)	10.74 (5)	0.0578 (5)	nm	nm	nm
BD10	7/22N/34E	649	Tubb	1.104 (6)	10.20 (2)	0.0537 (3)	6726 (106)	nm	nm
BD11	25/19N/30E	640	Tubb	3.784 (19)	11.88 (5)	0.0565 (4)	21560 (1591)	nm	nm
BD12	27/19N/30E	604	Tubb	3.627 (18)			21019 (1297)	nm	nm
BD13	22/18N/35E	725	Tubb	1.318 (7)	10.25 (5)	0.0579 (5)	7735 (277)	nm	0.425 (1)
BD14	16/18N/34E	766	Tubb	1.413 (7)	10.54 (12)	0.0583 (2)	8517 (645)	nm	nm
BD12b	27/19N/30E	604	Tubb	3.634 (18)	11.60 (6)	0.0537 (2)	22612 (3061)	nm	nm
<i>McElmo Dome</i>									
Doe Canyon	37.7392, -108.8259		Leadville	0.065 (1)	8.82 (8)	0.0788 (3)	8069 (15)	0.188 (1)	0.425 (2)
MC-1	37.4155, -108.7713	2439	Leadville	0.145 (2)	9.13 (12)	0.1044 (15)	15441 (30)	0.186 (1)	0.421 (2)
HE-2	37.5052, -108.9094	2543	Leadville	0.148 (1)	9.05 (5)	0.1119 (7)	14025 (141)	0.187 (3)	0.423 (2)
YC-4	37.4529, -108.8583	2443	Leadville	0.137 (3)	8.70 (7)	0.0910 (11)	2599 (5)	0.191 (1)	nm
SC-9	37.3934, -108.8733	2349	Leadville	0.150 (3)	8.62 (7)	0.1109 (13)	16296 (37)	0.188 (1)	0.418 (3)
YB-2	37.4472, -108.8075	2398	Leadville	0.125 (1)	8.90 (8)	0.1112 (6)	15513 (33)	0.190 (1)	0.423 (2)
YC-1	37.4529, -108.8583	2386	Leadville	0.142 (2)	8.94 (5)	0.1132 (5)	15148 (27)	0.186 (1)	nm
HF-1	37.4871, -108.8807	2509	Leadville	0.169 (1)	9.47 (10)	0.0810 (9)	14058 (75)	nm	nm
HD-2	37.4572, -108.9008	2533	Leadville	0.140 (3)	8.42 (8)	0.1070 (11)	20231 (651)	nm	nm
YA-2	37.4692, -108.7811	2394	Leadville	0.138 (3)	8.48 (15)	0.1084 (20)	18497 (69)	nm	nm
YE-1	37.4818, -108.8123	2429	Leadville	0.173 (3)	8.84 (9)	0.1147 (13)	18515 (151)	nm	nm
HA-1	37.5289, -108.8718	2524	Leadville	0.139 (3)	8.72 (5)	0.1062 (7)	18522 (85)	nm	nm
SC-10	37.3934, -108.8733		Leadville	0.139 (2)	9.15 (8)	0.1071 (41)	21179 (54)	nm	nm
HC-2	37.4734, -108.8860	2455	Leadville	0.140 (2)	9.21 (7)	0.1069 (34)	24744 (96)	nm	nm
HB-1	37.5087, -108.8802	2451	Leadville	0.148 (3)	8.85 (5)	0.1061 (17)	22198 (144)	nm	nm
YD-1	37.4619, -108.8224	2435	Leadville	0.145 (3)	8.84 (5)	0.1006 (6)	19708 (91)	nm	nm
<i>St. John's Dome</i>									
22-1X	34.4265, -109.2664	655	Supai	0.455 (8)	9.75 (9)	0.0408 (2)	1369 (13)	0.197 (3)	nm
10-22	34.2437, -109.1645	690	Supai	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 σ errors to last significant figure in brackets. nm, not measured.

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

Field & well	CO ₂ %	N ₂ %	CH ₄ %	C ₂ H ₆ %	⁴ He (× 10 ⁻⁴)cm ³ (STP)cm ⁻³	²⁰ Ne (× 10 ⁻⁸)cm ³ (STP)cm ⁻³	⁴⁰ Ar (× 10 ⁻⁴)cm ³ (STP)cm ⁻³	⁸⁴ Kr (× 10 ⁻¹⁰) cm ³ (STP)cm ⁻³	¹³⁶ Xe (× 10 ⁻¹²)cm ³ (STP)cm ⁻³
<i>McCallum mean gas composition from producers</i>									
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	—	—	—	—	15.6 (2)	2.71 (3)	3.98 (2)	37.8 (7)	nm
No. 36	—	—	—	—	1.32 (2)	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
<i>Sheep Mtn mean gas composition from Allis et al. (2001)</i>									
8-2-P	(97.0)	0.6	(1.7)	—	3.13 (3)	1.47 (2)	1.69 (1)	3.03 (25)	4.76 (8)
2-10-O	—	—	—	—	2.96 (3)	3.04 (3)	1.62 (1)	3.10 (30)	4.65 (8)
9-26	—	—	—	—	2.95 (3)	0.613 (10)	1.57 (2)	2.60 (15)	4.11 (7)
2-9-H	—	—	—	—	3.07 (3)	9.77 (10)	1.39 (1)	5.54 (144)	8.93 (15)
3-15-B	—	—	—	—	2.90 (3)	1.54 (2)	1.60 (2)	3.98 (75)	6.50 (11)
4-13	—	—	—	—	3.47 (4)	1.11 (2)	2.08 (2)	2.75 (32)	5.63 (10)
4-26-E	—	—	—	—	3.15 (3)	0.442 (5)	1.73 (1)	1.66 (47)	4.47 (8)
3-23-D	—	—	—	—	3.17 (3)	0.579 (9)	1.84 (2)	1.62 (30)	3.27 (6)
7-35-L	—	—	—	—	3.06 (3)	0.749 (12)	1.43 (1)	4.49 (44)	5.22 (9)
2-35-C	—	—	—	—	2.87 (3)	0.573 (8)	1.41 (1)	2.71 (48)	4.79 (8)
1-15-C	—	—	—	—	2.71 (3)	6.77 (10)	1.55 (2)	6.49 (90)	nm
3-4-O	—	—	—	—	2.99 (3)	2.64 (3)	1.57 (1)	8.61 (54)	4.89 (9)
4-14-M	—	—	—	—	3.00 (3)	1.11 (1)	1.63 (2)	1.76 (63)	10.6 (17)
5-15-O	—	—	—	—	2.92 (3)	4.33 (5)	1.51 (1)	3.69 (34)	5.44 (9)
4-4-P	—	—	—	—	2.52 (2)	1.31 (2)	1.60 (2)	2.73 (50)	5.52 (10)
5-9-A	—	—	—	—	2.94 (3)	1.28 (2)	2.06 (1)	3.05 (49)	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 (14)	1.55 (1)	5.72 (11)	nm
<i>Bravo Dome mean gas composition from Cassidy (2006)</i>									
BD01	(99.6)	(0.20)	(0)	—	0.944 (12)	0.169 (2)	0.303 (3)	1.01 (4)	nm
BD02	—	—	—	—	4.15 (5)	0.700 (7)	0.652 (6)	5.04 (14)	9.83 (40)
BD03	—	—	—	—	3.31 (4)	0.521 (5)	0.536 (5)	3.24 (8)	nm
BD04	—	—	—	—	0.961 (2)	0.181 (2)	0.286 (3)	1.03 (3)	2.09 (9)
BD05	—	—	—	—	2.70 (4)	0.446 (4)	0.538 (5)	3.33 (8)	6.15 (25)
BD06	—	—	—	—	1.20 (2)	0.202 (2)	0.350 (3)	1.35 (4)	nm

BD07	—	—	—	—	0.781 (10)	0.180 (2)	0.280 (3)	0.900 (36)	1.96 (10)
BD08	—	—	—	—	1.61 (2)	0.264 (3)	0.396 (4)	2.00 (5)	nm
BD09	—	—	—	—	0.981 (12)	0.180 (2)	nm	nm	nm
BD10	—	—	—	—	1.99 (3)	0.308 (3)	0.396 (3)	2.02 (5)	nm
BD11	—	—	—	—	0.391 (5)	0.103 (2)	0.241 (4)	0.455 (19)	9.94 (9)
BD12	—	—	—	—	0.415 (6)	—	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
<i>McElmo Dome</i>									
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)	3.01 (3)	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 (7)	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	98.1	1.72	0.14	0.0068	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
<i>St. John's Dome</i>									
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	91.7	8.0	0.0634	0	70.6 (7)	15.1 (21)	11.7 (1)	290 (9)	nm

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

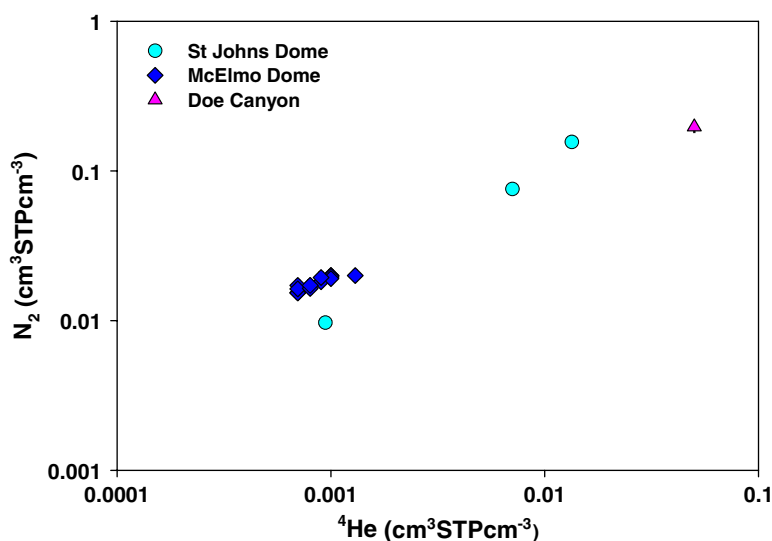


Fig. 2. Plot of N_2 against 4He concentration for the McElmo Dome, Doe Canyon and St. John's Dome fields, showing a positive correlation between N_2 and 4He . This relationship is attributed to the gas phase (CO_2) stripping old groundwater containing accumulated 4He and N_2 (Ballentine and Sherwood Lollar, 2002).

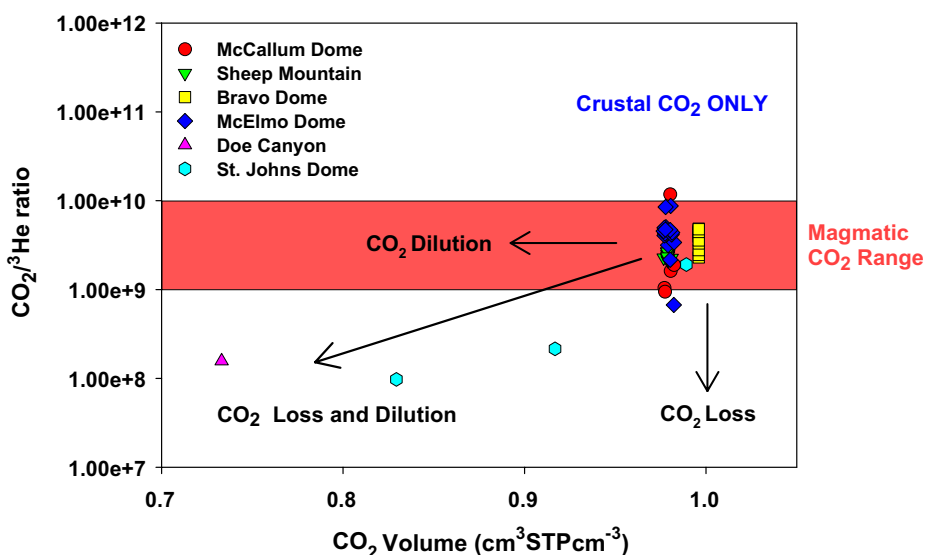


Fig. 3. Plot of $CO_2/{}^3He$ against CO_2 concentration for all of the reservoirs studied. All error bars are smaller than printed symbols. The shaded region highlights the range of $CO_2/{}^3He$ values measured in pure magmatic samples (MORB). All of the samples from the gas reservoirs plot within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

values of 2.89×10^7 to 5.08×10^7 within all of the fields are higher than both the measured average crust value of 1.71×10^7 and theoretical estimates of between 2.02 and 2.64×10^7 (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 except Sheep Mountain ${}^{40}Ar$ correlates directly with 4He and ${}^{20}Ne$. A similar relationship exists between ${}^{36}Ar$ and ${}^{20}Ne$ within all the reservoirs and is particularly strong within Bravo, McCallum and St.

John's Dome. As with ${}^{20}Ne$, ${}^{36}Ar$ increases with proximity to the gas/groundwater contact.

Measured ${}^{40}Ar/{}^{36}Ar$ ratios from all of the reservoirs are considerably above the air value of 295.5, as a result of a resolvable excess of ${}^{40}Ar$ (${}^{40}Ar^*$) (Fig. 4). Helium isotopes indicate both mantle and crustal contributions to the noble gases, the ${}^{40}Ar^*$ is therefore a mixture of mantle and crustal-derived ${}^{40}Ar$. In the case of Bravo Dome, ${}^{40}Ar^*/{}^4He$ correlates with ${}^3He/{}^4He$ isotope variation with a correlation coefficient of 0.993 (Ballentine et al., 2005). Extrapolating to ${}^3He/{}^4He_{crust} = 1 \times 10^{-8}$ (Ballentine and Burnard, 2002) resolves ${}^4He/{}^{40}Ar_{crust} = 22.0$. This is significantly above

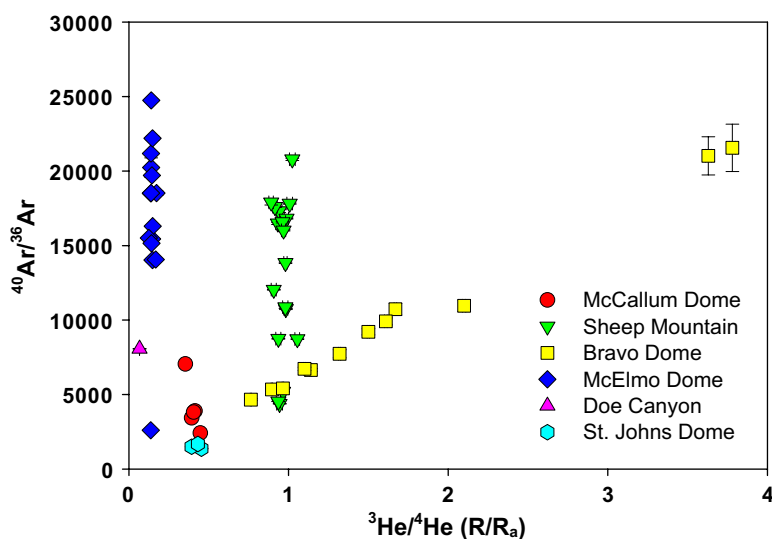


Fig. 4. Plot of ³He/⁴He (*R/R_a*) against ⁴⁰Ar/³⁶Ar for all samples. The clear correlation between ³He/⁴He and ⁴⁰Ar/³⁶Ar within Bravo Dome contrasts with the lack of variation measured in both Sheep Mountain and McElmo Dome and the anti correlation observed in McCallum.

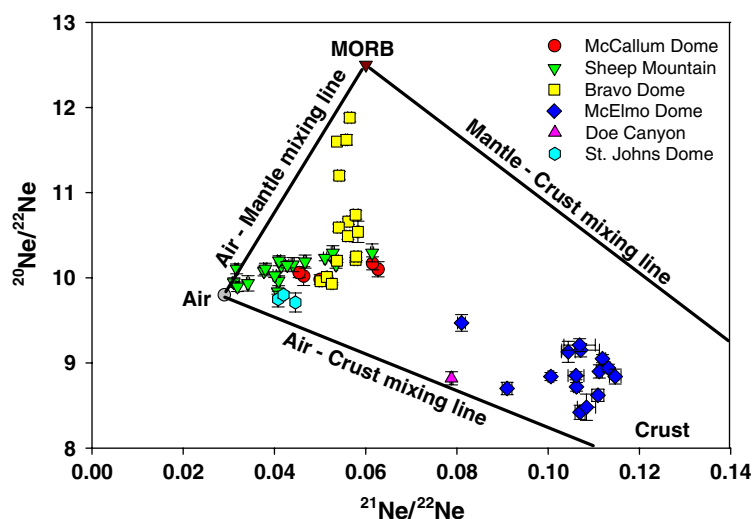


Fig. 5. Plot of ²⁰Ne/²²Ne ratio against ²¹Ne/²²Ne for all samples. Bravo Dome exhibits mixing between a pre-mixed crust/air component and the mantle. St. John's, Sheep Mountain and McCallum highlight mixing between a pre-mixed crust/mantle component and air. The distinct values measured from McElmo Dome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

average crustal production of $^4\text{He}/^{40}\text{Ar}_{\text{crust}} = 5$ and is consistent with the resolved $^4\text{He}/^{21}\text{Ne}_{\text{crust}}$ 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 ($^{40}\text{Ar}_{\text{crust} + \text{mantle}}$).

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 and groundwater noble gas components

⁸⁴Kr in all fields correlate with ³⁶Ar and also with ²⁰Ne within Bravo, McCallum and St. John's Domes. In both St. John's 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.

^{130}Xe within Bravo Dome exhibits a similar increase as observed in ^{20}Ne , ^{36}Ar and ^{84}Kr on moving eastwards towards the gas/water contact.

^{20}Ne and ^{36}Ar within crustal fluids are dominantly derived from the atmosphere, dissolved in groundwater at recharge (Ballentine et al., 2002). Nevertheless, in these mantle-derived CO_2 fluids, mantle and crustal ^{20}Ne and to a lesser extent ^{36}Ar may be present. Using the Ne isotope resolution technique outlined by Ballentine (1997) the atmospheric contribution to ^{20}Ne for each sample can be resolved. Within Bravo Dome a plot of $I/^{22}\text{Ne}$ vs $^{20}\text{Ne}/^{22}\text{Ne}$ vs $^{21}\text{Ne}/^{22}\text{Ne}$, 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 $^{36}\text{Ar}_{(\text{atm})}$ 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 ^{20}Ne mantle contribution to these fields is $\sim 10\%$. This is small compared to the range of observed $^{20}\text{Ne}/^{36}\text{Ar}$ and we make the simplifying assumption that ^{20}Ne and ^{36}Ar is entirely groundwater-derived. Observed (mantle-corrected in the case of Bravo Dome) $^{20}\text{Ne}/^{36}\text{Ar}$ ratios are compiled in Table 3.

Bravo Dome $^{20}\text{Ne}/^{36}\text{Ar}_{(\text{atm})}$ values range between 0.314 and 0.617 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 exhibit $^{20}\text{Ne}/^{36}\text{Ar}$ ranging from below ASW at 0.061, to 0.389, similar to the upper limit of Bravo Dome. McCallum Dome $^{20}\text{Ne}/^{36}\text{Ar}$ ratios range from 0.266 up to 0.403, again similar to the Bravo Dome upper limit, while St. John's 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 $^{20}\text{Ne}/^{36}\text{Ar}$ ratios in the range of 0.530 to 1.31. However, four samples show $^{20}\text{Ne}/^{36}\text{Ar}$ values ranging from 2.01 to 3.08. Similar extreme values have been observed before in natural gases with $^{20}\text{Ne}/^{36}\text{Ar}_{(\text{atm})}$ values up to 1.4 in $\text{CO}_2\text{-N}_2$ rich gases in the Indus Basin (Battani et al., 2000) and up to $^{20}\text{Ne}/^{36}\text{Ar}_{(\text{atm})}$ 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 $^{20}\text{Ne}/^{36}\text{Ar}$ in the gas phase from ASW are discussed in Section 5.1.

Similar to ^{36}Ar , ^{84}Kr in Bravo Dome samples can also be corrected for non-atmosphere (mantle) contributions using the Ne isotope system to define the $^{84}\text{Kr}/^{36}\text{Ar}_{\text{mntl}}$ ratio (0.051). ^{84}Kr in all other gas fields and ^{130}Xe in all gas fields are assumed to be dominantly atmospheric in origin. $^{84}\text{Kr}/^{36}\text{Ar}$ vs $^{20}\text{Ne}/^{36}\text{Ar}$ and $^{84}\text{Kr}/^{36}\text{Ar}$ vs $^{130}\text{Xe}/^{36}\text{Ar}$ is shown in Fig. 6a and b, respectively. Mantle corrected $^{84}\text{Kr}/^{36}\text{Ar}$ ratios in Bravo Dome range from 0.013 to 0.026 compared with the ASW value of 0.045. A wider range in $^{84}\text{Kr}/^{36}\text{Ar}$ is observed in St. John's Dome, McElmo Dome and McCallum Dome with $^{84}\text{Kr}/^{36}\text{Ar}$ ratios varying from 0.022 to 0.072 over a relatively narrow $^{20}\text{Ne}/^{36}\text{Ar}$ range. In contrast, with the exception of a few samples, the majority of Sheep Mountain data exhibit a

small range in $^{84}\text{Kr}/^{36}\text{Ar}$ ratios. The samples showing the greatest $^{20}\text{Ne}/^{36}\text{Ar}$ fractionation exhibit $^{84}\text{Kr}/^{36}\text{Ar}$ 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 $^{84}\text{Kr}/^{36}\text{Ar}$ and increasing $^{130}\text{Xe}/^{36}\text{Ar}$ (Fig. 6b). $^{130}\text{Xe}/^{36}\text{Ar}$ ratios from Bravo Dome exhibit a similarly narrow range to that observed in the $^{84}\text{Kr}/^{36}\text{Ar}$ (Fig. 6b).

4.3.5. Fractionation of groundwater and crustal-derived noble gases

The fractionation observed in the $^{20}\text{Ne}/^{36}\text{Ar}$ ratios within Bravo Dome and McCallum Dome correlates to some fractionation of the $^4\text{He}/^{40}\text{Ar}_{(\text{crust} + \text{mantle})}$, and to a lesser degree the $^4\text{He}/^{21}\text{Ne}_{(\text{crust} + \text{mantle})}$ ratios. Within Bravo Dome $^4\text{He}/^{40}\text{Ar}_{(\text{crust} + \text{mantle})}$ ratios range from 1.64 to 6.79, a fourfold increase, whereas the $^4\text{He}/^{21}\text{Ne}_{(\text{crust} + \text{mantle})}$ ratios double, from 8.90×10^7 to 2.19×10^7 . $^4\text{He}/^{40}\text{Ar}_{(\text{crust} + \text{mantle})}$ values from McCallum Dome more than double from an initial value of 2.70 to 5.93, with $^4\text{He}/^{21}\text{Ne}_{(\text{crust} + \text{mantle})}$ ratios only increasing from 2.24×10^7 to 3.14×10^7 . As the degree of $^4\text{He}/^{21}\text{Ne}_{(\text{crust} + \text{mantle})}$ fractionation is less than that of $^4\text{He}/^{40}\text{Ar}_{(\text{crust} + \text{mantle})}$ these fractionation trends are consistent with a solubility controlled gas/groundwater phase partition process (e.g. Ballentine et al., 1991). Coherent fractionation of the groundwater-derived and crustal radiogenic noble gases indicates that these differently sourced noble gases are pre-mixed prior to the fractionation event, probably in the groundwater. In contrast, the extreme fractionation of the $^{20}\text{Ne}/^{36}\text{Ar}_{(\text{atm})}$ ratios in the Sheep Mountain field does not correlate with any fractionation of the $^4\text{He}/^{40}\text{Ar}_{(\text{crust} + \text{mantle})}$ or $^4\text{He}/^{21}\text{Ne}_{(\text{crust} + \text{mantle})}$ ratios. Whilst $^{20}\text{Ne}/^{36}\text{Ar}$ fractionation in St. John's Dome is small (Table 3) there is nevertheless a clear correlation between the increase in $^{20}\text{Ne}/^{36}\text{Ar}$ and an increase in both $^4\text{He}/^{40}\text{Ar}$ and $^4\text{He}/^{21}\text{Ne}$ on moving towards the Gas/Groundwater contact. Observed McElmo Dome $^{20}\text{Ne}/^{36}\text{Ar}$ 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 $^{20}\text{Ne}/^{36}\text{Ar}$ values which are significantly above the ASW value of 0.152 no clear relationship between this fractionation and either $^4\text{He}/^{21}\text{Ne}$ or $^4\text{He}/^{40}\text{Ar}$ 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 $V_{\text{gas}}/V_{\text{water}} \rightarrow 0$ 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 through

Table 3
Calculated groundwater noble gas concentrations (cm³ STPcm⁻³) and ratios

Field & well	Observed ²⁰ Ne/ ³⁶ Ar	Proportion ³⁶ Ar lost to stage 2 water	Measured ³⁶ Ar cm ³ (STP) cm ⁻³ (× 10 ⁻⁸)	³⁶ Ar _{init} cm ³ (STP) cm ⁻³ (× 10 ⁻⁸)	Stage 1 <i>V</i> _{water} / <i>V</i> _{gas} (STP)	Stage 2 <i>V</i> _{water} / <i>V</i> _{gas} (STP)	Stage 2 <i>V</i> _{water} / <i>V</i> _{gas} (RTP)
<i>McCallum Dome</i>							
No. 3 (8-3)	0.403	0.862	2.92	21.1	0.1916	0.672	85.61
No. 5	0.266	0.678	10.2	31.8	0.2880	0.385	49.00
No. 13	0.315	0.773	13.8	60.9	0.5492	0.504	64.10
No. 79	0.281	0.714	8.98	31.4	0.2799	0.425	54.10
<i>Sheep Mtn</i>							
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	2.99	138	1.2555	1.372	153.09
3-4-O	0.762	0.846	3.46	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	1.73	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
<i>Bravo Dome</i>							
BD01	0.402	0.823	0.212	1.20	0.0109	1.416	97.73
BD02	0.439	0.849	1.25	8.28	0.0751	1.543	106.48
BD03	0.445	0.853	0.881	5.97	0.0542	1.565	107.98
BD04	0.444	0.852	0.222	1.49	0.0136	1.560	107.64
BD05	0.397	0.819	0.873	4.81	0.0437	1.395	96.23
BD06	0.379	0.804	0.299	1.52	0.0138	1.244	85.82
BD07	0.342	0.763	0.191	0.806	0.0073	1.178	81.27
BD08	0.334	0.754	0.505	2.05	0.0186	1.144	78.95
BD09							
BD10	0.416	0.833	0.499	2.99	0.0272	1.055	101.02
BD11	0.314	0.725	0.0549	0.199	0.0018	1.464	72.78
BD12							
BD13	0.369	0.794	0.406	1.97	0.0179	1.292	89.15
BD14	0.326	0.743	0.290	1.13	0.0102	1.110	76.58
BD12b	0.617	0.918	0.0494	0.600	0.0054	2.041	140.82
<i>McElmo Dome</i>							
Doe Canyon	0.197	0.427	41.1	71.7	0.6505	0.132	24.81
MC-1	0.257	0.678	1.46	4.55	0.0413	0.268	50.42
HE-2	0.354	0.840	8.66	54.1	0.4912	0.434	81.53
YC-4	0.061	0.000	9.34	9.34	0.0847		0.00
SC-9	0.307	0.783	1.62	7.44	0.0674	0.361	67.82
YB-2	0.253	0.669	1.47	4.42	0.0401	0.262	49.18
YC-1	0.267	0.704	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		0.00
YA-2	0.103	0.000	1.27	1.27	0.0115		0.00
YE-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

(continued on next page)

Table 3 (continued)

Field & well	Observed $^{20}\text{Ne}/^{36}\text{Ar}$	Proportion ^{36}Ar lost to stage 2 water	Measured ^{36}Ar cm ³ (STP) cm ⁻³ ($\times 10^{-8}$)	$^{36}\text{Ar}_{\text{init}}$ cm ³ (STP) cm ⁻³ ($\times 10^{-8}$)	Stage 1 $V_{\text{water}}/V_{\text{gas}}$ (STP)	Stage 2 $V_{\text{water}}/V_{\text{gas}}$ (STP)	Stage 2 $V_{\text{water}}/V_{\text{gas}}$ (RTP)
<i>St. John's Dome</i>							
22-1X	0.182	0.320	189	287	2.6012	0.314	16.19
10-22	0.136	0.000	16.9	16.9	0.1534		0.00
3-1	0.219	0.544	69.2	157	1.4276	0.619	31.93

phase equilibrium degassing is $K_{\text{Ne}}/K_{\text{Ar}}$ 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 $^{20}\text{Ne}/^{36}\text{Ar}$ values in McElmo Dome extend from groundwater elemental ratios to fractionated values that cannot be accounted for by simple equilibration between the CO_2 and groundwater phases. The preservation in some samples of ASW elemental ratios in this field and the near ASW ratios in the St. John's 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 CO_2 field is the same as that in the other gas fields, it is clear that Sheep Mountain is more complex: interaction between the CO_2 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 CO_2 storage.

5.1. Fractionation of $^{20}\text{Ne}/^{36}\text{Ar}$ (and $^{84}\text{Kr}/^{36}\text{Ar}$, $^{130}\text{Xe}/^{36}\text{Ar}$)

We now consider the different processes that have the potential to fractionate $^{20}\text{Ne}/^{36}\text{Ar}$ (and $^{84}\text{Kr}/^{36}\text{Ar}$, $^{130}\text{Xe}/^{36}\text{Ar}$) 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 $^{20}\text{Ne}/^{36}\text{Ar}$ in the water phase (Bosch and Mazor, 1988). Subsequent groundwater/ CO_2 phase equilibration could then produce higher $^{20}\text{Ne}/^{36}\text{Ar}$ in the CO_2 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 $^{20}\text{Ne}/^{36}\text{Ar}$ ratios have been attributed to oil involvement, there is a correlation between $^{20}\text{Ne}/^{36}\text{Ar}$ and $1/^{36}\text{Ar}$ ratios (Battani et al., 2000). There is no such correlation in the CO_2 gas fields of this study.

Similarly, $^{84}\text{Kr}/^{36}\text{Ar}$ and $^{130}\text{Xe}/^{36}\text{Ar}$ 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. $^{130}\text{Xe}/^{36}\text{Ar}$ 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 third 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 (Matsuda et al., 1989; Matsubara and Matsuda, 1995; Pinti et al., 1999). Torgersen et al. (2004) have proposed that variable enrich-

Table 4
Reservoir conditions used in models

Reservoir	Average depth (m)	Pressure (MPa)	Bore hole temp (K)	TDS (mg/l)	K_{Ne} (GPa)	K_{Ar} (GPa)	K_{Kr} (GPa)	K_{Xe} (GPa)
Bravo Dome ^a	700	8.03	314	85000	18.59	7.86	5.16	3.57
McCallum Dome ^c	1630	15.97	333	13300	13.33	6.56	4.86	3.28
McElmo Dome ^b	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. John's Dome ^b	630	6.17	322	4210	13.35	5.78	3.82	2.71

^a Broadhead (1993).

^b Stevens et al. (2004).

^c Field operators.

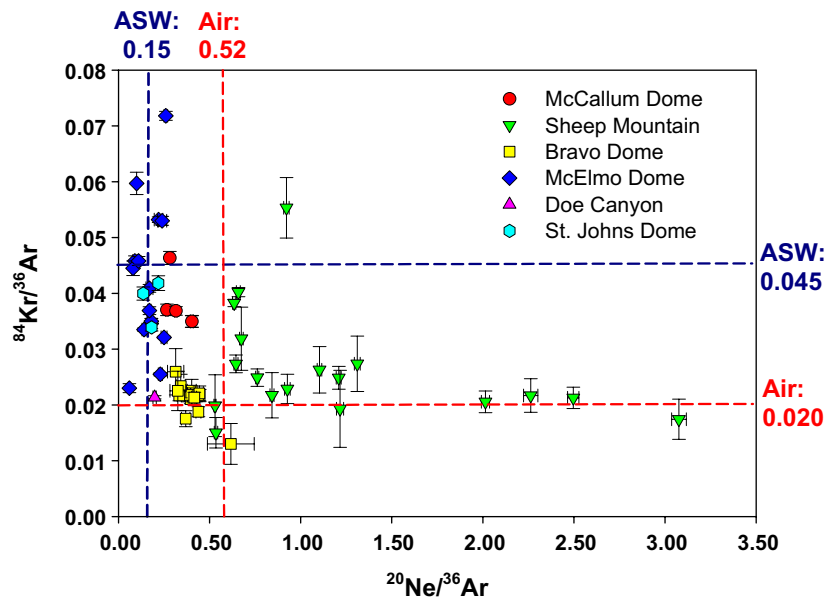


Fig. 6a. Plot of ²⁰Ne/³⁶Ar against ⁸⁴Kr/³⁶Ar for all reservoirs studied. The majority of the ²⁰Ne/³⁶Ar values lie close to the calculated ASW ratios. Sheep Mountain field shows extreme fractionation in ²⁰Ne/³⁶Ar.

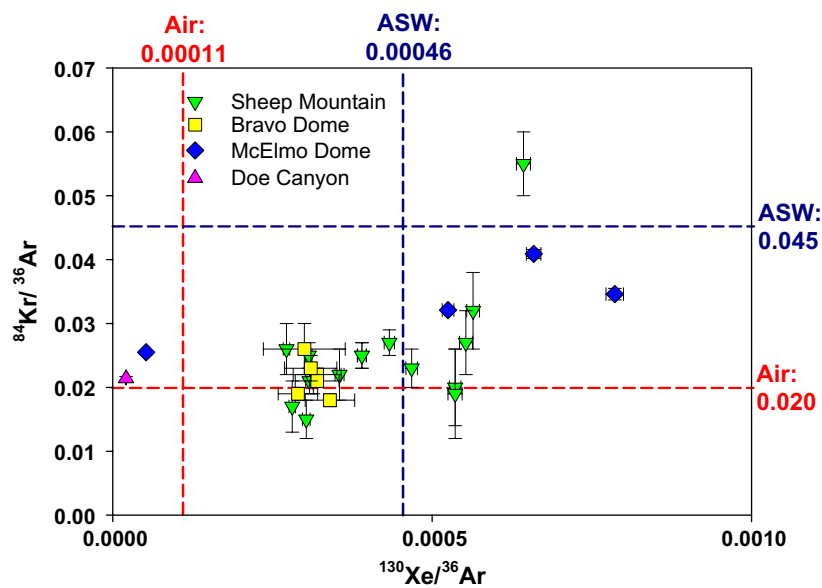


Fig. 6b. Plot of ⁸⁴Kr/³⁶Ar against ¹³⁰Xe/³⁶Ar for Sheep Mountain, McElmo Dome and Bravo Dome. The Xe and Kr systems are similar in both the McElmo Dome and Sheep Mountain fields. The extreme fractionation of ²⁰Ne/³⁶Ar observed in the Sheep Mountain field is not reflected in the other elemental ratios.

ments 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 $^{20}\text{Ne}/^{36}\text{Ar}$ ratio. This could be re-dissolved 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 significant fractionation (Ballentine et al., 2002). For these reasons 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

$^{20}\text{Ne}/^{36}\text{Ar}_{(\text{atm})}$ and low $^{84}\text{Kr}/^{36}\text{Ar}_{(\text{atm})}$ values can however, be explained by the re-dissolution model. Since CO_2 is a significantly better solvent than water (King et al., 1992), noble gases will preferentially partition into the CO_2 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 CO_2 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 ^{20}Ne 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

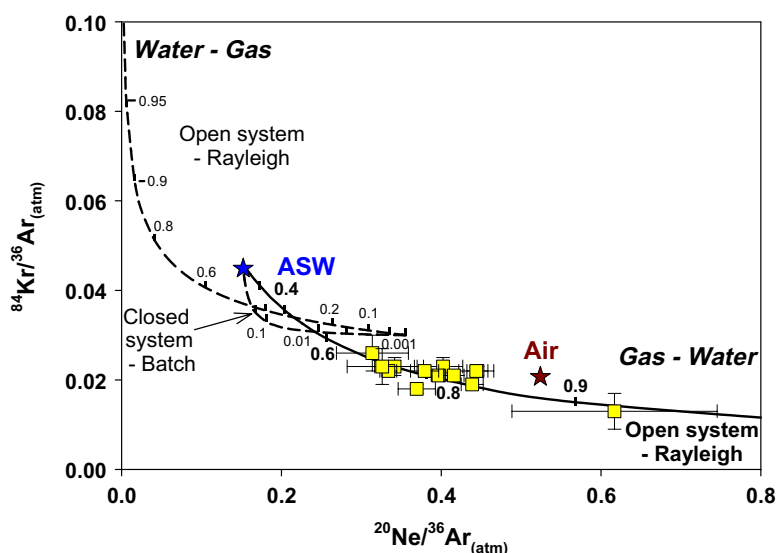


Fig. 7. Plot of mantle corrected $^{20}\text{Ne}/^{36}\text{Ar}_{(\text{atm})}$ against $^{84}\text{Kr}/^{36}\text{Ar}_{(\text{atm})}$ for the Bravo Dome field. Also plotted are the Air and ASW values and the calculated Rayleigh and Batch fractionation curves for a gas phase exsolving from a groundwater 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 **lost** from the gas phase. The fractionation pattern observed in the air derived ratios can be explained by the re-dissolution model.

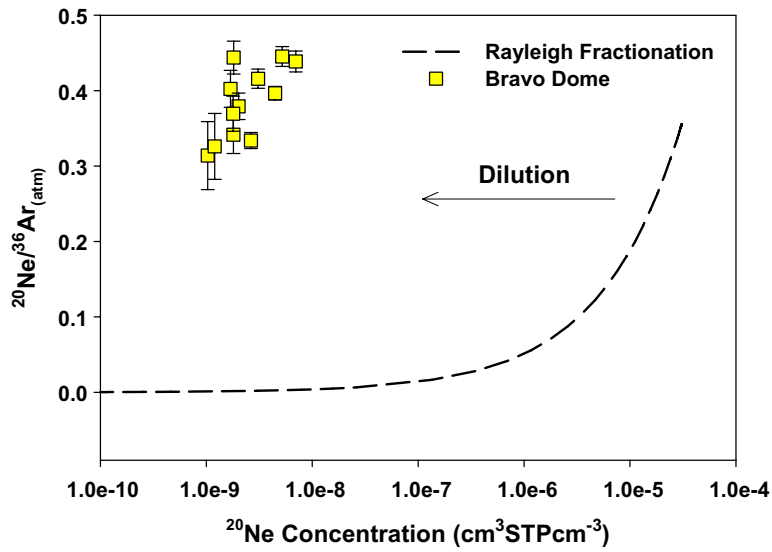


Fig. 8. Plot of $^{20}\text{Ne}/^{36}\text{Ar}_{(\text{atm})}$ against $^{20}\text{Ne}_{(\text{atm})}$ for the samples from the Bravo Dome field. Also plotted are the predicted ^{20}Ne concentration values assuming Rayleigh Fractionation of a gas phase exsolving from the groundwater. The predicted concentrations 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 CO₂.

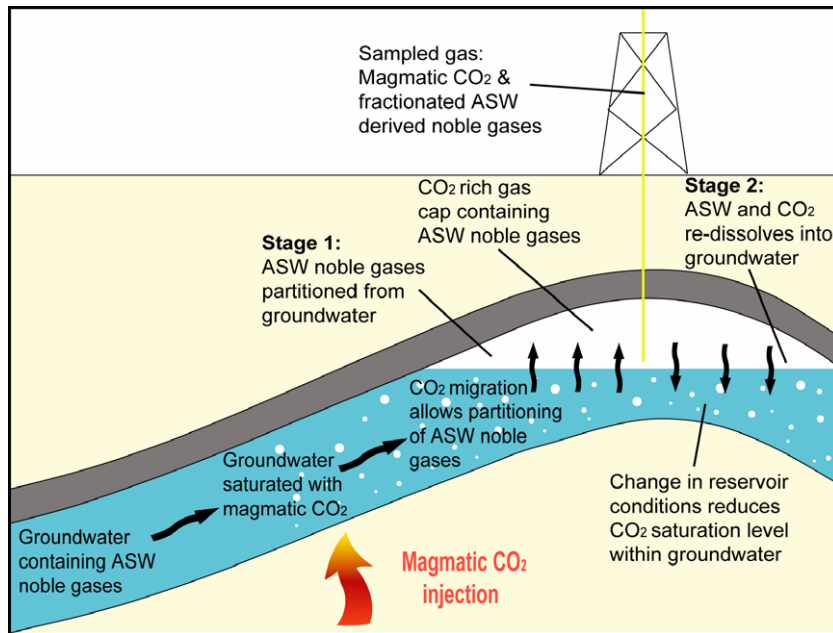


Fig. 9. Cartoon illustrating the two stage degassed groundwater and re-dissolution model. Stage 1: Magmatic CO₂ injection into the groundwater system causes the groundwater to become fully saturated in CO₂ with excess gas forming a free CO₂ gas phase. The free gas phase migrates upwards; stripping dissolved 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 gas rich CO₂. Reservoir scale preservation of concentration gradients in ASW-derived noble gases thus provide CO₂ filling direction (cf Bravo Dome, St. John's). 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.

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 Fig. 7 that the open system Rayleigh fractionation re-dissolution model accounts for all of the mantle corrected $^{20}\text{Ne}/^{36}\text{Ar}_{(\text{atm})}$ and $^{84}\text{Kr}/^{36}\text{Ar}_{(\text{atm})}$ ratios that are observed in the field. 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 $^{20}\text{Ne}/^{36}\text{Ar}$ ratios from the groundwater value defines the proportion of ^{36}Ar lost from the gas phase into solution. It is then straightforward to calculate the initial concentration of ^{36}Ar , $^{36}\text{Ar}_{\text{init}}$, within the gas phase prior to the fractionating (re-dissolution) process (Table 3) (e.g. Zhou et al., 2005). From the concentration of ^{36}Ar in ASW we then calculate for each sample the volume of water required to have been gas 'stripped' to supply the $^{36}\text{Ar}_{\text{init}}$ and present this as the Stage 1 water/gas volume ratio. For the Bravo Dome system, Stage 1 water/gas volume ratio ranges from 0.0018 to 0.075 cm^3 of water per cm^3 gas (STP) (Table 3). Under reservoir conditions 1 cm^3 of groundwater can hold 4.66 cm^3 of CO_2 (STP) in solution (Spycher and Pruess, 2005). This results in a Water/Gas ratio of 0.215 and is far higher than the largest estimated Stage 1 $V_{\text{water}}/V_{\text{gas}}$ Bravo Dome value. This is consistent with the CO_2 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 $^{20}\text{Ne}/^{36}\text{Ar}$ values from ASW (0.152) to that observed. For Bravo Dome this varies from 72 to 141 cm^3 water per cm^3 gas (RTP) (RTP = Reservoir Temperature and Pressure) (Table 3), which corresponds to 1.06 to 2.04 cm^3 water per cm^3 gas (STP). The volume of degassed water required to fractionate the $^{20}\text{Ne}/^{36}\text{Ar}$ 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, CO_2 will dissolve in this water while it remains CO_2 saturated. For the first time we quantify on a sample by sample basis the volume of water the gas in this CO_2 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 ASW-derived $^{20}\text{Ne}/^{36}\text{Ar}$ 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 Fig. 10a we show that the $^{20}\text{Ne}/^{36}\text{Ar}$ 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 $^{84}\text{Kr}/^{36}\text{Ar}$ values are below those observed (Fig. 10a). This could be explained by a higher initial groundwater excess air component or a sedimentary excess-air ^{84}Kr , possibly sourced from hydrocarbons associated with the nearby Oakdale natural gas field

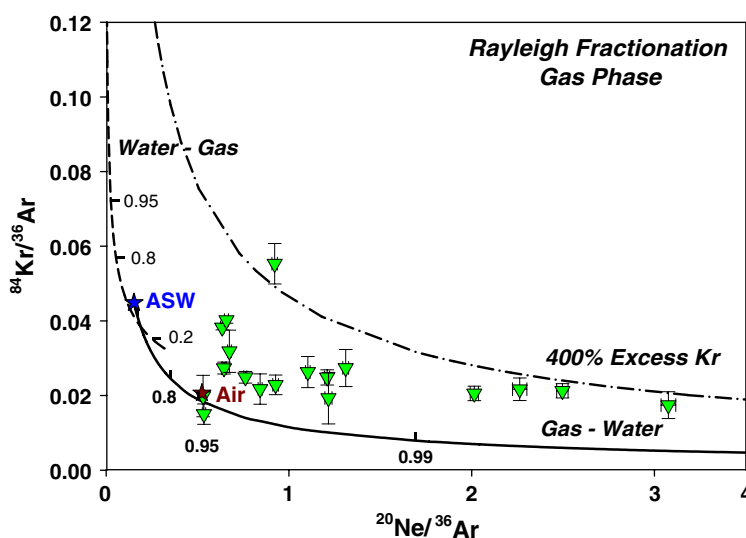


Fig. 10a. Plot of $^{20}\text{Ne}/^{36}\text{Ar}$ against $^{84}\text{Kr}/^{36}\text{Ar}$ for the Sheep Mountain field. Also plotted are the calculated Rayleigh fractionation curve for a gas phase evolving from an ASW groundwater (dashed line) and the Rayleigh fractionation curve for gas with an ASW composition re-dissolving into degassed water containing no noble gases (solid line). This second model accounts for the observed $^{20}\text{Ne}/^{36}\text{Ar}$. However, the observed $^{84}\text{Kr}/^{36}\text{Ar}$ values are up to 4 times higher than predicted, possibly as a result excess sedimentary Kr. In both figures ASW and air values are also plotted.

(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 0.026 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 most 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 re-dissolution ranges from 0.20 to 0.55 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 4) 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 (Table 3).

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 2.6 cm³ water per cm³ gas (STP), while re-equilibration requires zero to 32 cm³ water per cm³ gas (RTP) (Table 3). In a similar fashion to Bravo Dome, St. John's 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

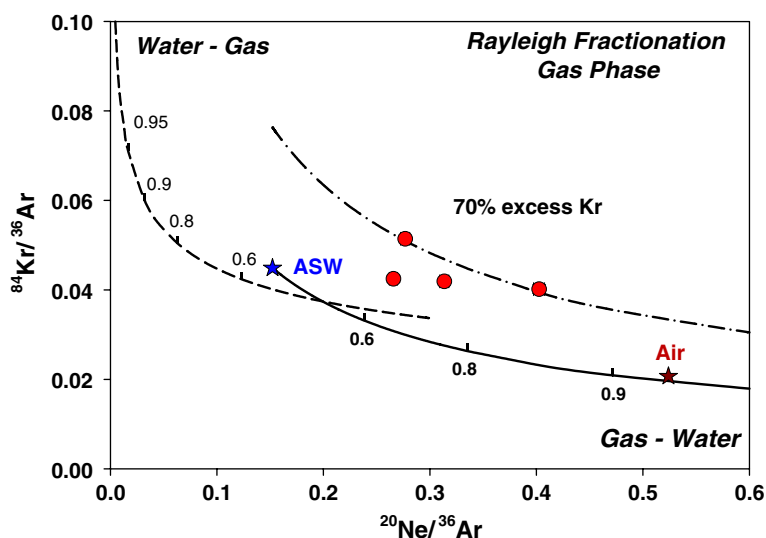


Fig. 10b. Plot of ²⁰Ne/³⁶Ar against ⁸⁴Kr/³⁶Ar for the McCallum field. ²⁰Ne/³⁶Ar ratios can be explained by a similar model of re-dissolution of noble gases into a previously stripped groundwater as outlined for Bravo Dome and Sheep Mountain. ⁸⁴Kr/³⁶Ar ratios are significantly above those predicted by 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.

some degree of perturbation of the groundwater system prior to stripping. With this caveat, we nevertheless calculate $^{36}\text{Ar}_{\text{init}}$ assuming an unperturbed ASW. The volume of ASW required to account for the $^{36}\text{Ar}_{\text{init}}$ 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. SUMMARY

Geological CO₂ storage requires the safe storage of CO₂ on a timescale in the region of a 1 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 storage 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. John's Dome and McCallum Dome CO₂ fields in the Colorado Plateau and Rocky Mountain provinces, USA provide a key set of analogues.

The CO₂/³He values of all of the well gas samples show that the CO₂ 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 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 several 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 CO₂ 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 as a result of subsequent charges of CO₂ 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 CO₂ 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.

ACKNOWLEDGMENTS

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APPENDIX A

A.1. Bravo Dome

The Bravo Dome field (originally named the Bueyeros field) is located south of Cortez in Harding County, north-east 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. CO₂ 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 (Broadhead, 1993; Broadhead, 1998; Baines and Worden, 2004). 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 CO₂ is believed to have migrated from vents associated with the nearby Rio Grande rift

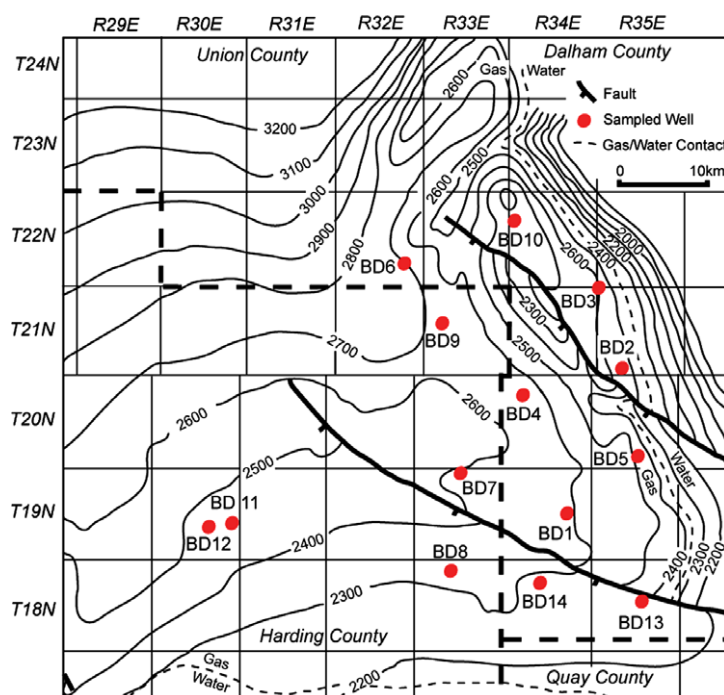


Fig. A1. Top surface map of the Tubb sandstone at Bravo Dome showing the folded and faulted structure of the field. Also shown is the approximate location of the Gas/Water contact which is poorly defined to the southwest. Contours are in feet above Mean Sea Level (MSL). Figure modified from Cassidy (2006).

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, 2006). CO₂ 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).

A.2. 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. A2). The reservoir produces almost pure CO₂ (~97%) from the Cretaceous Dakota and Jurassic Entrada sandstones at depths of 1400 m to 1800 m. Porosity within the reservoir varies from 16% to 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 aphanitic, intermediate-acidic igneous rocks and are named as a monzonite porphyry (Roth, 1983; Woodward, 1983; Johnston, 1959). Prior to this work the CO₂ source was thought to be the thermal breakdown of carbonates as a result of the nearby intrusives (Caffee et al., 1999).

A.3. 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

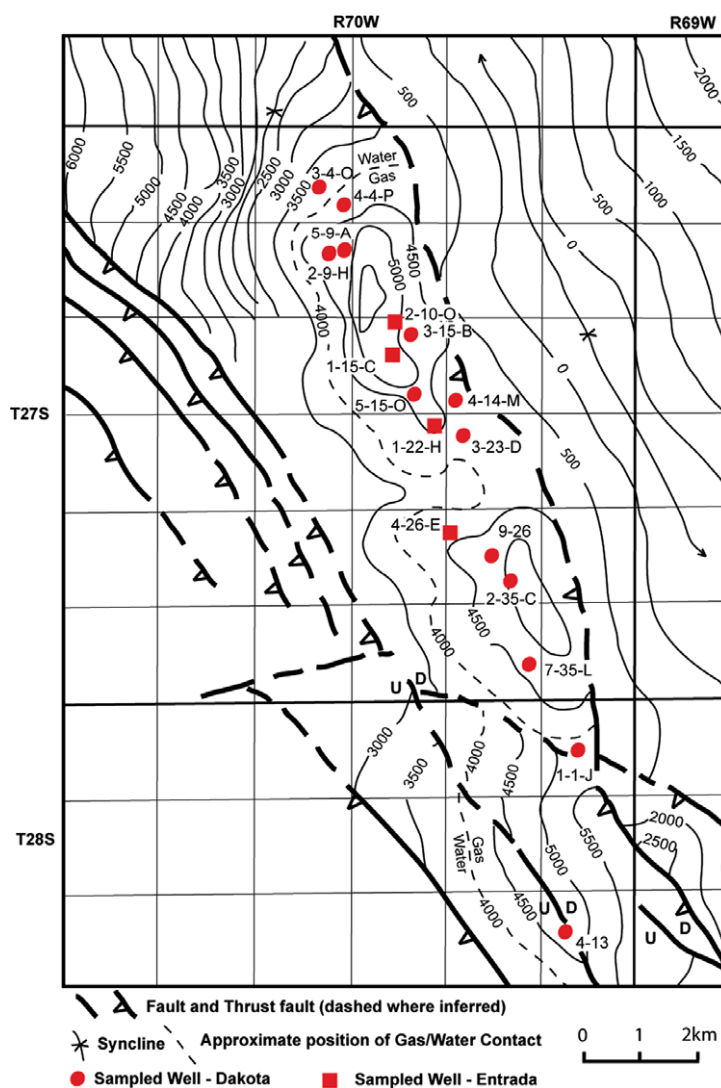


Fig. A2. Structure map of the top Dakota Formation at Sheep Mountain illustrating the well locations sampled for this study and the complex folded and thrust reservoir geology. Contours are in feet above MSL. The gas water contact is located at approximately 4000 feet across the reservoir. Figure modified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

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,b). 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, ther-

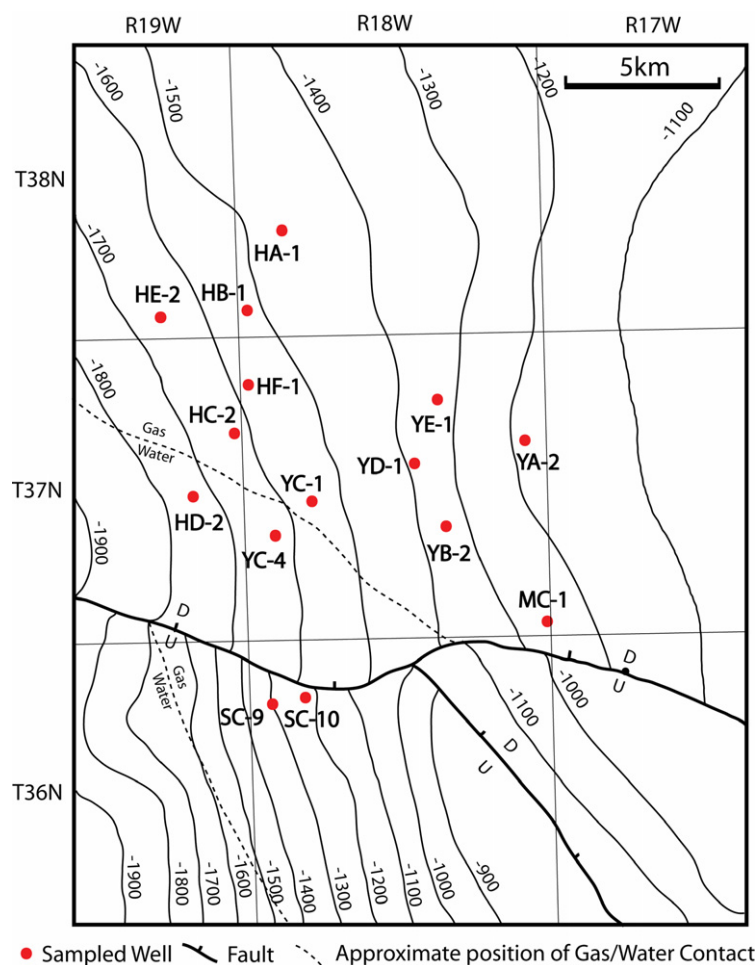


Fig. A3. Top surface map of the Leadville limestone at McElmo Dome showing the faulted complex structure of the field, approximate position of the gas/water contact and the wide distribution of wells sampled in this study. Contours are in feet below mean sea level. (Modified from Stevens et al. (2004)).

mal breakdown of carbonates as a result of this high heat flow regime had been highlighted as the most probable source of the CO₂ (Biggs, 1957; Maughan, 1988).

A.4. 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. CO₂ 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 1800 to 2600 m (Fig. A3). CO₂ is trapped by a combination of structural closure, permeability barriers within the Leadville Formation, CO₂-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 field was discovered in 1948 and is estimated to contain 476 billion m³ of CO₂ (Allis et al., 2001). The CO₂-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 to 72 Ma. Prior to this work, carbon isotope measurements have been used to suggest that the CO₂ 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).

A.5. St. John's Dome

St. John's Dome is a large (1800 km²), asymmetrical faulted anticline situated on the southern tip of the

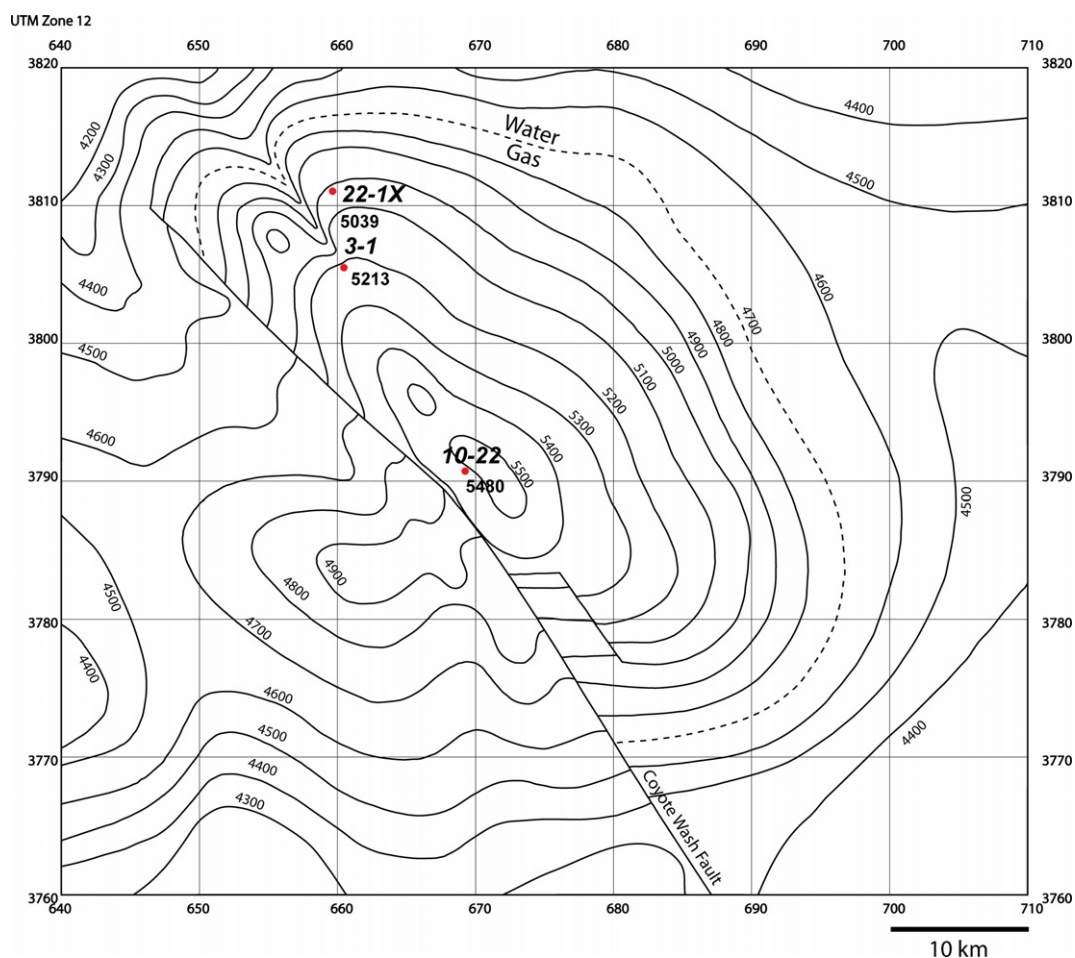


Fig. A4. Top surface map of Permian Supai formation at St. John's Dome showing the faulted anticlinal structure of the field and the position of the three wells sampled in this study. Contours are in feet above mean sea level. (Modified from Rauzi, 1999 by Reddy).

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 fine-grained alluvial sandstone intercalated with siltstone, anhydrite and dolomite. The reservoir is dissected by a major 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 m^3 (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 km^2 , with a volume of 300 km^2 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 CO_2 had not been investigated in detail (Rauzi, 1999).

REFERENCES

- Allis R., Chidsey T., Gwynn W., Morgan C., White S., Adams M. and Moore J. (2001) Natural CO_2 Reservoirs on the Colorado Plateau and Southern Rocky Mountains: Candidates for CO_2 sequestration. DOE/NETL: 1st National Conference of Carbon Sequestration. Proceedings Volume.
- Baars D. L. (2000) *The Colorado Plateau: A Geologic History*. University of New Mexico Press.
- Baines S. J. and Worden R. H. (2004) The long term fate of CO_2 in the subsurface: natural analogues for CO_2 storage. In *Geolog-*

- ical Storage of Carbon Dioxide*, vol. 233 (eds. S. J. Bains and R. H. Worden). Geological Society, pp. 59–85.
- Ballentine C. J., Burgess R. and Marty B. (2002) Tracing fluid origin, transport and interaction in the crust. In *Noble Gases in Geochemistry and Cosmochemistry* (eds. D. R. Porcelli, C. J. Ballentine, and R. Weiler), vol. 47, pp. 539–614.
- Ballentine C. J. and Burnard P.G. (2002) Production, release and transport of noble gases in the continental crust. In *Noble Gases in Geochemistry and Cosmochemistry* (eds. D. R. Porcelli, C. J. Ballentine, and R. Weiler). Vol. 47. pp. 481–538.
- Ballentine C. J., Marty B., Lollar B. S. and Cassidy M. (2005) Neon isotopes constrain convection and volatile origin in the Earth's mantle. *Nature* **433**, 33–38.
- Ballentine C. J., O'Nions R. K. and Coleman M. L. (1996) A Magnus opus: Helium, neon, and argon isotopes in a North Sea oilfield. *Geochim. Cosmochim. Acta* **60**(5), 831–849.
- Ballentine C. J., O'Nions R. K., Oxburgh E. R., Horvath F. and Deak J. (1991) Rare-gas constraints on hydrocarbon accumulation, crustal degassing and groundwater-flow in the Pannonian Basin. *Earth Planet. Sci. Lett.* **105**(1–3), 229–246.
- Ballentine C. J. (1997) Resolving the mantle He/Ne and crustal ²¹Ne/²²Ne in well gases. *Earth and Planet. Sci. Lett.* **152**, 233–249.
- Ballentine C. J., Schoell M., Coleman D. and Cain B. A. (2001) 300-Myr-old magmatic CO₂ in natural gas reservoirs of the west Texas Permian basin. *Nature* **409**, 327–331.
- Ballentine C. J. and Sherwood Lollar B. (2002) Regional groundwater focusing of nitrogen and noble gases into the Hugoton-Panhandle giant gas field, USA. *Geochim. Cosmochim. Acta* **66**(14), 2483–2497.
- Ballentine C. J., Mazurek M. and Gautschi A. (1994) Thermal constraints on crustal rare gas release and migration: evidence from Alpine fluid inclusions. *Geochim. Cosmochim. Acta* **58**, 4333–4348.
- Battani A., Sarda P. and Prinzhofer A. (2000) Basin scale natural gas source, migration and trapping traced by noble gases and major elements: the Pakistan Indus basin. *Earth Planet. Sci. Lett.* **181**(1–2), 229–249.
- Biggs P. (1957) CO₂ at North and South McCallum. In *Guidebook to the geology of North and Middle Parks Basin* (ed. W. C. Finch). Colorado, Rocky Mountain Association of Geologists, 9th Annual Field Conference, pp. 92–93.
- Bosch A. and Mazar E. (1988) Natural gas association with water and oil depicted by atmospheric noble gases: case studies from the southern Mediterranean Coastal Plain. *Earth Planet. Sci. Lett.* **87**, 338–346.
- Broadhead R. F. (1993) Carbon dioxide in northeast New Mexico. *West Texas Geol. Soc. Bull.* **32**, 5–8.
- Broadhead R. F. (1998) Natural accumulations of carbon dioxide in the New Mexico region—where are they, how do they occur and what are the uses for CO₂? *Lite Geol.* **20**, 2–6.
- Caffee M. W., Hudson G. U., Velsko C., Huss G. R., Alexander E. C. and Chivas A. R. (1999) Primordial noble gases from Earth's mantle: identification of a primitive volatile component. *Science* **285**, 2115–2118.
- Cappa J. and Rice D. (1995) Carbon dioxide in Mississippian rocks of the Paradox Basin and adjacent areas, Colorado, Utah, New Mexico and Arizona. U.S. Geological Survey Bulletin No. 2000-H.
- Carpen T. R. (1957a) North McCallum Field, Jackson County, Colorado. In *Guidebook to the geology of North and Middle Parks Basin* (ed. W. C. Finch). Colorado, Rocky Mountain Association of Geologists, 9th Annual Field Conference, pp. 109–112.
- Carpen T. R. (1957b) South McCallum Field, Jackson County, Colorado. In *Guidebook to the geology of North and Middle Parks Basin* (ed. W. C. Finch). Colorado, Rocky Mountain Association of Geologists, 9th Annual Field Conference, pp. 113–114.
- Cassidy M. (2006) Occurrence and origin of free carbon dioxide gas deposits in the earth's continental crust. PhD Thesis, University of Houston, Texas.
- Fanale F. P. and Cannon W. A. (1971) Physical adsorption of rare gases on terrigenous sediments. *Earth Planet. Sci. Lett.* **11**, 362–368.
- Fitton J. G., James D. and Leeman W. P. (1991) Basic magmatism associated with Late Cenozoic extension in the Western United-States - compositional variations in space and time. *J. Geophys. Res. Solid Earth Planets* **96**(B8), 13693–13711.
- Gerling C. R. (1983) McElmo Dome Leadville Carbon Dioxide Field, Colorado. In *Oil and Gas fields of the Four Corners Area* (ed. J. E. Fassett). Col. 3. Four Corners Geological Society, pp. 735–739.
- Haszeldine R. S., Quinn O., England G., Wilkonson M., Shipton Z. K., Evans J. P., Heath J. E., Crossey L., Ballentine C. J. and Graham C. M. (2005) Natural geochemical analogues for carbon dioxides storage in deep geological porous reservoirs, a UK perspective. In *Special Issue Oil and Gas Science and Technology (Revue de Inst Francais de Petrole)* (ed. E. Brosse), vol. 60, pp. 33–49.
- Holland G. and Ballentine C. J. (2006) Seawater subduction controls the heavy noble gas composition of the mantle. *Nature* **441**, 186–191.
- Intergovernmental Panel on Climate Change. (1996). Climate Change 1995: The Science of Climate Change, Summary for Policymakers and Technical Summary of the Working Group I report, pp. 56. Cambridge University Press, Cambridge, UK.
- Intergovernmental Panel on Climate Change. (2001) Climate Change 2001: The Scientific Basis, Summary for Policymakers and Technical Summary of the Working Group I Report. Cambridge University Press, Cambridge, UK.
- Intergovernmental Panel on Climate Change. (2007). Climate change 2007: Mitigation. Contribution of Working group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. In (eds. B. Metz, O. R. Davidson, P. R. Bosch, R. Dave, and L. A. Meyer). Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
- Jenden P. D., Hilton D. R., Kaplan I. R. and Craig H. (1993) Abiogenic hydrocarbons in and mantle helium in oil and gas fields. In *The Future of Energy Gases* (ed. D. G. Howell). U.S. Geological Survey Professional Paper 1570. U.S. Geological Survey, pp. 31–56.
- Johnson R. E. (1983) Bravo Dome carbon dioxide area, North east New Mexico. In *Oil and Gas Fields of the Four Corners area*, vol. 3 (ed. J. E. Fassett). Four Corners Geological Society, pp. 745–748.
- Johnston R. B. (1959) Geology of Huerfeno Park Area, Huerfeno and Custer County, Colorado. U.S. Geological Survey Bulletin No. 1071-D.
- Kennedy B. M., Hiyagon H. and Reynolds J. H. (1990) Crustal neon—a striking uniformity. *Earth Planet. Sci. Lett.* **98**(3–4), 277–286.
- Kennedy B. M., Torgersen T. and van Soest M. C. (2002) Multiple atmospheric noble gas components in hydrocarbon reservoirs: a study of the Northwest Shelf, Delaware Basin, SE New Mexico. *Geochim. Cosmochim. Acta* **66**(16), 2807–2822.
- King M. B., Mubarak A., Kim J. and Bott T. (1992) The mutual solubilities of water with supercritical and liquid carbon dioxide. *J. Supercrit. Fluids* **5**, 296–302.

- Marty B. and Jambon A. (1987) C^3He in volatile fluxes from the solid Earth: implications for carbon geodynamics. *Earth Planet. Sci. Lett.* **83**, 16–26.
- Matsubara K. and Matsuda J. (1995) Laboratory experiments on the Ne enrichments in terrestrial natural glasses. *Geochem. J.* **29**, 293–300.
- Matsuda J. I., Matsubara K., Yajima H. and Yamamoto K. (1989) Anomalous Ne enrichment in obsidians and Darwin glass: diffusion of noble gases in silica-rich glasses. **53**(11), p. 3025.
- Maughan E. K. (1988) Geology and Petroleum Potential, Colorado Park Basin Province, North-Central Colorado. U.S. Geological Survey Open-File Report 88-450 E.
- Parsons T. and McCarthy J. (1995) The active southwest margin of the Colorado Plateau: uplift of mantle origin. *Geol. Soc. Am. Bull.* **107**(2), 139–147.
- Phinney D., Tennyson J. and Frick U. (1978) Xenon. In: CO_2 Well Gas Revisited. *J. Geophys. Res.* **83**(NB5), 2313–2319.
- Pinti D. L. and Marty B. (1995) Noble-gases in crude oils from the Paris Basin, France—implications for the origin of fluids and constraints on oil–water–gas interactions. *Geochim. Cosmochim. Acta* **59**(16), 3389–3404.
- Pinti D. L., Wada N. and Matsuda J. (1999) Neon excesses in pumice: volcanological implications. *J. Volcanol. Geotherm. Res.* **88**, 279–289.
- Prinzhofer A., Vega M. A. G., Battani A. and Escudero M. (2000) Gas geochemistry of the Macuspana Basin (Mexico): thermogenic accumulations in sediments impregnated by bacterial gas. *Mar. Petrol. Geol.* **17**(9), 1029–1040.
- Rauzi S. L. (1999) Carbon dioxide in the St. John's - Springerville Area, Apache County, Arizona. Arizona Geological Survey, Open-File Report 99-2.
- Roth G. (1983) Sheep Mountain and Dike Mountain fields, Huerfano County, Colorado; a source of CO_2 for enhanced oil recovery. In *Oil and Gas Fields of the Four Corners Area*, vol. 3 (ed. J. E. Fassett). Four Corners Geological Society, pp. 740–744.
- Sherwood Lollar B., Ballentine C. J. and O'Nions R. K. (1997) The fate of mantle-derived carbon in a continental sedimentary basin: Integration of C/He relationships and stable isotope signatures. *Geochim. Cosmochim. Acta* **61**(11), 2295–2308.
- Sherwood Lollar B., Slater G. F., Ahad J., Sleep B., Spivack J., Brennan M. and MacKenzie P. (1999) Contrasting carbon isotope fractionation during biodegradation of trichloroethylene and toluene: Implications for intrinsic bioremediation. *Org. Geochem.* **30**(Part 1), 813–820.
- Shipton Z. K., Evans J. P., Kirschner D., Kolesar P. T., Williams A. P. and Heath J. (2004). Analysis of leakage through 'low-permeability' faults from natural reservoirs in the Colorado Plateau, east-central Utah. In *Geological Storage of Carbon Dioxide* (eds. S. J. Baines and R. H. Worden). Geological Society, vol. **233**, pp. 43–58.
- Spycher N. and Pruess K. (2005) CO_2 – H_2O mixtures in the geological sequestration of CO_2 . II Partitioning in chloride brines at 12–100 °C and up to 600 bar. *Geochim. Cosmochim. Acta* **69**(13), 3309–3320.
- Stevens S. H., Fox C., White T. and Melzer S. (2004) Natural CO_2 analogs for Carbon Sequestration. Midterm Report for USDOE.
- Stevens S. H., Pearce J. M. and Rigg A. A. J. (2001) Natural Analogues for Geologic Storage of CO_2 : an Integrated Global Research Program. In *Proceedings of the First National Conference on Carbon Sequestration*. Washington, D. C., May 14–17, 2001, p.12.
- Torgersen T., Kennedy B. and van Soest M. (2004) Diffusive separation of noble gases and noble gas abundance patterns in sedimentary rocks. *Earth Planet. Sci. Lett.* **226**(3–4), 477–489.
- Torgersen T. and Kennedy B. M. (1999) Air-Xe enrichments in Elk Hills oil field gases: role of water in migration and storage. *Earth Planet. Sci. Lett.* **167**(3–4), 239–253.
- Woodward L. A. (1983) Geology and hydrocarbon potential of the Raton Basin, New Mexico. In *Oil and Gas Fields of the Four Corners Area*, vol. 3 (ed. J. E. Fassett). Four Corners Geological Society, pp. 789–799.
- Worrall J. (2004). Preliminary Geology of Oakdale Field, Northwest Raton Basin, Huerfano County, Colorado. Search and Discovery Article #20017.
- Wycherley H., Fleet A. and Shaw H. (1999) Some observations on the origins of large volumes of carbon dioxide accumulations in sedimentary basins. *Mar. Petrol. Geol.* **16**(6), 489–494.
- Zartman R. E., Reynolds J. H. and Wasserburg G. J. (1961) Helium argon, and carbon in some natural gases. *J. Geophys. Res.* **66**(1), 277–306.
- Zhou Z. and Ballentine C. J. (2006) 4He dating of groundwater associated with hydrocarbon reservoirs. *Chemical Geology* **226**(3–4), 309–327.
- Zhou Z., Ballentine C. J., Kipfer R., Schoell M. and Thibodeaux S. (2005) Noble gas tracing of groundwater/coalbed methane interaction in the San Juan Basin, USA. *Geochim. Cosmochim. Acta* **69**(23), 5413–5428.

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