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## Solubility trapping in formation water as dominant CO<sub>2</sub> sink in natural gas fields

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**Injecting CO<sub>2</sub> into deep geological strata is proposed as a safe and economically favourable means to store CO<sub>2</sub> captured from industrial point sources<sup>1-3</sup>. However, it is difficult to assess the long term consequence of CO<sub>2</sub> flooding in the subsurface from decadal observations of existing disposal sites<sup>1,2</sup>. Both the site design and long term safety modelling critically depend on how and where CO<sub>2</sub> will be stored in the site over its lifetime<sup>2-4</sup>. Natural gas fields dominated by a CO<sub>2</sub> phase provide an essential natural analogue for assessing the safety and viability of the geological storage of anthropogenic CO<sub>2</sub> over millennia timescales<sup>1,2,5,6</sup>. Here, we show that the dominant subsurface sink of CO<sub>2</sub> in nine natural gas fields from North America, China and Europe is through dissolution (solubility trapping) in the formation water. All fields, whether siliciclastic or carbonate dominated reservoir lithologies, exhibit a reduction in CO<sub>2</sub> relative to <sup>3</sup>He, an inert and highly insoluble tracer that correlates with an increase in formation water-derived noble gases. Reservoir CO<sub>2</sub> phase loss, sometimes > 90% of that emplaced, is therefore quantitatively related to formation water involvement in the system. CO<sub>2</sub>/<sup>3</sup>He and δ<sup>13</sup>C(CO<sub>2</sub>) data for seven gas fields indicate that dissolution in formation water at pH=5-5.8 alone is the major sink for the CO<sub>2</sub> loss. Within two siliciclastic dominated reservoirs some CO<sub>2</sub> loss through precipitation as carbonate minerals cannot be ruled out, but may account for a maximum of 18% loss of the emplaced CO<sub>2</sub>. Long term anthropogenic CO<sub>2</sub> storage models in similar geological systems must consider the potential mobility of CO<sub>2</sub> dissolved in water and not geological mineral fixation, which is an insignificant CO<sub>2</sub> trapping mechanism.**

Noble gas and CO<sub>2</sub> carbon isotopes are powerful tracers of crustal fluid processes that act on subsurface CO<sub>2</sub><sup>5,7-10</sup>. Within a geological storage site, CO<sub>2</sub> injected as a free CO<sub>2</sub> phase (gas or supercritical) may over time be dissolved in solution (solubility trapping), or locked within carbonate minerals by precipitation (mineral trapping)<sup>4,11</sup>. By using noble gas and carbon

isotope tracers together to study naturally occurring CO<sub>2</sub> systems, we can uniquely identify and quantify the principal mechanism of the CO<sub>2</sub> phase removal, mineral or solubility trapping, over a time scale not accessible through extant injection studies.

We combine noble gas data from five natural CO<sub>2</sub> reservoirs located within the Colorado Plateau and Rocky Mountain provinces, (McCallum Dome, Sheep Mountain, McElmo Dome, CO., Bravo Dome, NM, and St Johns Dome, AZ.)<sup>7</sup> with new  $\delta^{13}\text{C}(\text{CO}_2)$  isotope data (Table 1). Previous work has shown that noble gas patterns in these gas fields are explained by CO<sub>2</sub> gas stripping of the formation water during reservoir filling, followed by partial dissolution of noble gases back into the formation water<sup>7</sup>. We also consider published noble gas and stable isotope information in a further four CO<sub>2</sub>-rich natural gas fields (JM-Brown Bassett field (JMBB), Permian Basin, Texas<sup>5</sup>; Kismarja field, Pannonian Basin, Hungary<sup>8</sup>; Jilin field, Jilin Province, Songliao Basin; and Subei Basin field, Jiangsu Province in China<sup>12,13</sup>).

CO<sub>2</sub>/<sup>3</sup>He ratios within the magmatic range of 1-10x10<sup>9</sup> have been used to identify a primary magmatic origin of the CO<sub>2</sub> contained within five natural CO<sub>2</sub> reservoirs of the Colorado Plateau and Rocky Mountain Provinces<sup>7</sup>. CO<sub>2</sub>/<sup>3</sup>He within the Subei Basin and JM-Brown Bassett field also indicate a magmatic origin, whilst the CO<sub>2</sub>/<sup>3</sup>He values within the Jilin and Kismarja fields are far higher, suggesting a predominantly crustal origin<sup>5,8</sup>. All of the reservoirs exhibit local variation in the CO<sub>2</sub> content relative to the inert tracer <sup>3</sup>He. As there is not a significant source of <sup>3</sup>He within the crust<sup>14</sup>, and as <sup>3</sup>He is inert and highly insoluble<sup>9</sup>, this variation must be due to changes in the CO<sub>2</sub> component within the reservoirs. While many sources and sinks of CO<sub>2</sub> exist in the subsurface<sup>4,8,9</sup> we argue later that the CO<sub>2</sub>/<sup>3</sup>He variation is caused by CO<sub>2</sub> loss from the reservoir. The difference between the highest CO<sub>2</sub>/<sup>3</sup>He and lower values can provide a minimum estimate of this CO<sub>2</sub> loss. In the case of Bravo Dome, a reduction of CO<sub>2</sub>/<sup>3</sup>He values from 4.82x10<sup>9</sup> (BD11) to 2.25x10<sup>9</sup> (BD02)

indicates a >50% loss of the original CO<sub>2</sub> charge in the portion of the reservoir represented by BD02 (Table 1). McElmo Dome samples exhibit a decrease from 8.5x10<sup>9</sup> (YD-1) to 0.68x10<sup>9</sup> (He-2) suggesting >90% emplaced CO<sub>2</sub> loss in portions of this field.

<sup>4</sup>He is continually produced in the subsurface by the radiogenic decay of U, Th and K<sup>14</sup>. <sup>20</sup>Ne is introduced into the subsurface as a component of air dissolved in water and, as such, can only enter the reservoir system via interaction with formation water<sup>9</sup>. While there is no *a-priori* reason to expect a correlation between <sup>4</sup>He and <sup>20</sup>Ne, this has been observed in natural gases on a regional scale<sup>15</sup>. This correlation is the result of <sup>4</sup>He accumulating in the formation water<sup>16</sup> which also contains atmosphere derived <sup>20</sup>Ne, and subsequent quantitative partitioning of both <sup>4</sup>He and <sup>20</sup>Ne into the reservoir phase<sup>7,15</sup>. Almost all CO<sub>2</sub> reservoirs for which we have <sup>20</sup>Ne and <sup>4</sup>He concentration data show a local <sup>20</sup>Ne correlation with <sup>4</sup>He (Table 1 and supplementary information). A decrease in CO<sub>2</sub>/<sup>3</sup>He is also correlated with <sup>20</sup>Ne in most CO<sub>2</sub> reservoirs (Fig. 1) and with <sup>4</sup>He in all CO<sub>2</sub> reservoirs (Fig. 2).

While there are various mechanisms to add crustal CO<sub>2</sub> (CO<sub>2</sub>/<sup>3</sup>He >> 10<sup>10</sup>) to these systems<sup>4,10</sup> there is no plausible mechanism that enables crustal CO<sub>2</sub> to be variably added to these systems while preserving a correlation of CO<sub>2</sub>/<sup>3</sup>He with the formation water-derived noble gases. Neglecting small amounts of <sup>3</sup>He dissolution back into the formation water<sup>7</sup>, changes in CO<sub>2</sub>/<sup>3</sup>He must therefore be due to CO<sub>2</sub> loss in the subsurface via a mechanism directly proportional to the amount of formation water that has been degassed. CO<sub>2</sub> is soluble and reactive. The most likely subsurface CO<sub>2</sub> phase removal mechanisms are solubility and mineral trapping<sup>4,11</sup>.

Reservoir lithology may exert a significant influence on how changes in CO<sub>2</sub>/<sup>3</sup>He relate to δ<sup>13</sup>C(CO<sub>2</sub>). The carbonate reservoirs (McElmo, JMBB, and St. Johns Domes) show little variance in δ<sup>13</sup>C(CO<sub>2</sub>) whilst the siliclastic fields (Jilin field, Subei Basin, Kismarja, Sheep

Mountain, McCallum and Bravo Domes) exhibit a greater range in  $\delta^{13}\text{C}(\text{CO}_2)$  (Table 1, Supplementary Fig. S1). We consider Bravo and McElmo Domes as case types for each reservoir lithology.

Emplacement of  $\text{CO}_2$  at Bravo Dome is believed to have occurred relatively recently (local volcanic activity dates from 8,000-10,000 years)<sup>7,17</sup> and the field may still be undergoing active  $\text{CO}_2$  recharge<sup>11</sup>. Decreasing  $\text{CO}_2/{}^3\text{He}$  within Bravo Dome correlates with more negative  $\delta^{13}\text{C}(\text{CO}_2)$  (Fig. 3a). Taking the highest  $\text{CO}_2/{}^3\text{He}$  of  $4.82 \times 10^9$  (BD11) to be the sample that experienced the least  $\text{CO}_2$  loss, we calculate the coherent change in  $\text{CO}_2/{}^3\text{He}$  and  $\delta^{13}\text{C}(\text{CO}_2)$  predicted for  $\text{CO}_2$  dissolution into the formation water at various pH and for  $\text{CO}_2$  precipitation as a carbonate (see Methods Summary). The data are not consistent with precipitation as carbonate being a major sink for  $\text{CO}_2$  at Bravo Dome (Figure 3a). However, while a significant number of the data points are consistent with  $\text{CO}_2$  dissolution into formation water at a pH between 6-7, it is not possible to rule out a degree of  $\text{CO}_2$  loss due to precipitation together with  $\text{CO}_2$  dissolution at a lower pH (e.g. pH=5). In such a two process model an upper limit to the proportion of  $\text{CO}_2$  lost to precipitation of approximately 18%, can be attributed (Fig. 3a). Hence, in all cases the major  $\text{CO}_2$  sink is dissolution. In situ precipitation of 18% reservoir  $\text{CO}_2$  would generate between 3.2-6.1% by mass of the whole rock, dependent on whether dolomite, calcite or dawsonite precipitation was favoured by the reservoir conditions. Whilst evidence for  $\text{CO}_2$  rich formation water interaction within the reservoir has been documented, to date no secondary carbonate has been identified<sup>18</sup>. Nevertheless, the volume control of the water suggests that the location of the precipitate, if any, is likely to be within the water leg which was not sampled. Lack of reservoir secondary mineralization cannot at this stage rule out any carbonate precipitation as a minor  $\text{CO}_2$  sink.

Similar to Bravo Dome, while many of the Sheep Mountain data can be accounted for by dissolution of CO<sub>2</sub> (at pH=5 in this case), a small component of precipitation cannot be ruled out. Adopting the same approach as Bravo Dome, the remaining Sheep Mountain data require a maximum of 10% precipitation and 20% dissolution of the original CO<sub>2</sub> charge (Table 1; Supplementary Fig. S2). In contrast, while minor data scatter may also be due to some small amount of CO<sub>2</sub> precipitation or dissolution at pH=7-8, almost all the data from the other siliciclastic fields of McCallum Dome, Subei basin, Kismarja and the Jilin field can be described by dissolution in the formation water only, within a narrow pH range of between 5-5.3 (Supplementary Figs S3-6).

McElmo Dome carbonate reservoir data show over an order of magnitude change in CO<sub>2</sub>/<sup>3</sup>He with invariant δ<sup>13</sup>C(CO<sub>2</sub>) (Figure 3b). This pattern is repeated in the two other carbonate-dominated fields (Supplementary Figures S7, S8). Invariant δ<sup>13</sup>C(CO<sub>2</sub>) in these fields allows us to discount a two process model of precipitation and dissolution such as at Bravo Dome (Fig. 3a). All data are consistent with CO<sub>2</sub> dissolution into formation water in the pH range of 5.4-5.8 (Figure 3b, Supplementary Figures 7,8), a value similar to the pH obtained for the siliciclastic reservoirs and to values observed (pH=5.7) in carbonate mineral buffered formation water observed in the recent Frio CO<sub>2</sub> injection studies on CO<sub>2</sub> breakthrough<sup>19</sup>.

On a reservoir engineering timescale, the early stages of CO<sub>2</sub> injection can result in a drop in pH and dissolution of carbonate minerals into the formation water<sup>18,20-22</sup>. Any significant CO<sub>2</sub> contribution to the reservoir CO<sub>2</sub> phase from re-dissolution of carbonates would be <sup>3</sup>He-free and therefore perturb the CO<sub>2</sub>/<sup>3</sup>He correlation with <sup>4</sup>He and <sup>20</sup>Ne. As there is a clear correlation between CO<sub>2</sub>/<sup>3</sup>He and <sup>4</sup>He in all fields and <sup>20</sup>Ne within the majority, we conclude that dissolution of carbonate minerals into the formation water cannot have had a major influence on δ<sup>13</sup>C(CO<sub>2</sub>) values. There is no evidence for any precipitation of CO<sub>2</sub> within the

carbonate dominated reservoirs, requiring that the dominant mechanism of reservoir CO<sub>2</sub> loss, up to 90%, is through dissolution into the formation water.

Even the most conservative model we have presented places an upper limit on the CO<sub>2</sub> removed by precipitation at approximately 18%, and then only in some samples, from all natural gas fields investigated in a variety of lithological settings. Precipitation of CO<sub>2</sub> over millennial timescales represents at most only a small subsurface trapping mechanism for CO<sub>2</sub>, and then only within siliciclastic lithologies. The dominant mechanism of CO<sub>2</sub> loss from most CO<sub>2</sub> natural gas fields can be accounted for through simple dissolution into the formation groundwater within a narrow pH window (pH=5-5.8). This study underscores that geological carbon storage requires careful investigation of existing geologic and hydrogeologic analogues that have naturally accumulated and stored CO<sub>2</sub> over timescales relevant to anthropogenic CO<sub>2</sub> storage facilities. We further demonstrate a means of testing trapping and storage mechanisms via coupled noble gas and carbon isotope measurements in the context of formation/reservoir water pH evolution.

## **Methods Summary**

Detailed descriptions of the sample collection and analysis procedures can be found in the original references<sup>5,7,8,21,23</sup>. In our calculations (Figure 3 and Supplemental Figures) we use the highest CO<sub>2</sub>/<sup>3</sup>He ratio measured in each field as a reference point to calculate the correlated reservoir CO<sub>2</sub>/<sup>3</sup>He and δ<sup>13</sup>C(CO<sub>2</sub>) ratios as the CO<sub>2</sub> phase is removed by either precipitation or dissolution. We assume open system loss. In the case of precipitation there is zero <sup>3</sup>He loss from the CO<sub>2</sub> phase and CO<sub>2</sub>/<sup>3</sup>He changes in proportion to the fraction of the remaining CO<sub>2</sub> phase (f). In the case of dissolution the change in CO<sub>2</sub>/<sup>3</sup>He is calculated following the Rayleigh equation.



Changes in  $\delta^{13}\text{C}(\text{CO}_2)$  are calculated using the Rayleigh fractionation equation expressed as:

$$\delta^{13}\text{C}(\text{CO}_2) = \delta^{13}\text{C}(\text{CO}_2)_0 + \epsilon \ln(f) \quad ^{24}$$

where  $\delta^{13}\text{C}(\text{CO}_2)_0$  is the original system value,  $f$  is the fraction of  $\text{CO}_2$  remaining in the reservoir, and  $\epsilon$  is the carbon isotope fractionation, either for precipitation or for dissolution.

Carbon isotope fractionation factors ( $\alpha$ ) are calculated as a function of temperature for  $\text{CO}_2(\text{g})$  precipitating to form  $\text{CaCO}_3(\text{s})$ , or dissolving to form either  $\text{H}_2\text{CO}_3(\text{aq})$  or  $\text{HCO}_3^- (\text{aq})$ <sup>25</sup>. Since all the fractionations are small the simplification can be made that  $\epsilon = 1000\ln(\alpha)$ <sup>26</sup>. For typical reservoir waters of pH range 5-8, the contribution of  $\text{CO}_3^{2-}(\text{aq})$  is negligible. Hence for  $\text{CO}_2$  dissolution, carbon isotope fractionation between the dissolved inorganic carbon (DIC) pool and  $\text{CO}_2$  gas used in the Rayleigh fractionation equation can be expressed as:

$$\epsilon^{13}\text{C}_{\text{DIC-CO}_2(\text{g})} = x(\epsilon^{13}\text{C}_{\text{H}_2\text{CO}_3(\text{aq})-\text{CO}_2(\text{g})}) + (1-x)(\epsilon^{13}\text{C}_{\text{HCO}_3^-(\text{aq})-\text{CO}_2(\text{g})}) \quad ^{24}$$

where  $x$  is the proportion of  $\text{CO}_2$  gas dissolving to  $\text{H}_2\text{CO}_3(\text{aq})$  at the relevant pH<sup>24</sup>.

Solubility as a function of temperature and salinity is given by the IUPAC solubility series for  $\text{CO}_2$ <sup>27</sup> and by Crovetto et al. and Smith for He<sup>28,29</sup>. The average well depth, reservoir pressure, temperature and salinity are presented in the supplementary information for each reservoir, with the corresponding Henry's Law constants  $K_{\text{He}}$ ,  $K_{\text{CO}_2}$ , and fractionation factor ( $1000\ln\alpha$ ) for  $\text{CO}_2(\text{g})$  forming  $\text{H}_2\text{CO}_3(\text{aq})$ ,  $\text{HCO}_3^-(\text{aq})$  and  $\text{CaCO}_3(\text{s})$  (Supplementary Table 1).

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**Supplementary Information** is linked to the online version of the paper at [www.nature.com/nature](http://www.nature.com/nature).

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**Author Contributions** S.G., C.B. and B.S.L. designed the study, analysed the samples, interpreted the data and wrote the paper. G.H., D.B., Z.D., Z.Z. and G.L.C. assisted with sample analysis and interpretation of the data. S.S., M.S. and M.C. assisted with sample collection and provided comments on the manuscript.

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**Table 1: Sample location, Producing formation, major gas species and CO<sub>2</sub>**

**carbon isotopes**

Field & Well	Location Twnshp-Rnge/Lat-Long	Producing Formation	CO <sub>2</sub> / <sup>3</sup> He x 10 <sup>5</sup>	<sup>3</sup> He/ <sup>4</sup> He (R/R <sub>a</sub> )	<sup>4</sup> He (x 10 <sup>-4</sup> ) cm <sup>3</sup> (STP)cm <sup>-3</sup>	<sup>20</sup> Ne (x 10 <sup>-8</sup> ) cm <sup>3</sup> (STP)cm <sup>-3</sup>	δ <sup>13</sup> C(CO <sub>2</sub> ) ‰
<b>Bravo Dome<sup>7</sup></b>							
BD01	23/19N/34E	Tubb	4.53 (10)	1.670 (8)	0.944 (12)	0.169 (2)	-3.96 (4)
BD02	32/21N/35E	Tubb	2.25 (5)	0.764 (4)	4.15 (5)	0.700 (7)	-4.93 (8)
BD03	36/22N/34E	Tubb	2.41 (5)	0.896 (4)	3.31 (4)	0.521 (5)	-4.89 (19)
BD04	8/20N/34E	Tubb	4.61 (10)	1.611 (8)	0.961 (2)	0.181 (2)	-4.23 (8)
BD05	34/20N/35E	Tubb	2.74 (6)	0.965 (5)	2.70 (4)	0.446 (4)	-4.95 (5)
BD06	26/22N/32E	Tubb	3.94 (8)	1.503 (8)	1.20 (2)	0.202 (2)	-4.55 (11)
BD07	3/19N/33E	Tubb	4.34 (9)	2.104 (11)	0.781 (10)	0.180 (2)	-4.85 (1)
BD08	9/18N/33E	Tubb	3.87 (8)	1.143 (6)	1.61 (2)	0.264 (3)	-3.88 (8)
BD09	17/21N/33E	Tubb	4.22 (9)	1.724 (9)	0.981 (12)	0.180 (2)	-4.44 (11)
BD10	7/22N/34E	Tubb	3.25 (6)	1.104 (6)	1.99 (3)	0.308 (3)	-4.88 (7)
BD11	25/19N/30E	Tubb	4.82 (10)	3.784 (19)	0.391 (5)	0.103 (1)	-3.66 (29)
BD12	27/19N/30E	Tubb	4.74 (10)	3.627 (18)	0.415 (6)		-3.94 (17)
BD13	22/18N/35E	Tubb	3.54 (8)	1.318 (7)	1.53 (2)	0.240 (3)	-4.42 (3)
BD14	16/18N/34E	Tubb	4.39 (9)	1.413 (7)	1.15 (2)	0.179 (4)	-4.04 (2)
BD12b	27/19N/30E	Tubb	4.75 (10)	3.634 (18)	0.413 (6)	0.120 (2)	-3.94 (17)
<b>McCallum Dome<sup>7</sup></b>							
No. 3 (8-3)	8/9N/78W	Lakota	1.52 (4)	0.354 (7)	12.3 (2)	1.17 (2)	-5.1 (3)
No. 5	3/9N/79W	Lakota	1.04 (3)	0.409 (7)	15.5 (2)	2.71 (3)	-5.2 (1)
No. 36	8/9N/79W	Dakota/Lakota		0.448 (8)	1.32 (12)	8.10 (8)	nm
No. 13	2/9N/79W	Lakota/Morrison	0.89 (2)	0.393 (7)	18.8 (2)	4.36 (5)	-5.3 (2)
No. 79	4/9N/79W	Dakota/Lakota	1.77 (6)	0.406 (6)	9.16 (21)	2.53 (3)	-5.7 (1)
<b>McElmo Dome<sup>7</sup></b>							
MC-1	37.4155, -108.7713	Leadville	5.04 (11)	0.145 (2)	9.58 (8)	0.376 (4)	-4.26 (10)
HE-2	37.5052, -108.9094	Leadville	0.68 (15)	0.148 (1)	70.5 (7)	0.307 (30)	-4.40 (10)
YC-4	37.4529, -108.8583	Leadville	4.96 (11)	0.137 (3)	10.2 (10)	0.573 (6)	-4.41 (10)
SC-9	37.3934, -108.8733	Leadville	3.17 (7)	0.150 (3)	14.8 (14)	0.497 (5)	-4.29 (10)
YB-2	37.4472, -108.8075	Leadville	8.74 (20)	0.125 (1)	6.42 (61)	0.371 (4)	-4.40 (10)
YC-1	37.4529, -108.8583	Leadville	4.07 (9)	0.142 (2)	12.1 (12)	0.423 (5)	-4.34 (10)
HF-1	37.4871, -108.8807	Leadville	2.16 (6)	0.169 (1)	19.3 (26)	0.564 (12)	-4.37 (10)
HD-2	37.4572, -108.9008	Leadville	4.28 (10)	0.140 (3)	11.7 (12)	0.128 (2)	-4.38 (10)
YA-2	37.4692, -108.7811	Leadville	3.39 (8)	0.138 (3)	15.0 (15)	0.130 (2)	-4.42 (10)
YE-1	37.4818, -108.8123	Leadville	4.16 (9)	0.173 (3)	9.75 (8)	0.143 (3)	-4.45 (10)
HA-1	37.5289, -108.8718	Leadville	4.56 (10)	0.139 (3)	11.0 (11)	0.205 (7)	-4.66 (10)
SC-10	37.3934, -108.8733	Leadville	4.37 (10)	0.139 (2)	11.6 (11)	0.413 (5)	-4.27 (10)
HC-2	37.4734, -108.8860	Leadville	4.68 (11)	0.140 (2)	10.7 (10)	0.409 (5)	-4.38 (10)
HB-1	37.5087, -108.8802	Leadville	4.74 (11)	0.148 (3)	9.94 (10)	0.247 (4)	-4.49 (10)
YD-1	37.4619, -108.8224	Leadville	8.50 (20)	0.145 (3)	5.68 (6)	0.366 (5)	-4.46 (10)
<b>JM Brown Basset<sup>5</sup></b>							
Turk State No. 1A	30.38758, -101.85642	Ellenberger	5.92 (47)	0.543 (16)	1.25 (9)	nm	-2.88
Bassett Goode No. 3	30.37852, -101.83068	Ellenberger	5.55 (43)	0.527 (16)	1.42 (10)	nm	-2.89
Brown Bassett No. 2*	30.34433, -101.7995	Ellenberger	5.82 (35)	0.502 (15)	1.33 (7)	nm	-2.90
Mayme K. Martin ETAL 1	30.35661, -101.74721	Ellenberger	5.29 (40)	0.372 (11)	1.42 (10)	nm	-2.97
Mitchell 109 No. 2*	30.33329, -101.69826	Ellenberger	4.58 (36)	0.400 (12)	1.53 (11)	nm	-2.92
Mitchell 5 No. 1X	30.32352, -101.68429	Ellenberger	5.61 (43)	0.478 (11)	1.40(10)	nm	-2.84
Mitchell 103 No. 2	30.3568, -101.63642	Ellenberger	4.20 (33)	0.246 (7)	1.39 (10)	nm	-2.70
Mitchell No. 6	30.351, -101.58835	Ellenberger	3.93 (31)	0.264 (8)	1.51 (11)	nm	-2.96
Mitchell No. 3	30.33966, -101.61307	Ellenberger	4.22 (33)	0.240 (7)	1.39 (10)	nm	-3.06
Mitchell A-11 No. 1	30.30286, -101.57677	Ellenberger	4.07 (32)	0.272 (8)	1.66 (12)	nm	-2.93
Mitchell No. 12	30.29118, -101.57295	Ellenberger	4.24 (130)	0.267 (8)	1.46 (10)	nm	-2.96
<b>Sheep Mountain<sup>7</sup></b>							
8-2-P	2/9-28S/70W	Dakota	2.31 (5)	0.981 (10)	3.13 (3)	1.47 (2)	-5.0 (2)
2-10-O	15/9-27S/70W	Entrada	2.44 (6)	0.984 (12)	2.96 (3)	3.04 (3)	-5.2 (1)
9-26	26/9-27S/70W	Dakota	2.57 (6)	0.934 (14)	2.95 (3)	0.613 (9)	nm
2-9-H	9/9-27S/70W	Dakota	2.44 (6)	0.945 (19)	3.07 (3)	9.77 (10)	nm
3-15-B	15/9-27S/70W	Dakota	2.61 (6)	0.937 (16)	2.90 (3)	1.54 (2)	-5.7 (4)
4-13		Dakota	2.17 (5)	0.942 (18)	3.47 (4)	1.11 (2)	nm
4-26-E	26/9-27S/70W	Entrada	2.20 (5)	1.024 (18)	3.15 (3)	0.442 (4)	-4.8 (1)
3-23-D	22/9-27S/70W	Dakota	2.26 (5)	0.988 (14)	3.17 (3)	0.579 (9)	nm
7-35-L	2/9-28S/70W	Dakota	2.53 (6)	0.916 (14)	3.06 (3)	0.749 (12)	-5.0 (2)
2-35-C	26/9-27S/70W	Dakota	2.57 (6)	0.963 (19)	2.87 (3)	0.573 (8)	nm
1-15-C	15/9-27S/70W	Entrada	2.71 (6)	0.967 (16)	2.71 (3)	6.77 (10)	nm
3-4-O	9/9-27S/70W	Dakota	2.53 (6)	0.937 (14)	2.99 (3)	2.64 (3)	-5.8 (3)
4-14-M	22/9-27S/70W	Dakota	2.65 (6)	0.892 (15)	3.00 (3)	1.11 (1)	nm
5-15-O	22/9-27S/70W	Dakota	2.30 (5)	1.056 (15)	2.92 (3)	4.33 (5)	-5.0 (1)

Field & Well	Location Twnshp-Rnge/Lat-Long	Producing Formation	CO <sub>2</sub> / <sup>3</sup> He x 10 <sup>9</sup>	<sup>3</sup> He/ <sup>4</sup> He (R/R <sub>a</sub> )	<sup>4</sup> He (x 10 <sup>-4</sup> ) cm <sup>3</sup> (STP)cm <sup>-3</sup>	<sup>20</sup> Ne (x 10 <sup>-8</sup> ) cm <sup>3</sup> (STP)cm <sup>-3</sup>	δ <sup>13</sup> C(CO <sub>2</sub> ) ‰
<b>Sheep Mountain</b> <sup>7</sup>			2.90 (7)				
4-4-P	9/9-27S/70W	Dakota		0.970 (14)	2.52 (2)	1.31 (2)	nm
5-9-A	9/9-27S/70W	Dakota	2.39 (6)	1.006 (18)	2.94 (3)	1.28 (2)	nm
1-1-J	2/9-28S/70W	Dakota	3.61 (8)	0.908 (16)	2.16 (2)	0.878 (12)	-5.2 (1)
1-22-H	22/9-28S/70W	Entrada	2.25 (5)	0.981 (17)	3.22 (3)	0.937 (13)	-4.5 (2)
<b>St. Johns Dome</b> <sup>7</sup>							
22-1X	34.4265, -109.2664	Supai	0.098 (2)	0.455 (8)	134 (13)	34.4 (47)	-3.65 (5)
10-22	34.2437, -109.1645	Supai	1.91 (42)	0.394 (8)	9.42 (9)	2.30 (4)	-3.79 (5)
3-1	34.3771, -109.2563	Supai	0.22 (3)	0.433 (9)	70.6 (7)	15.1 (21)	-3.85 (5)
<b>Jillin Field</b> <sup>12, 13, 23</sup>							
Wan 2		Cretaceous	1.44 (4)	4.91 (6)	1.00 (2)	nm	-3.6
Wan 5		Cretaceous	227 (7)	4.10 (4)	0.0076 (2)	0.0547 (15)	-5.0
Wan 6		Cretaceous	8.32 (3)	4.99 (5)	0.169 (4)	0.230 (6)	-3.8
Wan 8		Cretaceous	nm	4.30 (5)	nm	nm	-3.2
Wan 9		Cretaceous	36.6 (10)	4.08 (4)	0.047 (1)	0.130 (3)	-3.8
<b>Subai Basin</b> <sup>12, 23</sup>							
Huangqyan 1		Permian	2.17 (7)	3.52 (5)	3.13 (3)	1.47 (2)	-3.6
Sutail 74		Devonian	0.493(14)	3.59 (4)	2.96 (3)	3.04 (3)	-4.1
Su203		Eocene	0.459 (13)	2.61 (3)	2.95 (3)	0.613 (9)	-2.7
<b>Kismarja</b> <sup>8,30</sup>							
Kismarja 8		Up. Pannonian	20.2 (5)	1.33 (3)	0.226 (7)	nm	-5.0
Kismarja 79		Up. Pannonian	15.5 (4)	1.38 (3)	0.310 (10)	nm	-4.9
Kismarja 61		Up. Pannonian	27.3 (6)	1.16 (2)	0.205 (6)	nm	-5.1
Kismarja 55		Up. Pannonian	13.3 (3)	1.38 (3)	0.360 (11)	nm	-5.1
Kismarja 56		Up. Pannonian	1090 (3)	1.16 (2)	0.0052 (2)	nm	-6.8
Kismarja 74		Up. Pannonian	65.2 (2)	1.34 (3)	0.078 (3)	nm	-6.4
Kismarja 22		Up. Pannonian	1.52 (1)	1.02 (2)	1.31 (3)	nm	-6.6

nm = not measured

1σ error shown in brackets

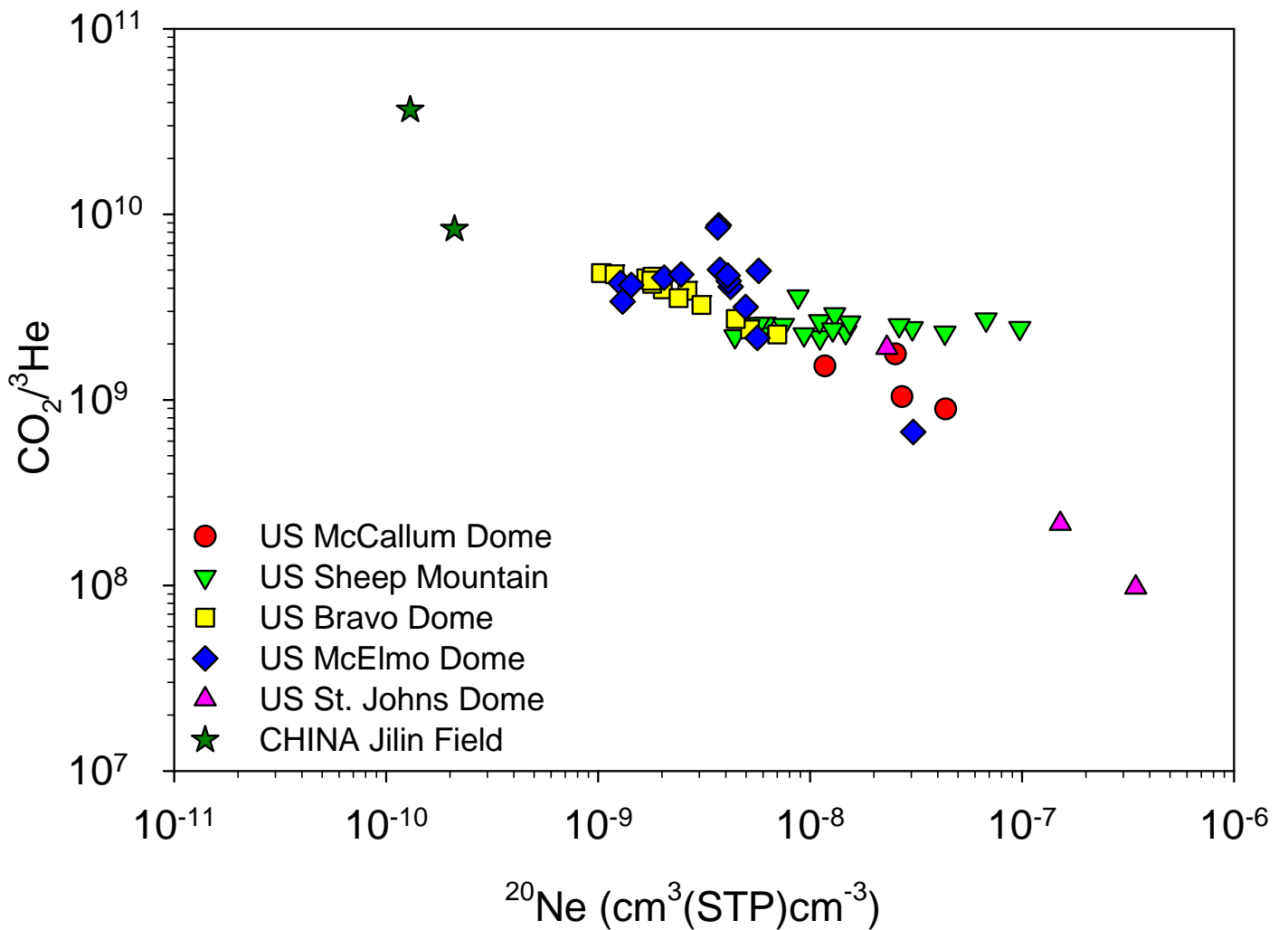
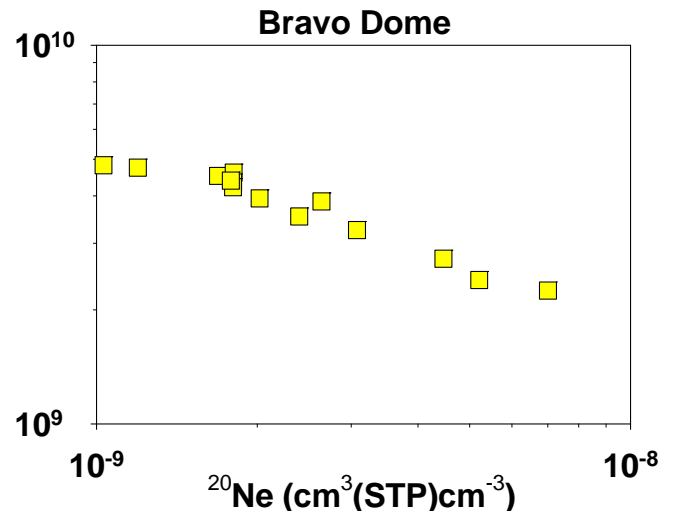
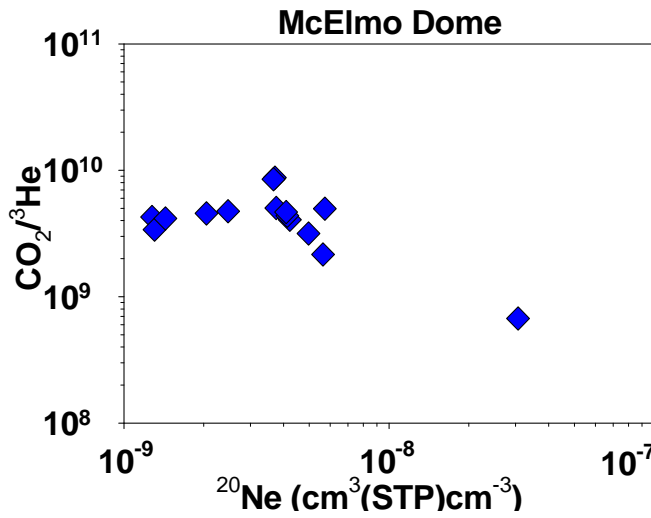
## Figure Captions

**Figure 1.**  $\text{CO}_2/{}^3\text{He}$  variation plotted against  ${}^{20}\text{Ne}$  in samples from the 'global' data set of  $\text{CO}_2$ -rich natural gas fields (see text). There is a general trend in this data set of decreasing  $\text{CO}_2/{}^3\text{He}$  with increasing  ${}^{20}\text{Ne}$ . This trend is most clearly apparent in the siliciclastic case type Bravo Dome data set (inset) but less clear in the carbonate case type reservoir, McElmo Dome (inset).  ${}^3\text{He}$  is conservative within the gas phase. Lower  $\text{CO}_2/{}^3\text{He}$  therefore represent subsurface reduction in  $\text{CO}_2$  concentration in the emplaced  $\text{CO}_2$  phase. Since the only subsurface source of the  ${}^{20}\text{Ne}$  now in the  $\text{CO}_2$  phase is the formation water, the  $\text{CO}_2$  sink must be linked to the formation water contacted by the gas phase.

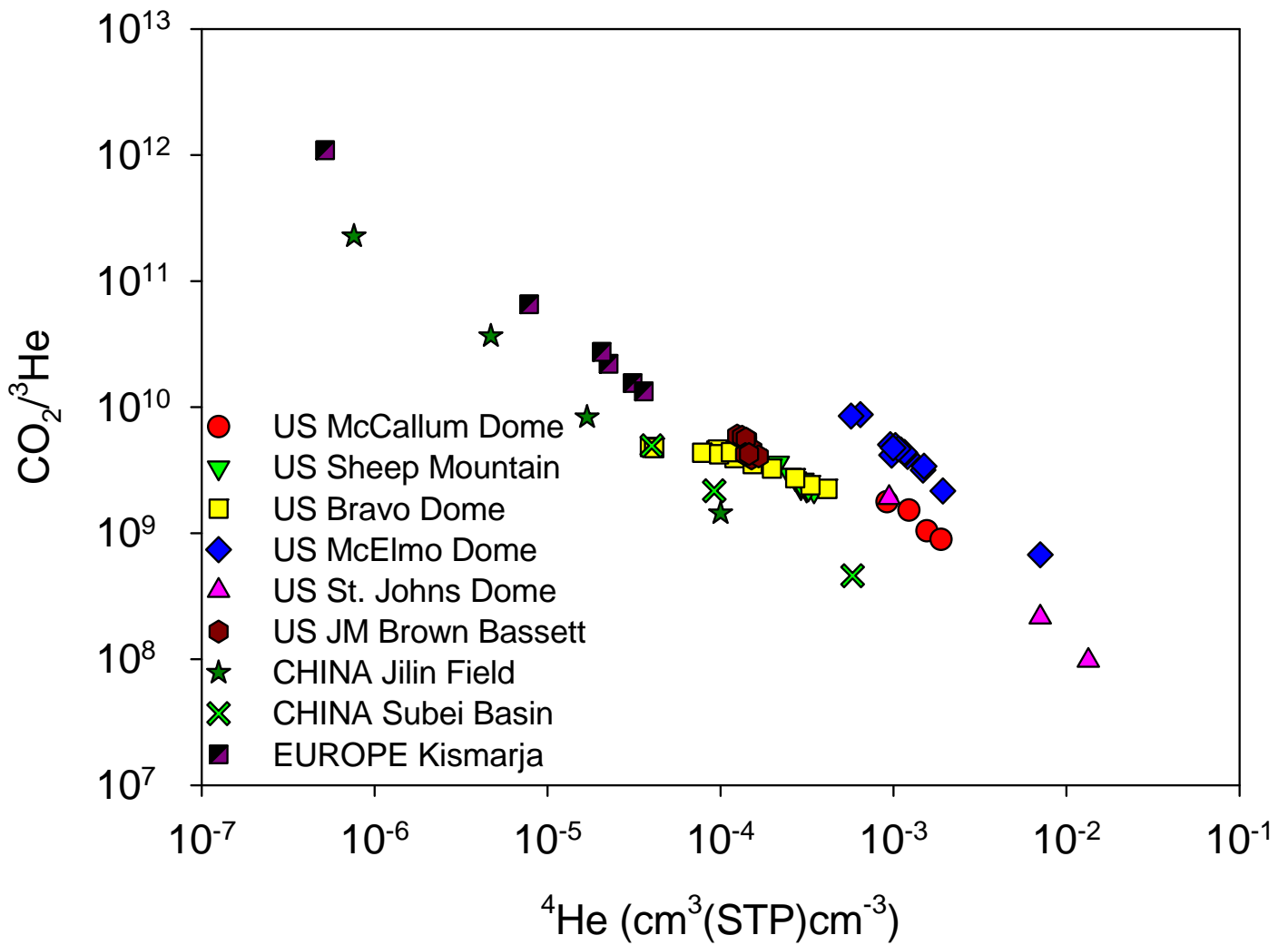
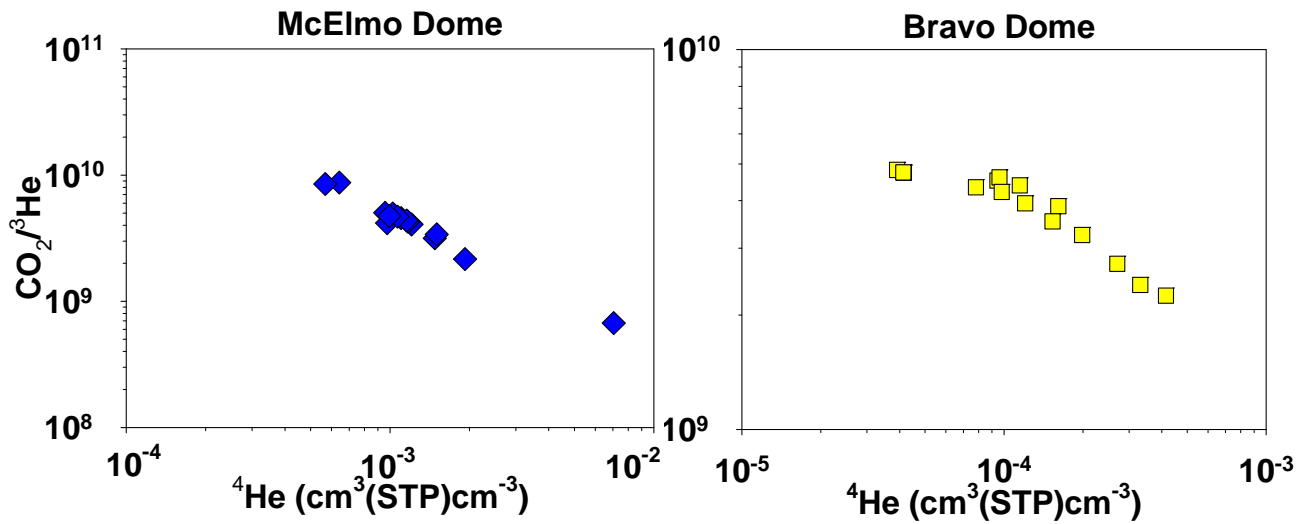
**Figure 2.** The 'global' data sets of  $\text{CO}_2$  gas fields also show a strong correlation between decreasing  $\text{CO}_2/{}^3\text{He}$  and increasing  ${}^4\text{He}$  concentration.  ${}^4\text{He}$  accumulates in formation water over time<sup>7,15,16</sup> and underscores the importance of formation water in controlling the mechanism of subsurface  $\text{CO}_2$  removal (Fig.1 and text). We speculate that the formation water  ${}^4\text{He}$  signature with  $\text{CO}_2/{}^3\text{He}$  is more coherent than the  ${}^{20}\text{Ne}$  (Fig. 1) due to perturbation of  ${}^{20}\text{Ne}$  in ancient formation water through non-water phase interaction<sup>9</sup> with subsequent  ${}^4\text{He}$  accumulation providing a homogenous regional scale formation water  ${}^4\text{He}$  signal<sup>15,16</sup>. Different  $\text{CO}_2/{}^3\text{He}$  vs.  ${}^4\text{He}$  gradients will be due to different local formation water  ${}^4\text{He}$  accumulation rates.

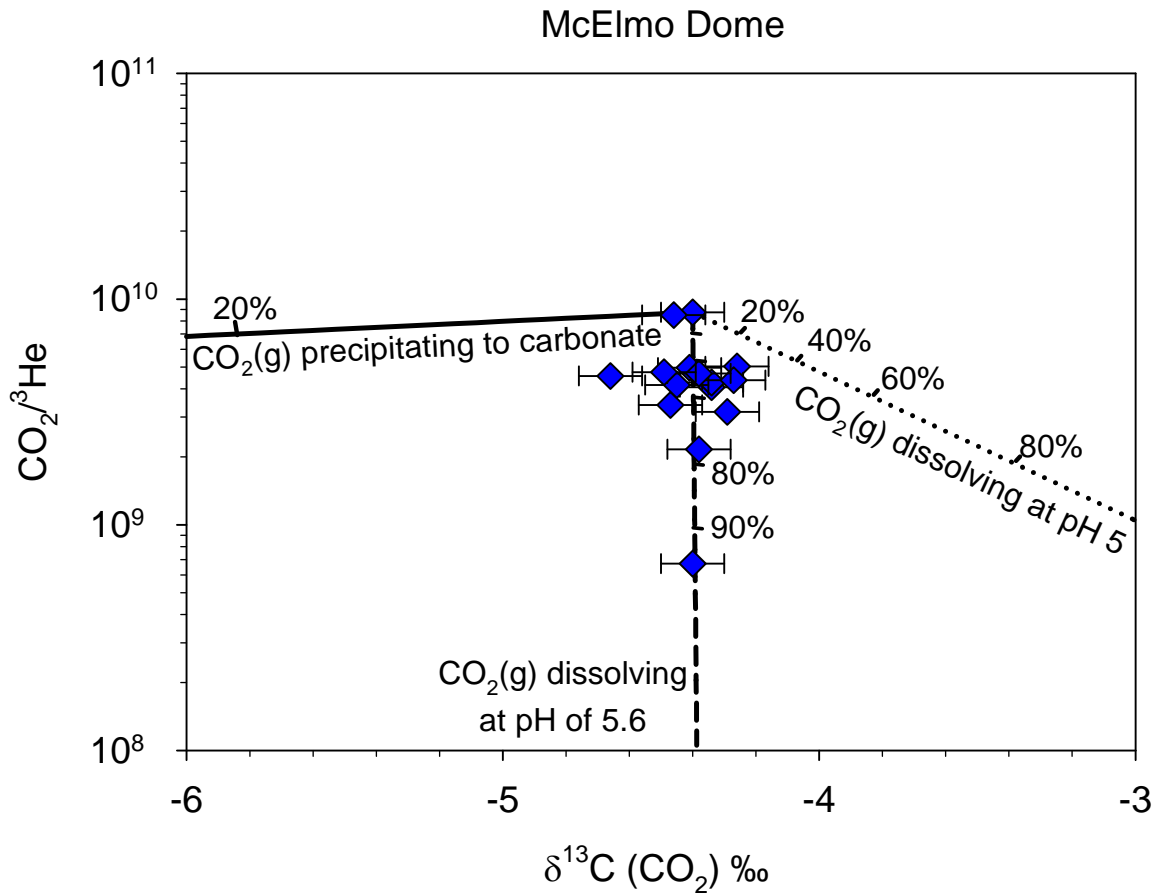
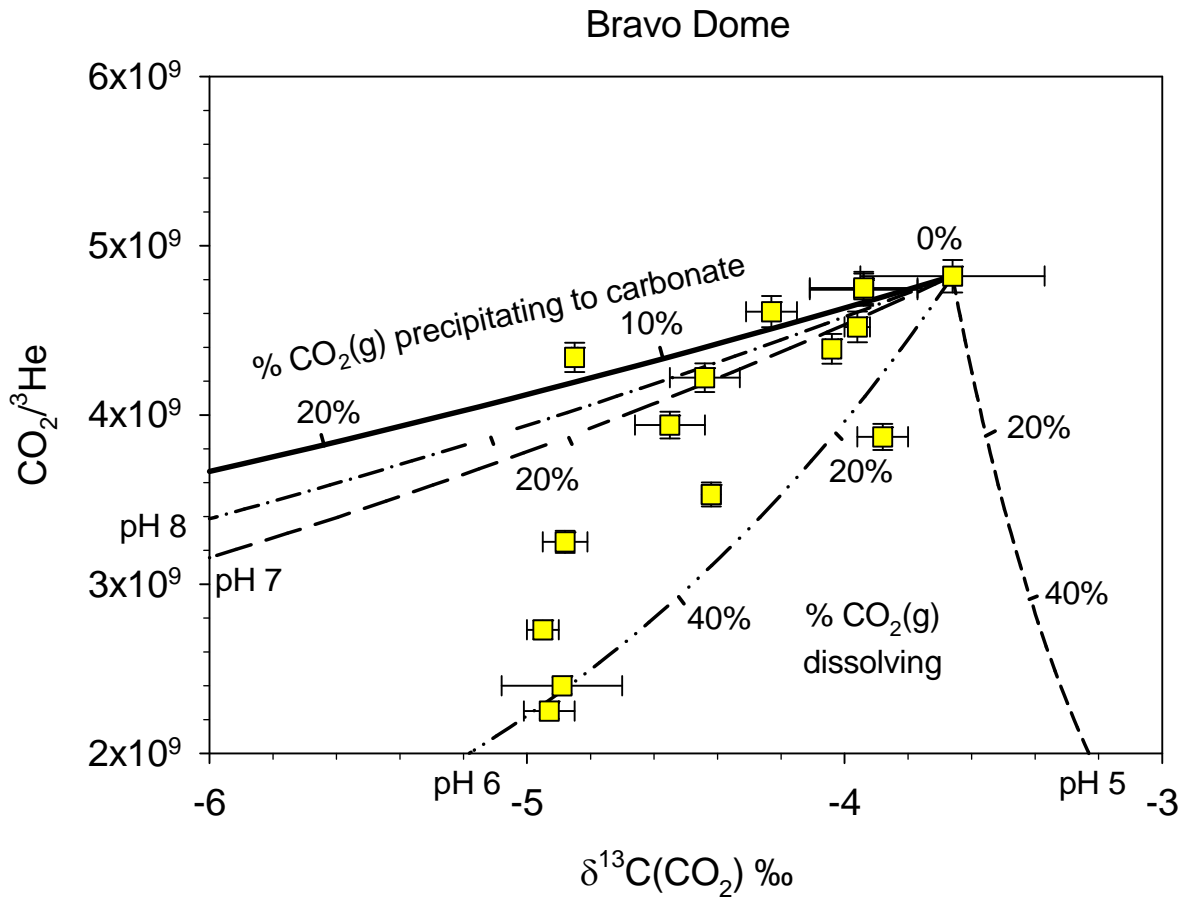
**Figure 3.**  $\delta^{13}\text{C}(\text{CO}_2)$  against  $\text{CO}_2/{}^3\text{He}$  for Bravo Dome (Top) and McElmo Dome (Bottom) Error bars are  $1\sigma$ . Top Panel: The solid line shows the predicted trend for carbonate mineral precipitation and the dashed lines show  $\text{CO}_2(\text{g})$  dissolution trends

for varying formation water pH (see methods). Bravo Dome data is not consistent with the major CO<sub>2</sub> sink being precipitation of carbonate (see text). Bottom Panel: Invariant  $\delta^{13}\text{C}(\text{CO}_2)$  with over an order of magnitude change in CO<sub>2</sub>/<sup>3</sup>He in McElmo Dome gases cannot be accounted for by precipitation (solid line). Dissolution of reservoir CO<sub>2</sub> into formation water at pH=5.6 would produce the observed results (see text).









## Supplementary Information:

**Supplementary Table 1**  
**Reservoir Conditions Used in Models**

Reservoir	Average Well Depth (m)	Pressure (MPa)	Borehole Temperature (K)	TDS (molar)	K <sub>He</sub> (GPa)	K <sub>CO2</sub> (GPa)	Fractionation (1000ln $\alpha$ ) for CO <sub>2(g)</sub> forming (‰) [24]		
							H <sub>2</sub> CO <sub>3(aq)</sub>	HCO <sub>3</sub> <sup>-</sup>	CaCO <sub>3</sub>
Bravo Dome <sup>30</sup>	820	8.03	314	1.45	20.1	0.349	-0.846	6.63	8.55
JM Brown Bassett <sup>5</sup>	2800*	27.4*	373	1.00*	14.0	0.774	-0.864	3.36	4.96
McCallum Dome <sup>7</sup>	1630	16.0	<a href="#">338</a>	0.228	14.1	0.460	-0.854	5.10	6.85
McElmo Dome <sup>7</sup>	2450	24.0	344	<a href="#">0.200</a>	11.9	0.487	-0.856	4.76	6.48
Sheep Mountain <sup>7</sup>	1400	13.7	331	0.0137	13.6	0.438	-0.852	5.51	7.29
St. Johns Dome <sup>31</sup>	630	6.17	322	0.0720	14.4	0.281	-0.849	6.08	7.92
Jilin Field <sup>21</sup>	840	8.23	333*	1.00*	17.4	0.491	- <a href="#">0.853</a>	5.39	7.16
Subei Basin <sup>12</sup>	2251	22.1	357*	1.00*	15.4	0.665	-0.860	4.09	5.75
Kismarja <sup>29</sup>	825	8.08	326*	1.00*	17.7	0.438	-0.850	5.82	7.63

\*JM Brown Bassett depth estimated from bottom hole temperature and 30°C/km geothermal gradient. Jilin Field, Subei Basin and Kismarja borehole temperatures estimated from depth and geothermal gradient. JM Brown Bassett, Jilin Field, Subei Basin and Kismarja salinity estimated.

### Additional References for Supplementary Table

30. Broadhead, R. F. Carbon dioxide in northeast New Mexico. *West Texas Geological Society Bulletin* **32**, 5-8 (1993).
31. Stevens, S. H., Fox, C., White, T. & Melzer, S. Natural CO<sub>2</sub> analogs for Carbon Sequestration. *Final Report for USDOE* (2006).