

LETTERS

Solubility trapping in formation water as dominant CO₂ sink in natural gas fields

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Injecting CO₂ into deep geological strata is proposed as a safe and economically favourable means of storing CO₂ captured from industrial point sources^{1–3}. It is difficult, however, to assess the long-term consequences of CO₂ flooding in the subsurface from decadal observations of existing disposal sites^{1,2}. Both the site design and long-term safety modelling critically depend on how and where CO₂ will be stored in the site over its lifetime^{2–4}. Within a geological storage site, the injected CO₂ can dissolve in solution or precipitate as carbonate minerals. Here we identify and quantify the principal mechanism of CO₂ fluid phase removal in nine natural gas fields in North America, China and Europe, using noble gas and carbon isotope tracers. The natural gas fields investigated in our study are dominated by a CO₂ phase and provide a natural analogue for assessing the geological storage of anthropogenic CO₂ over millennial timescales^{1,2,5,6}. We find that in seven gas fields with siliciclastic or carbonate-dominated reservoir lithologies, dissolution in formation water at a pH of 5–5.8 is the sole major sink for CO₂. In two fields with siliciclastic reservoir lithologies, some CO₂ loss through precipitation as carbonate minerals cannot be ruled out, but can account for a maximum of 18 per cent of the loss of emplaced CO₂. In view of our findings that geological mineral fixation is a minor CO₂ trapping mechanism in natural gas fields, we suggest that long-term anthropogenic CO₂ storage models in similar geological systems should focus on the potential mobility of CO₂ dissolved in water.

Noble gas and CO₂ carbon isotopes are powerful tracers of crustal fluid processes that act on subsurface CO₂ (refs 5, 7–10). Within a geological storage site, CO₂ injected as a free CO₂ phase (gas or supercritical) may over time be dissolved in solution (solubility trapping), or locked within carbonate minerals by precipitation (mineral trapping)^{4,11}. By using noble gas and carbon isotope tracers together to study naturally occurring CO₂ systems, we can uniquely identify and quantify the principal mechanism of the CO₂ phase removal (mineral or solubility trapping) over a timescale not accessible through extant injection studies.

We combine noble gas data from five natural CO₂ reservoirs located within the Colorado Plateau and Rocky Mountain provinces (McCallum dome, Sheep Mountain and McElmo dome, in Colorado; Bravo dome, in New Mexico; and St Johns dome, in Arizona and New Mexico)⁷ 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 the stripping of CO₂ gas from the formation water during reservoir filling, followed by partial dissolution of noble gases back into the formation water⁷. We also consider published noble gas and stable isotope information in a further four CO₂-rich

natural gas fields (the JM-Brown Bassett (JMBB) field in the Permian basin, Texas⁵; the Kismarja field in the Pannonian basin, Hungary⁸; and the Jilin field in the Songliao basin, Jilin Province, and the Subei basin field, Jiangsu Province, in China^{12,13}).

CO₂/³He ratios within the magmatic range of $(1–10) \times 10^9$ have been used to identify a primary magmatic origin of the CO₂ contained within five natural CO₂ reservoirs of the Colorado Plateau and Rocky Mountain provinces⁷. CO₂/³He ratios within the Subei basin and the JMBB field also indicate a magmatic origin, but the CO₂/³He ratios within the Jilin and Kismarja fields are much higher, suggesting a predominantly crustal origin^{5,8,12,13}. All of the reservoirs exhibit local variation in the CO₂ content relative to the inert tracer ³He. As there is not a significant source of ³He within the crust¹⁴, and as ³He is inert and highly insoluble⁹, this variation must be due to changes in the CO₂ component within the reservoirs. Although many sources and sinks of CO₂ exist in the subsurface^{4,8,9}, below we argue that the variation in CO₂/³He ratios is caused by CO₂ loss from the reservoir. The difference between the highest CO₂/³He ratio and lower values can provide a minimum estimate of this CO₂ loss. In the case of Bravo dome, a reduction in CO₂/³He values from 4.82×10^9 (well BD11) to 2.25×10^9 (BD02) indicates a loss of the original CO₂ charge of >50% in the portion of the reservoir represented by BD02 (Table 1). Samples from McElmo dome show a decrease from 8.5×10^9 (YD-1) to 0.68×10^9 (HE-2), suggesting a loss of emplaced CO₂ of >90% in portions of this field.

⁴He is continually produced in the subsurface by the radiogenic decay of U, Th and K (ref. 14). ²⁰Ne is introduced into the subsurface as a component of air dissolved in water and, as such, can only enter the reservoir system through interaction with formation water⁹. Although there is no *a priori* reason to expect a correlation between ⁴He and ²⁰Ne, one has been observed in natural gases on a regional scale¹⁵. This correlation is the result of ⁴He accumulating in the formation water¹⁶, which also contains atmosphere-derived ²⁰Ne, and subsequent quantitative partitioning of both ⁴He and ²⁰Ne into the reservoir phase^{7,15}. Almost all CO₂ reservoirs for which we have ²⁰Ne and ⁴He concentration data show a local ²⁰Ne correlation with ⁴He (Table 1 and Supplementary Information). A decrease in CO₂/³He is also correlated with ²⁰Ne in most CO₂ reservoirs (Fig. 1) and with ⁴He in all CO₂ reservoirs (Fig. 2).

There are various mechanisms by which crustal CO₂ (CO₂/³He > 10¹⁰) can be added to these systems^{4,10}, but there is no plausible mechanism that enables crustal CO₂ to be variably added to these systems while preserving a correlation of CO₂/³He with the noble gases derived from formation water. Neglecting small amounts of ³He dissolution back into the formation water⁷, changes in

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Table 1 | Sample location, producing formation, major gas species and CO₂ carbon isotopes

Field and well	Location	Producing formation	CO ₂ / ³ He (10 ⁹)	³ He/ ⁴ He (R/R _a)	⁴ He (10 ⁻⁴ cm ³ (STP) cm ⁻³)	²⁰ Ne (10 ⁻⁸ cm ³ (STP) cm ⁻³)	δ ¹³ C(CO ₂) (‰)
Bravo dome⁷							
BD01	35.8613, -103.2947	Tubb	4.53 (10)	1.670 (8)	0.944 (12)	0.169 (2)	-3.96 (4)
BD02	36.0058, -103.2305	Tubb	2.25 (5)	0.764 (4)	4.15 (5)	0.700 (7)	-4.93 (8)
BD03	36.0934, -103.2662	Tubb	2.41 (5)	0.896 (4)	3.31 (4)	0.521 (5)	-4.89 (19)
BD04	35.9766, -103.3480	Tubb	4.61 (10)	1.611 (8)	0.961 (2)	0.181 (2)	-4.23 (8)
BD05	35.9190, -103.2059	Tubb	2.74 (6)	0.965 (5)	2.70 (4)	0.446 (4)	-4.95 (5)
BD06	36.1080, -103.4988	Tubb	3.94 (8)	1.503 (8)	1.20 (2)	0.202 (2)	-4.55 (11)
BD07	35.9046, -103.4190	Tubb	4.34 (9)	2.104 (11)	0.781 (10)	0.180 (2)	-4.85 (1)
BD08	35.8037, -103.4368	Tubb	3.87 (8)	1.143 (6)	1.61 (2)	0.264 (3)	-3.88 (8)
BD09	36.0496, -103.4452	Tubb	4.22 (9)	1.724 (9)	0.981 (12)	0.180 (2)	-4.44 (11)
BD10	36.1519, -103.3557	Tubb	3.25 (6)	1.104 (6)	1.99 (3)	0.308 (3)	-4.88 (7)
BD11	35.8469, -103.7032	Tubb	4.82 (10)	3.784 (19)	0.391 (5)	0.103 (1)	-3.66 (29)
BD12	35.8469, -103.7387	Tubb	4.74 (10)	3.627 (18)	0.415 (6)	NM	-3.94 (17)
BD13	35.7749, -103.2059	Tubb	3.54 (8)	1.318 (7)	1.53 (2)	0.240 (3)	-4.42 (3)
BD14	35.7893, -103.3302	Tubb	4.39 (9)	1.413 (7)	1.15 (2)	0.179 (4)	-4.04 (2)
BD12b	35.8469, -103.7387	Tubb	4.75 (10)	3.634 (18)	0.413 (6)	0.120 (2)	-3.94 (17)
McCallum dome⁷							
No. 3 (8-3)	40.7632, -106.1717	Lakota	1.52 (4)	0.354 (7)	12.3 (2)	1.17 (2)	-5.1 (3)
No. 5	40.7777, -106.2479	Lakota	1.04 (3)	0.409 (7)	15.5 (2)	2.71 (3)	-5.2 (1)
No. 13	40.7777, -106.2289	Lakota/Morrison	0.89 (2)	0.393 (7)	18.8 (2)	4.36 (5)	-5.3 (2)
No. 79	40.7777, -106.2670	Dakota/Lakota	1.77 (6)	0.406 (6)	9.16 (21)	2.53 (3)	-5.7 (1)
McElmo dome⁷							
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)
JM-Brown Basset field⁶							
Turk State No. 1A	30.38758, -101.85642	Ellenberger	5.92 (47)	0.543 (16)	1.25 (9)	NM	-2.88 (3)
Bassett Goode No. 3	30.37852, -101.83068	Ellenberger	5.55 (43)	0.527 (16)	1.42 (10)	NM	-2.89 (3)
Brown Bassett No. 2*	30.34433, -101.7995	Ellenberger	5.82 (35)	0.502 (15)	1.33 (7)	NM	-2.90 (3)
Mayme K. Martin ETAL 1	30.35661, -101.74721	Ellenberger	5.29 (40)	0.372 (11)	1.42 (10)	NM	-2.97 (3)
Mitchell 109 No. 2*	30.33329, -101.69826	Ellenberger	4.58 (36)	0.400 (12)	1.53 (11)	NM	-2.92 (3)
Mitchell 5 No. 1X	30.32352, -101.68429	Ellenberger	5.61 (43)	0.478 (11)	1.40 (10)	NM	-2.84 (3)
Mitchell 103 No. 2	30.3568, -101.63642	Ellenberger	4.20 (33)	0.246 (7)	1.39 (10)	NM	-2.70 (3)
Mitchell No. 6	30.351, -101.58835	Ellenberger	3.93 (31)	0.264 (8)	1.51 (11)	NM	-2.96 (3)
Mitchell No. 3	30.33966, -101.61307	Ellenberger	4.22 (33)	0.240 (7)	1.39 (10)	NM	-3.06 (3)
Mitchell A-11 No. 1	30.30286, -101.57677	Ellenberger	4.07 (32)	0.272 (8)	1.66 (12)	NM	-2.93 (3)
Mitchell No. 12	30.29118, -101.57295	Ellenberger	4.24 (130)	0.267 (8)	1.46 (10)	NM	-2.96 (3)
Sheep Mountain⁷							
8-2-P	37.6383, -105.1836	Dakota	2.31 (5)	0.981 (10)	3.13 (3)	1.47 (2)	-5.0 (2)
2-10-O	37.6966, -105.2018	Entrada	2.44 (6)	0.984 (12)	2.96 (3)	3.04 (3)	-5.2 (1)
9-26	37.6675, -105.1836	Dakota	2.57 (6)	0.934 (14)	2.95 (3)	0.613 (9)	NM
2-9-H	37.7112, -105.2200	Dakota	2.44 (6)	0.945 (19)	3.07 (3)	9.77 (10)	NM
3-15-B	37.6966, -105.2018	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	37.6675, -105.1836	Entrada	2.20 (5)	1.024 (18)	3.15 (3)	0.442 (4)	-4.8 (1)
3-23-D	37.6820, -105.2018	Dakota	2.26 (5)	0.988 (14)	3.17 (3)	0.579 (9)	NM
7-35-L	37.6383, -105.1836	Dakota	2.53 (6)	0.916 (14)	3.06 (3)	0.749 (12)	-5.0 (2)
2-35-C	37.6675, -105.1836	Dakota	2.57 (6)	0.963 (19)	2.87 (3)	0.573 (8)	NM
1-15-C	37.6966, -105.2018	Entrada	2.71 (6)	0.967 (16)	2.71 (3)	6.77 (10)	NM
3-4-O	37.7112, -105.2200	Dakota	2.53 (6)	0.937 (14)	2.99 (3)	2.64 (3)	-5.8 (3)
4-14-M	37.6820, -105.2018	Dakota	2.65 (6)	0.892 (15)	3.00 (3)	1.11 (1)	NM
5-15-O	37.6820, -105.2018	Dakota	2.30 (5)	1.056 (15)	2.92 (3)	4.33 (5)	-5.0 (1)
4-4-P	37.7112, -105.2200	Dakota	2.90 (7)	0.970 (14)	2.52 (2)	1.31 (2)	NM
5-9-A	37.7112, -105.2200	Dakota	2.39 (6)	1.006 (18)	2.94 (3)	1.28 (2)	NM
1-1-J	37.6383, -105.1836	Dakota	3.61 (8)	0.908 (16)	2.16 (2)	0.878 (12)	-5.2 (1)
1-22-H	37.5946, -105.2018	Entrada	2.25 (5)	0.981 (17)	3.22 (3)	0.937 (13)	-4.5 (2)
St Johns dome⁷							
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)
Jilin field^{12,13,21}							
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

Table 1 is continued on page 616.

Table 1 | Continued

Field and well	Location	Producing formation	CO ₂ / ³ He (10 ⁹)	³ He/ ⁴ He (R/R _a)	⁴ He (10 ⁻⁴ cm ³ (STP) cm ⁻³)	²⁰ Ne (10 ⁻⁸ cm ³ (STP) cm ⁻³)	δ ¹³ C(CO ₂) (‰)
Wan 9	—	Cretaceous	36.6 (10)	4.08 (4)	0.047 (1)	0.130 (3)	-3.8
Subei field ^{12,21}							
Huangqian 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
Kismarja field ^{8,29}							
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

Location is given as latitude and longitude in decimal degrees, where north and east are positive and south and west are negative. The ³He/⁴He ratio, R, is shown relative to the ³He/⁴He ratio in air, R_a, which is taken to be 1.399 × 10⁻⁶. δ¹³C‰ = [(¹³C/¹²C_{sample} - ¹³C/¹²C_{standard})/(¹³C/¹²C_{standard})] × 1,000; the standard used is the Vienna PeeDee Belemnite. Errors (1σ) are shown in parentheses. NM, not measured.

* Average of two analyses for He and Ar.

CO₂/³He must therefore be due to CO₂ loss in the subsurface by an amount directly proportional to the amount of formation water that has been degassed. CO₂ is soluble and reactive. The most probable mechanisms of subsurface CO₂ fluid phase removal are solubility and/or mineral trapping^{4,11}.

Reservoir lithology may exert a significant influence on how changes in CO₂/³He ratio relate to δ¹³C(CO₂). The carbonate reservoirs (the JMBB field and the McElmo and St Johns domes) show little variance in δ¹³C(CO₂), whereas the siliciclastic fields (the Jilin, Subei basin and Kismarja fields, Sheep Mountain, McCallum dome

and Bravo dome) exhibit a greater δ¹³C(CO₂) range (Table 1 and Supplementary Fig. 1). We consider Bravo dome and McElmo dome as representative cases for each type of reservoir lithology.

Emplacement of CO₂ at Bravo dome is believed to have occurred relatively recently (local volcanic activity dates from 8,000 to 10,000 years ago)^{7,17}, and the field may still be undergoing active CO₂ recharge¹¹. The decreasing CO₂/³He ratio within Bravo dome correlates with more negative δ¹³C(CO₂) (Fig. 3a). Taking the highest CO₂/³He ratio, of 4.82 × 10⁹ (BD11), to be the sample that experienced

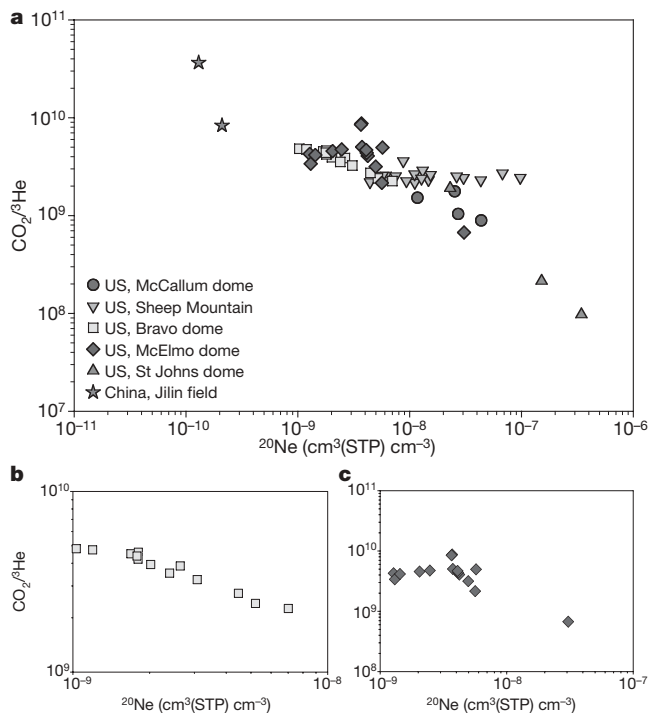


Figure 1 | CO₂/³He variation plotted against ²⁰Ne from CO₂-rich natural gas fields. a, There is a general trend in this data set of decreasing CO₂/³He with increasing ²⁰Ne. **b, c**, This trend is most clear in the siliciclastic-case data set, from Bravo dome (**b**), but less clear in the data from the carbonate-case reservoir, McElmo dome (**c**). ³He is conservative within the gas phase. Lower CO₂/³He ratios therefore represent subsurface reduction in CO₂ concentration in the emplaced CO₂ phase. Because the only subsurface source of the ²⁰Ne is the formation water, the CO₂ sink must be linked to the formation water contacted by the gas phase. STP indicates measurement at the International Union of Pure and Applied Chemistry (IUPAC) standard temperature (0 °C) and pressure (100 kPa).

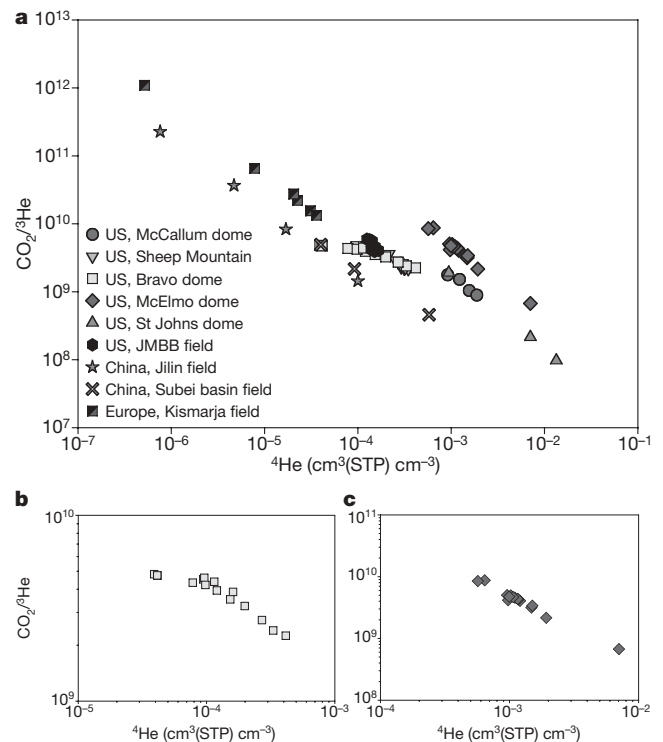


Figure 2 | CO₂/³He in CO₂-rich natural gas fields shows strong anticorrelation with ⁴He. a, ⁴He accumulates in formation water over time^{7,15,16} and underscores the importance of formation water in controlling the mechanism of subsurface CO₂ removal (Fig. 1 and main text). We speculate that the formation-water ⁴He signature with CO₂/³He is more coherent than the equivalent ²⁰Ne signature (Fig. 1) owing to perturbation of ²⁰Ne in ancient formation water through non-water phase interaction⁹, with subsequent ⁴He accumulation providing a homogenous, regional-scale formation-water ⁴He signal^{15,16}. Different CO₂/³He-versus-⁴He gradients are due to different local formation-water ⁴He accumulation rates. **b, c**, As in Fig. 1, but for ⁴He.

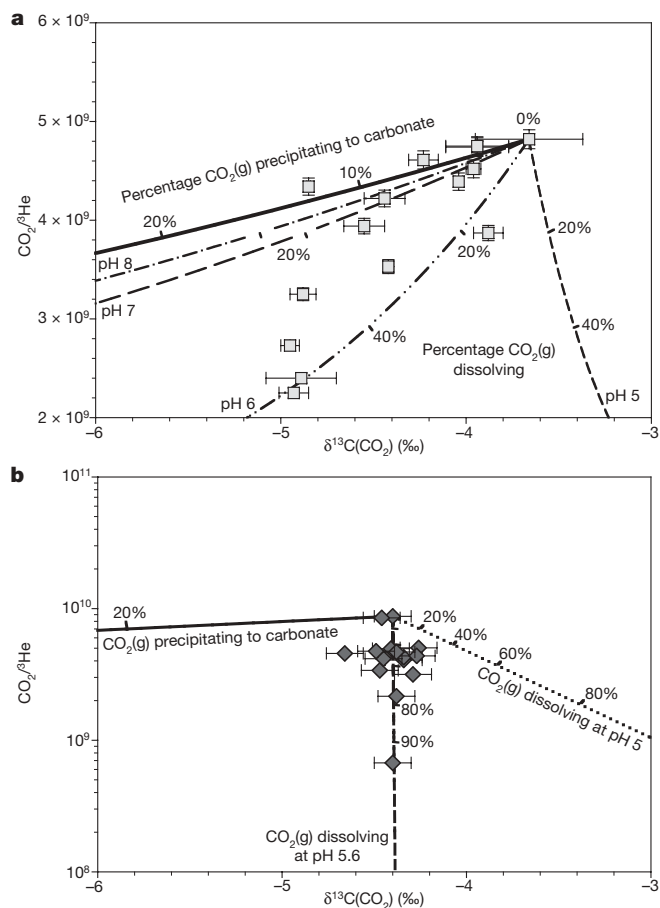


Figure 3 | Plot of $\delta^{13}\text{C}(\text{CO}_2)$ against $\text{CO}_2/{}^3\text{He}$ for Bravo dome and McElmo dome. **a**, Bravo Dome. The solid line shows the predicted trend for carbonate mineral precipitation and the broken lines show $\text{CO}_2(\text{g})$ dissolution trends for the indicated formation-water pH (see Methods Summary). This data limits the maximum effect of CO_2 precipitation in samples to approximately 18%. **b**, McElmo Dome. Invariant $\delta^{13}\text{C}(\text{CO}_2)$ with a change in $\text{CO}_2/{}^3\text{He}$ of over an order of magnitude in McElmo dome gases cannot be accounted for by precipitation (solid line). Dissolution of reservoir CO_2 into formation water at pH 5.6 is consistent with observed results. Error bars are 1σ .

the least 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 CO_2 dissolution into the formation water at various pH values and for CO_2 precipitation as a carbonate (Methods Summary). The data are not consistent with precipitation as carbonate being a major sink for CO_2 at Bravo dome (Fig. 3a). However, although a significant number of the data points are consistent with CO_2 dissolution into formation water at a pH between 6 and 7, it is not possible to rule out a degree of CO_2 loss due to precipitation together with CO_2 dissolution at a lower pH (for example pH 5). In such a two-process model, an upper limit of approximately 18% can be set on the proportion of CO_2 lost to precipitation (Fig. 3a). Hence, in all cases the major CO_2 sink is dissolution.

In situ precipitation of 18% of reservoir CO_2 would generate between 3.2 and 6.1% by mass of the whole rock, depending on whether dolomite, calcite or dawsonite precipitation was favoured by the reservoir conditions. Although evidence for CO_2 -rich formation water interaction within the reservoir has been documented, so far no secondary carbonate has been identified¹⁸. Nevertheless, the volume control of the water suggests that the location of the precipitate, if any, is likely to be within the water leg that was not sampled. Lack of reservoir secondary mineralization cannot at this stage rule out any carbonate precipitation as a minor CO_2 sink.

Similar to the case for Bravo dome, although many of the Sheep Mountain data can be accounted for by dissolution of CO_2 (at pH 5

in this case), a small component of precipitation cannot be ruled out. Adopting the same approach as used for Bravo dome, we find that the remaining Sheep Mountain data require a maximum of 10% precipitation and 20% dissolution of the original CO_2 charge (Table 1 and Supplementary Fig. 2). By contrast, although minor data scatter may also be due to some small amount of CO_2 precipitation or dissolution at pH 7–8, almost all the data from the other siliciclastic fields (McCallum dome and the Subei basin, Kismarja and Jilin fields) can be described by dissolution into the formation water alone, within a narrow pH range of 5–5.3 (Supplementary Figs 3–6).

Carbonate reservoir data from McElmo dome show a change in $\text{CO}_2/{}^3\text{He}$ ratio of over an order of magnitude, with invariant $\delta^{13}\text{C}(\text{CO}_2)$ (Fig. 3b). This pattern is repeated in the two other carbonate-dominated fields (Supplementary Figs 7, 8). Invariant $\delta^{13}\text{C}(\text{CO}_2)$ in these fields allows us to discount a two-process model of precipitation and dissolution such as at Bravo dome (Fig. 3a). These data are consistent with CO_2 dissolution only into formation water in the pH range of 5.4–5.8 (Fig. 3b and Supplementary Figs 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 CO_2 injection studies on CO_2 breakthrough¹⁹ in the Frio formation, Texas.

On a reservoir-engineering timescale, the early stages of CO_2 injection can result in a drop in pH and dissolution of carbonate minerals into the formation water^{18–20,22}. Any significant CO_2 contribution to the reservoir CO_2 phase from re-dissolution of carbonates would be ${}^3\text{He}$ free and would therefore perturb the correlation between $\text{CO}_2/{}^3\text{He}$ ratio and ${}^4\text{He}$ and ${}^{20}\text{Ne}$. As there is a clear correlation between $\text{CO}_2/{}^3\text{He}$ ratio and ${}^4\text{He}$ in all fields and ${}^{20}\text{Ne}$ within the majority, we conclude that dissolution of carbonate minerals into the formation water cannot have had a major influence on $\delta^{13}\text{C}(\text{CO}_2)$ values. There is no evidence for any precipitation of CO_2 within the carbonate-dominated reservoirs, requiring that the dominant mechanism of reservoir CO_2 loss, accounting for up to 90%, is through dissolution into the formation water.

Even the most conservative model we have presented places an upper limit of approximately 18% on the CO_2 removed by precipitation, and then only in some samples, from all natural gas fields investigated in a variety of lithological settings. Precipitation of CO_2 over millennial timescales represents at most only a small sub-surface trapping mechanism for CO_2 , and only within siliciclastic lithologies. The dominant mechanism of CO_2 loss from most CO_2 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 the fact that understanding geological carbon storage requires careful investigation of existing geological and hydrogeological analogues that have naturally accumulated and stored CO_2 over timescales relevant to anthropogenic CO_2 storage facilities. We have also demonstrated a means of testing trapping and storage mechanisms through coupled measurements of noble gas and carbon isotopes in the context of the pH evolution of formation/reservoir water.

METHODS SUMMARY

Detailed descriptions of the sample collection and analysis procedures can be found in the original references^{5,7,8,12,13,21}. In our calculations (Fig. 3 and Supplementary Figures) we use the highest $\text{CO}_2/{}^3\text{He}$ ratio measured in each field as a reference point to calculate the correlated reservoir $\text{CO}_2/{}^3\text{He}$ and $\delta^{13}\text{C}(\text{CO}_2)$ ratios as the CO_2 phase is removed by either precipitation or dissolution. We assume open system loss. In the case of precipitation there is zero ${}^3\text{He}$ loss from the CO_2 phase and $\text{CO}_2/{}^3\text{He}$ changes in proportion to the fraction of the remaining CO_2 phase. In the case of dissolution, the change in $\text{CO}_2/{}^3\text{He}$ ratio is calculated following the Rayleigh equation.

Changes in $\delta^{13}\text{C}(\text{CO}_2)$ are calculated using the Rayleigh fractionation equation expressed as $\delta^{13}\text{C}(\text{CO}_2) = \delta^{13}\text{C}(\text{CO}_2)_0 + \epsilon \ln f$ (ref. 23), where $\delta^{13}\text{C}(\text{CO}_2)_0$ is the original system value, f is the fraction of CO_2 remaining in the reservoir and ϵ is the carbon isotope fractionation, either for precipitation or for dissolution. Carbon isotope fractionation factors, α , are calculated as a function of temperature for

CO₂(g) precipitating to form CaCO₃(s), or dissolving to form either H₂CO₃(aq) or HCO₃⁻(aq) (ref. 24). Because all the fractionations are small, the simplification can be made that $\epsilon = 1,000 \ln \alpha$ (ref. 25). For typical reservoir waters of pH 5–8, the contribution of CO₃²⁻(aq) is negligible. Hence, for CO₂ dissolution, carbon isotope fractionation between the pool of dissolved inorganic carbon (DIC) and CO₂ gas used in the Rayleigh fractionation equation can be expressed as (ref. 23)

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

where x is the proportion of CO₂(g) dissolving to H₂CO₃(aq) at the relevant pH²³.

Solubility as a function of temperature and salinity is given by the IUPAC solubility series for CO₂ (ref. 26) and in refs 27, 28 for He. 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_{He} and K_{CO_2} and fractionation factor ($1,000 \ln \alpha$) for CO₂(g) forming H₂CO₃(aq), HCO₃⁻(aq) and CaCO₃(s) (Supplementary Table 1).

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- Schrag, D. P. Preparing to capture carbon. *Science* **315**, 812–813 (2007).
- Baines, S. J. & Worden, R. H. in *Geological Storage of Carbon Dioxide* (eds Baines, S. J. & Worden, R. H.) 1–6 (The Geological Society of London, 2004).
- Gale, J. in *Geological Storage of Carbon Dioxide* (eds Baines, S. J. & Worden, R. H.) 7–15 (The Geological Society of London, 2004).
- Bradshaw, J., Boreham, C. & La Pedalina, F. in *Proc. 7th Internat. Conf. Greenhouse Gas Control Technol. (GHGT-7)* (eds Rubin, E., Keith, D. & Gilboy, C.) 541–550 (Elsevier Science, 2004).
- Ballentine, C. J., Schoell, M., Coleman, D. & Cain, B. A. 300-Myr-old magmatic CO₂ in natural gas reservoirs of the west Texas Permian basin. *Nature* **409**, 327–331 (2001).
- Kintisch, E. The greening of synfuels. *Science* **320**, 306–308 (2008).
- Gilfillan, S. M. V. *et al.* The noble gas geochemistry of natural CO₂ gas reservoirs from the Colorado Plateau and Rocky Mountain provinces, USA. *Geochim. Cosmochim. Acta* **72**, 1174–1198 (2008).
- Sherwood Lollar, B., Ballentine, C. J. & O'Nions, R. K. The fate of mantle-derived carbon in a continental sedimentary basin: Integration of C/He relationships and stable isotope signatures. *Geochim. Cosmochim. Acta* **61**, 2295–2308 (1997).
- Ballentine, C. J., Burgess, R. & Marty, B. in *Noble Gases in Geochemistry and Cosmochemistry* (eds Porcelli, D. R., Ballentine, C. J. & Weiler, R.) 539–614 (Geochemical Society and Mineralogical Society of America, 2002).
- Cathles, L. M. & Schoell, M. Modeling CO₂ generation, migration and titration in sedimentary basins. *Geofluids* **7**, 441–450 (2007).
- Baines, S. J. & Worden, R. H. in *Geological Storage of Carbon Dioxide* (eds Baines, S. J. & Worden, R. H.) 59–85 (The Geological Society of London, 2004).
- Xu, S., Nakai, S., Wakita, H., Xu, Y. & Wang, X. Carbon isotopes of hydrocarbons and carbon dioxide in natural gases in China. *J. Asian Earth Sci.* **15**, 89–101 (1997).
- Xu, S., Nakai, S., Wakita, H. & Wang, X. Mantle-derived noble gases in natural gases from Songliao Basin, China. *Geochim. Cosmochim. Acta* **59**, 4675–4683 (1995).
- Ballentine, C. J. & Burnard, P. G. in *Noble Gases in Geochemistry and Cosmochemistry* (eds Porcelli, D. R., Ballentine, C. J. & Weiler, R.) 481–538 (Geochemical Society and Mineralogical Society of America, 2002).
- Ballentine, C. J. & Sherwood Lollar, B. Regional groundwater focusing of nitrogen and noble gases into the Hugoton-Panhandle giant gas field, USA. *Geochim. Cosmochim. Acta* **66**, 2483–2497 (2002).
- Torgersen, T. & Clarke, W. B. Helium accumulation in groundwater. I: An evaluation of sources and the continental flux of crustal ⁴He in the Great Artesian Basin, Australia. *Geochim. Cosmochim. Acta* **49**, 1211–1218 (1985).
- Broadhead, R. F. Natural accumulations of carbon dioxide in the New Mexico region - Where are they, how do they occur and what are the uses for CO₂? *Life Geol.* **20**, 2–6 (1998).
- Pearce, J. *et al.* Natural occurrences as analogues for the geochemical disposal of carbon dioxide. *Energy Convers. Manage.* **37**, 1123–1128 (1996).
- Kharaka, Y. K. *et al.* Gas-water-rock interactions in Frio Formation following CO₂ injection: Implications for the storage of greenhouse gases in sedimentary basins. *Geology* **34**, 577–580 (2006).
- Knauss, K. G., Johnson, J. W. & Steefel, C. I. Evaluation of the impact of CO₂, co-contaminant gas, aqueous fluid and reservoir rock interactions on the geologic sequestration of CO₂. *Chem. Geol.* **217**, 339–350 (2005).
- Xu, S., Shun'ichi, N., Wakita, H., Xu, Y. & Wang, X. Helium isotope compositions in sedimentary basins in China. *Appl. Geochem.* **10**, 643–656 (1995).
- Worden, R. H. & Smith, L. K. in *Geological Storage of Carbon Dioxide* (eds Baines, S. J. & Worden, R. H.) 211–224 (The Geological Society of London, 2004).
- Clark, I. D. & Fritz, P. *Environmental Isotopes in Hydrology* 55–61 (CRC, 1997).
- Deines, P., Langmuir, D. & Harmon, R. S. Stable carbon isotopes and the existence of a gas phase in the evolution of carbonate groundwaters. *Geochim. Cosmochim. Acta* **38**, 1147–1184 (1974).
- Fritz, P. & Fontes, J. C. *Handbook of Environmental Isotope Geochemistry* Vol. 1, 1–19 (Elsevier, 1980).
- Scharlin, P. & Cargill, R. W. *Carbon Dioxide in Water and Aqueous Electrolyte Solutions* (Solubility Data Series Vol. 62, IUPAC, 1996).
- Crovetto, R., Fernandez-Prini, R. & Laura Japas, M. Solubilities of inert gases and methane in H₂O and in D₂O in the temperature range of 300 to 600K. *J. Chem. Phys.* **76**, 1077–1086 (1982).
- Smith, S. P. Noble gas solubility in water at high temperature. *Eos* **66**, 397 (1985).
- Sherwood Lollar, B., O'Nions, R. K. & Ballentine, C. J. Helium and neon isotope systematics in carbon dioxide-rich and hydrocarbon-rich gas reservoirs. *Geochim. Cosmochim. Acta* **58**, 5279–5290 (1994).

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