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1 Estimating carbon dioxide residence times cales through
2 noble gas and stable isotope diffusion profiles

3 **Carmen A. Zwahlen^{1,2*}, Niko Kampman^{1,3}, Paul Dennis⁴, Zheng Zhou¹ and Greg**
4 **Holland^{1,2}**

5 ¹*Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, UK*

6 ²*School of Earth and Environmental Sciences, University of Manchester, Manchester*
7 *M13 9PL, UK*

8 ³*Shell Global Solutions International, Kessler Park 1, 2288 GS Rijswijk, Netherlands*

9 ⁴*School of Environmental Sciences, University of East Anglia, Norwich Research Park,*
10 *Norwich NR4 7TJ, UK*

11 E-mail: carmen.zwahlen@manchester.ac.uk

12 **ABSTRACT**

13 The study of natural carbon dioxide reservoirs provides fundamental insight into
14 processes involved in carbon capture and storage. However the calculations of process
15 rates such as dissolution of CO₂ into the formation water remain uncertain due to
16 indirectly determined ages of the CO₂ influx. The proposed ages for the Bravo Dome gas
17 field in New Mexico, USA, vary from 56 ka to 1.5 Ma. Here we demonstrate that
18 residence times can be estimated from simple modeling of noble gas and stable isotope
19 diffusion profiles from the gas water contact through the gas column. The Bravo Dome
20 gas field shows a gradient in noble gas concentrations and isotopic ratios from East to
21 West across the 70 km wide field. A mantle like endmember with a ³He/⁴He (R/R_A) ratio
22 of up to 4.7 is found in the west in contrast to a ground water endmember with high

23 concentrations of air and crustal derived noble gases in the east. The air and crustal
24 derived noble gases decrease gradually toward the west. Stable isotope compositions (C
25 and O) also vary across the field. Diffusion modeling of He, Ne, Ar, Kr, Xe and $\delta^{13}\text{C}$ data
26 yield residence times for the CO_2 between 14.1 ± 0.2 and $16.9^{+1.1}_{-0.5}$ ka. This is far less
27 than the previous estimates of 1.2–1.5 Ma based on apatite (U-Th)/He thermochronology,
28 leading to a dissolution rate of 29900^{+11800}_{-10700} t/a to 35900 ± 12300 t/a, implying that
29 28% of the total emplaced CO_2 dissolved. This new method can be applied to a wide
30 variety of gas fields with variation in the concentration of groundwater derived noble
31 gases and allow a better assessment of the timescale of other diffusive fluid-fluid
32 interactions.

33 INTRODUCTION

34 Natural carbon dioxide reservoirs serve as natural analogues for geological CO_2
35 storage and hence are studied extensively to understand processes that act over geological
36 timescales (Bickle et al., 2013). In order to quantify the rates of interactions between
37 carbon dioxide, subsurface fluids and the host rock, it is crucial to know the residence
38 time of the CO_2 in the reservoir. Previous estimates of CO_2 reservoir residence times
39 include dating of surface intrusive igneous rocks (Armstrong, 1969), dating of close-by
40 effusive igneous rocks (Condit, 1995; Stroud, 1997) and apatite (U-Th)/He
41 thermochronology (Sathaye et al., 2014). These methods have been used to infer
42 residence times for the Bravo Dome (New Mexico, USA) CO_2 reservoir ranging between
43 56 ka (Stroud, 1997) and 1.5 Ma (Sathaye et al., 2014). Petrographic studies on drill cores
44 suggest the carbon dioxide filling of Bravo Dome in mid Cenozoic (Hartig et al., 2011),
45 but rely exclusively on relative time constraints of diagenetic mineral growths with

46 poorly developed textures. Here we present a model for estimating directly the CO₂
47 residence time applied to the Bravo Dome gas field. The model relies on spatial sampling
48 of gases across the field and uses the diffusion of groundwater derived noble gases
49 entering the gas column at the gas water contact, with known diffusion constants, to
50 estimate residence ages.

51 **BRAVO DOME FIELD**

52 Bravo Dome is a well-studied sandstone hosted CO₂ reservoir in New Mexico,
53 USA (Baines and Worden, 2004; Cassidy, 2006; Dubacq et al., 2012; Gilfillan et al.,
54 2008; Gilfillan et al., 2009; Hartig et al., 2011; Holland and Ballentine, 2006; Kessler et
55 al., 2001; Sathaye et al., 2014). The gas is primarily of magmatic origin (Staudacher,
56 1987), has ³He/⁴He (R/R_A) ratios up to 4.7 and CO₂/³He ratios in the mid-oceanic ridge
57 basalt (MORB) range (Ballentine et al., 2001; Cassidy, 2006; Gilfillan et al., 2008;
58 Holland and Ballentine, 2006). The gas field comprises a thin laterally extensive reservoir
59 with an east-west extent of more than 70 km (Fig. 1) and supercritical reservoir
60 conditions (Broadhead, 1993). The western portion of the gas field is not in contact with
61 formation water since it overlies dry impermeable basement (Cassidy, 2006) and we
62 assume the most western fault on the map in Figure 1 represents the east-west gas water
63 contact (Appendix DR4). On the east side of this fault the water table is within the
64 sandstone formation and the CO₂ overlies water-saturated rock, with lateral juxtaposition
65 of CO₂ and formation water also occurring laterally to the extreme east (Fig. 1). Oxygen
66 isotope data of CO₂ gas confirm the western fault as a gas water contact since the gas
67 samples east of the fault have δ¹⁸O of 29‰ (Vienna standard mean ocean water, V-
68 SMOW) on average, which is the value predicted from CO₂-H₂O fractionation

69 (Brenninkmeijer et al., 1983) and complete equilibration with formation water of $\delta^{18}\text{O} =$
70 -11‰ at 33 °C (Cassidy, 2006) (Fig. 2A).

71 **MODEL**

72 **Data and Corrections**

73 The gas samples were collected in two different sampling campaigns (b and c) of
74 the Bravo Dome gas field (Gilfillan et al., 2008; Gilfillan et al., 2009; Holland and
75 Ballentine, 2006). Noble gas data of sample set b are from previous studies (Gilfillan et
76 al., 2008; Gilfillan et al., 2009; Holland and Ballentine, 2006), whereas sample set c has
77 been measured following previous methods (Holland and Ballentine, 2006) (Appendix
78 DR1). The oxygen isotopic and carbon isotopic analysis of sample set b were performed
79 at the University of East Anglia (Norwich, UK) using MIRA (multi- isotopologue ratio
80 analyzer) mass spectrometer (P. Dennis, unpublished data) with procedures following
81 Royle (2015) and precision for standard replicates of $<0.01\text{‰}$. The carbon isotopes of
82 sample set c were measured at Lancaster University (UK) using an Isoprime100 mass
83 spectrometer with a multiflow inlet. The data were corrected to V-PDB (Vienna Peedee
84 belemnite) using international standards LSVEC ($\delta^{13}\text{C} -46.6\text{‰}$), NBS 18 ($\delta^{13}\text{C}$
85 -5.014‰) and CO1 ($\delta^{13}\text{C} +2.492\text{‰}$). Precision for standard replicates ($n = 5$, 1 standard
86 deviation) was $<0.1\text{‰}$ for carbon isotopes.

87 The data for the model comprise the noble gas measurements and their sampling
88 distance to the gas water contact. The distance from the 26 selected wells to the gas water
89 contact have been measured horizontally for the wells west of the main fault and
90 vertically for the wells east of it, since these are the shortest distances to the gas water

91 contact (Fig. 1). The perforation interval depths from which the CO₂ is produced have
92 been considered for the wells with vertical distances to the gas water contact.

93 At the gas water contact, the air and crustal derived noble gases, which
94 accumulated in the formation water, degas into the CO₂ because of the higher
95 concentration and lower solubility in the formation water than in the CO₂ phase. In
96 addition to this increase in noble gas concentration in the CO₂, noble gas concentrations
97 in the gas phase are also enhanced by contemporaneous CO₂ dissolution into the
98 formation water. This solvent loss effect can be corrected based on ³He concentrations
99 (Appendix DR3) (Dubacq et al., 2012).

100 **Parameters and Error Calculation**

101 Following the noble gas concentration correction, the data can then be compared
102 to a diffusion profile based on Fick's second law of diffusion:

$$103 \quad \left[\frac{\partial C}{\partial t} = D_{eff} \frac{\partial^2 C}{\partial x^2} \right] (1)$$

104 where C stands for concentration, t for time, D_{eff} for the effective diffusion
105 coefficient and x for the distance. The solution of the equation involves two boundary
106 conditions which are set to be a constant noble gas concentration in the CO₂ at the gas
107 water contact (C_{start}) and a magmatic derived noble gas concentration (C_{end}) at the
108 western end of the gas field: $[C(x, t) = C_{start} - (C_{start} - C_{end}) * \text{erf}\left(\frac{x}{2\sqrt{t*D_{eff}}}\right)] (2)$

109 The effective diffusion coefficient compensates for the indirect travel paths of the
110 particles and differs from the common diffusion coefficient by taking into account the
111 porosity and tortuosity: $[D_{eff} = D \frac{\phi}{\tau}] (3)$ where D stands for the diffusion coefficient, ϕ
112 the porosity and τ the tortuosity. The diffusion coefficients have been calculated after the

113 method of He and Yu (1998) since no experimental data exists for diffusion of noble
114 gases in supercritical CO₂ (Appendix DR2). Poling et al. (2001) tested this approach for
115 the vitamin K₁ in supercritical CO₂ and found a low error of 0.4% compared to the
116 empirically determined diffusion coefficient. The calculated diffusion coefficients for the
117 noble gases in CO₂ are approximately one order of magnitude higher compared to those
118 in water. The reported porosity of the Tubb formation in New Mexico at Bravo Dome is
119 20% on average (Johnson, 1983; Cassidy, 2006) and the tortuosity has been calculated to
120 be 2.4 which is a typical value for sandstones (Cassidy, 2006; Epstein, 1989; Matthews
121 and Spearing, 1992).

122 Solutions for the diffusion profiles are calculated using a Monte Carlo simulation
123 in Matlab where both boundary conditions and the diffusion time multiplied by the
124 diffusion coefficient are fitted 1000 times to the data taking into account the error on
125 measurements through minimizing X^2 .

$$126 \quad X^2 = \sum_i^n \frac{(x_i - x_m)^2}{\frac{1}{2}x_{error\ range}^2} + \frac{(y_i - y(x_m))^2}{\sigma_y^2} \quad (4)$$

127 where x_m and $y(x_m)$ are model values for the distance and the concentration, x_i and
128 y_i are the distance and concentration of the data points, $x_{error\ range}$ is the error range of
129 the distance and σ_y is the standard error of the concentration measurements (Appendix
130 DR2). The data points in the simulation are picked randomly within the normal
131 distribution of their standard error for the concentration and within the error range of their
132 distance to the gas water contact. A second Monte Carlo simulation is set up to evaluate
133 the error of the diffusion coefficient on the diffusion time. The most probable diffusion
134 time, the diffusion coefficient, C_{start} and C_{end} are reported with asymmetric error brackets
135 defining the 95% quantile (Fig. 2, Appendix DR2). In the simulation for xenon, about

136 one-fifth of the C_{end} concentrations resulted in negative values which were excluded since
137 negative concentrations are meaningless. The model simplifies the field and does not
138 account for lithology heterogeneities, residual water, compartmentalization of the field,
139 lateral heterogeneities and temporal variation in the noble gas concentration in the
140 formation water which would have the tendency to increase the diffusion time.

141 The fitted carbon isotope C_{start} composition of -7.9‰ (Appendix DR2) fits well
142 with a CO_2 composition in equilibrium with formation water at Bravo Dome that is in
143 equilibrium with dolomite. Dolomite with an $\delta^{13}\text{C}$ of $\sim 2\text{‰}$ PDB (Hoefs, 2008) in
144 equilibrium with the formation water at Bravo Dome (Kessler et al., 2001; Hartig et al.,
145 2011) results in a CO_2 groundwater endmember of -8‰ based on a $\text{CO}_2(\text{g})$ -dolomite (g-
146 gaseous) fractionation of -10‰ (Sheppard and Schwarz, 1970; Clark and Fritz, 1997) at
147 33 °C (Cassidy, 2006). The fitted C_{end} composition of the carbon isotope is -4.1‰ which
148 is in the range of magmatic derived CO_2 (Jenden et al., 1993).

149 **AGE ESTIMATION**

150 The model generates noble gas diffusion profiles from the gas/water contact in the
151 east toward the western end of the field that are consistent with the observed well gas
152 concentrations and place age constraints for the CO_2 emplacement at between 14.1 ± 0.2
153 and $16.9^{+1.1}_{-0.5}$ ka (Fig. 2C-H, Appendices DR2 and DR4). The age difference between the
154 noble gases could arise from the uncertainty of the diffusion coefficients since the noble
155 gas diffusion coefficients are calculated and not empirically measured. The diffusion ages
156 are strongly influenced by the wells close to the gas water contact since these define the
157 curvature and hence the age of the diffusion profile.

158 The diffusion of the groundwater derived noble gases through the CO₂ most likely
159 started when the CO₂ first contacted the formation water. The gas water contact probably
160 moved down dip from the inferred entry point (see figure 4B in Sathaye et al., 2014)
161 throughout the filling of the CO₂ but this does not affect the diffusion of the noble gases
162 in the CO₂, assuming a slug like displacement of the formation water which is reasonable
163 given the likely slow rates of filling. Today the gas water contact is more than 30 km
164 away from the inferred entry point of the CO₂ (Sathaye et al., 2014). Therefore later CO₂
165 pulses, as proposed in previous studies (Baines and Worden, 2004; Sathaye et al., 2014),
166 would not alter the noble gas diffusion profile at the gas water contact. The water table in
167 the Bravo Dome field lies horizontally (Cassidy, 2006) and the anhydrite seal likely
168 prevents groundwater recharge which suggests a stagnant aquifer (Akhbari and Hesse,
169 2017). The estimated CO₂ emplacement ages are younger than the youngest dated
170 effusive rock in the area. Deep igneous activity, however, could have continued after the
171 last lava flow 56ka ago (Stroud, 1997).

172 Additionally, the change in carbon and oxygen isotopes has been investigated;
173 this can give insight into the source of the CO₂ and extent of gas water exchange and CO₂
174 dissolution. The $\delta^{13}\text{C}$ varies from -3.2‰ PDB in the west to -5.8‰ PDB in the east.
175 This isotopic difference originates from the presence of two sources of carbon. There is a
176 magmatic carbon input in the west, which is isotopically distinct from the formation
177 water derived carbon in the east. Similarly to the noble gases, diffusion controls the
178 mixing between these two endmembers (Fig. 2B). Diffusion modeling of the $\delta^{13}\text{C}$ profile
179 indicates a development period of $15.0^{+0.2}_{-0.5}$ ka (Fig. 2B). This age agrees well with the
180 age estimates derived from diffusion modeling of the noble gas concentration profiles.

181 However, the evolution of oxygen isotopes is more complex. The $\delta^{18}\text{O}$ varies
182 from a minimum of 18.6‰ in the west to 29‰ in the east. The wells in the west have
183 lighter isotopic composition but differ by more than 9–12‰ from an expected mantle like
184 CO_2 composition of 6–9‰ (Eiler, 2001). During the displacement of the formation water
185 by the invading CO_2 an irreducible water saturation of typically 5%–22% in sandstones
186 (Krevor et al., 2012) will be trapped in the CO_2 filled pores. The pores in the Tubb
187 formation thus contain an irreducible water saturation with a sufficient mass of oxygen
188 such that, O-isotopic exchange can modify the O-isotopic composition across the entire
189 CO_2 filled volume. A residual water content correction has been made to the O-isotope
190 ratios based on the mass balance equation $\delta^{18}\text{O}^f_{\text{CO}_2} = \delta^{18}\text{O}^i_{\text{CO}_2}(1-X^0_{\text{H}_2\text{O}}) + X^0_{\text{H}_2\text{O}}$
191 $(\delta^{18}\text{O}_{\text{H}_2\text{O}} + \epsilon)$ (5) (Johnson et al., 2011) where ϵ is the $\text{CO}_2(\text{g})\text{-H}_2\text{O}$ fractionation factor at
192 33 °C (Brenninkmeijer et al., 1983), $\delta^{18}\text{O}^i_{\text{CO}_2}$ and $\delta^{18}\text{O}^f_{\text{CO}_2}$ refer to initial and final
193 composition of the CO_2 respectively, and $X^0_{\text{H}_2\text{O}}$ is the fraction of oxygen in the system
194 from water. This amendment decreases the measured values only very little since the
195 residual water saturation is as low as 5–10 vol% (Sathaye et al., 2014). Due to this
196 complexity, the spatial trends in O-isotopic composition are not a useful constraint on the
197 emplacement age.

198 **DISSOLUTION RATE**

199 Combining the range of residence times of 14.1 ± 0.2 and $16.9^{+1.1}_{-0.5}$ ka with the
200 gas mass, which has been subject to dissolution, enables the estimation of the dissolution
201 rate. The dissolved gas can simply be estimated by subtracting the present mass of gas in
202 the reservoir from the mass of gas that was in place originally. The present gas volume in
203 the reservoir has previously been estimated to be 1.3 ± 0.6 Gt CO_2 (Sathaye et al., 2014).

204 The original gas mass can be calculated from the difference between the present gas and
205 the deviation from the highest CO₂/³He ratio (7.4*10⁹) (Appendix DR1), representing
206 dissolution of CO₂ through apparent increase in ³He. The dissolved gas mass has been
207 calculated in the past (Sathaye et al., 2014), however, the highest CO₂/³He ratio used was
208 5.35*10⁹ (Cassidy, 2006; Gilfillan et al., 2008; Gilfillan et al., 2009). Therefore the
209 dissolved mass is by one-third larger than previously estimated (Sathaye et al., 2014) and
210 equates to 506 ± 166 Mt CO₂. This amount is 28% of the new total estimated
211 emplacement of 1.8 ± 0.67 Gt CO₂. The resulting dissolution rate ranges from 29900
212 $\begin{matrix} +11800 \\ -10700 \end{matrix}$ t/a to 35900 ± 12300 t/a. The gas water contact covers an estimated area of 623
213 km² (Sathaye et al., 2014) and enables estimating the flux that ranges from 48 $\begin{matrix} +19 \\ -17 \end{matrix}$ to 58
214 ± 19.7 g/(m²a). This flux is over 500 times larger compared to previous estimates [0.1
215 g/(m²a)] (Sathaye et al., 2014) but still almost 400 times smaller than the estimates for the
216 permeable Sleipner CO₂ storage site in the North Sea [20 kg/(m²a)], (Neufeld et al.,
217 2010).

218 CONCLUSIONS

219 This diffusion model has, for the first time, been applied to estimation of the
220 residence time of CO₂ in Bravo Dome. This is key for quantifying the rate of CO₂
221 dissolution occurring in carbon dioxide reservoirs. Combining the range of residence
222 times of 14.1 ± 0.2 and 16.9 $\begin{matrix} +1.1 \\ -0.5 \end{matrix}$ ka with the gas volume, that has been subject to
223 dissolution, we could estimate the CO₂ dissolution rate of 29900 $\begin{matrix} +11800 \\ -10700 \end{matrix}$ t/a to 35900 ±
224 12300 t/a. Furthermore, the model can be tested on other natural CO₂ and enhanced oil
225 recovery (EOR) reservoirs to investigate gas-water interactions and quantify gas

226 dissolution rates into the formation waters that are ubiquitously found in subsurface gas
227 reservoirs.

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326

327 FIGURE CAPTIONS

328

329 Figure 1. A: Map of the Bravo Dome gas field (New Mexico, USA), showing the top of
330 the CO₂ hosting Tubb formation (black contour lines, in m above sea level [a.s.l.]), gas
331 water contact (short dashed line), the ³He/⁴He ratio (long dashed line) and the 26
332 sampling wells (circles). B: West-east cross-section highlighting the gas water contact
333 within the Tubb formation on the eastern side of the western most fault, as opposed to the
334 west side, where the gas reservoir is not in contact with the formation water. The
335 sampling wells are projected with their perforation depth (circles).

336

337 Figure 2. The CO₂ dissolution corrected noble gas concentrations and the measured stable
338 isotopes are plotted against the distance to the gas water contact (A-H). The groundwater

339 derived noble gases diffusing from the gas water contact through the gas column are
340 fitted by a Monte Carlo simulation to Fick's second law of diffusion equation (C-H). This
341 reveals the residence time of the CO₂. Additionally the Ne diffusion profile is drawn for
342 1.2 Ma (D). The carbon isotopes show a diffusive mixing between a magmatic carbon
343 source and a formation water carbon source that is in equilibrium with dolomite (B). The
344 time estimated using the $\delta^{13}\text{C}$ isotopes is within the range of ages estimated from the
345 noble gases. Oxygen isotopes show full equilibration with formation water in the eastern
346 part of the field close to the gas water contact (A). Concentration and distance errors are
347 smaller than symbols (circles). Symbol fillings correspond to well locations in Figure 1.
348 $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values are relative to: V-SMOW-Vienna standard mean ocean water; V-
349 PDB- Vienna Peedee belemnite. cm³STP-cubic centimeter at standard temperature and
350 pressure.
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352 1GSA Data Repository item 2017Appendices DR1-DR4, are available online at
353 <http://www.geosociety.org/datarepository/2017/> or on request from
354 editing@geosociety.org.







