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Estimating carbon dioxide residence time scales through noble gas and stable isotope diffusion profiles

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ABSTRACT

The study of natural carbon dioxide reservoirs provides fundamental insight into processes involved in carbon capture and storage. However, the calculations of process rates such as dissolution of CO_2 into formation water remain uncertain due to indirectly determined ages of the CO_2 influx. The proposed ages for the Bravo Dome gas field in New Mexico, USA, vary from 56 ka to 1.5 Ma. Here we demonstrate that residence times can be estimated from simple modeling of noble gas and stable isotope diffusion profiles from the gas-water contact through the gas column. The Bravo Dome gas field shows a gradient in noble gas concentrations and isotopic ratios from east to west across the 70-km-wide field. A mantle-like end member with a $^{3}He/^{4}He$ (R/R_A) ratio of up to 4.7 is found in the west in contrast to a groundwater end member with high concentrations of air- and crustal-derived noble gases in the east. The air- and crustal-derived noble gases decrease gradually toward the west. Stable isotope compositions (C and O) also vary across the field. Diffusion modeling of He, Ne, Ar, Kr, Xe, and $\delta^{13}C$ and data yield residence times for the CO_2 between 14.1 ± 0.2 ka and 16.9 +1.1/–0.5 ka. This is far less than the previous estimates of 1.2–1.5 Ma based on apatite (U-Th)/He thermochronology, leading to a dissolution rate of **[[Precede these values with "~" symbol, given that they are rounded from the values reported in Conclusions?]]**30,000 +12,000/–11,000 t/a to 36,000 ± 12,000 t/a, implying that 32% of the total emplaced CO_2 dissolved. This new method can be applied to a wide variety of gas fields with variation in the concentration of groundwater-derived noble gases and allow a better assessment of the time scale of other diffusive fluid-fluid interactions.

INTRODUCTION

Natural carbon dioxide reservoirs serve as natural analogues for geological CO_2 storage and hence are studied extensively to understand processes that act over geological time scales (Bickle et al., 2013). In order to quantify the rates of interactions between CO_2, subsurface fluids, and the host rock, it is crucial to know the residence time of the CO_2 in the reservoir. Previous estimates of CO_2 reservoir residence times include dating of surface intrusive igneous rocks from the Colorado Plateau (Armstrong, 1969), dating of close-by effusive igneous rocks (Condit, 1995; Stroud, 1997), and apatite (U-Th)/He thermochronology (Sathaye et al., 2014). These methods have been used to infer residence times for the Bravo Dome (New Mexico, USA) CO_2 reservoir ranging between 56 ka (Stroud, 1997) and 1.5 Ma (Sathaye et al., 2014). Petrographic studies on drill cores suggest the carbon dioxide filling of Bravo Dome in the mid-Cenozoic (Hartig et al., 2011), but rely exclusively on relative time constraints of diagenetic mineral growths with poorly developed textures. Here we present a model for estimating directly the CO_2 residence time applied to the Bravo Dome gas field. The model relies on spatial sampling of gases across the field and uses the diffusion of groundwater-derived noble gases entering the gas column at the gas-water contact, with known diffusion constants, to estimate residence ages.

BRAVO DOME FIELD

Bravo Dome is a well-studied sandstone-hosted CO_2 reservoir (Baines and Worden, 2004; Cassidy, 2006; Dubacq et al., 2012; Gilfillan et al., 2008, 2009; Hartig et al., 2011; Holland and Ballentine, 2006; Kessler et al., 2001; Sathaye et al., 2014). The gas is primarily of magmatic origin (Staudacher, 1987) and has $^3He/^4He$ (R/R_A) ratios up to 4.7 and $CO_2/^3He$ ratios in the mid-oceanic ridge basalt (MORB) range (Ballentine et al., 2001; Cassidy, 2006; Gilfillan et al., 2008; Holland and Ballentine, 2006). The gas field comprises a thin laterally extensive reservoir with an east-west extent of >70 km (Fig. 1) and supercritical reservoir conditions (Broadhead, 1993). The western portion of the gas field is not in contact with formation water because it overlies dry impermeable basement (Cassidy, 2006), and we assume that the most western fault on the map in Figure 1 represents the east-west gas-water contact (Appendix DR4 in the GSA Data Repository[1]). On the east side of this fault, the water table is within the sandstone formation and the CO_2 overlies water-saturated rock, with lateral juxtaposition of CO_2 and formation water also occurring laterally to the extreme east (Fig. 1). Oxygen isotope data of CO_2 gas confirm the western fault as a gas-water contact because the gas samples east of the fault have $\delta^{18}O$ of 29‰ **[[relative to?]]** standard mean ocean water

(SMOW)**[[Should this be “Vienna standard mean ocean water (V-SMOW) as indicated in fig. 2A?]]** on average, which is the value predicted from CO_2-H_2O fractionation (Brenninkmeijer et al., 1983) and complete equilibration with formation water of $\delta^{18}O = -11‰$ at 33 °C (Cassidy, 2006) (Fig. 2A).

MODEL

Data and Corrections

The gas samples were collected in two different sampling campaigns (*b* and *c*) of the Bravo Dome gas field (Gilfillan et al., 2008, 2009; Holland and Ballentine, 2006). Noble gas data of sample set *b* are from previous studies (Gilfillan et al., 2008, 2009; Holland and Ballentine, 2006), whereas sample set *c* has been measured following previous methods (Holland and Ballentine, 2006) (Appendix DR1). The oxygen isotopic and carbon isotopic analysis of sample set *b* was performed at the University of East Anglia (Norwich, UK) using a MIRA (multi-isotope ratio analyzer) mass spectrometer (Dennis, 2014) with procedures following Royle (2015) and precision for standard replicates of <0.01‰. The carbon isotopes of sample set *c* were measured at Lancaster University (UK) using an Isoprime100 spectrometer with a multiflow inlet. The data were corrected to PDB (Peedee belemnite**[[Or should it be “Vienna Peedee belemnite (V-PDB)”, as indicated in Fig. 2B? (all instances of “PDB” in text)]]**) using international standards LSVEC (lithium carbonate; $\delta^{13}C$ −46.6‰), NBS 18 (calcite; $\delta^{13}C$ −5.014‰) and CO1 (marble; $\delta^{13}C$ +2.492‰). Precision for standard replicates ($n = 5$, 1 standard deviation) was <0.1‰ for carbon isotopes.

The data for the model comprise the noble gas measurements and their sampling distance to the gas-water contact. The distance from the 26 selected wells to the gas-water contact has been measured horizontally for the wells west of the main fault and vertically for the wells east of it, because these are the shortest distances to the gas-water contact (Fig. 1). The perforation interval depths from which the CO_2 is produced have been considered for the wells with vertical distances to the gas-water contact.

At the gas-water contact, the air- and crustal-derived noble gases, which accumulated in the formation water, degas into the CO_2 because of the higher concentration and lower solubility in the formation water than in the CO_2 phase. In addition to this increase in noble gas concentration in the CO_2, noble gas concentrations in the gas phase are also enhanced by contemporaneous CO_2 dissolution into the formation water. This solvent loss effect can be corrected based on ^{3}He concentrations (Appendix DR3) (Dubacq et al., 2012).

Parameters and Error Calculation

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

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

where C is concentration, t is time, D_{eff} is the effective diffusion coefficient, and x is the **[[diffusion?]]** distance. The solution of the equation involves two boundary conditions which are set to be a constant noble gas concentration in the CO_2 at the gas-water contact (C_{start}) and a magmatic-derived noble gas concentration (C_{end}) at the western end of the gas field:

$$\left[C(x,t) = C_{\mathrm{start}} - (C_{\mathrm{start}} - C_{\mathrm{end}}) * \mathrm{erf}\left(\frac{x}{2\sqrt{t * D_{\mathrm{eff}}}}\right)\right]. \qquad (2)$$

The effective diffusion coefficient compensates for the indirect travel paths of the particles and differs from the common diffusion coefficient by taking into account the porosity and tortuosity:

$$[D_{\mathrm{eff}} = D\frac{\o}{\tau}]\,, \qquad (3)$$

where *D* is the diffusion coefficient, ø is porosity, and τ is tortuosity. The diffusion coefficients have been calculated after the method of He and Yu (1998) because no experimental data exist for diffusion of noble gases in supercritical CO_2 (Appendix DR2). Poling et al. (2001) tested this approach for the vitamin K_1 in supercritical CO_2 and found a low error of 0.4% compared to the empirically determined diffusion coefficient. The calculated diffusion coefficients for the noble gases in CO_2 are approximately one order of magnitude higher compared to those in water. The reported porosity of the Tubb Formation in New Mexico is 20% on average (Johnson, 1983; Cassidy, 2006), and the tortuosity has been calculated to be 2.4, which is a typical value for sandstones (Cassidy, 2006; Epstein, 1989; Matthews and Spearing, 1992).

Solutions for the diffusion profiles are calculated using a Monte Carlo simulation in Matlab where both boundary conditions and the diffusion time multiplied by the diffusion coefficient are fitted 1000× to the data, taking into account the error on measurements through minimizing χ^2:

$$\chi^2 = \sum_i^n \frac{(x_\mathrm{i} - x_\mathrm{m})^2}{\frac{1}{2}x^2_{(\mathrm{error\ range})}} + \frac{[y_\mathrm{i} - y(x_\mathrm{m})]^2}{\sigma_y{}^2}\,, \qquad (4)$$

where x_m and $y(x_\mathrm{m})$ are model values for the distance and the concentration, x_i and y_i are the distance and concentration of the data points, $x_{(\mathrm{error\ range})}$ is the error range of the distance, and σ_y is the standard error of the concentration measurements (Appendix

DR2). The data points in the simulation are picked randomly within the normal distribution of their standard error for the concentration and within the error range of their distance to the gas-water contact. A second Monte Carlo simulation is set up to evaluate the error of the diffusion coefficient on the diffusion time. The most probable diffusion time, the diffusion coefficient, C_{start}, and C_{end} are reported with asymmetric error brackets defining the 95% quantile (Fig. 2; Appendix DR2). In the simulation for xenon, about one-fifth of the C_{end} concentrations resulted in negative values which were excluded because negative concentrations are meaningless. The model simplifies the field and does not account for lithology heterogeneities, residual water, compartmentalization of the field, lateral heterogeneities, and temporal variation in the noble gas concentration in the formation water which would have the tendency to increase the diffusion time.

The fitted carbon isotope C_{start} composition of –7.9‰ (Appendix DR2) fits well with a CO_2 composition in equilibrium with formation water at Bravo Dome that is in equilibrium with dolomite. Dolomite with a $\delta^{13}C$ of ~2‰ PDB (Hoefs, 2008) in equilibrium with the formation water at Bravo Dome (Kessler et al., 2001; Hartig et al., 2011) results in a CO_2 groundwater end member of –8‰ based on a $CO_{2(g)}$-dolomite**[[Explain what “(g)” means]]** fractionation of –10‰ (Sheppard and Schwarz, 1970; Clark and Fritz, 1997) at 33 °C (Cassidy, 2006). The fitted C_{end} composition of the carbon isotope is –4.1‰ which is in the range of magmatic-derived CO_2 (Jenden et al., 1993).

AGE ESTIMATION

The model generates noble gas diffusion profiles from the gas-water contact in the east toward the western end of the field that are consistent with the observed well gas concentrations and place age constraints for **[[the beginning of?]]** the process at between 14.1 ± 0.2 ka and 16.9 +1.1/–0.5 ka (Figs. 2C–2H; Appendices DR2 and DR4). The age difference between the noble gases could arise from the uncertainty of the diffusion coefficients because the noble gas diffusion coefficients are calculated and not empirically measured. The diffusion ages are strongly influenced by the wells close to the gas-water contact because these define the curvature and hence the age of the diffusion profile.

The diffusion of the groundwater-derived noble gases through the CO_2 most likely started when the CO_2 first contacted the formation water. The gas-water contact probably moved down dip from the inferred entry point (see Sathaye et al., 2014, their figure 4b) throughout the filling of the CO_2 but this does not affect the diffusion of the noble gases in the CO_2, assuming a slug-like displacement of the formation water, which is reasonable given the likely slow rates of filling. Today the gas-water contact is >30 km away from the inferred entry point of the CO_2 (Sathaye et al., 2014). Therefore, later CO_2 pulses, as proposed in previous studies (Baines and Worden, 2004; Sathaye et al., 2014), would not alter the noble gas diffusion profile at the gas-water contact. The water table in the Bravo Dome field lies horizontally (Cassidy, 2006), and the anhydrite seal likely prevents groundwater recharge, which suggests a stagnant aquifer (Akhbari and Hesse, 2017). The estimated CO_2 residence times are younger than the youngest**[[Residence time is not an age, and therefore cannot be younger than something – please reword]]** dated effusive rock in the area. Deep igneous activity, however, could have continued after the last lava flow at 56 ka (Stroud, 1997).

Additionally, the change in carbon and oxygen isotopes has been investigated; this can give insight into the source of the CO_2 and extent of gas-water exchange and CO_2 dissolution. The $\delta^{13}C$ varies from –3.2‰ PDB in the west to –5.8‰ PDB in the east. This isotopic difference originates from the presence of two sources of carbon. There is a magmatic carbon input in the west, which is isotopically distinct from the formation water–derived carbon in the east. Similarly to the noble gases, diffusion controls the mixing between these two end members (Fig. 2B). Diffusion modeling of the $\delta^{13}C$ profile indicates a development period of 15.0 +0.2/–0.5 ka (Fig. 2B). This age**[[period?]]** agrees well with the age**[[Can't directly compare a "period" to an "age" – reword]]** estimates derived from diffusion modeling of the noble gas concentration profiles.

However, the evolution of oxygen isotopes is more complex. The $\delta^{18}O$ **[[Correct?]]** varies from a minimum of 18.6‰ in the west to 29‰ in the east. The wells in the west have lighter isotopic composition but differ by more than 9‰–12‰ from an expected mantle-like CO_2 composition of 6‰–9‰ (Eiler, 2001). During the displacement of the formation water by the invading CO_2, an irreducible water saturation of typically 5%–22% in sandstones (Krevor et al., 2012) will be trapped in the CO_2-filled pores. The pores in the Tubb Formation thus contain an irreducible water saturation with a sufficient mass of oxygen such that O-isotopic exchange can modify the O-isotopic composition of across the entire CO_2-filled volume. A residual water content correction has been made to the O-isotope ratios based on the mass balance equation:

$$\delta^{18}O^{f}_{CO_2} = \delta^{18}O^{i}_{CO_2}(1 - X^{0}_{H_2O}) + X^{0}_{H_2O}(\delta^{18}O_{H_2O} + \varepsilon), \qquad (5)$$

(Johnson et al., 2011**[[Johnson et al., 2011 is not in the reference list.]]**) where ε is the $CO_2(g)$-H_2O fractionation factor at 33 °C (Brenninkmeijer et al., 1983), $\delta^{18}O^{i}_{CO_2}$ and

$\delta^{18}O^{f}_{CO_2}$ refer to initial and final composition of the CO_2, respectively, and $X^{0}_{H_2O}$ is the fraction of oxygen in the system from water. This amendment decreases the measured values only very little because the residual water saturation is as low as 5–10 vol% (Sathaye et al., 2014). Due to this complexity, the spatial trends in O-isotopic composition are not a useful constraint on the emplacement age.

DISSOLUTION RATE

Combining the range of residence times of 14.1 ± 0.2 ka and 16.9 +1.1/–0.5 ka with the gas mass, which has been subject to dissolution, enables the estimation of the dissolution rate. The dissolved gas can simply be estimated by subtracting the present mass of gas in the reservoir from the mass of gas that was in place originally. The present gas volume in the reservoir has previously been estimated to be 1.3 ± 0.6 Gt CO_2 (Sathaye et al., 2014). The original gas mass can be calculated from the difference between the present gas and the deviation from the highest $CO_2/^3He$ ratio (7.4×10^9) (Appendix DR1), representing dissolution of CO_2 through apparent increase in ^3He. The dissolved gas mass has been calculated in the past (Sathaye et al., 2014), however, the highest $CO_2/^3He$ ratio used was 5.35×10^9 (Cassidy, 2006; Gilfillan et al., 2008, 2009). Therefore, the dissolved mass is one-third larger than previously estimated (Sathaye et al., 2014) and equates to 506 ± 166 Mt CO_2. This amount is 32% of the total estimated emplacement of 1.6 ± 0.67 Gt CO_2 (Sathaye et al., 2014). The resulting dissolution rate ranges from 23,000 +1200/–1100 t/a to 36,000 ± 12,000 t/a. The gas-water contact covers an estimated area of 623 km^2 (Sathaye et al., 2014) and enables estimating the flux that ranges from 48 +19/–17 $g/(m^2a)$ to 58 ± 19.7 $g/(m^2a)$. This flux is >500× larger compared to previous estimates [0.1 $g/(m^2a)$] (Sathaye et al., 2014) but still almost 400× smaller than the estimates for the permeable Sleipner CO_2 storage site in the North Sea [20 kg/(m^2a)] (Neufeld et al., 2010).

CONCLUSIONS

This diffusion model has, for the first time, been applied to estimation of the residence time of CO_2 in Bravo Dome. This is key for quantifying the rate of CO_2 dissolution occurring in carbon dioxide reservoirs. Combining the range of residence times of 14.1 ± 0.2 ka and 16.9 +1.1/–0.5 ka with the gas volume that has been subject to dissolution, we could estimate the CO_2 dissolution rate of 29,900 +11,800/–10,700 t/a to 35,900 ± 12,300 t/a. Furthermore, the model can be tested on other natural CO_2 and enhanced oil recovery (EOR) reservoirs to investigate gas-water interactions and quantify gas dissolution rates into the formation waters that are ubiquitously found in subsurface gas reservoirs.

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FIGURE CAPTIONS

Figure 1. A: Map of Bravo Dome gas field (New Mexico, USA), showing top of CO_2-hosting Tubb Formation (black contour lines, in m above sea level [a.s.l.]), gas-water contact (short dashed line), the $^3He/^4He$ ratio (long dashed line), and 26 sampling wells (circles). B: West-east cross-section highlighting gas-water contact within Tubb Formation on eastern side of westernmost fault, as opposed to west side, where gas reservoir is not in contact with formation water. Sampling wells are projected with their perforation depth (circles).

[[In the figure, label panels A and B with uppercase letters; change all instances of “gas/water” to “gas-water”. In panel A, insert hyphen in “east-west” on the gas-water fault contact; in symbol explanation, insert space between “Fm” and “[m a.s.l.]”, between “water” and “contact”, and between “10” and “km” on the scale bar. In panel B, sense of slip on the faults doesn’t seem to match that shown in panel A (barbs typically on upthrown side); change “Tubb Sandstone” to “Tubb Formation” for consistency; include horizontal scale bar (or reference the one in panel A if the same)]]

Figure 2. A–H: CO_2 dissolution–corrected noble gas concentrations and measured stable isotopes plotted against distance to gas-water contact. Groundwater-derived noble gases diffusing from gas-water contact through gas column are fitted by Monte Carlo simulation to Fick's second law of diffusion equation (C–H). This reveals residence time of CO_2. Additionally, Ne diffusion profile is drawn for 1.2 Ma (D). Carbon isotopes show diffusive mixing between magmatic carbon source and formation water carbon source that is in equilibrium with dolomite (B). Time estimated using $\delta^{13}C$ isotopes is within range of ages estimated from noble gases. Oxygen isotopes show full equilibration with formation water in eastern part of field close to gas-water contact (A). Concentration and distance errors are smaller than symbols (circles). Symbol fills correspond to well locations in Figure 1. $\delta^{18}O$ and $\delta^{13}C$ values are relative to: V-SMOW—Vienna standard mean ocean water; V-PDB—Vienna Peedee belemnite. cm^3STP—standard cubic centimeter.

[[In the figure, change "gas/water" to "gas-water"]]

[1] GSA Data Repository item 2017, Appendices DR1–DR4, is available online at http://www.geosociety.org/datarepository/2017/ or on request from editing@geosociety.org.