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

Carmen A. Zwahlen1,2*, Niko Kampman1,3, Paul Dennis4, Zheng Zhou1 and Greg Holland1,2

1Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, UK
2School of Earth and Environmental Sciences, University of Manchester, Manchester M13 9PL, UK
3Shell Global Solutions International, Kessler Park 1, 2288 GS Rijswijk, Netherlands
4School of Environmental Sciences, University of East Anglia, Norwich Research Park,
Norwich NR4 7TJ, UK

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

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 CO₂ into the formation water remain uncertain due to indirectly determined ages of the CO₂ 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 endmember with a ³He/⁴He (R/Rₐ) ratio of up to 4.7 is found in the west in contrast to a ground water endmember 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 data yield residence times for the CO$_2$ between $14.1 \pm 0.2$ and $16.9 \pm 1.1$ 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 $29900 ^{+11800}_{-10700}$ t/a to $35900 \pm 12300$ t/a, implying that $28\%$ 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 timescale 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 timescales (Bickle et al., 2013). In order to quantify the rates of interactions between carbon dioxide, 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 (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 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 in New Mexico, USA (Baines and Worden, 2004; Cassidy, 2006; Dubacq et al., 2012; Gilfillan et al., 2008; Gilfillan et al., 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), has $^3$He/$^4$He (R/R$_A$) ratios up to 4.7 and CO$_2$/$^3$He 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 more than 70 km (Fig. 1) and supercritical reservoir conditions (Broadhead, 1993). The western portion of the gas field is not in contact with formation water since it overlies dry impermeable basement (Cassidy, 2006) and we assume the most western fault on the map in Figure 1 represents the east-west gas water contact (Appendix DR4). 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 since the gas samples east of the fault have $\delta^{18}$O of 29‰ (Vienna standard mean ocean water, V-SMOW) on average, which is the value predicted from CO$_2$-H$_2$O 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; Gilfillan et al., 2009; Holland and Ballentine, 2006). Noble gas data of sample set b are from previous studies (Gilfillan et al., 2008; Gilfillan et al., 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 were performed at the University of East Anglia (Norwich, UK) using MIRA (multi-isotopologue ratio analyzer) mass spectrometer (P. Dennis, unpublished data) with procedures following Royle (2015) and precision for standard replicates of $<$0.01‰. The carbon isotopes of sample set c were measured at Lancaster University (UK) using an Isoprime100 mass spectrometer with a multiflow inlet. The data were corrected to V-PDB (Vienna Peedee belemnite) using international standards LSVEC ($\delta^{13}C$ −46.6‰), NBS 18 ($\delta^{13}C$ −5.014‰) and CO1 ($\delta^{13}C$ +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 have been measured horizontally for the wells west of the main fault and vertically for the wells east of it, since 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:

$$\frac{\partial C}{\partial t} = D_{eff} \frac{\partial^2 C}{\partial x^2}$$

(1)

where $C$ stands for concentration, $t$ for time, $D_{eff}$ for the effective diffusion coefficient and $x$ for the 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:

$$C(x, t) = C_{start} - (C_{start} - C_{end}) \times \text{erf}\left(\frac{x}{2\sqrt{\pi D_{eff} t}}\right)$$

(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: $D_{eff} = D \frac{\phi^a}{\tau}$

(3) where $D$ stands for the diffusion coefficient, $\phi$ the porosity and $\tau$ the tortuosity. The diffusion coefficients have been calculated after the
method of He and Yu (1998) since no experimental data exists for diffusion of noble
gases in supercritical CO₂ (Appendix DR2). Poling et al. (2001) tested this approach for
the vitamin K₁ in supercritical CO₂ and found a low error of 0.4% compared to the
empirically determined diffusion coefficient. The calculated diffusion coefficients for the
noble gases in CO₂ are approximately one order of magnitude higher compared to those
in water. The reported porosity of the Tubb formation in New Mexico at Bravo Dome 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 times to the data taking into account the error on
measurements through minimizing \( \chi^2 \).

\[
\chi^2 = \sum_{i} \frac{(x_i - x_m)^2}{\sigma_x^2 \text{error range}} + \frac{(y_i - y(x_m))^2}{\sigma_y^2} \tag{4}
\]

where \( x_m \) and \( y(x_m) \) are model values for the distance and the concentration, \( x_i \) and
\( y_i \) are the distance and concentration of the data points, \( x_{\text{error range}} \) is the error range of
the distance and \( \sigma_y \) 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, \( C_{\text{start}} \) and \( C_{\text{end}} \) 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 since 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 an $\delta^{13}C$ of $\sim2\%$ 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 endmember of $-8\%$ based on a CO$_2$(g)-dolomite (g-gaseous) 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 CO$_2$ emplacement at between $14.1 \pm 0.2$ and $16.9^{+1.1}_{-0.5}$ ka (Fig. 2C-H, Appendices DR2 and DR4). The age difference between the noble gases could arise from the uncertainty of the diffusion coefficients since 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 since 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 figure 4B in Sathaye et al., 2014) 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 more than 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$_2$ emplacement ages are younger than the youngest dated effusive rock in the area. Deep igneous activity, however, could have continued after the last lava flow 56ka ago (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 δ$^{13}$C varies from $\sim$3.2‰ PDB in the west to $\sim$5.8‰ PDB in the east. This isotopic difference originates from the presence of two sources of carbon. There is a magmatic carbon input in the west, which is isotopically distinct from the formation water derived carbon in the east. Similarly to the noble gases, diffusion controls the mixing between these two endmembers (Fig. 2B). Diffusion modeling of the δ$^{13}$C profile indicates a development period of $15.0^{+0.2}_{-0.5}$ ka (Fig. 2B). This age agrees well with the age estimates derived from diffusion modeling of the noble gas concentration profiles.
However, the evolution of oxygen isotopes is more complex. The $\delta^{18}$O 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 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 $\delta^{18}\text{O}_{\text{CO}_2}^f = \delta^{18}\text{O}_{\text{CO}_2}^i (1 - X_0^H2O) + X_0^H2O$ ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$$+$6) (5) (Johnson et al., 2011) where $\varepsilon$ is the CO$_2$(g)-H$_2$O fractionation factor at 33 °C (Brenninkmeijer et al., 1983), $\delta^{18}\text{O}_{\text{CO}_2}^i$ and $\delta^{18}\text{O}_{\text{CO}_2}^f$ refer to initial and final composition of the CO$_2$ respectively, and $X_0^H2O$ is the fraction of oxygen in the system from water. This amendment decreases the measured values only very little since 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 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$_2$/$^3$He ratio (7.4*10$^9$) (Appendix DR1), representing dissolution of CO$_2$ through apparent increase in $^3$He. The dissolved gas mass has been calculated in the past (Sathaye et al., 2014), however, the highest CO$_2$/$^3$He ratio used was 5.35*10$^9$ (Cassidy, 2006; Gilfillan et al., 2008; Gilfillan et al., 2009). Therefore the dissolved mass is by one-third larger than previously estimated (Sathaye et al., 2014) and equates to 506 ± 166 Mt CO$_2$. This amount is 28% of the new total estimated emplacement of 1.8 ± 0.67 Gt CO$_2$. The resulting dissolution rate ranges from 29900 ± 12300 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 to 58 ± 17 g/(m$^2$a). This flux is over 500 times larger compared to previous estimates [0.1 g/(m$^2$a)] (Sathaye et al., 2014) but still almost 400 times smaller than the estimates for the permeable Sleipner CO$_2$ storage site in the North Sea [20 kg/(m$^2$a)], (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 and 16.9 ± 0.5 ka with the gas volume, that has been subject to dissolution, we could estimate the CO$_2$ dissolution rate of 29900 ± 12300 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.

ACKNOWLEDGMENTS

We would like to thank Dr. Alina Marca from the University of East Anglia and Dave Hughes from Lancaster University for technical assistance. We are also grateful to the Statistics department at Lancaster University, Dr. Benoit Dubacq from the Centre national de la recherche scientifique (CNRS) and Prof. Jamie Gilmour from the University of Manchester for their helpful advice regarding the fitting procedure. We thank and Marc Hesse, Junji Yamamoto and one anonymous reviewer for valuable comments on this manuscript.

REFERENCES CITED


Bickle, M., Kampman, N., and Wigley, M., 2013, Natural analogues: Reviews in
Mineralogy and Geochemistry, v. 77, no. 1, p. 15–71.


Gilfillan, S.M.V., Ballentine, C.J., Holland, G., Blagburn, D., Lollar, B.S., Stevens, S.,
reservoirs from the Colorado Plateau and Rocky Mountain provinces, USA:
Geochimica et Cosmochimica Acta, v. 72, p. 1174–1198,
Gilfillan, S.M.V., Lollar, B.S., Holland, G., Blagburn, D., Stevens, S., Schoell, M.,
276 Cassidy, M., Ding, Z., Zhou, Z., Lacrampe-Couloume, G., and Ballentine, C.J.,
2009, Solubility trapping in formation water as dominant CO2 sink in natural gas
Hartig, K.A., Soreghan, G.S., Goldstein, R.H., and Engel, M.H., 2011, Dolomite in
Permian paleosols of the Bravo Dome CO2 field, USA: Permian reflux followed by
late recrystallization at elevated temperature: Journal of Sedimentary Research, v.
Coefficients in Supercritical and High-Temperature Liquid Solvents: Industrial &
Media, 288 p.
Holland, G., and Ballentine, C.J., 2006, Seawater subduction controls the heavy noble gas
and mantle helium in oil and gas fields, in Howell, D.G., et al., eds., U.S. Geological


FIGURE CAPTIONS

Figure 1. A: Map of the Bravo Dome gas field (New Mexico, USA), showing the top of the CO$_2$ hosting Tubb formation (black contour lines, in m above sea level [a.s.l.]), gas water contact (short dashed line), the $^3$He/$^4$He ratio (long dashed line) and the 26 sampling wells (circles). B: West-east cross-section highlighting the gas water contact within the Tubb formation on the eastern side of the western most fault, as opposed to the west side, where the gas reservoir is not in contact with the formation water. The sampling wells are projected with their perforation depth (circles).

Figure 2. The CO$_2$ dissolution corrected noble gas concentrations and the measured stable isotopes are plotted against the distance to the gas water contact (A-H). The groundwater
derived noble gases diffusing from the gas water contact through the gas column are fitted by a Monte Carlo simulation to Fick’s second law of diffusion equation (C-H). This reveals the residence time of the CO$_2$. Additionally the Ne diffusion profile is drawn for 1.2 Ma (D). The carbon isotopes show a diffusive mixing between a magmatic carbon source and a formation water carbon source that is in equilibrium with dolomite (B). The time estimated using the $\delta^{13}$C isotopes is within the range of ages estimated from the noble gases. Oxygen isotopes show full equilibration with formation water in the eastern part of the field close to the gas water contact (A). Concentration and distance errors are smaller than symbols (circles). Symbol fillings 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$^3$STP-cubic centimeter at standard temperature and pressure.

1GSA Data Repository item 2017Appendices DR1-DR4, are available online at http://www.geosociety.org/datarepository/2017/ or on request from editing@geosociety.org.
Appendix DR1 (Table DR1)

Table DR1. Noble gas concentrations, carbon and oxygen stable isotopes and distance to the gas water contact of the 26 Bravo Dome samples with errors and corrected noble gas concentrations.

Appendix DR2 (Table DR2)

Table DR2. Results from 1000 fold Monte Carlos simulation for time, diffusion coefficient and start and end concentrations of the diffusion profile with asymmetric error estimates of the 95% quantile.

Appendix DR3 (Noble gas correction)

Since the $^3$He solubility is two orders of magnitude lower in the formation water than in the CO$_2$ and the $^3$He concentration in the formation water is several orders of magnitude lower than in the CO$_2$, the $^3$He concentration increase toward the gas water contact reflects the loss of CO$_2$ by dissolution into the formation water (Fig. DR3A) (Gilfillan et al., 2009). Starting with the lowest noble gas concentration, present in the western part of the field, the concentration increase due to the loss of CO$_2$ can be determined for $^3$He and used to calculate the relative increase for the other noble gases (Fig. DR3B-G). This calculated increase is subtracted from the measured values to get the CO$_2$ loss corrected value (Fig. DR3B-G, Table DR1, Equation 1) to give corrected noble gas concentrations. The equation for the CO$_2$ loss correction is:

\[
GNG_c = GNG_m - \left[ GNG_{\text{mc}} \times \frac{\text{CO}_2}{^3\text{He} (GNG_{\text{mc}})} - GNG_{\text{mc}} \right]
\]

where $GNG$ stands for groundwater derived noble gas, subscripts $c$, $m$ and $\text{mc}$ stand for the corrected, measured and lowest measured concentration, respectively.
Fig. DR3. Noble gas concentration correction for CO₂ loss by dissolution into the formation water. The ³He concentration in the formation water is several magnitudes lower than in the gas phase and therefore the ³He concentration increase toward the gas water contact represents the loss of CO₂ to the formation water (A). The increase in ⁴He is calculated proportional to the ³He increase, starting at the lowest ⁴He concentration (black line) (B). This is the increase in ³He concentration due to CO₂ dissolution (gray area) and is therefore subtracted from the measured ⁴He concentrations. (C-G) Correction for ²⁰Ne, ³⁶Ar, ⁴⁰Ar, ⁸⁴Kr and ¹³²Xe concentrations due to solvent loss (CO₂ dissolution into the formation water) in the same way as for ⁴He in (B). Note that ⁴⁰Ar is not present in excess to the relative ³He increase (E). One Kr measurement lies far from the expected concentration and is excluded due to potential measuring problems (F).

Appendix DR4 (Discussion of gas/water contact)

The western portion of the gas field is not in contact with formation water since it overlies dry impermeable basement (Cassidy, 2006), however it remains unclear how permeable the fault zone is and whether some water remains above the basement close to the fault in the south western end of the field (Sathaye et al., 2014; Akhbari and Hesse, 2017). In Figure DR4 there is one sample that does not fit the model very well and shows an enhanced noble gas concentration for its distance to the gas water contact. This sample is well 13b on the south western side of the field close to the fault. This could indicate either a more permeable fault zone or water that remains above the basement in that part of the field.

Fig DR4. The corrected concentrations of noble gases and the measured stable isotopes are plotted against the distance to the gas water contact in logarithmic scale (A–H) (Fig. 2). The data point with higher noble gas concentration than expected by the model corresponds to well 13b and might indicate a more permeable fault zone or that water remains above the basement in the south western end of the field.

References


<table>
<thead>
<tr>
<th>Sample id</th>
<th>( \delta^{13}C ) [%]</th>
<th>Error [‰]</th>
<th>( \delta^{18}O ) [%]</th>
<th>Error [‰]</th>
<th>Distance to groundwater [km]</th>
<th>Error range on distance to groundwater [km]</th>
<th>( \gamma^{18}O ) [cm(^2)STP cm(^{-3})]</th>
<th>Error [cm(^2)STP cm(^{-3})]</th>
<th>( \gamma^{18}C ) [cm(^2)STP cm(^{-3})]</th>
<th>Error [cm(^2)STP cm(^{-3})]</th>
<th>( \gamma^{18}Ne ) [cm(^2)STP cm(^{-3})]</th>
<th>Error [cm(^2)STP cm(^{-3})]</th>
<th>( \gamma^{18}Ar ) [cm(^2)STP cm(^{-3})]</th>
<th>Error [cm(^2)STP cm(^{-3})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4b</td>
<td>1.04</td>
<td>4.01</td>
<td>1.19</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
</tr>
<tr>
<td>12b</td>
<td>1.00</td>
<td>4.00</td>
<td>1.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
</tr>
<tr>
<td>15b</td>
<td>1.00</td>
<td>4.00</td>
<td>1.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
</tr>
<tr>
<td>13b</td>
<td>1.00</td>
<td>4.00</td>
<td>1.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
</tr>
<tr>
<td>7b</td>
<td>1.00</td>
<td>4.00</td>
<td>1.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
</tr>
<tr>
<td>5b</td>
<td>1.00</td>
<td>4.00</td>
<td>1.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
</tr>
<tr>
<td>W1b</td>
<td>1.00</td>
<td>4.00</td>
<td>1.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
</tr>
<tr>
<td>W1b</td>
<td>1.00</td>
<td>4.00</td>
<td>1.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
</tr>
<tr>
<td>6b</td>
<td>1.00</td>
<td>4.00</td>
<td>1.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
</tr>
<tr>
<td>3c</td>
<td>1.00</td>
<td>4.00</td>
<td>1.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
</tr>
<tr>
<td>12c</td>
<td>1.00</td>
<td>4.00</td>
<td>1.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
</tr>
<tr>
<td>14c</td>
<td>1.00</td>
<td>4.00</td>
<td>1.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
</tr>
<tr>
<td>10c</td>
<td>1.00</td>
<td>4.00</td>
<td>1.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
</tr>
<tr>
<td>7c</td>
<td>1.00</td>
<td>4.00</td>
<td>1.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
</tr>
<tr>
<td>3c</td>
<td>1.00</td>
<td>4.00</td>
<td>1.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
</tr>
<tr>
<td>5c</td>
<td>1.00</td>
<td>4.00</td>
<td>1.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
<td>4.00</td>
<td>2.18</td>
</tr>
</tbody>
</table>

**Table DR1**
<table>
<thead>
<tr>
<th>element</th>
<th>$t$</th>
<th>$t$ (95% Quantile)</th>
<th>Diffusion coefficient</th>
<th>Effective diffusion coefficient</th>
<th>$D$ (95% Quantil)</th>
<th>$C_{\text{start}}$</th>
<th>$C_{\text{start}}$(95% Quantili)</th>
<th>$C_{\text{end}}$</th>
<th>$C_{\text{end}}$(95% Quantili)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4\text{He}$</td>
<td>14.1</td>
<td>-0.2</td>
<td>0.2</td>
<td>5.7E-08</td>
<td>4.7E-09</td>
<td>1.7E-11</td>
<td>1.7E-11</td>
<td>4.5E-04</td>
<td>7.7E-06</td>
</tr>
<tr>
<td>$^{20}\text{Ne}$</td>
<td>14.6</td>
<td>-0.4</td>
<td>0.5</td>
<td>2.6E-08</td>
<td>2.1E-09</td>
<td>5.0E-12</td>
<td>5.0E-12</td>
<td>9.4E-09</td>
<td>8.8E-11</td>
</tr>
<tr>
<td>$^{36}\text{Ar}$</td>
<td>15.1</td>
<td>-0.8</td>
<td>3.4</td>
<td>1.9E-08</td>
<td>1.6E-09</td>
<td>5.0E-12</td>
<td>5.0E-12</td>
<td>3.0E-08</td>
<td>1.1E-08</td>
</tr>
<tr>
<td>$^{84}\text{Kr}$</td>
<td>16.9</td>
<td>-0.5</td>
<td>1.1</td>
<td>1.2E-08</td>
<td>1.0E-09</td>
<td>5.0E-12</td>
<td>5.0E-12</td>
<td>1.0E-09</td>
<td>9.0E-11</td>
</tr>
<tr>
<td>$^{132}\text{Xe}$</td>
<td>15.5</td>
<td>-7</td>
<td>6.8</td>
<td>9.9E-09</td>
<td>8.2E-10</td>
<td>1.9E-12</td>
<td>3.9E-12</td>
<td>6.5E-11</td>
<td>4.0E-12</td>
</tr>
<tr>
<td>$\delta^{13}\text{C}$</td>
<td>15.0</td>
<td>-0.5</td>
<td>0.2</td>
<td>3.6E-08</td>
<td>3.0E-09</td>
<td>1.0E-11</td>
<td>1.0E-11</td>
<td>-7.9</td>
<td>0.5</td>
</tr>
</tbody>
</table>