Residence times of groundwater along a flow path in the Great Artesian Basin determined by 81Kr, 36Cl and 4He: Implications for palaeo hydrogeology

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Residence times of groundwater along a flow path in the Great Artesian Basin determined by $^{81}$Kr, $^{36}$Cl and $^4$He: Implications for palaeo hydrogeology

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HIGHLIGHTS

- The first time that the whole suite of radio-noble gases $^{81}$Kr, $^{39}$Ar $^{82}$Kr was measured along a groundwater flow path
- Identification of spatial and temporal occurrence of ephemeral river recharge based on water velocities along a flow line
- Reconstruction of changing Palaeo-recharge conditions in an arid area
- Determination of critical input values for the $^{36}$Cl and $^4$He dating methods

GRAPHICAL ABSTRACT

Ephemeral River Recharge  Diffuse Recharge

The Great Artesian Basin  Australia

Low $^{36}$Cl/Cl, $^{34}$O  High $^{36}$Cl/Cl, $^{34}$O

Radio Noble Gas Sampling

$^{81}$Kr, $^{39}$Ar, $^{14}$C, $^{81}$Kr Age Scale

Subsurface Cl Accumulation

Basal $^4$He Flux

ABSTRACT

Understanding the age distribution of groundwater can provide information on both the recharge history as well as the geochemical evolution of groundwater flow systems. Of the few candidates available that can be used to date old groundwater, $^{81}$Kr shows the most promise because its input function is constant through time and there are less sources and sinks to complicate the dating procedure in comparison to traditional tracers such as $^{36}$Cl and $^4$He. In this paper we use $^{81}$Kr in a large groundwater basin to obtain a better understanding of the residence time distribution of an unconfined-confined aquifer system. A suite of environmental tracers along a groundwater flow path in the south-west Great Artesian Basin of Australia have been sampled. All age tracers ($^{36}$Kr, $^{39}$Ar, $^{14}$C, $^{81}$Kr, $^{36}$Cl and $^4$He) display a consistent increase in groundwater age with distance from the recharge area indicating the presence of a connected flow path. Assuming that $^{81}$Kr is the most accurate dating technique the $^{36}$Cl/Cl systematics was unravelled to reveal information on recharge mechanism and chloride concentration at the time of recharge. Current-day recharge occurs via ephemeral river recharge beneath the Finke River, while diffuse recharge is minor in the young...
1. Introduction

The Great Artesian Basin (GAB) is a continental-scale multi-layered aquifer system, one of the largest groundwater basins in the world (Habermehl, 1980). Because of its large size and relatively easy access to free-flowing artesian waters it has been considered an ideal "field laboratory" for the application and assessment of dating old groundwater. Previous investigations have included seminal studies on Chlorine-36 (36Cl) (Bentley et al., 1986a; Torgersen et al., 1991), Helium-4 (4He) (Torgersen and Clarke, 1985) and in more recent times Krypton-81 (81Kr) (Collon et al., 2000; Lehmann et al., 2003). In the latter study accelerator mass spectrometry (AMS) measurements of the 81Kr abundances were conducted for the first time in a regional study of the same part of the GAB as presented here. Of these three isotopes, 81Kr is the most suitable for age interpretation of old groundwater, because 36Cl and 4He are often not straightforward to untangle as they are complicated by uncertain model assumptions. Along a hydraulic transect from the Finke River recharge zone in the south-western GAB (Fig. 1), we constrained groundwater flow velocities by a set of dating tracers that cover time ranges from decades (36Cl) to over hundreds and thousands of years (39Ar, 14C), and to hundreds of thousands of years (81Kr, 36Cl).

The most used tracer for dating very old groundwater is 36Cl (half-life 301 kyr). The widespread availability of Accelerator Mass Spectrometry (AMS) from the late 1980s meant that 36Cl could henceforth not only be sampled easily but analysed relatively routinely. This combined with the high solubility of chloride resulted in widespread optimism in the research community that the ultimate methodology for dating old groundwater was within reach. However, this optimism soon faded when it was realised that much more complementary information would be required to interpret 36Cl, including the spatial and temporal variability of the 36Cl input as well as information about sources and sinks of chloride. The reader is referred to a number of comprehensive reviews on 36Cl (Aggarwal et al., 2013; Phillips, 2000). In this paper we demonstrate that with independent knowledge of the groundwater age chronology from 81Kr measurements, we have the potential to unravel the chloride isotope systematics and the chloride input into the groundwater system. This procedure provides additional information on the groundwater flow system not possible by other methodologies, and under ideal situations it may provide "proxy" evidence for paleoclimate.

Helium-4 is another isotope commonly used to obtain information on old groundwater (Kipfer et al., 2002). The basic principle of this method is that, as 4He is produced in the sub surface by the decay of uranium (U) and thorium (Th) its concentration increases with increasing residence time. For quantitative age dating the local accumulation rate of 4He needs to be determined as well as the He influx to the aquifer from various sources. The production rate can be calculated from U and Th concentrations in the aquifer. However, the He influx from neighbouring strata is far more difficult to quantify. As a result, 4He is often considered to be a semi-quantitative indicator of groundwater age at best. Many previous studies in the GAB have been devoted to the accumulation of He in groundwater (Torgersen and Clarke, 1985, 1987; Torgersen and Ivey, 1985). However, up until the present, it has not been possible for the 4He clock to be calibrated against a reliable residence time indicator, not only for the GAB, but also for other large aquifers systems around the globe (Torgersen, 2010).

It is only recently that the detection of 81Kr at natural levels has been developed with a precision sufficient to date groundwater (Gerber et al., 2017; Jiang et al., 2020; Matsumoto et al., 2018; Ram et al., 2021; Sturchio et al., 2014; Yechieli et al., 2019; Yokochi et al., 2019; Yokochi et al., 2021), but it has for a long time been potentially considered to be the most reliable isotope to quantify long groundwater residence times (Lehmann et al., 1993; Lehmann et al., 2003). This is because krypton (Kr), being a noble gas is inert and as a result does not undergo chemical reactions. Furthermore, it has a well-known atmospheric concentration of 1.099 ± 0.009 ppm (Aoki and Makide, 2005). Variations of the 81Kr/Kr ratio over time are relatively small (Buziart et al., 2013; Zappala et al., 2020). In addition, both subsurface and anthropogenic sources of 81Kr are considered minimal in most cases (Aggarwal et al., 2015; Purtschert et al., 2013; Purtschert et al., 2021; Sturchio et al., 2004).

However the application of this potentially ideal groundwater tracer has been limited in the past because of poor detection efficiency of 81Kr which has resulted in large volumes of water required for degassing (Purtschert et al., 2013). Nevertheless, recent development of Atom Trap Trace Analysis method (ATTA) has improved the detection efficiency, which has resulted in a much lower volume of water being required for sampling and processing (Lu et al., 2014; Zappala et al., 2020; Zhang et al., 2020).

Our study area is in the south-western GAB. This region may represent an ideal area for testing the application of 81Kr in groundwater studies because: a) the hydrogeology of the region is relatively well known (Love et al., 2013); b) there have been previous studies on the source and sinks of chloride (Love et al., 2000); c) there have been numerous hydro-chemical and environmental tracers studies in the region (Pristley et al., 2017; Radke et al., 2000; and, d) the first successful set of groundwater 81Kr samples were analysed by AMS in this region (Collon et al., 2000; Lehmann et al., 2003). It is assumed that there has been effectively zero diffuse recharge in the region since the end of the Pleistocene and that modern day recharge only occurs beneath isolated riverbeds referred to as ephemeral river recharge (ERR).

In this paper we show that 81Kr ages provide a reasonable representation of the groundwater residence time. Our confidence in this comes from the lack of major sources or sinks of Kr in the subsurface and that the input function is known and constant through time. Furthermore, a previous study in this area, provided the first 81Kr dates from four wells in the region, indicating that this new dating tool was worthy of further consideration (Lehmann et al., 2003).

The aim of this paper is to:

- Assess the feasibility of radioactive noble gas tracers (85Kr, 81Kr and 39Ar) for the determination of groundwater flow velocities over a large range of flow distances.
- Use the calculated 81Kr ages to calibrate the 36Cl and 4He groundwater clocks.
- Obtain a better understanding of the palaeo-hydrogeology and in particular the history of recharge from the Finke River over time.

2. Study area

Our study area is the western margin of the GAB in the Finke River recharge zone and extends hundreds of kilometres towards the interior of the GAB where the aquifer becomes confined (Fig. 1). The study section starts near the Finke River recharge zone and extends about 300 km downstream. At the beginning of the transect the main aquifer of the GAB (referred to as the Cadna-Owie Formation–Albeguckina Sandstone or J aquifer in this section of the GAB) crops out and is unconfined for approximately 40 km until it becomes a confined system overlain by the confined Bulldog Shale. The study area is arid with potential evapotranspiration ranging up to 3000 mm/yr. Average annual rainfall is 200 mm/yr, with approximately 85% occurring in the months of January to March. In this area of the GAB the only effective recharge occurring today is via
groundwaters. Towards the end of the transect the influence of ephemeral recharge is less while diffuse recharge and the initial chloride concentration at recharge were higher.
ephemeral river recharge (ERR). This recharge to the main J aquifer of the GAB occurs in the outcrop area beneath the Finke River where the main J aquifer outcrops during infrequent times of intense rainfall that originate from monsoons that travel across the continent from the north. Stable isotope data indicate that this typically occurs in the months of January to March (Fulton et al., 2013).

Fulton et al. (2013) mapped the potential recharge zone to be 13 km², with a length of 36 km and an average river bed width of 370 m (Fulton et al., 2013). Ephemeral river recharge beneath the Finke River recharge zone was estimated to be 380–850 mm per annum, in contrast to diffuse recharge surrounding the river which is in the order 0.1–0.25 mm/yr (Wohling et al., 2013). Groundwater flows in a southeast direction from the Finke River recharge zone to towards a more central portion of the GAB. Clearly, modern day ERR occurs beneath the Finke River today but how significant this recharge has been in the past remains unresolved.

Previous studies in the arid central Australia have shown that subsurface production of $^{36}$Cl, as well as diffusion of solutes from adjacent aquitards, complicates the interpretation of $^{36}$Cl dating results (Love et al., 2000; Priestley et al., 2017). Furthermore, it has been shown that there are spatial variations in the $^{36}$Cl/Cl input value, and in all cases, the input values are below what could be expected from latitudinal variation of the $^{36}$Cl/Cl input ratio alone. Based on Cl/Br in samples upstream from

**Fig. 1.** Map of the study area showing the different groundwater groups. The dashed line represents the potentiometric contours (Rousseau-Gueutin et al., 2013) where the generalised direction of groundwater flow is at right angles to these contour lines. A-B represents the hydrogeological cross section. The boundary between confined-unconfined conditions is also shown.
the Finke River recharge zone halite dissolution has occurred from the Bitter Springs Formation and has been discharged to the river. This effect can account for the lower $^{36}$Cl/Cl input value of $60 \times 10^{-15}$ (Fulton et al., 2013; Wohling et al., 2013). While in the region to the south–west of the Finke River recharge zone there is no evidence of young groundwater being influenced by dissolution of evaporites. In this area the $^{36}$Cl/Cl input ratio was determined to be $125 \times 10^{-15}$ based on measurements on selected young groundwater samples in the unconfined part of this aquifer where an anthropogenic component can be ruled out (Lehmann et al., 2003; Love et al., 2000).

3. Field and analytical methods

Groundwater was sampled in November 2009 from unconfined and confined sections (including artesian wells) of the main J aquifer of the GAB (Fig. 1). The sampling sites were selected along a transect in the direction of groundwater flow. The transect begins in the Finke River recharge area and extends past Dalhousie Springs. A total of 19 wells were purged several times until stable field parameters of pH, temperature and salinity were achieved (Table 1).

Samples for $^4$He were taken in copper tubes using standard techniques (Aeschbach-Hertig and Solomon, 2013). He isotopes, as well as the main isotopes of Ne and the heavy noble gases were measured at the Institute of Environmental Physics, Heidelberg University, following the methods described by (Beyerle et al., 2000). Radioactive noble gases $^{86}$Kr, $^{39}$Ar and $^{81}$Kr were sampled in the field using a large volume gas extraction system (Purtschert et al., 2013). The vacuum cylinder gas extraction system was optimized for remote fieldwork and achieved an extraction efficiency of 80–90 % at a water flow rate of 20 L/min. Approximately 2000–3000 L of groundwater were degassed in the field and gases were collected in pre-evacuated steel containers.

The gas obtained by degassing was analysed for major gas composition on a quadrupole mass spectrometer before separating the Ar and Kr gases for further analysis. Krypton was extracted from the bulk gas at the University of Bern by multistep gas chromatography (Loosli and Purtschert, 2005), and the isotope ratios $^{81}$Kr/Kr and $^{85}$Kr/Kr were determined using the ATTA-3 instrument in the Laboratory for Radiokrypton Dating, Argonne National Laboratory (Jiang et al., 2012). Based on the Atom Trap Trace Analysis method (Du et al., 2003), ATTA-3 is a selective and efficient atom counter capable of measuring both $^{81}$Kr/Kr and $^{85}$Kr/Kr ratios of environmental samples in the range of $10^{-14}$–$10^{-16}$. In the apparatus, atoms of a targeted isotope $^{81}$Kr, $^{85}$Kr, or the control isotope $^{83}$Kr were captured by resonant laser light into an atom trap and counted by observing the fluorescence of the trapped atoms. For $^{81}$Kr dating in the age range of 50 kyr – 1500 kyr, the required sample size was at the time of analyses $5–10$ micro-L STP of krypton gas, which could be extracted from approximately 100–200 kg of water or 40–80 kg of ice. Both the reliability and reproducibility of the method were examined with an inter-comparison study among different methods and instruments. The $^{85}$Kr/Kr ratios of 12 samples, in the range of $10^{-15}$ to $10^{-16}$, were measured independently in three laboratories: a low-level counting (LLC) laboratory in Bern, Switzerland, and two ATTA laboratories, one in Argonne and the other in Hefei, China. The results agree at the precision level of 7 % (Du et al., 2003; Jiang et al., 2012).

The detection limit of ATTA-3, defined as the lowest isotope ratio detectable by ATTA-3, is approximately 1 dpm/cc for $^{85}$Kr/Kr. Here we use the conventional units of dpm/cc, which stands for the number of $^{85}$Kr decays per minute per mL-STP of Kr gas. For conversion, 100 dpm/cc corresponds to the $^{85}$Kr/Kr ratio of $3.03 \times 10^{-11}$. This detection limit, caused by the instrument memory effect, was determined with measurements of an $^{85}$Kr-dead sample. Argon was also extracted from the bulk gas by cryogenic distillation. $^{39}$Ar activities were measured by low-level gas proportional counting at the Physics Institute, University of Bern (Loosli, 1983; Loosli and Purtschert, 2005).

Radiocarbon ($^{14}$C) was collected in 1 L bottles in the field and analysed by AMS at the Rafter Radiocarbon Laboratory in New Zealand. An additional aliquot collected for Carbon 13 ($^{13}$C) was also analysed by AMS at the same laboratory. $^{36}$Cl samples were filtered with 0.45 μm membrane filters and then the chlorine was prepared as AgCl according to the preparation scheme reported in (Tosaki et al., 2011). The $^{36}$Cl/Cl ratios were analysed with the AMS (accelerator mass spectrometry) system at the Tandem Accelerator Complex, University of Tsukuba (Sasa et al., 2010), along with diluted NIST $^{36}$Cl standards ($^{36}$Cl/Cl = $1.60 \times 10^{-12}$).

4. Results

For ease of comparison and discussion the sampled wells were split into three groups (Fig. 1):

- Group I samples located closest to the Finke River recharge zone (red dots in figures)
- Group II represent the intermediate wells (green triangles in figures)
- Group III represent the wells furthest along the transect (blue triangles in figures)

Table 1

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Local Name</th>
<th>Total Depth m</th>
<th>Boretype</th>
<th>Temperature °C</th>
<th>Specific EC μS/cm</th>
<th>Cl mg/L</th>
<th>$^{36}$O ‰</th>
<th>$^{36}$H ‰</th>
<th>$^{36}$C ‰</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>New Townsend</td>
<td>143.3</td>
<td>S</td>
<td>29.08</td>
<td>666</td>
<td>84</td>
<td>−10.3</td>
<td>−71.8</td>
<td>−11.4</td>
</tr>
<tr>
<td>2</td>
<td>Sandy Bore</td>
<td>91.5</td>
<td>S</td>
<td>29.06</td>
<td>595</td>
<td>86</td>
<td>−9.8</td>
<td>−67.8</td>
<td>−10.8</td>
</tr>
<tr>
<td>3</td>
<td>Roads Bore</td>
<td>196</td>
<td>S</td>
<td>33.14</td>
<td>3017</td>
<td>760</td>
<td>−8.3</td>
<td>−58.8</td>
<td>−9.7</td>
</tr>
<tr>
<td>5</td>
<td>Maryanne Stock Bore</td>
<td>96</td>
<td>S</td>
<td>30.25</td>
<td>1303</td>
<td>250</td>
<td>−9.6</td>
<td>−66.9</td>
<td>−10.5</td>
</tr>
<tr>
<td>6</td>
<td>Willoughby Bore</td>
<td>79</td>
<td>S</td>
<td>29.35</td>
<td>582</td>
<td>86</td>
<td>−9.4</td>
<td>−66.8</td>
<td>−10.6</td>
</tr>
<tr>
<td>7</td>
<td>139.8</td>
<td></td>
<td>M</td>
<td>28.72</td>
<td>781</td>
<td>110</td>
<td>−10.6</td>
<td>−73.6</td>
<td>−11.6</td>
</tr>
<tr>
<td>8</td>
<td>Bore 8 (Finke)</td>
<td>157</td>
<td>T</td>
<td>28.04</td>
<td>801</td>
<td>150</td>
<td>−9.4</td>
<td>−65.1</td>
<td>−13.3</td>
</tr>
<tr>
<td>9</td>
<td>Mt Dare HS</td>
<td>237</td>
<td>T</td>
<td>41.86</td>
<td>1489</td>
<td>280</td>
<td>−8.4</td>
<td>−57.6</td>
<td>−10.7</td>
</tr>
<tr>
<td>10</td>
<td>3 O’Clock Creek Bore</td>
<td>441.4</td>
<td>M</td>
<td>40.57</td>
<td>1638</td>
<td>330</td>
<td>−7.5</td>
<td>−53.3</td>
<td>−11.0</td>
</tr>
<tr>
<td>12</td>
<td>Stevenson Bore</td>
<td>363.6</td>
<td>M</td>
<td>46.04</td>
<td>2136</td>
<td>440</td>
<td>−6.8</td>
<td>−50.7</td>
<td>−11.7</td>
</tr>
<tr>
<td>13</td>
<td>Oodnadatta #3</td>
<td>498</td>
<td>T</td>
<td>41.81</td>
<td>2998</td>
<td>630</td>
<td>−6.85</td>
<td>−48.8</td>
<td>−11.7</td>
</tr>
<tr>
<td>14</td>
<td>Snake Creek No.2</td>
<td>676</td>
<td>S</td>
<td>60.4</td>
<td>4335</td>
<td>950</td>
<td>−6.4</td>
<td>−44.9</td>
<td>−11.0</td>
</tr>
<tr>
<td>15</td>
<td>Horshoe Bore 2</td>
<td>202.1</td>
<td>S</td>
<td>38.08</td>
<td>4090</td>
<td>950</td>
<td>−5.9</td>
<td>−43.5</td>
<td>−11.0</td>
</tr>
<tr>
<td>16</td>
<td>Apperinna Bore 2</td>
<td>489.5</td>
<td>M</td>
<td>49.83</td>
<td>3609</td>
<td>810</td>
<td>−6.6</td>
<td>−49.2</td>
<td>−10.3</td>
</tr>
<tr>
<td>17</td>
<td>Duckhole No. 2</td>
<td>250.8</td>
<td>S</td>
<td>38.83</td>
<td>3704</td>
<td>830</td>
<td>−6.8</td>
<td>−47.8</td>
<td>−9.9</td>
</tr>
<tr>
<td>18</td>
<td>Watson Creek 2</td>
<td>289</td>
<td>S</td>
<td>39.94</td>
<td>4417</td>
<td>1100</td>
<td>−6.5</td>
<td>−44.4</td>
<td>−9.3</td>
</tr>
<tr>
<td>19</td>
<td>Raspberry Creek 2</td>
<td>126.8</td>
<td>S</td>
<td>29.36</td>
<td>5032</td>
<td>1200</td>
<td>−6.11</td>
<td>−45.7</td>
<td>−8.2</td>
</tr>
</tbody>
</table>
Well 19 is an outlier and does not belong to any group. The groundwater there most likely originates from a westerly recharge source (black square in figures).

### 4.1. Radionuclides data consistency and reduction

The purpose of this section is to review the internal consistency of the data set and to apply corrections to the data where required. The activities of the radioactive noble gases $^{85}$Kr, $^{39}$Ar, $^{81}$Kr as well as $^{14}$C activities and $^{36}$Cl/Cl ratios are summarized in Table 2, and tracer-tracer plots are compared with each other in order of increasing half-lives in Fig. 2.

![Fig. 2](image-url)

**Fig. 2.** Tracer -Tracer plots showing the comparison of tracers with sequential half-lives. Red circles represent Group 1 close to the recharge zone, the green triangles represent the intermediate wells of Group 2 while the blue triangles represent the most distal wells of Group 3. The black square represents a well most likely from a more westerly recharge zone.

Table 2

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>$^{39}$Ar pmAr</th>
<th>$^{85}$Kr dpm/cc</th>
<th>$^{81}$Kr pmKr</th>
<th>$^{14}$C pmC</th>
<th>$^{36}$Cl/Cl $\times 10^{-15}$</th>
<th>$^3$He/$^4$He cm$^3$/yr/g</th>
<th>$^3$He pmKr</th>
<th>$^3$He pmC $\times 10^{-9}$</th>
<th>$^8$Ne</th>
<th>$^{39}$Ar age yrs</th>
<th>$^{14}$C age kyr</th>
<th>$^{81}$Kr age kyr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>&lt;10</td>
<td>1.6 ± 0.6</td>
<td>98 ± 7</td>
<td>74.5</td>
<td>55 ± 4</td>
<td>147.3</td>
<td>&lt;0.2</td>
<td>58.2</td>
<td>&gt;894</td>
<td>1.2</td>
<td>6.7</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>24 ± 6</td>
<td>&lt;0.9</td>
<td>100 ± 7</td>
<td>84.64</td>
<td>61 ± 4</td>
<td>158.6</td>
<td>&lt;0.2</td>
<td>37.8</td>
<td>550 ± 100</td>
<td>0.1</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>55 ± 6</td>
<td>&lt;1.5</td>
<td>85 ± 7</td>
<td>82.08</td>
<td>91 ± 5</td>
<td>149.2</td>
<td>&lt;0.2</td>
<td>20.5</td>
<td>230 ± 40</td>
<td>0.4</td>
<td>51.8</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>&lt;4</td>
<td>0.8 ± 0.5</td>
<td>99 ± 8</td>
<td>17.65</td>
<td>38 ± 3</td>
<td>85</td>
<td>6.1 ± 0.2</td>
<td>65.3</td>
<td>&gt;1249</td>
<td>14.8</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>26 ± 7</td>
<td>&lt; 0.9</td>
<td>107 ± 8</td>
<td>42.09</td>
<td>61 ± 4</td>
<td>116</td>
<td>0.8 ± 0.1</td>
<td>54.7</td>
<td>520 ± 100</td>
<td>6.3</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>&lt;6</td>
<td>1.2 ± 0.5</td>
<td>91 ± 8</td>
<td>67.43</td>
<td>52 ± 4</td>
<td>148.1</td>
<td>&lt;0.2</td>
<td>7.6</td>
<td>&gt;1092</td>
<td>2.1</td>
<td>31.2</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>19 ± 8</td>
<td>34.0 ± 2.6</td>
<td>72 ± 9</td>
<td>63.07</td>
<td>57 ± 4</td>
<td>136.7</td>
<td>&lt;0.2</td>
<td>155.3</td>
<td>645 ± 160</td>
<td>2.7</td>
<td></td>
<td></td>
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<tr>
<td>8</td>
<td>65 ± 7</td>
<td>1.8 ± 0.6</td>
<td>105 ± 7</td>
<td>89.94</td>
<td>160</td>
<td>&lt;0.2</td>
<td>60.7</td>
<td>&gt;167</td>
<td>-0.4</td>
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<tr>
<td>9</td>
<td>&lt;8</td>
<td>10.3 ± 0.9</td>
<td>87 ± 7</td>
<td>9.94</td>
<td>73 ± 4</td>
<td>32.4</td>
<td>32 ± 0.5</td>
<td>77.6</td>
<td>&gt;980</td>
<td>21.7</td>
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<td>&lt;14</td>
<td>&lt;0.8</td>
<td>87 ± 7</td>
<td>4.74</td>
<td>49 ± 5</td>
<td>9.3</td>
<td>176.8 ± 2.3</td>
<td>83.1</td>
<td>&gt;763</td>
<td>38.8</td>
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<td>11</td>
<td>&lt;5</td>
<td>1.2 ± 0.6</td>
<td>69 ± 6</td>
<td>7.74</td>
<td>49 ± 5</td>
<td>4.7</td>
<td>377.2 ± 5.4</td>
<td>52.4</td>
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<td>25.5</td>
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<tr>
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<td>&lt;1.1</td>
<td>56 ± 5</td>
<td>2.59</td>
<td>62 ± 4</td>
<td>1.8</td>
<td>1650 ± 20.4</td>
<td>61.1</td>
<td>50 ± 20</td>
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<td>4.73</td>
<td>55 ± 3</td>
<td>2.6</td>
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<td>75.9</td>
<td>&gt;894</td>
<td>39.0</td>
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<tr>
<td>14</td>
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<td>12.3 ± 1.2</td>
<td>47 ± 6/37 ± 7</td>
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<td>34 ± 2</td>
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<td>15</td>
<td>&lt;10</td>
<td>40 ± 3</td>
<td>92 ± 10</td>
<td>nm</td>
<td>37 ± 3</td>
<td>1.4</td>
<td>4759. ± 52</td>
<td>46.8</td>
<td>&gt;894</td>
<td>-</td>
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<tr>
<td>16</td>
<td>&lt;3</td>
<td>0.8 ± 0.5</td>
<td>36 ± 5</td>
<td>2.87</td>
<td>27 ± 2</td>
<td>2.2</td>
<td>2831 ± 35</td>
<td>50.8</td>
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<td>&lt;1.5</td>
<td>47 ± 5</td>
<td>6.84</td>
<td>32 ± 2</td>
<td>1.4</td>
<td>3981 ± 43</td>
<td>49.3</td>
<td>&gt;894</td>
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<tr>
<td>19</td>
<td>&lt;10</td>
<td>1.3 ± 0.6</td>
<td>87 ± 8</td>
<td>4.34</td>
<td>53 ± 4</td>
<td>&gt;894</td>
<td>45.3</td>
<td>46</td>
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</table>

$^{36}$Cl/Cl ratios are summarized in Table 2, and tracer-tracer plots are compared with each other in order of increasing half-lives in Fig. 2. Fig. 2a displays three samples with elevated $^{85}$Kr values in combination with $^{39}$Ar values <20 % of the activity in the modern atmosphere (pmAr). These are possibly the result of contamination of the Kr gas fraction which was purified and shipped to Argonne National Laboratory after the Ar gas fraction was separated at the University of Bern from the crude gas which implies that only the $^{81}$Kr activities need to be corrected (and not $^{39}$Ar). This is the case for samples 9 and 14. The $^{81}$Kr value of the highly
air contaminated sample 7 was neglected. Since it is assumed that the contamination occurred in the northern hemisphere the corresponding atmospheric \(^{81}\)Kr activity in the northern hemisphere (\(^{85}\)Kratm) of 75 dpm/cc Kr (Winger et al., 2005) was used to calculate the fraction \(\alpha\) of air contamination in the \(^{81}\)Kr sample (\(\alpha = \frac{^{85}\text{Kratm} - ^{81}\text{Kran}}{^{85}\text{Kratm}}\)).

\[ \text{Krcorr} = \left( \frac{^{81}\text{Kran} \cdot \alpha - 100}{1 - \alpha} \right) \]

Here the indices \(m\) and \(corr\) refer to the measured and corrected \(^{81}\)Kr values, respectively. \(^{85}\)Kr activity is given in percent of the modern atmospheric value (pmKr).

The comparison of \(^{39}\)Ar and \(^{14}\)C activities reveals a rather consistent pattern (Fig 2b). The \(^{39}\)Ar active samples show the highest \(^{14}\)C activities ranging from 40 to 90 pmC (percent modern carbon). Three samples from Group 1 and all samples from Group 2–3 have \(^{39}\)Ar activities (given in percent of the modern atmospheric activity concentration pmAr) below the detection limit except for sample 12 which has an elevated \(^{39}\)Ar value. Since this sample is \(^{39}\)Kr free, air contamination during sampling can be excluded. The \(^{39}\)Ar activity was measured twice with reproducible results so we are confident that the value is real. One possibility could be that this sampling location represents modern recharge from vertical flow from the surface. However, this seems very unlikely as this location is a zone of upward hydraulic head which would negate downward flow today. This site also has 320 m of overlying low permeability units. Furthermore, all the other dating tracers indicate old groundwater. Locally elevated underground in-situ production of \(^{39}\)Ar within in the aquifer at great depth (Lehmann et al., 1993) cannot be excluded but seems to be unlikely because the \(^{39}\)Ar activity of all other samples from Groups 2–3 are below detection limit in agreement with previous findings (Lehmann et al., 2003). However, this site also has elevated \(^{36}\)Cl/Cl in comparison to the depleted \(^{81}\)Kr value (Fig 2d). This may possibly support the existence of a locally elevated neutron flux (Purtschert et al., 2021). We interpret this as a local phenomenon and assume negligible underground production of \(^{39}\)Ar for all other samples. The \(^{39}\)Ar values of Group 1 were therefore interpreted in terms of groundwater residence time without corrections for underground production.

Elevated \(^{14}\)C activities of Group 1 waters coincide with the highest \(^{81}\)Kr values (Fig. 2c). Samples with \(^{81}\)Kr values <80 % modern are strongly depleted in \(^{14}\)C with values between 3 and 10 pmC. However, even the most \(^{81}\)Kr depleted waters have \(^{14}\)C concentrations significantly above the detection limit of \(-0.5\) pmC. The origin of this offset of \(-4\) pmC remains a conundrum but may be an analytical artefact rather than representing the real situation in the aquifer. \(^{14}\)C contamination e.g. during sampling was observed in other studies (Aggarwal et al., 2014; Yokochi et al., 2017) in particular when conventional sampling and counting techniques were applied. Such an effect was however not expected for the radiocarbon AMS technique as applied in our study. The comparison with the \(^{81}\)Kr data in combination with the improbability of the admixture of young water components in the downstream part of the artesian aquifer allows us to conclude that samples with \(^{14}\)C activities below 4 pmC are older than the practical upper end of the \(^{14}\)C dating range of 40 kyrs.

\(^{81}\)Kr activities and \(^{36}\)Cl/Cl ratios correlate well (Fig. 2d). The largest scatter is observed for Group 1 where \(^{36}\)Cl/Cl ratios range between 40 and 90 \(\times 10^{-15}\) for a relatively small range of \(^{81}\)Kr values between 80 and 100% modern. Further downstream (Groups 2–3) the activities of both tracers decrease simultaneously. A more detailed discussion of both tracers in terms of groundwater residence time and flow velocity will follow in Section 5.1.

\(^{38}\)C values of DIC (Table 1) are relatively constant along the flow line and range mostly between \(-10\) and \(-12\) \%. This is comparable to the assumed signature of soil CO\(_2\) (Fulton et al., 2013). This indicates that dissolution of carbonate minerals during recharge beneath the Finke River is minimal. As a result, we present \(^{14}\)C ages (Table 2) calculated with a constant initial activity of 86 pmC calculated from the mean of \(^{39}\)Ar active samples under consideration of an offset of 4 pmC (Section 5.1).

4.2. Spatial distribution of tracer activities

In Fig. 3 the contamination corrected tracer activities are plotted as a function of distance from the recharge area (RA), where the Finke River crosses the J aquifer outcrop. \(^{81}\)Kr values (Table 2, not shown in the graph) below 2.4 dpm/ccKr indicate a lower age limit of 40 years for all waters. This is also supported by the highest \(^{39}\)Ar activity of 65 \pm 7 pmAr which corresponds to a residence time of \(-170\) years. With increasing distance from the recharge area, the \(^{39}\)Ar values decrease rapidly to the below detection limit around 40 km from the Finke River. This is also the location where a sharp decrease of \(^{14}\)C activities is observed. Within 10–20 km, the \(^{14}\)C activities decrease from 70 to 17 pmC (Fig 3c). This rapid decrease in \(^{14}\)C corresponds to the approximate location where the aquifer transfers from an unconfined to a confined system (Fig. 1). In this section the aquifer thickness increases from 30 m to almost 200 m which may imply a reduction of the flow velocity.

All Group 1 waters show modern or slightly sub-modern \(^{81}\)Kr activities (Fig 3d). For Group 2 groundwater wells the \(^{14}\)C ages increase beyond the dating range of the radiocarbon method. This is consistent with the decreasing \(^{81}\)Kr activities in this area (Fig 3d and e). The lowest \(^{81}\)Kr values of 34 and 36 pmKr are observed for Group 3 groundwaters. This corresponds to an \(^{81}\)Kr age of \(-350\) kyrs. Sample number 13 appears to be closely related to Sample 19 being sourced from the west (Fig 1). It has a higher \(^{81}\)Kr value than would be expected if it were along a common flow transect from the north. Fig 3c shows that the highest \(^{36}\)Cl/Cl ratios are found close to the recharge area. Most samples of Group 1 cluster at \(^{36}\)Cl/Cl ratios in the range 50–60 \(\times 10^{-15}\). Similarly to \(^{81}\)Kr, the ratios decrease within Group 2 and reach the lowest values in Group 3 wells down gradient. Although there is considerably more scatter in the \(^{36}\)Cl/Cl values.

Concentrations of dissolved \(^{4}\)He also show a very pronounced evolution with distance (Fig 3f). Group 1 water close to the recharge area are low in \(^{4}\)He with concentrations < \(-10^{-6}\) cm\(^{-3}\)/gm. Within Group 2 an increase is observed after approximately 150 km from the Finke River recharge area. Waters of Group 3 are most enriched in \(^{4}\)He by three orders of magnitude in relation to air saturated water (ASW). Also here, sample 13 is an outlier with a lower \(^{4}\)He concentration suggesting a shorter flow path from a westerly source as indicated by the potentiometric surface (Fig. 1, note no \(^{4}\)He data are available for sample 19).

4.3. Stable isotopes

The stable isotope composition of the groundwater varies over a large range between \(-10.7\) ‰ to \(-6\) ‰ for \(^{81}\)O and \(-74\) ‰ to \(-43\) ‰ and for \(^{8}\)D (Table 1 and Fig. 4). The most depleted waters are from Group 1 close to the recharge area. Further downgradient (Group 2 & 3), the stable isotope composition is characterised by more enriched values. The best fit of the data has a slope of \(6.4 \pm 0.2\), while the deuterium excess (defined by \(^{8}\)D \(-8 \times ^{18}\)O) decreases from +11 ‰ in the recharge area to +3.5 ‰ for the oldest waters. This indicates that groundwater that infiltrated in the past was subject to greater evaporation than the younger waters. This is also supported by the highest Cl concentrations found for Group 2 and Group 3 waters. However, it must be considered that part of the chlorine accumulated in the subsurface. This distinction is made in the discussion, taking into account the \(^{36}\)Kr ages.

5. Discussion

5.1. Groundwater residence times and flow velocities

The comprehensive set of dating tracers covering age ranges of decades (\(^{36}\)Kr) to centuries (\(^{39}\)Ar) to millennia’s (\(^{14}\)C) and up to hundreds of thousands of years (\(^{81}\)Kr, \(^{36}\)Cl and \(^{4}\)He) along a groundwater flow path consistently indicate increasing residence time with decreasing piezometric heads and distance from the Finke River recharge area (Table 2). This unique dataset allows for the inter-comparison of the suitability of the different dating tracers, particular in relation to \(^{81}\)Kr data, and for an
understanding of the recharge and flow dynamic of this part of the GAB.
The very old apparent residence times imply recharge over different
climate periods.

In this paper, the term “tracer age” refers to the decay (or accumulation
in the case of $^{4}$He) time of the individual tracer that has been elapsed
between groundwater recharge and the sampling location in the aquifer
system. The distinct half-lives (and decay constants $\lambda$) of $^{39}$Ar, $^{14}$Ca
and $^{81}$Kr cover very different ranges of residence times, $t$. The $^{39}$Ar, $^{14}$C and
$^{81}$Kr percent modern values are converted directly to groundwater ages
using the radioactive decay law:

$$t = \frac{1}{\lambda} \cdot \ln \left( \frac{C_0}{C} \right)$$  \hspace{1cm} (2)

where $C$ and $C_0$ are the measured and initial concentration respectively. For
$^{39}$Ar and $^{81}$Kr, initial activities $C_0$ of 100 pmAr and 100 pmKr were
assumed. An initial $^{14}$C concentration of 86 pmC was calculated from the
mean of samples with a detectable $^{39}$Ar activity (samples 2, 3 and 8 in
Fig. 8). From this initial value and from all measured activities an offset
of 4 pmC was subtracted as outlined in Section 4.1. The resulting tracer
ages for $^{39}$Ar, $^{14}$C and $^{81}$Kr are listed in Table 2 and are compared in
Fig. 5 with age bands considering the analytical uncertainties. The
Figure demonstrates consistent tracer ages for most wells without consider-
ation of mixing, but it becomes also obvious how the application of tracers
with suitable half-life reduces the age uncertainties for the individual age
ranges.

A fit through the decay ages of sampling points reveal the mean flow
velocity between those sampling points, which is independent of the initial
concentration $C_0$ (Fig. 6). Thereby it is assumed that the observed gradient
of tracer concentrations along a flow line is mainly the result of aging rather
than mixing of different water masses (i.e. piston flow). The age gradients
are determined individually for $^{39}$Ar, $^{14}$C and $^{81}$Kr (Fig. 6 A, B and C). For

Fig. 3. Tracer concentrations versus distance from the Finke River Recharge area (RA). The top left-hand panel shows the location of the wells as a reference. Note all the
tracers show an increase in age with distance travelled along the transect.
Table 3

<table>
<thead>
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<th>Parameter</th>
<th>Value</th>
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<tr>
<td>R_{36Cl}</td>
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</tr>
<tr>
<td>R_{81Kr}</td>
<td>$10 \times 10^{-15}$</td>
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<tr>
<td>R_{87Br}</td>
<td>$60 \times 10^{-15}$</td>
</tr>
<tr>
<td>R_{0}</td>
<td>$120 \times 10^{-15}$</td>
</tr>
<tr>
<td>C_{GLOBAL}</td>
<td>100 mg/L</td>
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</table>

$^{14}$C, two different slopes were calculated for the first part of the transect and the further downstream part, respectively. The fitting results are depicted in Fig. 6 and show a clear trend as function of flow distance, time and dating tracer. On short timescales and as calculated from the $^{39}$Ar data a flow velocity of $\sim 90$ m/yr close to the recharge can be derived. Downstream, the $^{14}$C data indicate a further decrease of the flow velocity to $\sim 10.9$ m/yr up to $\sim 30$ km, while further down gradient ($\sim 30–90$ km) flow velocities decrease to $\sim 4$ m/yr. A similar pattern for the $^{81}$Kr data can be observed where, on $^{81}$Kr timescales of hundreds of thousands of years an average flow velocity of $\sim 1$ m/yr can be concluded. Further downstream ($\sim 150–300$ km) these decreases to $\sim 0.3$ m/yr (Fig. 6). Fig. 6D, displays the various calculated velocities from the different tracers versus an analytical model of tracer velocity (see Section 5.2). The decrease of flow velocities (or increase of spatial age gradients) as function of flow and tracer timescales may have several reasons:

- The assumption of conservative flow within the aquifer is not fulfilled. If significant quantities of water seep through the aquitards (leaky aquitards) the flow velocity within the aquifer would decrease according to the mass conservation law. The observed reduction of flow velocity along the flow line by two orders of magnitude would imply that 99 % of the recharge is lost by upward leaking through the aquitard.
- Transient hydrodynamic conditions either due to naturally changing recharge rates and/or the change from pre-exploitation conditions to a situation with heavy groundwater abstraction would modify the age gradient within the system. A new tracer steady state in the whole system is only achieved after a transient phase during which the new hydraulic state propagates through the system (Rousseau-Gueutin et al., 2013; Zuber et al., 2010). However, if the mean groundwater age is large in comparison with the characteristic timescale of the changes in the system, as it is the case here, a hydrologic quasi-steady state can still be assumed.
- Also, the progressive admixture of older water along the flow line would cause a faster aging along the flow than anticipated in a piston flow scenario. Towards the centre of the basin the regional flow directions from the western and the north-eastern recharge areas converge (Radke et al., 2000; Torgersen et al., 1991) which could cause an apparent spatial aging.
- Dominant recharge at a point source, as it is postulated in our study area today, into a 3-dimensional aquifer system would also lead to a decreasing flow velocity as function of distance from the source.

We judge the last possibility to be the most likely and this scenario is investigated in more detail in the following section.

5.2. Finke River recharge source

One of the key questions that remains unresolved in understanding ephemeral river recharge (ERR) in this part of the GAB is how long the Finke River has been a source of groundwater recharge. For the following analyses we hypothesize that the Finke River recharge zone is a point source. This seems reasonable considering that the section where the Finke River crossed the outcrops of the J-aquifer is only 36 km long and 350 m in width which is relatively small considering a transect distance of >300 km. Then, if we assume steady state groundwater flow in an aquifer with constant porosity and recharge from a point source with strength $S$ ($\text{m}^3/\text{yr}$) and the law of mass conservation it follows that:

$$S = v_D(R) \cdot A(R)$$

(3)

where $v_D(R)$ is the Darcy velocity and $A(R)$ the cross section where groundwater moves as function of distance $R$ from the point source (Fig. 7). The cross-sectional area $A(R)$ may increase because of radial flow away from the point source (which is strictly not fulfilled) it follows from Eq. (3) that the local Darcy velocity, $v_D(R)$, decreases inversely proportional with distance $R$ from the point source: $v_D(R) \sim \frac{1}{R}$. For constant porosity $\phi$, this

Fig. 4. a) Plot of stable isotopic composition of the water molecule in $\delta^2$H-$\delta^{18}$O space. The dashed-dotted line is the global meteoric water line (GMWL) $\delta^2$H = $83\delta^{18}$O + 10, the dashed line represents the local meteoric water line (LMWL) $\delta^2$H = 6.9 $\delta^{18}$O + 4.5 (Harrington et al., 2013), while the solid red line represents the best fit through the data. b) Displays the relationship between the $\delta^{18}$O and the Cl concentration at recharge. The evaporation line was calculated for an equilibrium liquid-water fraction factor $\varepsilon$ = 1 % and an initial composition of $C_{\text{Cl},0}$ = 5 mg/L and $-10.5$ % respectively.
relationship is also valid for the water flow velocity \( v = v_D/\phi \). Then, the total flow time \( T \) to a certain distance \( R \) from the point source is:

\[
T(R) \sim \int_0^R \frac{1}{v(R)} \, dR \sim \int_0^R R \, dR \sim R^2
\]

implying that \( R(T) \sim T^{0.5} \). Consequently, the flow velocity decreases as function of residence time \( T \) according to:

\[
v(T) = \frac{dR(T)}{dT} \sim T^{-n}
\]
with \( n = 0.5 \). In a three-dimensional case (where H is also increasing with distance) \( n \) would be 0.66. The analytical model above is plotted against the observed tracer velocity data in Fig. 6D. We note that this distribution follows one that we would expect from a point source and conclude that our data are consistent with the presence of the actual Finke River recharge plume (Radke et al., 2000). Whether ERR was also the dominating recharge mechanism in the past or for group 2–3 waters cannot be concluded from the dating tracers alone. For this purpose, methods and tracers that are sensitive to recharge mechanisms are required.

### 5.3. Systematics of \(^{36}\text{Cl} \) and \( \text{Cl} \)

If we accept that \(^{81}\text{Kr} \) provides the most accurate chronology of old groundwater residence times of up to 400,000 years between the Finke River and Dalhousie Springs, we can then try to evaluate the temporal evolution of \(^{36}\text{Cl} \) (expressed as the \(^{36}\text{Cl}/\text{Cl} \) and \( \text{Cl} \) concentration) as well as the different source of chloride. The chloride mass balance as function of groundwater residence time can generally be expressed as (Bentley et al., 1986b; Phillips, 2000).

\[
\frac{R \cdot C}{a} = \frac{R_i \cdot C_i}{b} \cdot \exp\left(-\lambda_{36} \cdot t\right) + \frac{R_{se} \cdot C_i \cdot \left(1 - \exp\left(-\lambda_{36} \cdot t\right)\right)}{c} + \frac{(C - C_i) \cdot R_{Ex}}{d}
\]  

where:

- \( a \): Measured \(^{36}\text{Cl} \) concentration in the sample (atoms/L water) expressed as the product of \(^{36}\text{Cl}/\text{Cl} \) ratio \( R \) and chloride concentration \( C \).
- \( b \): Decay of the initial \(^{36}\text{Cl} \) concentration in recharge water, which is defined by the \(^{36}\text{Cl}/\text{Cl} \) ratio at recharge \( (R_i) \) and the initial chloride concentration \( C_i \).
- \( c \): In-growth of a secular subsurface equilibrium \(^{36}\text{Cl} \) concentration within the aquifer, which is given by the equilibrium ratio \( R_{se} \) and the initial concentration \( C_i \).
- \( d \): \(^{36}\text{Cl} \) accumulation due to the addition of \( \text{Cl} \) from subsurface sources \( (C_m = C - C) \) with a \(^{36}\text{Cl}/\text{Cl} \) ratio from the external source of \( R_{Ex} \).

If \( \text{Cl} \) behaves physically and chemically conservative (no sources or sinks of \( \text{Cl} \) within the aquifer) only the term \( b \) must be considered. However, even in this simple case, assumptions must be made about the local \(^{36}\text{Cl}/\text{Cl} \) initial ratio \( R_i \) which could vary spatially and temporally. Neutron activation of the dissolved \(^{35}\text{Cl} \) by the reaction \(^{35}\text{Cl}(n,\gamma)^{36}\text{Cl} \) would continuously add \(^{36}\text{Cl} \) atoms until a secular production decay equilibrium \( R_{se} \) is reached, as described by term \( c \). It is thereby again assumed that the \( \text{Cl} \) concentration in the water is constant over time. \( R_{se} \) can be estimated based on the elemental composition of the aquifer rocks (Lehmann et al., 1993). However, in the investigated part of the GAB the assumption of constant \( \text{Cl} \) concentration is not fulfilled (Fig. 9). The \( \text{Cl} \) concentration increases quasi-linearly with groundwater residence time at an apparent growth rate of \( -3.1 \text{ mg/L/kyr} \) (Fig. 9). This increase can either be because of \( \text{Cl} \) accumulation from subsurface sources (Love et al., 2000) and/or due to changes of the initial chloride concentration \( C_i \) as a result of varying evaporative enrichment at recharge time.

Without additional information from other tracers, it is impossible to separate both \( b \) and \( c \) processes (and \(^{36}\text{Cl} \) dating is not possible in this case). However, our \(^{81}\text{Kr} \) data now offer the unique opportunity to better constrain the \( \text{Cl} \) accumulation history and to deconvolute the relative importance of both processes as a function of groundwater flow time and distance. This information is not only crucial for the characterization of the accumulation processes along the flow path but also for the reconstruction of past recharge conditions which affect the evaporative enrichment of \( C_i \). This in turn, provides information about the dominant recharge mechanism as function of time i.e., the importance of ERR versus diffusive recharge. For this purpose, the initial \(^{36}\text{Cl} \) and \( \text{Cl} \) concentration of the different recharge sources need to be defined.

### 5.4. Initial parameters

The initial \(^{36}\text{Cl}/\text{Cl} \) at recharge must be estimated based on recent samples which infiltrated prior to 1950 to exclude the contribution of bomb derived \(^{36}\text{Cl} \) to estimate groundwater residence times of old groundwater. Previous estimates (Love et al., 2000) concluded an average initial \( R_i \) in precipitation and groundwater of \( 125 \pm 10 \times 10^{-15} \) to the south-west of our study area. In this area, the dominant recharge mechanism is diffuse.

The best candidates in our study area are \(^{85}\text{Kr} \) free samples (thus free of \(^{36}\text{Cl} \) from the nuclear tests in the 1960’s) with detectable \(^{39}\text{Ar} \) and \(^{14}\text{C} \) activities (therefore containing fresh recharge on the \(^{36}\text{Cl} \) timescale). Almost all samples of Group 1 fulfill these criteria (Fig. 8). The highest \(^{36}\text{Cl}/\text{Cl} \) ratio was measured at site 3 with a value of \( 91 \pm 5 \times 10^{-15} \). However, most samples with young \(^{39}\text{Ar} \) and \(^{14}\text{C} \) signatures have a much lower \(^{36}\text{Cl}/\text{Cl} \) ratio or are \(^{85}\text{Kr} \) free as expected for groundwater that has infiltrated prior to 1950.
ratio around 55–60 $\times 10^{-15}$ (Figs. 3 and 8). Considering the half-lives of $^{36}$Cl (310 kyr), $^{39}$Ar (269 yr) and $^{14}$C (5730 yr), $^{36}$Cl decay can be excluded as the reason for the $^{36}$Cl/Cl depletion of those samples compared to sample 3 or samples found elsewhere in this part of the GAB (Love et al., 2000 and Fig. 7). The admixture of old groundwater is also unlikely because Group 1 water are located close to the outcrop and presumed recharge area of the J aquifer and because the quasi modern $^{81}$Kr activities do not indicate the presence of a substantial old water component (Fig. 3 and Fig. 6).

The only reasonable explanation is that the source of recharge is not direct precipitation, but water with a low $^{36}$Cl/Cl due to the addition of chloride with a depleted $^{36}$Cl signature. Indeed, water sampled along the Finke River (New Crown Station and Old Crown Town) showed $^{36}$Cl/Cl of $60 \times 10^{-15}$ and $64 \times 10^{-15}$, respectively (Fulton et al., 2013). The depleted $^{36}$Cl/Cl ratio of the Finke River, compared to local precipitation, originates from halide dissolution e.g. from the Bitter Springs Formation which crops out along the Finke River further upstream (Fulton et al., 2013). That way ERR from the Finke River is tagged with an initial ratio $R_{ERR} = (60 \times 10^{-15})$ and a relatively low Cl concentration of $\sim 100$ mg/L (Ci) Table 3. Significantly higher initial concentrations are likely due to a different recharge process, with initial ratio $^{36}$Cl/Cl ratio ($R_i$) and chloride concentration ($C_i$). Confirming the finding of the previous dating section, this indicates that ERR dominates under present climate conditions with an initial $^{36}$Cl/Cl ratio $R_i$ of $60 \times 10^{-15}$ as indicated by the mean of Group 1 samples (Fig. 2 and Fig. 8). The average Cl concentration of Group 1 is $\sim 100$–200 mg/L which most likely represents the initial concentration $C_i$ for ERR ($C_{ERR}$ in Eq. (8)). Since ERR is a relatively rapid recharge mechanism, it is unlikely that the higher Cl concentrations found further down the groundwater flow path are caused by changes of $C_{ERR}$ in the past. The Cl increase of Group 2 and Group 3 samples further downstream may have two reasons: (i) temporal variations of environmental conditions triggering a different recharge mechanism that leads to higher Cl concentrations at recharge, or (ii) accumulation of Cl originating from subsurface sources.

In case of a more humid climate in the past, diffusive recharge over large surface areas would dominate and the initial $R_i$ would have been closer to the typical value of local precipitation (120–130 $\times 10^{-15}$). This would also imply higher Cl concentrations at recharge $C_i$. The potential $^{36}$Cl evolutionary pathways are depicted in Fig. 10 where the $^{36}$Cl/Cl ratios are plotted as function of the $^{36}$Cl concentration. Also shown are the $^{36}$Cl/Cl signatures of ERR, precipitation and data from other studies in the area (Love et al., 2000). Those data indicate diffuse recharge with a high initial ratio $R_i$ first followed by evaporative enrichment and then followed by a combination of Cl accumulation in the subsurface and radioactive decay (indicated by arrows in Fig. 10). The exact pathways to the data points are ambiguous without additional data (i.e., the solid and dashed paths in Fig. 10 are both possible). However, since evaporative enrichment for ERR is limited (crossed out arrow in the figure), it is clear, that data of group 2–3 must partly originate from diffuse recharge which is characterised be high a $^{36}$Cl/Cl ratio of $120 \times 10^{-15}$ and elevated Cl concentration (and thus high $N_{36Cl}$). With that, a new $^{36}$Cl budget can be

![Fig. 9. (a) Measured chloride concentration as function of $^{81}$Kr ages, (b) Calculated Cl ($C_C$) accumulated in the subsurface and (c) Calculated Cl that was already present at recharge ($C_i$) as a function of $^{81}$Kr ages. The dashed lines in a) and b) represent different Cl accumulation rates as a function of $^{81}$Kr ages.](image-url)
formulated in which the $^{36}$Cl contributions from ERR and diffuse recharge are separated:

$$R \cdot C = \left( R_{\text{ERR}} \cdot C_{\text{ERR}} + R_{\text{D}} \cdot C_{\text{D}} \right) \cdot \exp(-\lambda_{36} \cdot t) + R_{\text{D}} \cdot C / 2 \cdot \left( 1 - \exp(-\lambda_{36} \cdot t) \right) + (C - C_{\text{ERR}} - C_{\text{D}}) \cdot R_{\text{D}}$$

The second term describes the ingrowth to secular-production-decay equilibrium $R_{\text{D}}$ in the aquifer which also depends on the timing of the increase of Cl along the flow path which is a priori unknown. The factor of two assumes an $^{36}$Cl-in-situ production rate corresponding to a time averaged Cl concentration of C/2. Eq. (7) can be solved for the concentration $C_{\text{D}}$ contributed from diffuse recharge:

$$C_{\text{D}}(t) = \frac{C \left( R_{\text{ERR}} - R_{\text{D}} / 2 \right) \cdot \left( 1 - \exp(-\lambda_{36} \cdot t) \right) - R_{\text{ERR}} \cdot C_{\text{ERR}} \cdot \exp(-\lambda_{36} \cdot t) - (C - C_{\text{ERR}}) \cdot R_{\text{D}}}{R_{\text{D}} - \exp(-\lambda_{36} \cdot t) - R_{\text{ERR}} - R_{\text{D}} / 2}$$

Fig. 9 shows the resulting $C_{\text{D}}(t)$ and $C(t) = C - C_{\text{ERR}} - C_{\text{D}}(t)$ as function of the $^{81}$Kr ages. Cl accumulation in the subsurface contributes about 2/3 to the observed Cl increase along the flow path. The chloride accumulation rate of $\sim 1.8 \pm 1$ mg/L kyr is consistent with values found in other studies in the western GAB (Lehmann et al., 2003; Love et al., 2000). Up to 400 mg/L Cl are attributed to changes of the initial Cl concentration at recharge $C_{\text{D}}$, which first increases with groundwater age but levels off for the oldest waters as indicated in the figure. The groundwater samples towards the centre of the basin (group 2–3) are partly originating from areas with diffuse recharge under varying climatic conditions. This is strongly supported by the stable isotope data shown in Fig. 4a where a strong correlation between $\delta^{18}$O values and $C$ can be observed. Group 3 samples fall along the LMWL and are isotopically depleted. Moving away from the Finke River recharge plume, the isotope signature becomes more enriched along a line with slope 6.4. This correlation might be partly caused by evaporation but is rather a mixing line than an evaporation line as demonstrated in Fig. 4b. The slope of the stable isotope signature parallels an increase of the initial Cl concentration $C_{\text{D}}$. Also shown are calculated evaporation and transpiration trends. Transpiration will increase the $^{36}$Cl concentration without affecting the $^{81}$O but unrealistic large fractions of water need to be transpired to explain the observed scatter (Sultan et al., 2000). The slope of the evaporation line is too small to explain the observed variation in Cl concentration. This suggests that mixing of water that recharged at different conditions is going on and/or the additions of salt come from dust solutes dissolved during the recharge process (Sultan et al., 2000).

Sample 19, for example, which has one of the highest Cl concentrations and a higher Cl accumulation rate is geographically separated from the main transect towards the south. According to the recent piezometric head distribution (Fig. 1) the water originates from a recharge area further south where there is no evidence for any ERR source water (Love et al., 2000) and Fig. 10.

5.5. Origin and rate of accumulated helium

The isotope signature of accumulated helium indicates two distinct endmembers: atmospheric helium with a $^{4}$He/$^{3}$He ratio of air saturated water (ASW) (1.36 $\times$ 10 $^{-5}$) plus a radiogenic component (Fig. 11a). A linear fit in the $^{4}$He/$^{3}$He vs. Ne/$^{3}$He plot reveals a ratio of 1.5 $\times$ 10 $^{-8}$ for the radiogenic components which is typical for crustal production (Stute et al., 1992). No mantle helium contribution is indicated by the data.

Using the Ne excess ($\Delta$Ne) from excess air (Table 2) and assuming recharge temperature and elevation of 20 °C and 400 m respectively, the fraction of radiogenic $^{4}$He can be calculated (Kipfer et al., 2002) which is plotted in Fig. 11b as a function of $^{81}$Kr derived tracer ages. There is a systematic increase of $^{4}$He with increasing $^{81}$Kr age which highly supports the chronology of $^{81}$Kr ages and is indicative for a relatively homogeneous groundwater flow path. The $^{4}$He in-situ accumulation rate ($A_{\text{He}}$) can be calculated based on the [U] and [Th] concentrations of the aquifer rocks of 0.8 ppm and 6 ppm respectively (Andrews and Lee, 1979; Lehmann et al., 2003), an aquifer density of $\rho = 2.6$ g/cm$^{3}$, a porosity of $\phi = 0.2$, and a helium release factor of 1 into the water filled pore space (Mazor and Bosch, 1992).

$$A_{\text{He}} = \rho / \phi \cdot (1.19 \times 10^{-12} \cdot [U] + 2.88 \times 10^{-14} \cdot [Th])$$

The resulting helium in situ accumulation rate $A_{\text{He}}$ of $4 \times 10^{-12}$ cm$^{3}$/g$_{\text{w}}$/yr, is depicted in Fig. 11b.

It is obvious that in-situ production is not sufficient to explain the observed $^{4}$He increase rate, a situation found in other aquifers (Aggarwal et al., 2015; Torgersen, 2010; Torgersen and Clarke, 1985). In particular for the samples further away from the recharge area (group 2–3 waters), the helium accumulation rate exceeds the expected value from in-situ production by almost two orders of magnitude, which is in line with observations made in other parts of the GAB, Torgersen and Ivey, (1985) proposed a model in which an external $^{4}$He flux of 3 $\times$ 10$^{-5}$ cm$^{3}$/STP/ cm$^{2}$/yr originating from the underlying strata enters the aquifer from below. Their model assumes a transversal dispersion coefficient of 0.1 m$^{2}$/yr and $^{4}$He no-flow upper boundary (Torgersen and Ivey, 1985). This leads to a nonlinear $^{4}$He accumulation rate with age and flow distance with a transition from an in-situ accumulation rate to an accumulation rate determined by the basal $^{4}$He flux strength. The point in time (and flow distance) where the transition occurs is determined by the depth of the screened borehole interval in relation to the total depth of the aquifer. A borehole that intersects only the upper part of the aquifer “sees” the basal $^{4}$He flux later than a well completed deeper in the formation. The corresponding model line for an aquifer thickness $H = 400$ m and a well tapping 6 cm$^{3}$/STP/ cm$^{2}$/yr originating from the underlying strata enters the aquifer from below. Their model assumes a transversal dispersion coefficient of 0.1 m$^{2}$/yr and $^{4}$He no-flow upper boundary (Torgersen and Ivey, 1985). This leads to a nonlinear $^{4}$He accumulation rate with age and flow distance with a transition from an in-situ accumulation rate to an accumulation rate determined by the basal $^{4}$He flux strength. The point in time (and flow distance) where the transition occurs is determined by the depth of the screened borehole interval in relation to the total depth of the aquifer. A borehole that intersects only the upper part of the aquifer “sees” the basal $^{4}$He flux later than a well completed deeper in the formation. The corresponding model line for an aquifer thickness $H = 400$ m and a well tapping to the top layer of the aquifer is shown in Fig. 11b. There is a reasonable agreement between the Torgersen and Ivey model and the data, also the transition point to the higher accumulation rate between groups 1 and 2 waters is well represented. Thus, our $^{81}$Kr data support the general concept.
of a (crustal) He influx as developed in the past at other parts of the GAB (Torgersen and Clarke, 1985; Torgersen and Ivey, 1985). Other scenarios where e.g. the source of $^4$He (and chloride) occurs in the overlying Bulldog Shale (Lehmann et al., 2003; Love et al., 2000) or in impermeable layers within the aquifer which pre-accumulated $^4$He in the past cannot be completely excluded but are less supported by the data. The good correlation between the concentration of radiogenic helium $^4$He$_{rad}$ and the reconstructed chloride accumulation ($C_r$) points to a common source and transport process of helium and chloride (Fig. 11c) (Lehmann et al., 2003; Zhang et al., 2007).

6. Conclusions

The quantification and reconstruction of amount and mechanism of groundwater recharge in arid areas is fundamental for the life and economies in those areas. Such aquifers typically include a very large range of groundwater residence times and different climatic zones in the recharge regimes over time. However, the characterization of the age structure of groundwater over extended spatial and temporal scales is a very difficult task. Various tracers need to be combined which cover different dating ranges, but which are also affected by different process that may affect the interpretation in terms of groundwater residence times. One of these is changing recharge conditions which can only be deconvoluted if multiple tracers covering the same time scales are applied. In this study a complete tracer set in incrementally increasing half-lives and dating ranges from decades to millions of years was applied to a large aquifer along a presumed groundwater flow path. In order of increasing dating range this includes the measurements of $^{85}$Kr, $^{39}$Ar, $^{14}$C, $^{81}$Kr, $^{36}$Cl and $^4$He$_{rad}$. This unique combination with partly overlapping and complementing dating ranges allows for a deeper understanding of the hydrogeology of the studied area, and also for the first time, for a comprehensive comparison and assessment of the age information obtained by different applied dating methods.

Generally, the data indicate a consistent age chronology with distance from the Finke River recharge area. The continued increase of groundwater residence times with distance from the Finke River implies the existence of a connected flow system in contrast to the possibility of having partly isolated subsystems. Flow velocities determined by the spatial gradients of the concentrations of $^{39}$Ar, $^{14}$Ca and $^{81}$Kr decrease with increasing half-life of the used tracer and thus with increasing distance from recharge area. Despite the inherent uncertainties of the individual dating methods this is attributed to a diverging mass flow from a localized recharge point. In the investigated western part of the GAB ERR was the dominant recharge mechanism over long timescales. In the down gradient part of the system where groundwater residence times exceed 100,000 years as indicated by the $^{81}$Kr data the influence and contribution of ERR becomes less important due to the admixture of water originating from other recharge areas. At such timescales transient recharge conditions, water rock interaction, hydrodynamic dispersion and diffusive exchange with the aquitards become increasingly important. As already pointed out in other studies (Phillips, 2000; Phillips et al., 1986) the application of $^{36}$Cl for old groundwater dating is highly complicated in this part of the GAB because the initial parameters $R_i$ and $C_i$ are not well defined and variable due the multitude of processes and recharge mechanisms which may affect those parameters.

The $^{81}$Kr dating methods allowed deconvoluting the complicated $^{36}$Cl/C systematics in this part of the GAB. The $^{36}$Cl data underpin the decreasing influence of ERR towards the centre of the basin, where groundwater originating from diffuse recharge becomes more important. Varying recharge conditions and related recharge mechanisms are also reflected in variations of the stable isotope signature of the water molecule and the chloride concentration at recharge. However, >50% of the observed chloride increase...
along the flow line is caused by subsurface processes. This Cl accumulation rate is accompanied by increasing $^{3}He_{ad}$ concentrations. The rate as well as the temporal and spatial pattern of the $^{3}He$ concentrations is in good agreement with the assumption of a previously postulated crustal helium flux entering the system from underlying strata. Diffusive exchange with those layers may also affect the $^{81}$Kr ages, but was neglected in this study (Purtschert et al., 2013). This work also demonstrates the potential of very old groundwater as an archive of paleoclimatic conditions over long timescales. The $^{81}$Kr dating method not only provides a reliable age chronology but also increases the potential for meaningful climate proxies such as the Cl and stable isotope concentration at time of recharge.

CRediT authorship contribution statement

Roland Purtschert: conceptualization, writing original draft, investigation; Andrew Love: conceptualization, writing, funding acquisition; Wei Jiang: methodology, editing, writing; Z-T. Lu: methodology, editing, writing; G-M Yang: methodology; Werner Aeschbach: editing, writing; Peter Müller: methodology, editing, writing; Paul Shand: investigation, writing, editing; Daniel Wohling: investigation, editing; Simon Fulton: investigation editing, Lisa Broder: methodology; Yuki Tosaki: methodology.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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