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Earth and Planetary Science Letters 211 (2003) 237–250

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## A comparison of groundwater dating with $^{81}\text{Kr}$ , $^{36}\text{Cl}$ and $^4\text{He}$ in four wells of the Great Artesian Basin, Australia

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Received 29 May 2002; received in revised form 11 March 2003; accepted 7 April 2003

### Abstract

The isotopic ratios  $^{81}\text{Kr}/\text{Kr}$  and  $^{36}\text{Cl}/\text{Cl}$  and the  $^4\text{He}$  concentrations measured in groundwater from four artesian wells in the western part of the Great Artesian Basin (GAB) in Australia are discussed. Based on radioactive decay along a water flow path the  $^{81}\text{Kr}/\text{Kr}$  ratios are directly converted to groundwater residence times. Results are in a range of 225–400 kyr with error bars in the order of 15% primarily due to counting statistics in the cyclotron accelerator mass spectrometer measurement. Additional uncertainties from subsurface production and/or exchange with stagnant porewaters in the confining shales appear to be of the same order of magnitude. These  $^{81}\text{Kr}$  ages are then used to calibrate the  $^{36}\text{Cl}$  and the  $^4\text{He}$  dating methods. Based on elemental analyses of rock samples from the sandstone aquifer as well as from the confining Bulldog shale the in situ flux of thermal neutrons and the corresponding  $^3\text{He}/^4\text{He}$  and  $^{36}\text{Cl}/\text{Cl}$  ratios are calculated. From a comparison of: (i) the  $^3\text{He}/^4\text{He}$  ratios measured in the groundwater samples with the calculated in situ ratios in rocks and (ii) the measured  $\delta^{37}\text{Cl}$  ratios with the  $^4\text{He}$  concentrations measured in groundwater it is concluded that both helium and chloride are most likely added to the aquifer from sources in the stagnant porewaters of the confining shale by diffusion and/or mixing. Based on this ‘working hypothesis’ the  $^{36}\text{Cl}$  transport equation in groundwater is solved taking into account: (i) radioactive decay, (ii) subsurface production in the sandstone aquifer (with an in situ  $^{36}\text{Cl}/\text{Cl}$  ratio of  $6 \times 10^{-15}$ ) and (iii) addition of chloride from a source in the confining shale (with a  $^{36}\text{Cl}/\text{Cl}$  ratio of  $13 \times 10^{-15}$ ). Lacking better information it is assumed that the chloride concentration increased linearly with time from an (unknown) initial value  $C_i$  to its

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measured present value  $C = C_i + C_a$ , where  $C_a$  represents the (unknown) amount of chloride added from subsurface sources. Using the  $^{81}\text{Kr}$  ages of the four groundwater samples and a reasonable initial  $^{36}\text{Cl}/\text{Cl}$  ratio of  $125 \times 10^{-15}$ , which is consistent with other studies in this part of the GAB, it is then possible to determine ( $C_i, C_a$ ) parameter sets for all four samples and consequently to simulate the Cl and the  $^{36}\text{Cl}$  evolution with time. Strong evidence that the whole procedure is adequate comes from: (i) a comparison of  $C_i$  with the calculated noble gas recharge temperatures (NGRT) indicating that a higher NGRT is related to higher input chloride concentrations  $C_i$  (because of higher evapotranspiration) and (ii) a comparison of  $C_a$  with the measured  $^4\text{He}$  concentration confirming the idea that both chloride and helium are added to the groundwater in parallel. It turns out that the four samples fall into two groups: (i) for two of the samples (Raspberry Creek and Oodnadatta) initial  $^{36}\text{Cl}$  concentrations are high and  $^{36}\text{Cl}$  dating based on radioactive decay is possible. The  $^4\text{He}$  accumulation rate for these two samples is low ( $0.2 \times 10^{-10} \text{ cm}^3 \text{ STP } ^4\text{He}/(\text{cm}^3 \text{ water yr})$ ); (ii) for the other two samples (Duck Hole and Watson Creek) the initial  $^{36}\text{Cl}$  concentration is low and therefore subsurface processes dominate resulting in almost constant  $^{36}\text{Cl}$  concentrations with time;  $^{36}\text{Cl}$  groundwater dating is not possible. The  $^4\text{He}$  accumulation rate for these two samples is about 10 times higher ( $1.9 \times 10^{-10} \text{ cm}^3 \text{ STP } ^4\text{He}/(\text{cm}^3 \text{ water yr})$ ).  $^{129}\text{I}$  concentrations are interpreted as a simple mixing between an atmospheric and a subsurface source.

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**Keywords:** geochemistry; groundwater dating; krypton-81; chlorine-36; helium-4; Great Artesian Basin, Australia; isotope hydrology

## 1. Introduction

The concentrations of the two naturally occurring radionuclides  $^{81}\text{Kr}$  (half-life 229 kyr) and  $^{36}\text{Cl}$  (half-life 301 kyr), produced by cosmic rays in the atmosphere and present in surface waters, are expected to decrease in groundwater along a water flow line due to radioactive decay. In parallel,  $^4\text{He}$  concentrations generally increase due to the accumulation of helium generated in the natural decay series of uranium and thorium in rocks. Groundwater dating is possible if the input values at recharge ( $^{81}\text{Kr}$ ,  $^{36}\text{Cl}$ ) and/or the accumulation rate ( $^4\text{He}$ ) in the subsurface are known. However, other processes that could also change isotope concentrations in groundwater (e.g. subsurface production, diffusive exchange with porewaters or mixing processes) also need to be quantified.

Among the three nuclides,  $^{81}\text{Kr}$  lends itself to the most straightforward age interpretation because fewer assumptions are required. At the same time it is by far the most difficult to analyse due to the very low concentrations of  $< 1000$  atoms/l of water. Converting measured  $^{81}\text{Kr}/\text{Kr}$  ratios into a groundwater age is comparatively simple because: (i) the ratio in atmospheric air is known and was most likely constant over the

past several hundred thousand years because the atmosphere is the only important reservoir for Kr and possible short-term fluctuations in the cosmic ray production rate will therefore be averaged out on such time scales, (ii) this input ratio into an aquifer does in particular not depend on the climatic conditions at the time of recharge and (iii) subsurface production in rocks or groundwater is small. In contrast, hydrogeologists working with  $^{36}\text{Cl}$  always have to address the ‘initial value problem’ [1] and in many cases, in particular in deeper and more saline groundwaters, disentangling the atmospheric  $^{36}\text{Cl}$  signal is difficult due to subsurface production of  $^{36}\text{Cl}$  by the  $^{35}\text{Cl}(n,\gamma)^{36}\text{Cl}$  reaction and transport from adjacent aquifers or porewater reservoirs.

For helium it has been demonstrated that concentrations often increase with water residence times (for a recent review see [2]), however, accumulation rates in different aquifers vary or are not known. In particular, a very small admixture of ancient groundwater with an extremely high concentration of  $^4\text{He}$  can drastically change the  $^4\text{He}$  concentration along a water flow path. Consequently,  $^4\text{He}$  groundwater dating is generally considered to be a ‘semi-quantitative’ method only.

In this work we present for the first time a complete set of data for all three isotopes from

groundwaters sampled from four wells in the Great Artesian Basin (GAB) in Australia. This enables a comparison of possibilities and limitations of the different nuclides in dating old groundwaters.

## 2. Field work

A  $^{81}\text{Kr}$  sampling campaign was organised in January 1998 by researchers from the Department of Water, Land and Biodiversity Conservation of South Australia (DWLBC) in Adelaide as part of a Coordinated Research Program ('Isotope Techniques for the Assessment of Slow Moving Deep Groundwaters') of the International Atomic Energy Agency (IAEA) in Vienna, Austria. Water degassing equipment of the University of Bern, Switzerland, was used to extract gases from water samples of 16000 litres each at four wells in the western part of the GAB some 1200 km northwest of Adelaide. Krypton gas was separated from the extracted gases at the Physics Institute in Bern, and  $^{81}\text{Kr}/\text{Kr}$  ratios were measured at the Michigan State University (MSU) Cyclotron by a group from the Institute for Isotope Research and Nuclear Physics in Vienna. Details of the analytical procedure have been reported by Collon et al. [3].

Three of the four wells (Oodnadatta (OD), Duck Hole (DH), Watson Creek (WC)) were selected based on earlier  $^{36}\text{Cl}$  data [4] which indicated ages in the dating range of the  $^{81}\text{Kr}$  technique (approx. 50–700 kyr). Furthermore, by sampling from artesian wells, contamination with modern atmospheric air during the field de-

gassing operation can be minimised. Due to difficult road conditions in the area it was not possible to sample additional wells along the northern transect investigated by Love et al. [4] as was planned. Instead, a fourth well (Raspberry Creek (RC)) was selected further to the southwest. No map and no hydrogeological cross-section are included in this work because it is the key purpose of this contribution to discuss how much one can learn about groundwater residence times from a set of isotope data without a hydrodynamic model of the area. The locations of the wells together with additional relevant data of the field sampling are summarised in Table 1.

All wells tap the well-known J-K aquifer in a sandstone of the GAB which is confined by some 200–400 m of overlying 'Bulldog shale' acting as an aquitard. Rock samples from both units were made available for elemental and noble gas analyses after the field trip by DWLBC. For a more detailed description of the local hydrogeological situation we refer to [4].

## 3. Data

After the field campaign samples were shipped to the various laboratories in the different countries. Table 2 summarises all available isotope data of the four groundwater samples and Table 3 those of nine rock samples from the sandstone of the aquifer and from the confining Bulldog shale. The analyses were made in the following laboratories (number in parentheses refers to the parameter number in Table 2):

Table 1  
Well data from samples collected in the western margin of the GAB

	RC	OD	DH	WC
Longitude (°E)	135.08	135.44	136.09	135.95
Latitude (°S)	28.12	27.55	27.61	27.73
Well depth (m)	126.8	478.84	250.8	289
Sample date	18.01.98	14.01.98	20.01.98	19.01.98
Water temperature (°C)	29.6	45	36.1	38
Pressure (kPa)	155	74	440	182
Use of well	stock	town water supply	stock	stock
Discharge	low	continuous	low	low

All four wells are artesian.

## 1. Long-lived radionuclides

$^{81}\text{Kr}/\text{Kr}$  (#18) at the National Superconducting Cyclotron Laboratory at Michigan State University;  $^{36}\text{Cl}/\text{Cl}$  (#9) at the Department of Nuclear Physics of the Australian National University in Canberra;  $^{129}\text{I}/\text{I}$  (#24) at Lawrence Livermore National Laboratory.

From the respective concentrations of the stable isotopes krypton (#20, Swiss Federal Institute of Environmental Science and Technology), chloride (#10, University of Waterloo, Ontario) and iodide (#25, Lawrence Livermore National Laboratory) the atomic concentrations of  $^{81}\text{Kr}$  (#21),  $^{36}\text{Cl}$  (#11) and  $^{129}\text{I}$  (#26) in groundwater were calculated.

## 2. Stable noble gas isotopes

$^4\text{He}$  (#4) and  $^{40}\text{Ar}$  (#15) concentrations were

measured at the Swiss Federal Institute of Environmental Science and Technology together with the ratios  $^3\text{He}/^4\text{He}$  (#5) and  $^{40}\text{Ar}/^{36}\text{Ar}$  (#16). From these data the  $^3\text{He}$  concentration (#3) and the fraction of radiogenic  $^{40}\text{Ar}$  (#17) were calculated.

## 3. Additional isotope data

$\delta^{37}\text{Cl}$  (#12) was measured at the University of Waterloo, Ontario;  $^{37}\text{Ar}$  (#13),  $^{39}\text{Ar}$  (#14) and  $^{85}\text{Kr}$  (#23) at the Physics Institute in Bern;  $^{14}\text{C}$  (#7) and  $\delta^{13}\text{C}$  (#6) at CSIRO in Adelaide; tritium  $^3\text{H}$  (#2) as well as the stable isotope ratios  $\delta^2\text{H}$  (#1) and  $\delta^{18}\text{O}$  (#8) at the Isotope Hydrology Section of the IAEA in Vienna and  $^{222}\text{Rn}$  (#27) at CSIRO in Adelaide.

Table 2 further shows the calculated  $^{81}\text{Kr}$  age (#22) based on radioactive decay only and the

Table 2

Isotope concentrations and ratios measured in the four groundwater samples (see text for details)

	Factor	RC	OD	DH	WC		
1	$\delta^2\text{H}$ (‰)		−46.3	−50.7	−46.0	−46.3	m−
2	$^3\text{H}$ (TU)		0.05		0.01		m−
3	$^3\text{He}$ (cc/g water)	E−13	1.55 (3.0)	3.40 (1.9)	7.68 (1.4)	12.0 (2.5)	c+
4	$^4\text{He}$ (cc/g water)	E−5	0.42 (0.9)	1.19 (0.8)	5.37 (0.8)	7.75 (0.9)	m+
5	$^3\text{He}/^4\text{He}$ (atomic ratio)	E−8	3.70 (2.9)	2.86 (1.7)	1.43 (1.1)	1.55 (2.3)	m+
6	$\delta^{13}\text{C}$ (‰)			−11.6	−11.0		m−
7	$^{14}\text{C}$ (pmC)			2.0	1.7		m−
8	$\delta^{18}\text{O}$ (‰)		−5.93	−6.56	−6.33	−6.33	m−
9	$^{36}\text{Cl}/\text{Cl}$ (atomic ratio)	E−15	66 (8)	55 (7)	19 (11)	19 (11)	m+
10	Cl (mg/l water)		1250	676	848	1040	m+
11	$^{36}\text{Cl}$ (atoms/l water)	E+8	14.0	6.3	2.7	3.4	c+
12	$\delta^{37}\text{Cl}$ (‰)		−0.10	−0.26	−1.35	−1.56	m+
13	$^{37}\text{Ar}$ (dpm/l Ar)					0.007 (57)	m−
14	$^{39}\text{Ar}$ (‰ modern)		< 4	22 (14)	11 (18)	< 8	m−
15	Ar (cc/g water)	E−4	2.83 (1.1)	3.69 (1.0)	3.41 (1.0)	3.31 (1.1)	m+
16	$^{40}\text{Ar}/^{36}\text{Ar}$ (atomic ratio)		295.73 (0.14)	295.89 (0.06)	296.92 (0.09)	297.65 (0.19)	m+
17	$^{40}\text{Ar}$ -rad (cc/g water)	E−7	2.2 (180)	4.9 (45)	16 (19)	24 (26)	c+
18	$^{81}\text{Kr}/\text{Kr}$ (atomic ratio)	E−13	2.63 (12.2)	1.78 (14.6)	2.19 (12.8)	1.54 (14.3)	m+
19	$^{81}\text{Kr}/\text{Kr}$ (‰ modern)		50.6	34.2	42.1	29.6	c+
20	Kr (cc/g water)	E−8	6.0	7.3	7.0	6.8	m+
21	$^{81}\text{Kr}$ (atoms/l water)		420	350	410	280	c+
22	$^{81}\text{Kr}$ age (kyr)		225	354	287	402	c+
23	$^{85}\text{Kr}$ (dpm/cc Kr)		4.2 (14)		1.4 (29)		m−
24	$^{129}\text{I}/\text{I}$ (atomic ratio)	E−13	6.7	6.3	4.6	7.6	m+
25	I (mg/l)		0.76	0.49	0.51	0.55	m+
26	$^{129}\text{I}$ (atoms/l water)	E+6	2.4	1.5	1.1	2.0	c+
27	$^{222}\text{Rn}$ (Bq/l water)		15.8	10.4	6.50	6.73	m−
28	NGRT (°C)		27.1 (3.0)	24.1 (5.8)	22.8 (4.0)	23.3 (4.3)	c+

Values in parentheses are relative errors in per cent. Last column indicates measured values (m), calculated values (c), data discussed in this study (+) and data that were added for completeness but will not be discussed (−).

dpm is decays per minute; pmC is per cent modern carbon.

Table 3  
Isotope concentrations and ratios measured in rock samples and calculated K/Ar age  $t$

	1	2	3	4	5	6	7	8	9
	RC	OD	OD	OD	OD	DH	DH	DH	DH
	sandstone	sandstone	sandstone	shale	shale	shale	shale	shale	shale
Depth (m)	104	425	429	275	366	200	202	241	244
U (ppm)	0.78	0.85	0.72	2.5	2.1	2.1	2.2	1.9	1.5
Th (ppm)	4.4	8.2	5.3	11	9.6	9.9	11.2	14.3	14.6
K (%)	0.83	0.97	0.87	1.7	1.5	1.4	1.4	1.1	1.4
Li (ppm)	6.1	12.4	8.4	54	30	35	36	28	24
$^4\text{He}$ (cc/g)	5.0E-07	2.1E-06	1.0E-06		2.1E-06	3.0E-05	1.7E-05	2.0E-05	2.6E-05
$^3\text{He}/^4\text{He}$	< 1E-08	2.2E-08	4.3E-08		3.9E-08	3.2E-08	3.0E-09	3.7E-08	1.6E-08
$^{40}\text{Ar}$ (cc/g)	6.7E-05	1.9E-05	2.0E-05	1.5E-05	2.0E-05	2.3E-05	2.0E-05	2.2E-05	
$^{40}\text{Ar}/^{36}\text{Ar}$	5030	1930	5870	3050	5210	13000	6580	5410	
$t$ (Ma)	1390	390	520	200	320	400	350	490	

noble gas recharge temperature (NGRT) [5,6] (#28, Swiss Federal Institute of Environmental Science and Technology) for which additional noble gas data (Ne, Xe) were used (not listed in Table 2). All data from rocks in Table 3 are from the Geological Institute in Apatity, Russia.

#### 4. Subsurface production of radionuclides

Based on the available U, Th and K concentrations in rock it is easy to calculate the in situ  $^4\text{He}$  and  $^{40}\text{Ar}$  production rates. Using the concentrations of all the other elements (based on rock analyses performed at Activation Laboratories Ltd in Canada) one can also estimate the flux

$\Phi_n$  of thermal neutrons in the respective rock formations and consequently the in situ  $^{36}\text{Cl}/\text{Cl}$  and  $^3\text{He}/^4\text{He}$  ratios [7]. Subsurface production of  $^{81}\text{Kr}$  by spontaneous fission of  $^{238}\text{U}$  is expected to be small based on estimates of the independent fission yield. However, such estimates have not been confirmed by field data up to now. The measured  $^{81}\text{Kr}/\text{Kr}$  ratios in GAB groundwaters down to 30% of the atmospheric value for the first time demonstrate that  $^{81}\text{Kr}$  subsurface production indeed must be small.

Nine rock samples were available for elemental analysis. Table 4 lists the average U, Th, K and Li concentrations for both formations (calculated from the data in Table 3) together with the calculated fluxes of thermal neutrons, the in situ  $^{36}\text{Cl}/\text{Cl}$  ratios, the  $^3\text{He}$ ,  $^4\text{He}$  and  $^{40}\text{Ar}$  production rates

Table 4  
Average measured U, Th, K and Li concentrations for sandstone and shale

	Sandstone	Shale
U (ppm)	0.78	2.0
Th (ppm)	6.0	12
K (%)	0.89	1.4
Li (ppm)	9.0	34
n flux (n/cm <sup>2</sup> s)	1.3E-05	2.9E-05
$^{36}\text{Cl}/\text{Cl}$ (ratio)	6.0E-15	1.3E-14
$^3\text{He}$ production (cc STP/cm <sup>3</sup> rock yr)	2.2E-21	1.9E-20
$^4\text{He}$ production (cc STP/cm <sup>3</sup> rock yr)	6.9E-13	1.5E-12
$^{40}\text{Ar}$ production (cc STP/cm <sup>3</sup> rock yr)	9.2E-14	1.5E-13
$^3\text{He}/^4\text{He}$ production ratio	3.2E-09	1.2E-08
$^4\text{He}/^{40}\text{Ar}$ production ratio	7.5	10.4

Calculated thermal neutron flux, in situ production rates and ratios.

and the corresponding  $^3\text{He}/^4\text{He}$  and  $^4\text{He}/^{40}\text{Ar}$  production ratios.

## 5. $^{81}\text{Kr}$ ages

The  $^{81}\text{Kr}$  isotope with a half-life of 229 000 years has several unique advantages for dating old groundwaters as already listed in Section 1. After the first measurement in atmospheric air by low level decay counting [8] efforts to develop a routine analytical tool include both laser-based optical techniques [9–14] as well as accelerator mass spectrometry [15,16]. Most of these efforts are still in progress and a routine analytical facility is currently not available.

In a first attempt one can calculate  $^{81}\text{Kr}$  groundwater residence times simply by using the exponential law for radioactive decay ignoring other possible processes that might affect the  $^{81}\text{Kr}/\text{Kr}$  ratio in the subsurface. According to this approach the groundwaters sampled at Raspberry Creek, Oodnadatta, Duck Hole and Watson Creek are  $225 \pm 42$ ,  $354 \pm 50$ ,  $287 \pm 38$  and  $402 \pm 51$  kyr old, respectively. The uncertainty in the calculated groundwater age is about 10–20% because of the analytical error in this first  $^{81}\text{Kr}$  measurement using cyclotron accelerator mass spectrometry.

Other processes that might change the isotopic concentration in the aquifer include subsurface production (by spontaneous fission of  $^{238}\text{U}$ ) and exchange or mixing with the porewaters of the confining shale. In Fig. 1 we quantify such effects using a simple numerical diffusive–advective transport model. The lowest curve is for a situation where  $^{81}\text{Kr}$  is lost from the aquifer to the porewaters of the shale by diffusion because a  $^{81}\text{Kr}$  gradient between the groundwater and the porewater would exist if there is absolutely no subsurface production of  $^{81}\text{Kr}$ . We assume a diffusion coefficient of  $D = 2 \times 10^{-11} \text{ m}^2/\text{s}$  for this situation, a value which is slightly lower than was observed for He diffusion in porewaters of a shale [17]. Note that a characteristic diffusion length is only about  $x = 16 \text{ m}$  in a time interval of 400 kyr estimated from  $x = (Dt)^{1/2}$  under these conditions. The calculated ages based on decay

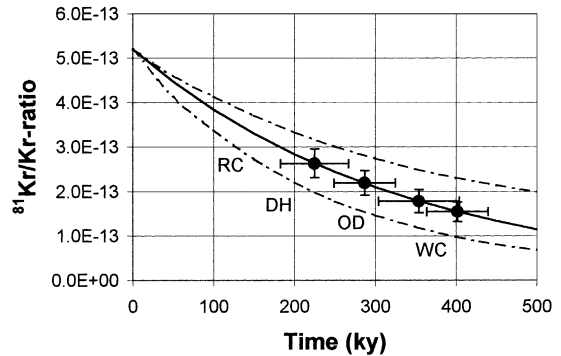


Fig. 1.  $^{81}\text{Kr}/\text{Kr}$  ratio vs time. Solid line: calculated decrease of the ratio based on radioactive decay only; lower dashed line: calculated decrease of the ratio based on radioactive decay and additional diffusive loss to the porewaters of the confining Bulldog shale; upper dashed line: calculated decrease of the ratio based on radioactive decay and taking into account a possible input of  $^{81}\text{Kr}$  from a subsurface source in the confining Bulldog shale.

only (circles) would then overestimate the groundwater age.

In contrast, decay ages would underestimate the true groundwater age when  $^{81}\text{Kr}$  is produced in the subsurface (highest curve in Fig. 1). From the fact that the measured  $^{81}\text{Kr}/\text{Kr}$  ratio is at a level of 30% of the atmospheric input ratio at recharge, high production rates can be excluded for  $^{81}\text{Kr}$ . At most 0.7 atoms of  $^{81}\text{Kr}$  per  $\text{m}^3$  of water per year can be added to the groundwater.

Overall, we conclude that the systematic uncertainty caused by processes other than radioactive decay for the age range of our four samples appears to be in the order of about 20%, not much larger than the current analytical error. We therefore are not in a position to discuss in more detail such processes with the present small set of data. For the following discussions we use the calculated  $^{81}\text{Kr}$  ages based on radioactive decay only as given above (circles in Fig. 1).

## 6. $^4\text{He}$ dating

As observed in various studies before [2]  $^4\text{He}$  concentrations in an aquifer often increase with time; however, rates are variable and depend on the importance of exchange and mixing processes.

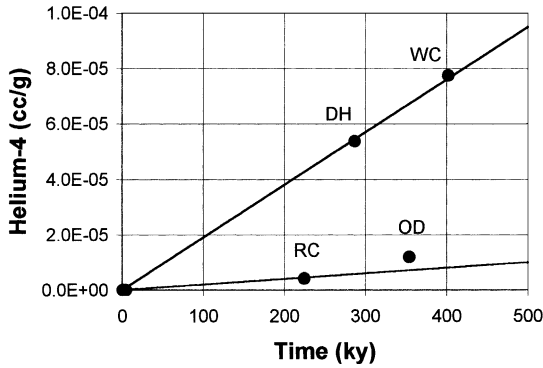


Fig. 2. Measured <sup>4</sup>He concentrations vs calculated <sup>81</sup>Kr age. Two trend lines indicate maximum and minimum helium accumulation rates.

For our four samples for the first time a calibration is possible using <sup>81</sup>Kr. In Fig. 2 the <sup>4</sup>He concentrations are plotted vs the <sup>81</sup>Kr ages. Obviously, different accumulation rates result of about  $1.9 \times 10^{-10}$  cc STP/(cm<sup>3</sup> water yr) (for Duck Hole and Watson Creek) and  $0.2 \times 10^{-10}$  cc STP/(cm<sup>3</sup> water yr) (for Raspberry Creek and Oodnadatta).

The <sup>4</sup>He production rate in sandstone of  $6.9 \times 10^{-13}$  cm<sup>3</sup> STP/(cm<sup>3</sup> rock yr) (Table 4) multiplied with a groundwater flow time of e.g. 400 kyr would only yield  $2.8 \times 10^{-6}$  cm<sup>3</sup> STP <sup>4</sup>He/(cm<sup>3</sup> water) providing complete transfer from rock to the corresponding volume of water (assuming an average porosity of 10%). For the sample from Watson Creek this would be a contribution of only about 4%. Obviously, in situ production of helium in the aquifer is too small; external sources must exist. By comparing the measured <sup>3</sup>He and <sup>4</sup>He concentrations in the four groundwater samples to the calculated in situ <sup>3</sup>He/<sup>4</sup>He production ratio (Fig. 3) it appears very likely that the source of the extra helium is located in the rocks and porewaters of the Bull-

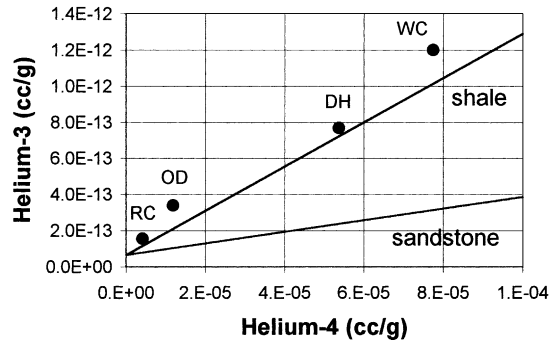


Fig. 3. Measured concentrations of <sup>3</sup>He and <sup>4</sup>He in the four groundwater samples. Upper straight line: <sup>3</sup>He/<sup>4</sup>He in situ production ratio in shale; lower straight line: <sup>3</sup>He/<sup>4</sup>He in situ production ratio in sandstone (from Table 4).

dog shale. A very similar situation was observed in the Molasse basin in Northern Switzerland [18] where shale sections in a sedimentary core were identified as the major source of helium isotopes in groundwater of an adjacent sandstone aquifer.

### 7. <sup>36</sup>Cl dating

For some 20 years <sup>36</sup>Cl has been used to study groundwater movement over time scales of several hundred thousand years. A number of researchers have addressed the potential and possible limitations of a <sup>36</sup>Cl dating technique [19–24]; most recently in [25]. In many situations it is possible to disentangle all the various interfering processes. However, evolutionary scenarios which cannot unambiguously be reduced to one consistent picture sometimes result and <sup>36</sup>Cl dating might only be possible for successive samples along a reasonable water flow path [4].

With the present set of data we have for the first time the unique opportunity to calibrate <sup>36</sup>Cl data by <sup>81</sup>Kr ages. As will be shown the

Table 5

Input chloride concentrations  $C_i$  consistent with the calculated <sup>81</sup>Kr age and the measured <sup>36</sup>Cl concentration (assuming  $R_i = 125 \times 10^{-15}$ ) and the corresponding calculated fraction  $C_a$  of chloride from subsurface sources

	RC	OD	DH	WC
$C_i$ (mg/l)	1047	624	119	206
$C_a$ (mg/l)	213	52	729	834
$C = C_i + C_a$ (mg/l)	1260	676	848	1040

four samples happen to cover the full range of uncertainties that possibly can limit the  $^{36}\text{Cl}$  technique. Two of the samples can be dated by  $^{36}\text{Cl}$  using radioactive decay, for the other two subsurface processes dominate. Furthermore, large variations in the input values over such long time scales clearly need to be considered.

The  $^{36}\text{Cl}$  concentration in groundwater decreases with time due to radioactive decay as the water moves downstream from the recharge area into an aquifer. At the same time,  $^{36}\text{Cl}$  atoms might also be added: (i) by in situ production in the aquifer during the travel time of the groundwater as a result of the  $^{35}\text{Cl}(n,\gamma)^{36}\text{Cl}$  reaction when thermal neutrons are captured by stable  $^{35}\text{Cl}$  atoms in dissolved chloride or (ii) by transport of  $^{36}\text{Cl}$  from external sources where over time intervals longer than a few half-lives the same nuclear reaction produced equilibrium  $^{36}\text{Cl}/\text{Cl}$  ratios in the respective geologic formations [21].

In Section 6 it was argued that the source of extra helium most likely is in the porewaters of the shale aquitard (Fig. 3). The same conclusion is drawn for chloride from the trend observed in a plot of  $\delta^{37}\text{Cl}$  vs  $^4\text{He}$  (Fig. 4). Low  $\delta^{37}\text{Cl}$  values of  $-1.95\text{‰}$  were found in rocks from the Bulldog shale (Frape, personal communication). Helium and chloride both appear to be transported to the GAB groundwaters from the confining shales.

The actual measured chloride concentration  $C(t)$  in groundwater is generally higher than the input concentration  $C_i$  by an amount  $C_a$  added

from subsurface sources. However, there is usually no information about the details of the temporal evolution of the chloride concentration for a given groundwater sample. For a simple approach we postulate that the chloride concentration increased linearly with time according to:

$$C(t) = C_i + C_a = C_i + kt \quad (1)$$

The in situ  $^{36}\text{Cl}/\text{Cl}$  atomic ratios have been calculated based on elemental analyses of the respective rocks (Table 4):

$R_{\text{shale}} = 13 \times 10^{-15}$  =  $^{36}\text{Cl}/\text{Cl}$  atomic ratio in secular equilibrium with the neutron flux in shale

$R_{\text{sand}} = 6 \times 10^{-15}$  =  $^{36}\text{Cl}/\text{Cl}$  atomic ratio in secular equilibrium with the neutron flux in sandstone

The temporal evolution of the  $^{36}\text{Cl}$  concentration in groundwater is then controlled by:

$$dN_{36}/dt = -\lambda N_{36}(t) + \alpha k R_{\text{shale}} + \alpha \lambda R_{\text{sand}}(C_i + kt) \quad (2)$$

(rate of change = radioactive decay + addition from shale + in situ production in sandstone),  $N_{36}$  = number of  $^{36}\text{Cl}$  atoms per litre of water,  $\lambda$  = decay constant for  $^{36}\text{Cl} = 2.3 \times 10^{-6}/\text{yr}$ ,  $C_i$  = initial chloride concentration in water entering the aquifer (mg/l),  $k$  = rate of chloride increase [(mg/l)/yr].

The constant ( $\alpha = 0.017 \text{ mg}^{-1}$ ) converts the units such that the value for  $N_{36}$  results in  $10^6$  atoms per litre of water, when  $C$  is entered in mg/l and  $R$  in units of  $10^{-15}$ . (One litre of water with e.g.  $C = 500 \text{ mg/l}$  of chloride and  $R = 100 \times 10^{-15}$  contains  $N_{36} = \alpha RC = 850 \times 10^6$  atoms of  $^{36}\text{Cl}$ ).

The following numerical example illustrates the relative importance of the various contributions.

During a time interval of 5 kyr a sample that at time  $t$  contains a chloride concentration of 600 mg/l and a  $^{36}\text{Cl}$  concentration of  $600 \times 10^6$  atoms/l (equivalent to a  $^{36}\text{Cl}/\text{Cl}$  ratio of  $59 \times 10^{-15}$ ) will lose  $6.91 \times 10^6$  atoms/l of  $^{36}\text{Cl}$  by decay (first term of the equation), will gain  $0.38 \times 10^6$   $^{36}\text{Cl}$  atoms/l from the shale (using a value of  $k = 0.34 \text{ mg}/(\text{l kyr})$  in the second term of the equation) and will gain  $0.71 \times 10^6$   $^{36}\text{Cl}$  atoms/l by in situ production in the sandstone aquifer (third term of the equation). Overall a net loss of  $5.82 \times 10^6$   $^{36}\text{Cl}$  atoms/l would result in this situation during a

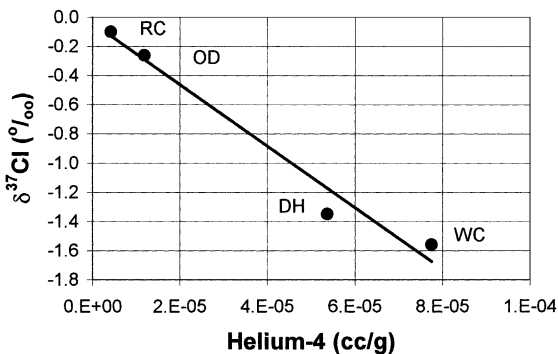


Fig. 4.  $\delta^{37}\text{Cl}$  vs  $^4\text{He}$  measured in the four groundwater samples with calculated trend line.

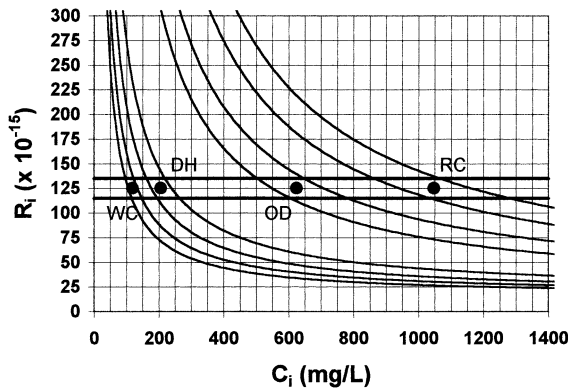


Fig. 5. Range of acceptable parameters for the  $^{36}\text{Cl}$  input values ( $R_i, C_i$ ) which are compatible with the  $^{81}\text{Kr}$  age according to Eq. 3. The four circles mark the best values for the four groundwater samples (centred between the respective two curves which represent the analytical uncertainty of the  $^{81}\text{Kr}$  data and for a selected representative input ratio  $R_i$  of  $125 \times 10^{-15}$  for all four samples).

5 kyr time interval illustrating that radioactive decay is more important than addition or ingrowth of  $^{36}\text{Cl}$ .

As mentioned earlier, it turns out that for two of our four samples such a situation is realised; for the two other samples subsurface processes dominate the  $^{36}\text{Cl}$  evolution as will now be shown.

The solution of Eq. 2 with a  $^{36}\text{Cl}$  input to the aquifer of  $N_{36}(0) = \alpha R_i C_i$  is:

$$N_{36}(t) = \alpha [R_i C_i + R_{\text{sand}} k t - A(1 - e^{-\lambda t})] \quad (3)$$

where  $A = (R_i - R_{\text{sand}})C_i - (R_{\text{shale}} - R_{\text{sand}})(k/\lambda)$  and  $R_i =$  initial  $^{36}\text{Cl}/\text{Cl}$  atomic ratio at recharge.

By inserting the measured value for  $N_{36}(t_{81})$  as well as the calculated ratios  $R_{\text{shale}}$  and  $R_{\text{sand}}$  into Eq. 3 one is left with a mathematical function which makes it possible to calculate pairs of parameters ( $R_i, C_i$ ) for the  $^{36}\text{Cl}$  input into the aquifer which are consistent with the  $^{81}\text{Kr}$  age of the sample and the measured  $^{36}\text{Cl}$  concentration. Note that  $k$  can be calculated from  $k = (C(t_{81}) - C_i)/t_{81}$  according to the postulated linear increase of the chloride concentration with time from Eq. 1.

Acceptable pairs ( $R_i, C_i$ ) for each sample must lie in the respective band marked by the two lines for each of the four samples in Fig. 5. The upper

and lower curves of a band represent the range of uncertainty caused by the analytical error in the  $^{81}\text{Kr}$  measurement.

In the next step a reasonable initial  $^{36}\text{Cl}/\text{Cl}$  ratio  $R_i$  must be selected. It is determined by three factors according to  $R_i = F_{36}/(P C_p)$ , namely:

1. the fall-out rate  $F_{36}$  of  $^{36}\text{Cl}$  atoms by dry and/or wet deposition which depends on the cosmic ray production rate and its variations due to e.g. a variable magnetic field intensity and atmospheric distribution patterns (stratosphere/troposphere exchange, tropospheric circulation)
2. the annual precipitation  $P$  which over such long time scales might have been affected by climatic changes
3. the chloride concentration  $C_p$  in precipitation which is essentially controlled by the distance to the seashore. All these factors are known to be variable; however, some of the variations might cancel or will be partially smoothed out by dispersion in the aquifer.

Love et al. [4] use an initial  $^{36}\text{Cl}/\text{Cl}$  ratio of  $R_i = (125 \pm 10) \times 10^{-15}$  based on measurements on selected young samples in the unconfined part of this aquifer where an anthropogenic component can be ruled out. As a working hypothesis we postulate that this same value of  $R_i$  is representative for all four of our samples. The corresponding band parallel to the horizontal axis in Fig. 5 determines those input chloride concentrations  $C_i$  to the aquifer which are in accordance with the  $^{81}\text{Kr}$  age. Obviously very different numerical values result for our four samples (range: 120–1050 mg/l).

In their analysis of  $^{36}\text{Cl}$  data Love et al. [4] also estimated the numerical values for other relevant input parameters in this part of the GAB:

$$P = \text{annual precipitation} = 200 \text{ mm/yr} (= 200 \text{ l}/(\text{m}^2 \text{ yr}))$$

$$C_p = \text{average chloride concentration in precipitation} = 0.625 \text{ mg/l.}$$

The product represents the annual deposition of Cl onto the land surface:

$$P C_p = 200 \times 0.625 = 125 \text{ mg Cl}/(\text{m}^2 \text{ yr}) = 6.7 \times 10^{13} \text{ stable Cl atoms}/(\text{m}^2 \text{ s}).$$

By multiplying with the best estimate of the initial  $^{36}\text{Cl}/\text{Cl}$  ratio of  $R_i = (125 \pm 10) \times 10^{-15}$  a

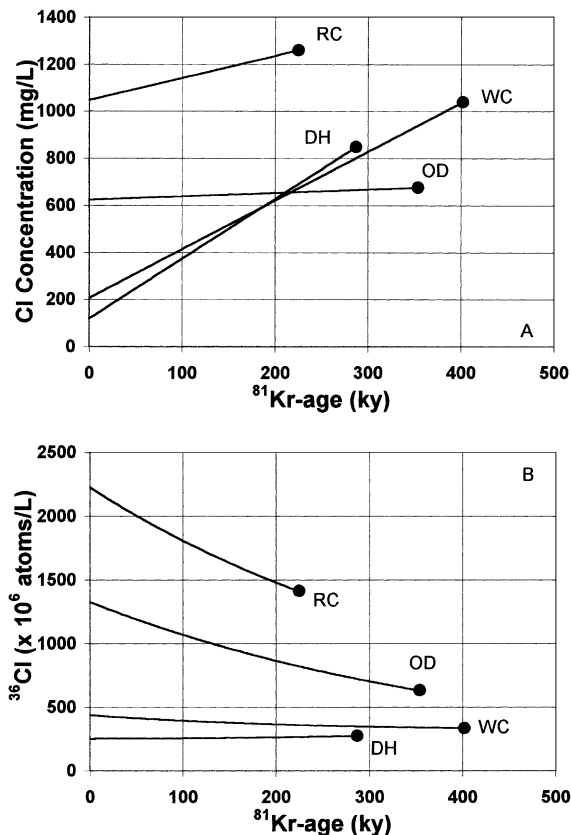


Fig. 6. Simulated temporal evolution of the chloride (A) and the  $^{36}\text{Cl}$  concentrations (B). Circles represent measured values in the four groundwater samples.

$^{36}\text{Cl}$  flux to the land surface in the recharge region of  $F_{36} = 8.4$   $^{36}\text{Cl}$  atoms/( $\text{m}^2$  s) results.

For the actual recharge into the aquifer the authors propose a value of  $0.16 \pm 0.08$  mm/yr, a fraction of only 0.08% of the annual precipitation. Obviously, evapotranspiration in this arid area is extremely high. Consequently, the initial chloride concentration  $C_i$  is high:

$$C_i = (125 \text{ mg Cl}/(\text{m}^2 \text{ yr})) / (0.16 \text{ l}/(\text{m}^2 \text{ yr})) = 781 \text{ mg/l}$$

(min 520 mg/l, max 1560 mg/l, errors from [4]) and high  $^{36}\text{Cl}$  input concentrations result:

$$R_i C_i = 1670 \times 10^6 \text{ }^{36}\text{Cl} \text{ atoms/l of water.}$$

For two of the four samples (Raspberry Creek and Oodnadatta) their analysis is not in conflict with the  $^{81}\text{Kr}$  dating of this work. For the other two samples, however (Duck Hole and Watson Creek), acceptable input parameters for  $C_i$  are

outside their estimated range; lower values obviously must be adopted. Rather small variations in the magnitude of evapotranspiration through time or even local differences between the respective recharge areas would affect the input chloride concentration  $C_i$  to the aquifer.

In Table 5 our values for  $C_i$  are listed that are consistent with the  $^{81}\text{Kr}$  ages (from Fig. 5). By subtracting  $C_i$  from the measured Cl concentration  $C(t_{81})$  we calculate  $C_a$ , the fraction of Cl accumulated by each sample from sources in the subsurface.

With these  $^{81}\text{Kr}$ -derived input values  $C_i$  for chloride, the initial  $^{36}\text{Cl}$  input concentrations can be calculated ( $N_{36}(0) = \alpha R_i C_i$ ) and the  $^{36}\text{Cl}$  evolution of the four samples be reconstructed: for two of the four samples decay of atmospheric  $^{36}\text{Cl}$  dominates subsurface input; for the other two the input  $^{36}\text{Cl}$  concentration is low and the Cl increase over time is substantial (Fig. 6A) and therefore subsurface sources become equally important resulting in an almost constant  $^{36}\text{Cl}$  concentration over time (Fig. 6B). Obviously  $^{36}\text{Cl}$  dating for those two samples is not possible.

## 8. Discussion

Strong evidence that the Cl and  $^{36}\text{Cl}$  evolution derived from  $^{81}\text{Kr}$  decay ages are valid comes from Figs. 7 and 8.

In Fig. 7 the input value  $C_i$  is plotted vs the calculated NGRT (Table 3). Higher recharge temperatures reflect higher rates of evapotranspiration yielding higher Cl input concentrations. In Fig. 8 the amount  $C_a$  of chloride added from subsurface sources is plotted vs the  $^4\text{He}$  concentration of the four samples. The correlation is in agreement with Figs. 3 and 4 clearly pointing to a common source of the two elements (the porewaters of the Bulldog shale). A representative Cl/He atomic ratio for this source is about 7000:1 which is in a range found in other aquifers [26].

Note that the higher  $^4\text{He}$  accumulation rate in Fig. 2 happens to be close to the value reported by Torgerson et al. [27]. However, in contrast to the hypothesis presented by these authors the

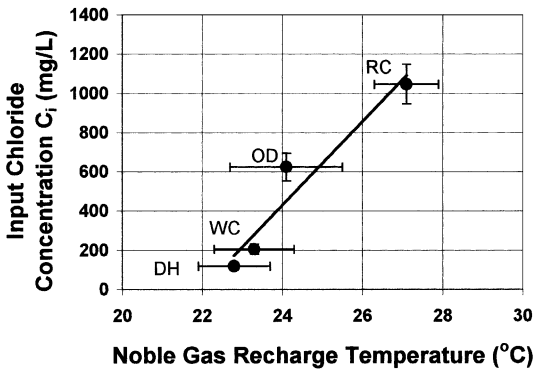


Fig. 7.  $^{81}\text{Kr}$ - $^{36}\text{Cl}$ -derived initial chloride concentration  $C_i$  vs calculated NGRT (see Table 2) with calculated trend line.

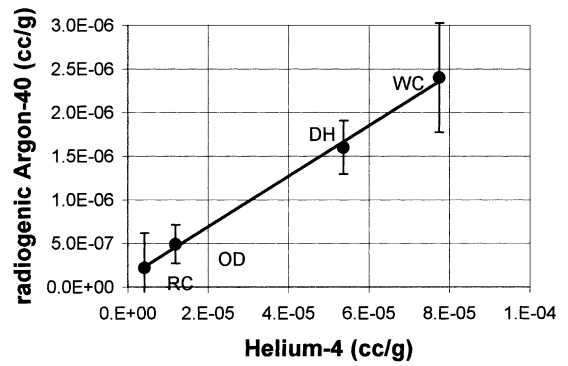


Fig. 9. Calculated radiogenic  $^{40}\text{Ar}$  concentrations (based on measured Ar concentrations and  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios) vs measured  $^4\text{He}$  concentrations with calculated trend line.

model with a local reservoir of Cl and He in the nearby stagnant porewaters does not need large-scale helium transport.

In Fig. 9 the amount of radiogenic  $^{40}\text{Ar}$  is plotted vs the  $^4\text{He}$  concentration. The correlation indicates that the two nuclides are added in parallel to the groundwater samples. The two samples where little Cl is added from subsurface sources (RC, OD) have lower concentrations of  $^4\text{He}$  and of radiogenic  $^{40}\text{Ar}$ ; the other two samples, where subsurface Cl sources are stronger (DH, WC), also have higher  $^4\text{He}$  and  $^{40}\text{Ar}$  concentrations. The  $^4\text{He}/^{40}\text{Ar}_{\text{rad}}$  ratios of the four samples increase from a value of about 20 to 33 which may indicate that diffusion partly is responsible for the addition of the two gases from shale;

the lighter element is more enriched in older samples.

The trend in Fig. 4 might be explained accordingly:  $^{35}\text{Cl}$  diffuses faster from the shale to the aquifer than  $^{37}\text{Cl}$  causing a decrease of the  $\delta^{37}\text{Cl}$  value in groundwater with time. Based on first numerical estimates using a diffusive-advective transport model we conclude, however, that diffusion alone is not fast enough to supply enough chloride in the time available.

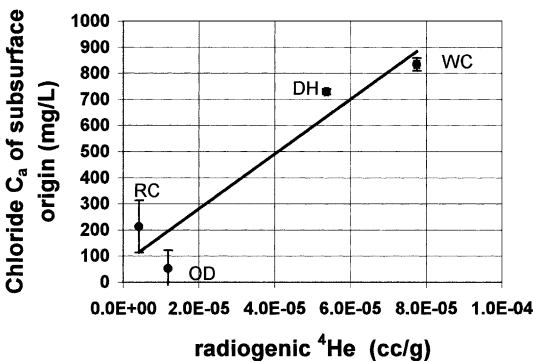


Fig. 8.  $^{81}\text{Kr}$ - $^{36}\text{Cl}$ -derived chloride concentration  $C_a$  of subsurface origin vs measured concentration of radiogenic  $^4\text{He}$  with calculated trend line.

### 9. Iodine-129

The isotope  $^{129}\text{I}$  has a half-life of 15.7 million years. In the atmosphere it is mainly produced by cosmic ray-induced spallation of xenon atoms [20]. The initial pre-bomb  $^{129}\text{I}/\text{I}$  ratio is in a range of  $R_i = (600-1000) \times 10^{-15}$  based on theoretical considerations which is supported by several field studies. Values in a range of  $(1200-1500) \times 10^{-15}$  have been measured in pre-bomb marine sediments [28]. In the underground, subsurface production by spontaneous fission of  $^{238}\text{U}$  yields in situ equilibrium ratios  $^{129}\text{I}/\text{I}$  which depend on the elemental concentrations of uranium and iodine in the host rock. For a shale with 2 ppm uranium and 1 ppm iodine an equilibrium ratio of  $R_{\text{shale}} = 620 \times 10^{-15}$  would result after several half-lives of  $^{129}\text{I}$  [7]. Because of the long half-life decay of  $^{129}\text{I}$  in the aquifer during the residence times discussed in this study can be neglected (in contrast to  $^{36}\text{Cl}$ ).

Furthermore, in situ production and release of nuclides to the groundwater during such time intervals (several hundred thousand years) clearly is not important. The corresponding calculated  $^{129}\text{I}/\text{I}$  ratios are about 100 times smaller than the ones measured in our four samples.

As can be seen in Table 2 the measured  $\text{Cl}/\text{I}$  ratios in the four groundwater samples are fairly constant at a value of 1650 ( $\pm 15\%$ ). At recharge, the same concentration increase due to strong evapotranspiration in the semi-arid climate will take place for iodide as for chloride. The initial  $(\text{Cl}/\text{I})_i$  ratio in precipitation is not known and the  $(\text{Cl}/\text{I})_a$  ratio of the saline porewaters where the source of subsurface chloride is assumed to be is not known either. As a simple first approximation we assume that both ratios are the same and that the  $^{81}\text{Kr}$ -derived splitting of the measured  $\text{Cl}$  concentration  $C$  in groundwater into an input concentration  $C_i$  and a component accumulated in the subsurface  $C_a$  according to  $C = C_i + C_a$  (Table 5) also holds for iodide. In accordance with the situation discussed for chloride the source for iodide is assumed to be in the porewaters of the Bulldog shale. Such a situation appears to be very similar to the one postulated for the halogens in the Milk River aquifer in Canada [29] or for the Anadarko Basin in Oklahoma [30]. For each sample we then get a simple mixing equation (neglecting radioactive decay):

$$N_{129} = \beta(I_i R_{\text{atm}} + I_a R_{\text{shale}}) \quad (4)$$

$N_{129}$  = number of  $^{129}\text{I}$  atoms per litre of water;  $I_i$  = iodide concentration at recharge;  $R_{\text{atm}}$  = atmospheric  $^{129}\text{I}/\text{I}$  ratio;  $I_a$  = iodide concentration accumulated in the subsurface;  $R_{\text{shale}}$  = in situ  $^{129}\text{I}/\text{I}$  ratio in the porewaters of the shale;  $\beta$  = numerical constant =  $4.7 \times 10^{-3} \text{ (mg/l)}^{-1}$ , which converts the units such that  $N_{129}$  results in  $10^6$  atoms/l when  $I$  is entered in  $\text{mg/l}$  and  $R$  in units of  $10^{-15}$ .

Note that  $I_i/\text{Cl}_i = I_a/\text{Cl}_a$  with the respective elemental ratios for iodide and chloride according to the above hypothesis. Mixing lines which would yield the correct measured  $^{129}\text{I}$  concentration according to Eq. 4 are plotted in Fig. 10 for all four samples. The circle marks the best consistent pair of  $R_{\text{shale}} = (600 \pm 200) \times 10^{-15}$  and  $R_{\text{atm}} = (660 \pm 30) \times 10^{-15}$  for which all calculated concentrations

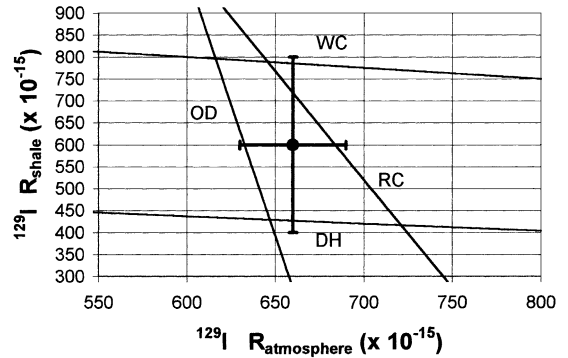


Fig. 10. Mixing lines for  $^{129}\text{I}$  between an atmospheric component (with  $R_{\text{atm}}$ ) and a subsurface component (with  $R_{\text{shale}}$ ). The circle represent a best pair of values for which the  $^{129}\text{I}$  concentrations measured in all four samples can be reproduced with deviations of less than 20%.

according to Eq. 4 are within 20% of the measured value for the four samples. Comparing these best estimates with the expected ratios listed in the first paragraph of this section both ratios  $R_{\text{shale}}$  and  $R_{\text{atm}}$  appear to be very reasonable giving confidence that the hypothetical splitting of the measured iodide concentration into two fractions equal to the splitting of the chloride concentrations and a simple mixing model should be quite close to the real situation for  $^{129}\text{I}$ .

## 10. Summary

Measured  $^{81}\text{Kr}/\text{Kr}$  ratios are converted to water residence times based on a decrease of  $^{81}\text{Kr}$  by radioactive decay only. These ages are then used to simulate the  $^{36}\text{Cl}$  and the  $\text{Cl}$  evolution. Based on  $^3\text{He}/^4\text{He}$  data of rocks and groundwaters and on  $\delta^{37}\text{Cl}$  data of groundwaters it is concluded that  $\text{Cl}$  and  $\text{He}$  both are transported from the porewaters of the shale (by diffusion and/or advection) and mixed into the flowing groundwaters. As a result, the measured chloride concentration  $C_m$  of each sample can be split into two components  $C_i$  and  $C_a$ , the fractions that infiltrated at recharge or were added in the subsurface respectively. Strong evidence that the procedure is valid comes from the facts that: (i) the NGRTs correlate with  $C_i$  and (ii) the measured  $^4\text{He}$  concentrations correlate with  $C_a$ . An interpretation of the

$^{129}\text{I}$  data in a simple mixing model is not in disagreement with the overall interpretation of  $^{81}\text{Kr}$ ,  $^{36}\text{Cl}$  and  $^4\text{He}$  data.

## Acknowledgements

The authors thank Sergei Tarakanov for numerical estimates with a simple diffusive–advective transport model to quantify the uncertainties of the  $^{81}\text{Kr}$  ages (Fig. 1) and Beat Ihly for analytical solutions of the  $^{36}\text{Cl}$  transport equation in groundwater (Fig. 5). The Isotope Hydrology Section of the IAEA substantially supported the fieldwork of this study. The Russian collaborators were supported by a grant from SCOPEs, the Scientific Cooperation between Eastern Europe and Switzerland. A very particular feature of this study is that it never went through a regular funding procedure due to time constraints at the National Superconducting Cyclotron Laboratory at Michigan State University. Less than nine months were available between the first idea of such a field project and the deadline for measurements. All participating groups thank their respective organisations for a very flexible handling of the financial budgets which enabled a coordinated international effort with hardly any ‘paperwork’. [BOYLE]

## References

- [1] S.N. Davis, C. DeWayne, M. Zreda, P. Sharma, Chlorine-36 and the initial value problem, *Hydrogeol. J.* 6 (1998) 1330–1332.
- [2] K. Solomon,  $^4\text{He}$  in groundwater, in: P.G. Cook, A.L. Herczeg (Eds.), *Environmental Tracers in Subsurface Hydrology*, Kluwer Academic, Dordrecht, 2000, pp. 299–348.
- [3] P. Collon, W. Kutschera, H.H. Loosli, B.E. Lehmann, R. Purtschert, A. Love, L. Sampson, D. Anthony, D. Cole, B. Davids, D.J. Morrissey, B.M. Sherrill, M. Steiner, R.C. Pardo, M. Paul,  $^{81}\text{Kr}$  in the Great Artesian Basin, Australia: a new method for dating very old groundwater, *Earth Planet. Sci. Lett.* 182 (2000) 103–113.
- [4] A.J. Love, A.L. Herczeg, L. Sampson, R.G. Cresswell, L.K. Fifield, Sources of chloride and implications for  $^{36}\text{Cl}$  dating of old groundwater, southwestern Great Artesian Basin, Australia, *Water Resour. Res.* 36 (2000) 1561–1574.
- [5] U. Beyerle, W. Aeschbach-Hertig, D.M. Imboden, H. Baur, T. Graf, R. Kipfer, A mass spectrometric system for the analysis of noble gases and tritium from water samples, *Environ. Sci. Technol.* 34 (2000) 2042–2050.
- [6] W. Aeschbach-Hertig, F. Peeters, U. Beyerle, R. Kipfer, Palaeotemperature reconstruction from noble gases in ground water taking into account equilibration with entrapped air, *Nature* 405 (2000) 1040–1044.
- [7] B.E. Lehmann, S.N. Davis, J. Fabryka-Martin, Atmospheric and subsurface sources of stable and radioactive nuclides used for groundwater dating, *Water Resour. Res.* 29 (1993) 2027–2040.
- [8] H.H. Loosli, H. Oeschger,  $^{37}\text{Ar}$  and  $^{81}\text{Kr}$  in the atmosphere, *Earth Planet. Sci. Lett.* 7 (1969) 67–71.
- [9] B.E. Lehmann, H. Oeschger, H.H. Loosli, G.S. Hurst, S.L. Allman, S.D. Kramer, M.G. Payne, R.C. Phillips, R.D. Willis, N. Thonnard, Counting  $^{81}\text{Kr}$  atoms for analysis of groundwater, *J. Geophys. Res.* 90 (B13) (1985) 11547–11551.
- [10] B.E. Lehmann, H.H. Loosli, D. Rauber, N. Thonnard, R.D. Willis,  $^{81}\text{Kr}$  and  $^{85}\text{Kr}$  in groundwater, Milk River aquifer, Alberta, Canada, *Appl. Geochem.* 6 (1991) 419–423.
- [11] N. Thonnard, R.D. Willis, M.C. Wright, W.A. Davis, B.E. Lehmann, Resonance ionization spectroscopy and the detection of  $^{81}\text{Kr}$ , *Nucl. Instr. Methods B* 29 (1987) 398–406.
- [12] A.I. Ludin, B.E. Lehmann, High-resolution diode laser spectroscopy on a fast beam of metastable atoms for detecting very rare krypton isotopes, *Appl. Phys. B* 61 (1995) 461–465.
- [13] W.M. Fairbank Jr., C.S. Hansen, R.D. Labelle, X.J. Pan, Y. Zhang, E.P. Chamberlin, N.S. Nogar, C.M. Miller, B.L. Feary, H. Oona, Photon burst mass spectrometry for the measurement of  $^{85}\text{Kr}$  at ambient levels, *Proc. Soc. Photo.-Opt. Instr. Eng.* 3270 (1998) 2–8.
- [14] C.Y. Chen, Y.M. Li, K. Bailey, T.P. O’Connor, L. Young, Z.-T. Lu, Ultrasensitive isotope trace analysis with a magneto-optical trap, *Science* 286 (1999) 1139–1141.
- [15] W. Kutschera, M. Paul, I. Ahmad, T.A. Antaya, P.J. Billquist, B.G. Glagola, R. Harkewicz, M. Hellstrom, D.J. Morrissey, R.C. Pardo, K.E. Rehm, B.M. Sherrill, M. Steiner, Long-lived noble gas radionuclides, *Nucl. Instr. Methods B* 29 (1994) 241–248.
- [16] P. Collon, T. Antaya, B. Davids, M. Fauerbach, R. Harkewicz, M. Hellstrom, W. Kutschera, D.J. Morrissey, R.C. Pardo, M. Paul, B.M. Sherrill, M. Steiner, Measurement of  $^{81}\text{Kr}$  in the atmosphere, *Nucl. Instr. Methods B* 123 (1997) 122–127.
- [17] A. Rübel, Ch. Sonntag, J. Lippmann, F.J. Pearson, A. Gautschi, Solute transport in formations of very low permeability: Profiles of stable isotope and dissolved noble gas contents of pore water in the Opalinus Clay, Mont Terri, Switzerland, *Geochim. Cosmochim. Acta* 66 (2002) 1311–1321.
- [18] I. Tolstikhin, B.E. Lehmann, H.H. Loosli, A. Gautschi,

- Helium and argon isotopes in rocks, minerals, and related groundwaters: a case study in Northern Switzerland, *Geochim. Cosmochim. Acta* 60 (1996) 1497–1514.
- [19] H. Bentley, F.M. Phillips, S.N. Davis, M.A. Habermehl, P.L. Airey, G.E. Calf, D. Elmore, H.E. Gove, T. Torgersen, Chlorine-36 dating of very old groundwater: The Great Artesian Basin, Australia, *Water Resour. Res.* 22 (1986) 1991–2001.
- [20] J. Fabryka-Martin, S.N. Davis, D. Elmore, Applications of  $^{129}\text{I}$  and  $^{36}\text{Cl}$  to hydrology, *Nucl. Instr. Methods B* 29 (1987) 361–371.
- [21] J.N. Andrews, J.-C. Fontes, Importance of the in situ production of  $^{36}\text{Cl}$ ,  $^{36}\text{Ar}$  and  $^{14}\text{C}$  in hydrology and hydrogeochemistry, in: *Proceedings of Symposium on Isotope Techniques in Water Resources Development*, IAEA-SM-319/12, Vienna, 1991, pp.245–269.
- [22] T. Torgersen, M.A. Habermehl, F.M. Phillips, D. Elmore, P. Kubik, B. Geoffrey-Jones, T. Hemmick, H.E. Gove, Chlorine-36 dating of very old groundwater. Further studies in the Great Artesian Basin, Australia, *Water Resour. Res.* 27 (1991) 3201–3213.
- [23] J.N. Andrews, J.-C. Fontes, Comment on ‘Chlorine-36 dating of very old groundwater, 3, Further results on the Great Artesian Basin, Australia’, by Torgersen et al, *Water Resour. Res.* 29 (1993) 1871–1874.
- [24] T. Torgersen, F.M. Phillips, Reply, *Water Resour. Res.* 29 (1993) 1875–1877.
- [25] F.M. Phillips, Chlorine-36 in subsurface hydrology, in: P.G. Cook, A.L. Herczeg (Eds.), *Environmental Tracers in Subsurface Hydrology*, Kluwer Academic, Dordrecht, 2000, pp. 299–348.
- [26] B.E. Lehmann, H.H. Loosli, R. Purtschert, J.N. Andrews, A comparison of chloride and helium concentrations in deep groundwaters, in: *Proceedings of the Symposium on Isotopes in Water Resources Management*, IAEA-SM-336/44, Vienna, 1995, pp. 3–17.
- [27] T. Torgersen, W.B. Clarke, Helium accumulation in groundwater, I: An evaluation of sources and the continental flux of crustal  $^4\text{He}$  in the Great Artesian Basin, Australia, *Geochim. Cosmochim. Acta* 49 (1985) 1211–1218.
- [28] J.E. Moran, U. Fehn, R.T.D. Teng, Variation in  $^{129}\text{I}/\text{I}$ -ratios in recent marine sediments: Evidence for a fossil organic component, *Chem. Geol.* 152 (1998) 193–203.
- [29] J. Fabryka-Martin, D.O. Whittemore, S.N. Davis, P. Kubik, P. Sharma, Geochemistry of halogens in the Milk River aquifer, Alberta, Canada, *Appl. Geochem.* 6 (1991) 447–464.
- [30] J.E. Moran, Origin of iodine in the Anadarko Basin, Oklahoma: An  $^{129}\text{I}$  study, *AAPG Bull.* 80 (1995) 685–694.