Gas Concentrations and Ages of Groundwaters in Beaufort Group Sediments, South Africa

T.H.E. HEATON AND J.C. VOGEL
[NATURAL ISOTOPES DIVISION, NATIONAL PHYSICAL RESEARCH LABORATORY, COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH, P.O. BOX 395, PRETORIA 0001]

Abstract

Twenty eight groundwater samples from Beaufort group rocks were analysed for their dissolved He, Rn, Ra, CH_4, N_2, O_2, and Ar concentrations, and their ^{14}C and ^{3}H ages. Along the 120 km long sampling line large variations in He concentrations were measured, ranging over three orders of magnitude, and correlate with similarly large variations in CH_4 concentrations. Higher He and CH_4 concentrations are characteristic of the older waters. However, unless the rocks are unusually radioactive or have very low porosities, the He concentrations appear to be too high for a system where the dissolved He was only that produced during the residence time of the water by the rock with which the water was in contact.

The high He concentrations may be the result of He migration associated with CH_4 migration. The magnitude and uniformity of the Rn concentrations suggest that the Rn is of near-surface origin. N_2 and Ar concentrations are generally higher than those to be expected for waters originally in equilibrium with the atmosphere; excess air may be trapped in the waters during their initial infiltration.

Introduction

In recent years increasing attention has been paid to the study of He and Rn concentrations in soils and groundwaters as aids to locating faults and predicting earthquakes, and in prospecting for gas, geothermal and uranium resources (Tanner, 1964; Bulashevich and Bashorin, 1971; Clarke and Kugler, 1973; Eremeev *et al.*, 1973; Craig *et al.*, 1975; Dyck, 1976; Friedman and Denton, 1976; Noguchi and Wakita, 1977). Gas concentration data have also been used in hydrological investigations, but most of these studies have been carried out on thermal or other unusual waters (e.g. Mazor and Verhagen, 1976; Mazor *et al.*, 1974). The samples studied in this report may be regarded, with a few exceptions, as more 'normal' groundwaters.

As part of a geophysical and hydrological study centred along the middle-upper stretches of the Orange River, groundwater samples were collected from 25 sites along a line approximately 120 km long in the Cape Province and Orange Free State (Fig. 1). The samples were analysed for their dissolved He, Rn, Ra, CH_4, N_2, O_2 and Ar concentrations, and also their ^{14}C and ^{3}H ages.

The authors were particularly interested in:

- the range in concentration of a gas to be found over an area with relatively uniform rock types;
- the possible relationship between gas concentration and the age of the water; and
- whether any concentration anomalies were associated with waters from a fracture zone which is believed to cross the sampling area.

Geology

Country rocks of the sampling area are near-horizontal sandstones, siltstones and shales of the Katberg Formation, part of

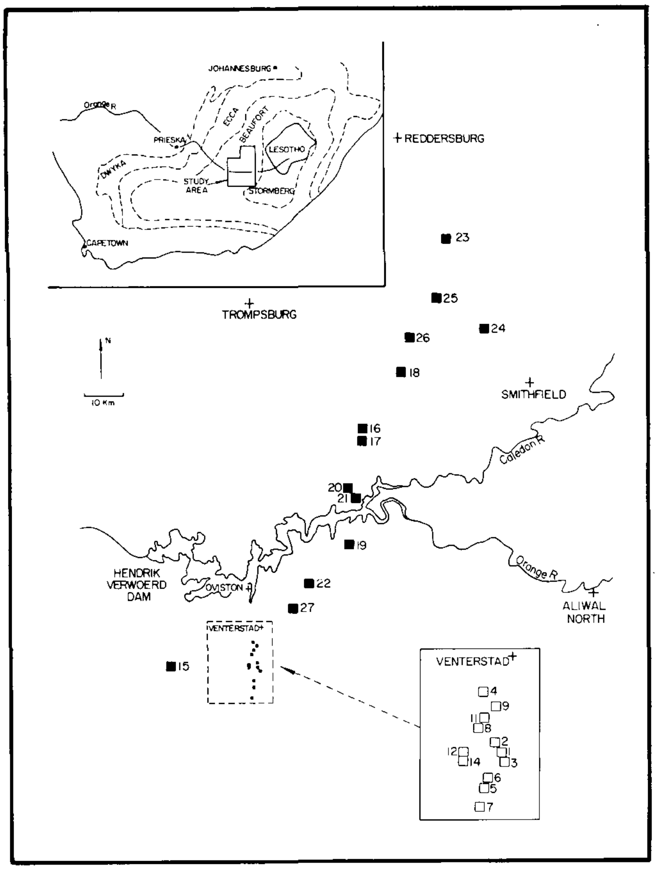

Figure 1
Sample locality map. Inset shows the position of the study area in relation to the main divisions of the Karoo supergroup: the Dwyka formation, Ecca group and Beaufort group; Stormberg = the Molteno, Elliot, Clarens formations and the Drakensberg group.

the Beaufort group (Fig. 1). The sediments are intruded by dolerite sheets and by a large number of near-vertical dykes. Individual dykes, which range up to ~10 m thick, are traceable over tens of kilometres.

Karoo sediments have undergone low grade burial metamorphism with the production of methane-rich gas, and traces of oil. These factors are discussed in detail by Rowsell and De Swardt (1976). In a deep borehole 30 km south of Aliwal North (Fig. 1) the sediment thickness from the top of the Katberg Formation to the gneissic basement was measured as 3,1 km (Winter and Venter, 1970).

During drilling of the Orange Fish Tunnel south from Oviston (Fig. 1), a highly permeable fracture zone yielding an initial water inflow of 3 090 m^3/h was encountered at sampling localities 12—14, Fig. 1 (Olivier, 1972). The fracture zone consisted of a number of E-W striking near-vertical open joints. It has been tentatively suggested that this zone may represent reactivation of an extension of the pre-karoo Doornberg fault exposed near Prieska, Fig. 1 (Olivier, 1972).

Hydrology

Hydrological investigations have been carried out in the Venterstad area (Fig. 1) by a number of authors (Boehmer, 1971; Bredenkamp, 1971; Olivier, 1972; Van der Linde and Hodgson, 1976, 1977; this report). The overall conclusions may be summarised as follows.

In the area of the Orange Fish Tunnel fracture zone there appears to be a correlation between groundwater age and temperature. This suggests that the groundwater's age increases with depth. The overall situation, of course, may be more complex. There is some evidence to suggest that two groundwater bodies exist, an upper and lower one. In the tunnel fracture zone area they may be divided by semi-permeable shale horizons.

Much of the recent groundwater may be stored in the upper weathered zone of the sedimentary rocks below the overlying alluvium, but the chemical and isotopic data, and the presence of thermal waters, indicate that some of the water has a deeper and older history. The movement and mixing of water is greatly facilitated along vertical fractures and along the contact zones between dykes and sediments. These contact zones are often highly permeable, and many of the boreholes in the sampling area draw water from them.

Sample selection

During June 22 to July 2, 1977, samples 1 to 11 were collected in the vicinity of the Orange Fish Tunnel fracture zone south of Venterstad (Fig. 1). The samples were chosen to be representative of the different water chemistries found in this area by Van der Linde and Hodgson (1976, 1977).

To test whether waters in the Venterstad area were in any way unusual, further samples were collected during November 29 to December 7, 1977. These were from locations along a line running northwards from Venterstad, approximately parallel with the strike of the Beaufort group (Fig. 1). In seleclting these boreholes preference was given to those with a relatively high water yield. In addition, samples 12 and 14 were collected from boreholes on the Orange Fish Tunnel fracture zone, together with repeat samples 3b, 7b and 11b.

Experimental

Sample collection

Water from the borehole pump was run into a bucket and allowed to overflow. 200—300 ml of water from the bottom of the bucket was drawn into an evacuated 500 ml glass flask sealed with a greased stopcock. Two samples (4 and 5) were filled by drawing water directly from the borehole pump through a tube connected to the glass joint of the flasks, and both showed evidence of air contamination during sampling; their major atmospheric gas concentration data (N_2, O_2 and Ar) are not discussed further. Flasks containing H_3PO_4 and $HgCl_2$ are used for He, CH_4, N_2, O_2 and Ar analysis, with a separate flask collected for Rn and Ra analysis. Additional water samples were collected for ^{14}C and ^3H analysis.

Gas analysis

The flasks were connected to a glass extraction line, and the gases from the water pumped through dry-ice and liquid nitrogen traps with a Toepler pump into a manometer where the non-condensable gas yield is measured. Gas analysis was performed in an Atlas M86 mass spectrometer with a viscous flow

TABLE 1
AIR EQUILIBRATED WATERS (A.E.W.) AND WITKLIPBANK FARM WATERS

Sample	He	N_2	O_2	Ar	CH_4
	Mean (ml STP/kg H_2O) and av. % deviation from mean				
3 A.E.W., 25 °C	4,10 x 10^{-5}	9,62	4,88	0,24	
	(12 %)	(1,6 %)	(1,0 %)	(2,5 %)	
(Expected A.E.W., 25 °C)*	3,81 x 10^{-5}	9,44	5,00	0,25	
2 A.E.W., 21 °C	4,48 x 10^{-5}	10,09	5,10	0,26	
	(6,3 %)	(1,8 %)	(5,5 %)	(0,8 %)	
(Expected A.E.W., 21 °C)*	3,85 x 10^{-5}	10,11	5,39	0,26	
6 Laboratory spring waters	6,01 x 10^{-5}	14,01	1,02	0,31	
	(8,2 %)	(0,15 %)	(4,8 %)	(0,8 %)	
7 Witklipbank Farm waters collected on 21/10/77					
3 analysed 22/10/77	0,398	5,79	0,09	0,20	26,01
	(2,7 %)	(5,4 %)	(75 %)	(0,8 %)	(2,8 %)
2 analysed 22/11/77	0,407	5,89	0,05	0,20	26,91
	(2,0 %)	(5,2 %)	(82 %)	(1,2 %)	(2,4 %)
2 analysed 9/1/78	0,416	5,90	0,08	0,20	26,36
	(1,2 %)	(1,4 %)	(42 %)	(1,7 %)	(3,5 %)

*Solubility for moist air at 656 mm Hg (Weiss 1970, 1971)

TABLE 2
SAMPLE LOCALITY DATA

Sample [a] No.	Farm	Pump type [b]	Temp. °C [c]	Water level [d] (m)	Borehole [e] depth (m)	Dolerite [f] dyke	H_2S smell
1	Badsfontein	Spring	27,1	0		X	X
2	Badsfontein	w.	16		24 5		
3	Badsfontein	d.	27,0			X	X
4	Wildebeesvlei	d.	16	3,0	24 5	X	
5	Elandsfontein	d.	16,0				
6	Elandsfontein	d.	15,8				
7	Valekrans	w.	16			X	
8	Badsfontein	e.	16				
9	Wildebeesvlei	d.	18			X	X
11	Badsfontein	w.	17,8				X
12	Badsfontein	e.	19,9	15	> 50		X
14	Badsfontein	e.	19,4	6	54		
15	Roodewal	spring-d	30,2	0-3	38	X	X
16	Diepfontein	w.	19,2			X	
17	Heuningfontein	w.	18,8				X
18	Uitkyk	w.	17,2			X	
19	Klipbanksfontein	w.	17,9			X	
20	Kareefontein	d.	19,0		30		
21	Katfontein	w.	18,5				X
22	Vaalbank	spring-d	20,2	0	27,5		X
23	Suiddeel	w.	16,8		24,5		
24	Kleinbadfontein	spring-w	18,2	0	36	X	X
25	Poortjie	w.	18,2				
26	Die Bad	w.	16,7	1-3	27	X	X
27	Vaalrand	d.	18,2			X	

a. Sample localities, see Fig. 1.
b. w = wind; e = electric; d = diesel. Electric or diesel pump generally implies a high-yield borehole.
c. Mean annual air temperature at Oviston over 6 year period = 17 – 20 °C, av. 18,5 °C (Olivier, 1972).
d. Average water level depth ~7 m in sampling area 1 – 14 (Van der Linde and Hodgson, 1976).
e. Where borehole depths are not known the majority may be expected to be in the range 20 – 30 m.
f. X-Borehole close to, and probably taps water from, dolerite dyke. Lack of evidence for a dyke does not prove its absence.

inlet system. The instrument was calibrated using atmospheric air and gas mixtures of known composition.

Analytical precision was tested by analysing air equilibrated water (A.E.W.), water from a spring below the laboratory's radioisotope counting cellar, and water from a 2 km deep artesian borehole at Witklipbank Farm (near Delmas, Transvaal). The data are shown in Table 1.

For higher He concentrations and the major atmospheric gases the precision is generally better than 5%. For the lowest He concentrations to be expected in natural waters, ~ 4×10^{-5} ml He STP/kg H_2O, and for very low O_2 concentrations, the precision is reduced. The measured gas concentrations in air equilibrated water are in close agreement with the values to be expected from published solubility data (Table 1).

The Witklipbank Farm water has a particularly high He concentration and was used to test whether there is a significant loss of He, during sample storage, by diffusion through the glass walls of the sample flask. No significant change in the He concentration, greater than the limit of precision, was measured after 78 days (Table 1). The majority of samples discussed in this report were analysed within three weeks of collection.

^{222}Rn, ^{226}Ra, ^{14}C and ^{3}H analysis

CO_2 is added to the flasks containing the samples for Rn analysis. The gases are pumped through a liquid nitrogen trap where the CO_2, and the Rn removed by stripping are retained. The CO_2 + Rn mixture is transferred to a proportional counter for analysis (Vogel, unpublished). A decay correction is applied to the measured Rn concentrations to give the Rn concentration in the water at the time of collection. The water samples are reanalysed for Rn after a further known storage time. This allows calculation of their Ra concentration.

The analytical and interpretive methods for ^{14}C and ^{3}H age determinations have been discussed elsewhere (Vogel, 1967, 1970; Vogel and Marais, 1971; Vogel *et al.*, 1974).

Results and discussion

Data on the sampled wells are given in Table 2, the localities are shown in Fig. 1. Dissolved gas concentrations, ^{14}C, ^{3}H and Ra data are given in Table 3.

TABLE 3
GROUNDWATER DATA

Sample No.	He	N_2 ml STP/kg H_2O	O_2 [a]	Ar	CH_4 [b]	Rn [c] cpm/kg H_2O	^{14}C % modern	^{3}H [d] T.U.	Corrected [e] age (yrs)
1	$5{,}68 \times 10^{-2}$	16,62		0,28	33,74	3 636	70,8 (±0,5)	0,5 (±1,0)	1 475
2	$3{,}93 \times 10^{-4}$	12,20		0,29	0,02	1 621	115,4 (±0,9)	0,0 (±1,2)	<20
3	$9{,}88 \times 10^{-2}$	9,51		0,22	42,80	2 246	53,5 (±0,7)	4,1 (±1,0)	3 730
4	$1{,}10 \times 10^{-4}$	20,83		0,46	0,10	8 665	111,2 (±0,9)	12,0 (±1,0)	<20
5	$1{,}97 \times 10^{-4}$	23,67		0,53	n.d.	5 892	117,7 (±0,9)	10,3 (±1,1)	<20
6	$8{,}91 \times 10^{-5}$	17,62		0,39	0,04	3 320	122,2 (±0,6)	14,1 (±1,1)	<20
7	$5{,}0 \times 10^{-5}$	14,61		0,34	n.d.	3 047	122,6 (±0,6)	16,3 (±1,0)	<20
8	$7{,}64 \times 10^{-3}$	15,10		0,30	1,10	11 524	105,2 (±0,8)	3,4 (±1,0)	<20
9	$4{,}37 \times 10^{-3}$	17,59		0,34	1,35	6 675	95,1 (±0,8)	7,0 (±1,3)	<20
11	$8{,}52 \times 10^{-3}$	7,73		0,24	32,54	5 574	63,3 (±0,5)	0,7 (±1,0)	2 375
3b	$7{,}73 \times 10^{-2}$	8,40	0,32	0,20	43,00	6 614		0,0 (±1,0)	
7b	$7{,}69 \times 10^{-5}$	15,00	0,67	0,34	0,002				
11b	$5{,}70 \times 10^{-3}$	5,19	0,54	0,16	26,17	7 943			
12	$8{,}98 \times 10^{-3}$	13,37	2,46	0,30	1,82	10 211	101,0 (±0,9)	3,7 (±1,0)	<20
14	$7{,}57 \times 10^{-5}$	11,65	5,30	0,29	n.d.	5 139		4,7 (±1,0)	<20
15	$1{,}90 \times 10^{-2}$	14,81	0,73	0,32	4,82	3 936	77,0 (±0,7)	2,0 (±1,0)	800
16	$2{,}02 \times 10^{-4}$	14,14	1,53	0,33	0,11	8 903		5,8 (±1,0)	<20
17	$3{,}34 \times 10^{-3}$	16,67	0,91	0,37	0,30	9 099	120,8 (±0,8)	7,2 (±1,1)	<20
18	$4{,}68 \times 10^{-4}$	13,27	3,63	0,32	n.d.	7 167		3,3 (±1,0)	<20
19	$8{,}04 \times 10^{-5}$	12,39	2,73	0,30	n.d.	3 211		7,4 (±1,1)	<20
20	$7{,}15 \times 10^{-5}$	13,91	2,61	0,33	n.d.	15 461		10,8 (±1,0)	<20
21	$3{,}45 \times 10^{-2}$	11,25	0,23	0,26	15,08	15 472	89,1 (±0,8)	1,2 (±1,0)	<20
22	$3{,}55 \times 10^{-2}$	10,70	<0,01	0,26	19,27	8 937	59,5 (±0,5)	1,9 (±1,0)	2 875
23	$2{,}61 \times 10^{-4}$	16,60	4,95	0,36	n.d.	10 161		4,8 (±1,1)	<20
24	$7{,}99 \times 10^{-3}$	17,10	0,27	0,36	2,87	10 915	47,2 (±0,6)	0,0 (±1,0)	4 740
25	$7{,}91 \times 10^{-5}$	14,49	4,05	0,34	n.d.	14 844		3,5 (±1,0)	<20
26	$8{,}48 \times 10^{-3}$	15,80	0,12	0,35	1,70	4 588	63,4 (±0,8)	1,0 (±1,0)	2 362
27	$6{,}59 \times 10^{-5}$	13,75	1,19	0,29	0,01	13 841		8,0 (±1,0)	<20

a Samples 1—11 did not contain $HgCl_2$; some O_2 may have been organically consumed. Samples 3b, 7b, 11b and 12—27 contained $HgCl_2$.
b n.d. = not detectable. ^{15}N places lower detection limit of ~0,002 ml CH_4/kg H_2O.
c Corrected to time of collection. Figures include disintegrations of ^{218}Po and ^{214}Po.
d 1 T.U. $^{3}H/H = 10^{-18}$.
e assumes initial groundwater ^{14}C = 85 %.
f Ra (cpm/kg H_2O): Sample 1 = 1,76 (±0,3); 7 = 8,08 (±0,3); 8 = 1,62 (±0,1); 9 = 1,95 (±0,1). See note c.
Note: cpm = counts/min. Divide by ~ 2 for disintegrations per minute.

^{14}C and ^{3}H ages

The ^{14}C ages in Table 3 are calculated on the basis of an initial ^{14}C concentration of (85 ± 5)% modern, in accordance with experience (Vogel, 1970). A large proportion of the samples (16 out of 26) contain ^{14}C and ^{3}H derived from nuclear weapon tests. These waters are therefore less than 20 years old and must be of very superficial origin. The other waters are also of relatively recent date, the oldest having an inferred ^{14}C age of 4 740 years. There is no obvious correlation with locality.

He, CH_4 and Rn

He concentrations range over three orders of magnitude, from $5x10^{-5}$ ml STP/kg H_2O, close to the value to be expected for air-equilibrated water, to as high as 10^{-1} ml STP/kg H_2O in the thermal waters at Badsfontein. CH_4 also shows a wide range in concentrations and has a marked positive correlation with He (Fig. 2). The He and CH_4 rich waters are characterised by an H_2S odour and elevated reduced sulphur concentrations (Fig. 2). (Sulphur analyses were made by the Hydrological Research Institute of the Department of Water Affairs.) Rn concentrations are comparatively uniform, in the range 1 621—15 472 counts/min/kg H_2O, and show no apparent correlation with He concentrations (Fig. 3).

N_2, Ar and O_2

N_2 and Ar concentrations are shown in Fig. 4. Whilst some of the waters have N_2 and Ar concentrations close to the values to be expected for air equilibrated waters, most of the samples have higher concentrations. There is no apparent correlation between N_2 and Ar concentrations and He concentrations (Fig. 4). O_2 contents are generally lower than those for air equilibrated waters, and there is a general tendency for He and CH_4 rich waters to have lower O_2 concentrations (Table 3).

CH_4 — $^{13}C/^{12}C$ ratios

CH_4 from the gas of samples 3b and 11b was analysed for its $^{13}C/^{12}C$ ratio and yielded $\delta^{13}C$ values of −35,7 and −32,2 ‰ (vs. PDB standard) respectively. These values are within the range −28,3 to −41,3 ‰ for CH_4 from a number of boreholes and warm springs in the Beaufort group (Vogel and Talma, unpublished).

Whilst such values are not *totally* unambiguous, CH_4 of biogenic origin, produced by low temperature decay of organic matter in anoxic waters, usually has lower $^{13}C/^{12}C$ ratios (< −50 ‰). The carbon isotope ratios of samples 3b and 11b are more typical of CH_4 of thermal origin (Fuex, 1977; Stahl, 1977).

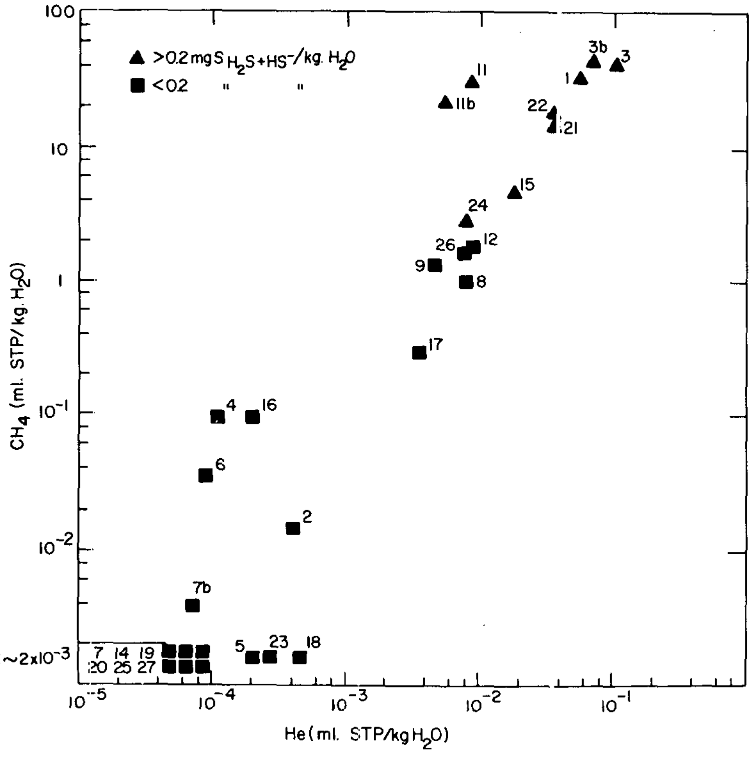

Figure 2
He and CH_4 concentrations, showing waters with higher reduced sulphur contents.

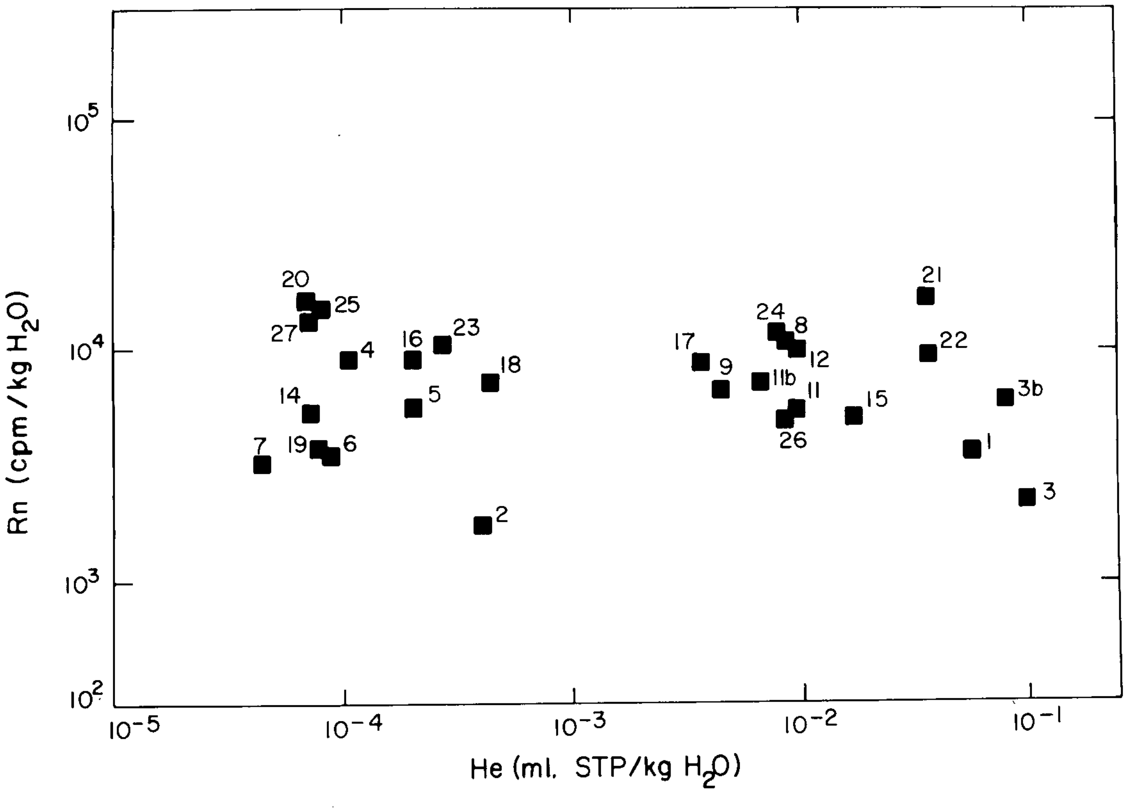

Figure 3
He and Rn concentrations.

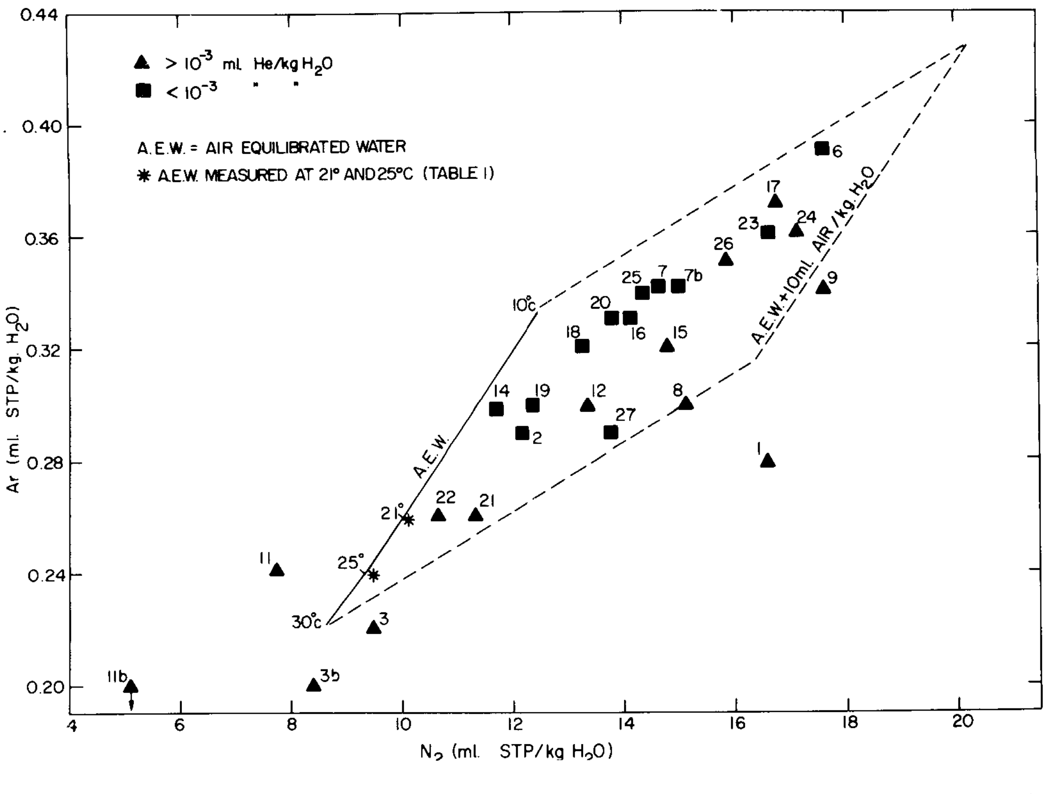

Figure 4
N_2 and Ar concentrations and the relative He concentrations in the sampled waters. N_2 and Ar concentrations are compared with the N_2 and Ar concentrations for water in equilibrium with air (A.E.W.) at 660 mm Hg, 10—30°C. The composition of A.E.W. to which 10 ml STP/kg H_2O of excess air has been added is also known.

He Concentrations

The initial He concentration in groundwater, infiltrating as rain water, must be expected to be about 3,8 x 10^{-5} ml STP/kg H_2O. This is the He concentration for water in equilibrium with air at our ground surface conditions. A number of the waters analysed have concentrations close to this value. For samples with higher He concentrations, however, He produced as alpha particles by radioactive decay of uranium and thorium in the rocks must have been added to the water during its subsurface history.

He concentration vs. age of water

On the basis of their He concentrations the samples superficially separate into two groups: those with less than 5 x 10^{-4} ml He STP/kg H_2O all contain more than 2 T.U. and/or over 90 % ^{14}C, and are therefore of recent origin (< 20 years old); whilst those with more than 5 x 10^{-3} ml He STP/kg H_2O contain less than 2 T.U. and less than 90 % ^{14}C, and are therefore older than 20 years. An intermediate group (samples 8, 9, 12 and 17) have relatively high He concentrations (3 — 9 x 10^{-3} ml STP/kg H_2O) as well as elevated ^3H and ^{14}C contents, and apparently represent mixtures (Fig. 5).

The very high He concentrations in the old waters have the effect that only a small addition of old water to recent water will substantially increase the He concentration of the recent water without significantly affecting its ^{14}C or ^3H concentration. The solid lines in Fig. 5 illustrate the effect of such mixing. The composition of sample 17, for example, can be adequately explained by the addition of about 2 % of water similar to sample 3 to water similar to sample 6. Such admixture of waters with different ages can easily occur in the borehole from which the sample is collected, especially if it penetrates the water table to some depth.

Those waters which have ages between 1 000 and 5 000 years contain between 10^{-2} and 10^{-1} ml He STP/kg H_2O (Fig. 5). On the average, therefore, about 3 x 10^{-2} ml He STP/kg H_2O is added per 2 000 years, or 1,5 x 10^{-5} ml He STP/kg H_2O per year. The different mechanisms which could account for this are discussed below.

Non-He migration model

This model assumes that the He removed by groundwater is derived only from the rocks through which the water passes (i.e. no migration of He to produce areas with anomalously high He

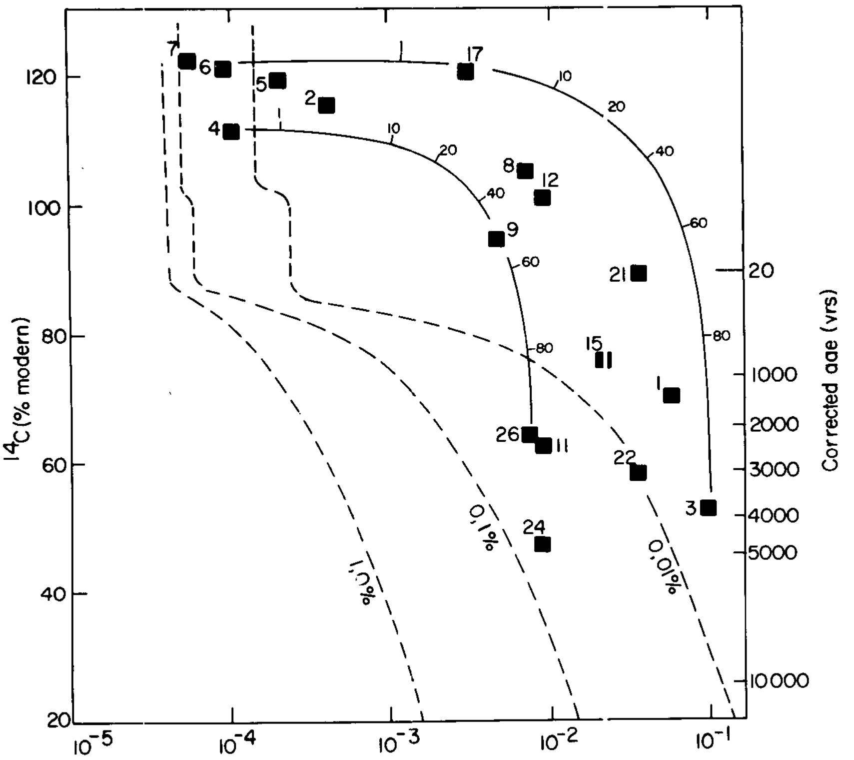

Figure 5

He concentrations in the sampled waters compared with their ^{14}C concentrations and calculated ages. The solid lines show the compositions of mixtures of samples 6 and 3, and 4 and 26, with the % component of the older water; calculated on the basis that the older waters contain about 2,5 times less dissolved carbon than the younger waters (Talma, 1979). The broken lines show the theoretical maximum He concentration in water as a function of its age for a non-He migration model (see text), where the rocks contain 2 p.p.m. U, 7 p.p.m. Th and have porosities of 1,0 to 0,01 %.

concentrations). Then the He concentration in the water will depend on its age, i.e.:

$$He_w = 3,8 \times 10^{-5} + \frac{\alpha}{p}. f.t, \text{ where:}$$

He_w = final He concentration in the groundwater (ml STP/kg)
α = amount of He (ml STP) produced per year per kg rock
p = amount of water (kg) per kg rock (a measure of porosity)
f = $\frac{\text{amount of He removed by groundwater}}{\text{amount of He produced by rocks}}$
t = age of groundwater (years)

The theoretical He concentration in a groundwater as a function of its age for a non-He migration model is shown by the broken lines in Fig. 5. The rocks are assumed to have typical radioactivities of 2p.p.m. U and 7p.p.m. Th (Rogers and Adams, 1969); then $\alpha = 4,3 \times 10^{-10}$. Estimates of the porosity of the rocks are difficult to make, but storage coefficients of Beaufort group sediments in other areas suggest effective porosities of the order of 0,1 to 0,01 % (Boehmer, 1970; Leskiewicz, 1979); then $p = 3,7 \times 10^{-4}$ to $3,7 \times 10^{-5}$.

Whilst most rocks probably retain some of their He (i.e. $f < 1$) the theoretical curves in Fig. 5 assume $f = 1$, so that the calculated He concentration in the water is a *maximum* value for the assumed rock radioactivity and porosity.

The data in Fig. 5 suggest the following:

1. The He content of samples 11, 22, 24 and 26 could be accounted for with this model if the very low porosities of 0,1 to 0,01 % are applicable, and there is negligible retention of He in the rocks.

2. Samples 1, 3 and 15 would require even lower porosities, unless the rocks are anomalously radioactive.

In general, it may be stated that it is difficult, though not impossible, to explain the high He concentrations of the older waters by a non-He migration model.

Release of accumulated He from a fracture zone

High He concentrations could be accounted for if a small part of the sampled water had penetrated and dissolved He from rocks which had previously been accumulating He for several million years. Such a situation, where He is removed from rocks in which it had previously been retained, would be particularly favourable along an active fault zone. In such a zone rocks become fractured, exposing new surfaces to water, and mineral structures are stressed, favouring release of He.

It has been suggested that the warm springs at Badsfontein (samples 1 and 3) and Roodewal (sample 15) may be related to an E-W extension of the fracture zone encountered during drilling of the Orange Fish Tunnel (Olivier, 1972). If this fracture exists, and is active, it could explain the high He concentrations in the waters at Badsfontein and Roodewal, and in sample 12 from above the fracture zone in the tunnel.

Waters with high He concentrations, however, also occur up to 100 km away from this possible fracture zone (samples 17, 21, 24 and 26). These are to the north of the Orange River where there is, to the authors' knowledge, no evidence for a major fault. Therefore, although the thermal waters at Badsfontein contain the highest measured He concentrations they are not markedly anomalous when compared with other waters away from the fracture zone. In this respect the He data has not *detected* a *localised* anomaly in the vicinity of the tunnel fracture zone. It would appear that a more widespread process is required to explain the high He concentrations throughout the sampling area.

He and CH_4 migration

The world's most abundant sources of He are CH_4 rich natural gas deposits, and the correlation between He and CH_4 concentrations in the groundwaters (Fig. 2) suggests that these gases are associated with one another in the sampling area. The high He concentrations in the groundwaters could result from the passage of water through rocks where He and CH_4 have accumulated through migration of gas from depth.

CH_4/He ratios in the sampled waters vary from about 50 to 3 800, but the majority are in the range 200 – 600. Whilst the He concentrations in natural gas are quite variable, and gas solubilities have to be taken into account, such ratios are quite reasonable for natural gas deposits. Zartman *et al.* (1961) calculated the mean He content of natural gas deposits to be 0,2 %, which would suggest a mean CH_4/He ratio of about 400 – 500.

Pockets of CH_4 gas were encountered during oil/gas exploration drilling in the Karoo sediments, and during construction of the Orange Fish Tunnel (Rowsell and De Swardt, 1976). The formation of this CH_4 during diagenesis of the sediments has been discussed by Rowsell and De Swardt (1976). The $^{13}C/^{12}C$ ratios for CH_4 in two of the water samples (discussed above) are consistent with such a thermal origin.

The source of the He is uncertain. It may have been produced in the Karoo sediments themselves, along with CH_4, or have originated in the underlying gneissic basement rocks. However, even though the He may have been originally derived from different source rocks to the CH_4, the migration paths and areas of entrapment of the gases in the Karoo sediments may be largely the same. Impermeable barriers, such as thick shale horizons or dolerite sills, could constitute such traps.

This process of gas migration could be widespread and would account for the distribution of high He and CH_4 concentrations in groundwaters throughout the sampled area. The correlation between the He and CH_4 concentration of a sample and its age suggests that the older waters have either:

1. penetrated to greater depths where higher He and CH_4 concentrations may be expected to occur; and/or

2. have had longer subsurface paths, thereby removing gas from a greater volume of rock.

Rn Concentrations

The radium concentrations in the groundwater samples are low (Table 3) and can account for very little of the Rn in the water. Most of the Rn, therefore, must have been dissolved directly from the rocks.

High Rn concentrations have been reported from some natural gas deposits, and may be associated with faulting (Zartman *et al.* 1961; Bulashevich *et al.* 1976). The Rn concentrations in the sampled groundwaters, however, are quite uniform and show no correlation with the large variations in He and CH_4 concentrations (Fig. 3). In addition, the Rn concentrations are similar to those reported from other groundwater sampling areas (Tanner, 1964; Dyck 1976).

The data suggest that the Rn is not associated with a localised anomaly, such as a fault, and is not particularly associated with natural gas migration. The short half-life of Rn (3,82 days) suggests that Rn from deep sources would have to be communicated fairly rapidly to the surface for such sources to be detectable. In general, the Rn concentrations in the groundwaters of the sampling area are consistent with the Rn being derived essentially from the rocks through which the water passed during the last, near-borehole stage of the water's history.

N_2 and Ar Concentrations

The N_2 and Ar concentrations in the sampled waters are shown in Fig. 4, and are compared with the concentrations for water in equilibrium with air at 10 °C to 30 °C (solid line). Whilst some of the samples have N_2 and Ar concentrations close to those for air equilibrated waters (A.E.W.), most show a trend for an excess of N_2 and Ar above these concentrations.

This excess N_2 and Ar has a N_2/Ar ratio similar to that of air; the effect of adding 10 ml air STP/kg H_2O to air equilibrated water is shown in Fig. 4. The data suggest, therefore, that excess air has been incorporated into the waters during some stage of their history. Air contamination during collection, or leakage during storage of the samples are not suspected.

Air bubbles may be incorporated in rainwater during its infiltration to the groundwater reservoir, a process somewhat analagous to air 'injection' into ocean waters (Craig and Weiss, 1971; Bieri, 1974). The entrapment of air beneath percolating water is a well-known phenomenon to soil scientists, and can play an important part in determining the rate of infiltration (Wilson and Luthin, 1963; Dixon and Linden, 1972; Vachaud *et al.* 1974). Rainfall in the sampling area occurs mainly as intermittent heavy downpours in the summer months October to May, and maximum seasonal water level fluctuations of up to 9 m have been recorded (Olivier, 1972). It is possible that rainwater, originally having N_2 and Ar concentrations in equilibrium with air, may trap air occurring in the pore-space of the soil or subsoil. These air bubbles, if carried down to the water table, could dissolve under the increased hydrostatic pressure.

Evidence for this excess air is not restricted to waters in this study area, it is also found in the spring water below the laboratory basement (Table 1), and elsewhere. The amount of excess air trapped during infiltration may be expected to depend on the nature of the recharge and the structure of the unsaturated zone. Measurements of the amount of excess air may, therefore, provide a means of distinguishing between waters recharged under different conditions.

CH_4 'stripping'

Samples from sites 1, 3 and 11 have N_2 and Ar concentrations distinct from those discussed above (Fig. 4). These three sites are all characterised by particularly high CH_4 concentrations (Table 3), and solubility data (Morrison and Billet, 1952) suggest that the partial pressure of CH_4 in these waters exceeds atmospheric pressure. Under such conditions bubbles of CH_4 may form in the water and, if they are lost to the surface, they will remove N_2 and Ar in proportion to their solubilities. CH_4 'stripping' may also have reduced the amount of He in CH_4-rich waters. This mechanism can explain the N_2 and Ar concentra-

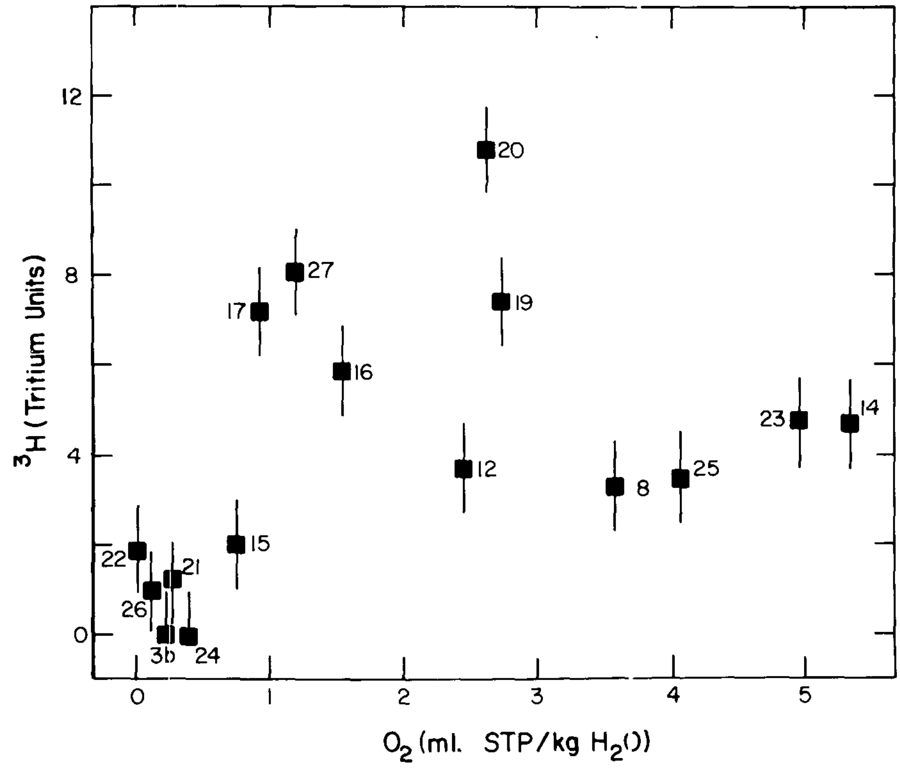

Figure 6
Oxygen and tritium concentrations

tions at sites 3 and 11, and those at Witklipbank Farm (Table 1). Water from site 1, which is an open spring, may have a more complicated CH_4 stripping and atmospheric exchange history.

O_2 Concentrations

O_2 concentrations range from less than 0,01 ml STP/kg H_2O up to 5,30 ml STP/kg H_2O; the latter value being close to the concentration for air equilibrated water (Table 1). Within this range there is a qualitative correlation with the age of the water. O_2 and tritium concentrations are shown in Fig. 6. Young waters with $> 2-3$ T.U. have O_2 concentrations > 1 ml STP/kg H_2O, whilst the older waters with < 2 T.U. have O_2 concentrations < 1 ml STP/kg H_2O.

Such a pattern, with O_2 concentrations decreasing with the age of the water, might be expected in a system where O_2 is progressively removed by oxidation of organic matter in the water. The presence of organic matter in some of the samples to which $HgCl_2$ and H_3PO_4 had not been added was suggested by the growth of a green slime during storage.

Summary

Large variations have been found in the concentrations of He and CH_4 in groundwaters from Beaufort group sediments along a sampling line of 120 km, and a correlation exists between the He $-$ CH_4 concentrations and the ^{14}C $-$ ^3H age of the sample. An order of magnitude gap in the He concentrations may indicate the presence of two groundwater types. The data suggest that low He and CH_4 concentrations are characteristic of the young, recently recharged near-surface waters, with high He and CH_4 concentrations characteristic of the old, deeper groundwaters. The three orders of magnitude range in He and CH_4 concentrations, however, makes these gases particularly sensitive to the mixing of small amounts of old groundwater with large amounts of recent groundwater. This process can account for the high He concentrations of some of the waters.

In sampling areas where there has been no significant migration of He, or release of accumulated He, He concentration data could provide a useful method for the qualitative age determination of groundwaters. In the present sampling area, however, the He concentrations in many of the groundwaters appear to be too high to be accounted for solely by the age of the groundwater. He appears to be associated with CH_4, and the high He concentrations may be explained in terms of the passage of water through Beaufort sediments where He has accumulated with the upward migration of CH_4. The good correlation between He and CH_4 supports the belief that the detection of He anomalies may be useful in petroleum gas exploration.

The magnitude of the Rn concentrations in the groundwaters are *consistent* with the Rn being derived only from the rocks with which the water was last in contact. The relatively narrow range in Rn concentrations, therefore, suggests that the near-surface environment of different waters is fairly uniform throughout the sampling area, as far as the uranium content of the rock is concerned.

Whilst high He concentrations are found in waters possibly associated with the Orange Fish Tunnel fracture zone, similar concentrations are also found in waters away from the fracture zone. This, together with the lack of any Rn anomalies, means that the gas concentration study was not successful in locating a fracture zone.

N_2 and Ar concentration data indicate that an excess component of air has been added to the waters during some part of their history. It is suggested that under certain conditions air bubbles may be trapped by water during infiltration, be carried down to below the water table, and then dissolve under the increased hydrostatic pressure. Since the amount of excess air trapped during infiltration should depend on the local infiltration conditions, studies on the N_2 and Ar concentrations in groundwaters may provide information on these conditions. Under favourable circumstances it may be possible to distinguish between waters from different recharge areas on the basis of N_2 and Ar concentration data.

The older groundwaters in the sampling area are generally found to have low O_2 concentrations, possibly as a result of the progressive oxidation of organic matter in the water. Dissolved O_2 concentration determinations can be made in the field, and provides a qualitative method for distinguishing between recently recharged and older groundwaters.

Acknowledgements

The Water Research Commission are thanked for their financial support of this study. We also gratefully acknowledge: assistance in sample collection from, and discussion with A.S. Talma; the analytical services of other members of the division; access to water chemistry data of P.J. van der Linde and F.D.I. Hodgson; and the co-operation and hospitality afforded by farmers in the sampling area, particularly the Lessings of Badsfontein.

References

BIERI, R.H. (1974) Dissolved conservative gases in seawater. In *The Sea,* Vol. 5, Ed. D. Goldberg, Wiley and Sons, New York.

BOEHMER, W.K. (1970) *Application of the channel method for determining the hydrological characteristics of Karoo sediments tapped by a dyke/dyke-contact aquifer.* Unpubl. proceedings Convention: Water for the Future (Republic of South Africa, Water Year 1970, Pretoria).

BOEHMER, W.K. (1971) *Report on geohydrological investigations along the route of the Orange-Fish Tunnel.* Unpubl. Interim Rep., Geol. Surv. S. Afr.

BREDENKAMP, D.B. (1971) *An investigation of the origin of groundwater and nature of the aquifer system in the vicinity of shaft no. 2 of the Orange-Fish Tunnel.* Unpubl. Rep., Hydro. Research Div., Dept. of Water Affairs, S. Afr.

BULASHEVICH, Yu. P. and BASHORIN, V.N. (1971) Correlation of high helium concentrations in subsurface waters with intersections of disjunctive fractures. *Dokl. Akad. Nauk. S.S.S.R.* **201** (4) 840.

BULASHEVICH, Yu. P., CHALOV, P.I., TUZOVA, T.V., ALEKHINA, V.M., MERKULOVA, K.I. and SVETLICHNAYA, N.A. (1976) The helium content and the ratio of the uranium series isotopes in the water of the north Kirgizian fracture zone. *Izv., Earth Physics* **1** 78.

CLARKE, W.B. and KUGLER, G. (1973) Dissolved helium in groundwater: a possible method for uranium and thorium prospecting. *Econ. Geol.* **68** 243.

CRAIG, H. and WEISS, R.F. (1971) Dissolved gas saturation anomalies and excess helium in the ocean. *Earth Planet. Sci. Letters* **10** 289.

CRAIG, H., LUPTON, J.E., CHUNG, Y. and HOROWITZ, R.M. (1975) *Investigation of radon and helium as possible fluid-phase precursors to earthquakes.* Tech. report I. Scripps Institution of Oceanography. 27 pp.

DIXON, R.M. and LINDEN, D.R. (1972) Soil air pressure and water infiltration under border irrigation. *Proc. Soil Sci. Soc. Amer.* **36** 948.

DYCK, W. (1976) The use of Helium in mineral exploration. *J. Geochem. Exploration* 5 3.

EREMEEV, A.N., SOKOLOV, V.A., SOLOVOV, A.P. and YANITSKII, I.N. (1973) Application of helium surveying to structural mapping and ore deposit forecasting. In: *Geochemical Exploration 1972.* (Inst. Min. Metall., London) 183.

FRIEDMAN, I. and DENTON, E.H. (1976) A portable helium sniffer. *Jour. Res. U.S. Geol. Survey* 4 35.

FUEX, A.N. (1977) The use of stable carbon isotopes in hydrocarbon exploration. *J. Geochem. Exploration* 7 155.

LESKIEWICZ, A.F. (1979) Department of Water Affairs, Republic of South Africa. Personal communication.

MAZOR, E. and VERHAGEN, B. Th. (1976) Hot springs of Rhodesia: their noble gases, isotopic and chemical composition. *J. Hydrol.* **28** 29.

MAZOR, E., VERHAGEN, B. Th. and NEGREANU, E. (1974) *Hot springs of the igneous terrain of Swaziland — their noble gases, hydrogen, oxygen and carbon isotopes and dissolved ions.* Isotope Techniques in Groundwater Hydrology (Proc. Symp. Vienna) I.A.E.A., 29.

MORRISON, T.J. and BILLETT, F. (1952) The salting-out of non-electrolytes. Part II. The effect of variation in non-electrolyte. *J. Chem. Soc.* 3819.

NOGUCHI, M. and WAKITA, H. (1977) A method for continuous measurement of radon in groundwater for earthquake prediction. *J. Geophys. Res.* 82 1353.

OLIVIER, H.J. (1972) Geohydrological investigation of the flooding of Shaft 2, Orange-Fish Tunnel, north-eastern Cape Province. *Trans. Geol. Soc. S. Afr.* 75 197.

ROGERS, J.J.W. and ADAMS, J.A.S. (1969) Thorium : Uranium. In *Handbokok of Geochemistry* K.H. Wedepohl (ed). (Springer, Berlin), 90-K and 92-K.

ROWSELL, D.M. and DE SWARDT, A.M.J. (1976) Diagenesis in Cape and Karoo Sediments, South Africa, and its bearing on their hydrocarbon content. *Trans. Geol. Soc. S. Afr.* **79** 81.

STAHL, W.J. (1977) Carbon and nitrogen isotopes in hydrocarbon research and exploration. *Chem. Geol.* **20** 121.

TALMA, A.S. (1979) National Physical Research Laboratory, C.S.I.R. Personal communication.

TANNER, A.B. (1964) Radon migration in the ground: a review. In *The Natural Radiation Environment* (Adams and Lowder (eds) (University of Chicago press) 161.

VACHAUD, G., GAUDET, J.P. and KURAZ, V., (1974) Air and water flow during ponded infiltration in a vertical bounded column of soil. *J. Hydrol.* **22** 89.

VAJNER, V. (1974) The Doringberg fault and its relation to the post-Waterburg deformation. *Trans. Geol. Soc. S. Afr.* **77** 295.

VAN DER LINDE, P.J. and HODGSON, F.D.I. (1976) 'n Geohidrologiese ondersoek van die Oranje-Visriviertonnelgebied in die omgewing van Venterstad, Kaapprovinsie. *Bull. Inst. Groundwater Stud.*, Bloemfontein 2 42p.

VAN DER LINDE, P.J. and HODGSON, F.D.I. (1977) Die gebruik van hidrochemiese tegnieke in grondwatereksplorasie in die Venterstad omgewing, Kaapprovinsie. *Water S.A.* 3 (3) 166.

VOGEL, J.C. (1967) *Investigation of groundwater flow with radiocarbon.* Isotopes in Hydrology (Proc. Symp. Vienna, 1966) I.A.E.A., 355.

VOGEL, J.C. (1970) *Carbon-14 dating of groundwater.* Isotope Hydrology 1970 (Proc. Symp. Vienna) I.A.E.A., 225.

VOGEL, J.C. and MARAIS, M. (1971) Pretoria radiocarbon Dates 1. *Radiocarbon,* **13** 378.

VOGEL, J.C., THILO, L. and VAN DIJKEN, M. (1974) Determination of groundwater recharge with tritium. *J. Hydrol.* **23** 131.

WEISS, R.F. (1970) The solubility of nitrogen, oxygen and argon in water and seawater. *Deep-Sea Res.* **17** 721.

WEISS, R.F. (1971) Solubility of helium and neon in water and seawater. *J. Chem. Eng. Data* **16** 235.

WILSON, L.G. and LUTHIN, J.N. (1963) Effect of air flow ahead of the wetting front on infiltration. *Soil Sci.* **96** 137.

WINTER, H. DE LA R. and VENTER, J.J. (1970) *Lithostratigraphic correlation of recent deep boreholes in the Karoo-Cape sequence.* In Proceedings and Papers, I.U.G.S. 2nd. Gondwana symposium (Ed. S.H. Haughton, Publ. C.S.I.R. Pretoria) 395.

ZARTMAN, R.E., WASSERBURG, G.J. and REYNOLDS, J.H., (1961) Helium, argon and carbon in some natural gases. *J. Geophys. Res.* **66** 277.