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DISSOLVED IONS, STABLE AND RADIOACTIVE ISOTOPES AND NOBLE GASES IN THERMAL WATERS OF SOUTH AFRICA

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ABSTRACT

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Sixteen thermal springs of South Africa were studied. Chemically, two salinity groups were found; one group at 3—13 meq l^{-1} TDI issuing in crystalline terrains, and a more saline group, 30—80 meq l^{-1} TDI, mostly associated with sedimentary rocks.

Stable hydrogen and oxygen isotopic compositions indicate direct recharge by heavy rains and negligible intermixing with water from adjacent rivers.

Tritium concentrations are generally low. In a few cases, tritium at the limit of detection, combined with sub-recent ^{14}C, might indicate some admixture of recent water.

Dissolved Ne, Ar, Kr and Xe occur at atmospheric isotopic composition and at concentrations indicating intake temperatures of 15—35°C. These intake temperatures show a clear dependence of climatic and geographical factors. Some of the springs contain significant amounts of radiogenic helium, accompanied by radiogenic argon. The ($^{4}He/^{40}Ar$) radiogenic values are in the range of 1—7, indicating common rocks as the origin rather than concentrates (ores) of U and Th. Low helium values in some of the thermal springs are explained by large flows and short residence times.

INTRODUCTION

South Africa has over 87 thermal springs, with temperatures in the range of 25—61°C. These springs have been the subject of many studies by a number of investigators, e.g. Gevers (1942, 1963), Kent (1942, 1946, 1949, 1962a, b, 1972, 1979), Visser (1962), von Backström (1962), Temperley (1964, 1975) and Kent et al. (1966). These workers described the geology, chemical composition and medical aspects of individual thermal springs, data which have been collected in a review paper by Kent (1969) and more recently by Hoffmann (1979).

The major emphasis in the present study was the measurement of parameters not measured previously. These included the stable hydrogen, oxygen

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TABLE I

Thermal spring data

No.	Spring	Sampling date	Temperature (°C)	Geology (after Kent, 1969)
26	Tshipise	03.1972	58	junction of two faults in Karoo System
30	Eiland (Letaba)	03.1972	39	fissure associated with dyke and fault in Archaean granite-gneiss
20	Warmbad	12.1971	36	thrust—fault in Bushveld granite
18	Natal Spa	12.1971	37	shear zone in Archaean granitic gneiss
23	Lilani	12.1971	40	fracture zone in Archaean gneiss and amphibolite
1	Florisbad	12.1971	29	fractures, associated with a fault (?) in dolerite intruding Karoo System
16	Beersheba	12.1971	26	
13	Aliwal North	12.1971	34	dolerite dyke in Karoo System
12	The Springs	12.1971	24	
9	Olifants	12.1971	48	fault in Table Mountain Series
43	Montagu Baths	12.1971	42	fault (?) in Table Mountain Series
42	Caledon	12.1971	49	fault in Table Mountain Series
2,40	Brandvlei	12.1971,72	61	fault in Table Mountain Series
3,41	Goudini	12.1971,72	37	fault in Table Mountain Series
4,44	Malmesbury	12.1971.72	31	fracture zone in Cape granite
45	Die Bad, Citrusdal	12.1972	43	fault cutting syncline in Cape System
50	Warmbaths	11.1972	50	fault separating Bushveld granite from Karoo System

and carbon isotopes, tritium and ^{14}C and the dissolved noble gases (He, Ne, Ar, Kr and Xe). The dissolved ions were also measured.

Many thermal springs elsewhere occur in volcanically active areas and the heat and at least part of the dissolved ions are taken to be of volcanic origin; many others issue in marine sedimentary rocks and at least a part of the dissolved ions is attributed to flushing from these rocks. The South African thermal springs occur, in contrast, in areas with no recent volcanism and many of them issue in crystalline terrains.

CHEMICAL COMPOSITION

The chemical composition of the spring waters studied can be classified into two groups (Tables I—II; Fig. 1):

(a) A relatively saline group, containing 936—2364 $mg\,l^{-1}$ total dissolved ions (TDI), or 30—80 $meq\,l^{-1}$ TDI. In this group NaCl is the dominating salt. To this group belong (in increasing order of salinity): Eiland, Malmesbury, Aliwal North and Florisbad. Tshipise, with almost 400 $mg\,l^{-1}$ TDI, is also NaCl-dominated and could be classified in this group.

TABLE II

Chemical composition, meq l^{-1} and mg l^{-1}*

No.	Spring	K	Na	Mg	Ca	Cl	SO_4	Alk.	Total cations	Total anions	Total ions
3, 41	Goudini	0.03	0.26	0.66	0.50	0.40	0.52	0.44	1.45	1.41	2.9
		1	6	8	10	14	25	27			91
2, 40	Brandvlei	0.05	0.30	0.74	0.40	0.59	0.40	0.56	1.50	1.60	3.1
		2	7	9	8	21	19	34			100
12	The Springs	0.03	0.78	0.82	0.20	1.21	0.31	0.23	1.83	1.81	3.6
		1	18	10	4	43	15	14			105
9	Olifants	0.23	0.74	1.15	0.65	1.21	0.46	1.13	2.77	2.86	5.63
		9	17	14	13	43	22	62			170
18	Natal Spa	0.05	2.26	0.58	0.40	1.01	0.77	1.10	3.29	3.10	6.4
		2	52	7	8	36	37	54			196
20	Warmbad	0.05	2.61	0.41	0.40	0.60	0.65	2.03	3.47	3.48	6.9
		2	60	5	8	21	31	96			223
23	Lilani	0.05	3.91	0.25	0.20	1.21	1.81	1.10	4.41	4.33	8.7
		2	90	3	4	43	87	39			268
26	Tshipise	0.10	6.22	0.082	0.10	3.83	0.48	1.66	6.51	6.35	12.9
		4	143	1	2	136	23	88			397
16	Beersheba	0.03	3.70	1.97	0.85	1.80	1.60	3.15	6.54	6.76	13.31
		1	85	24	17	64	77	164			432
30	Eiland	0.36	13.3	0.16	1.60	13.3	0.85	1.13	15.4	15.5	30.9
		14	305	2	32	473	41	69			936
4, 44	Malmesbury	0.28	14.8	1.07	2.54	16.1	1.17	1.10	18.7	18.5	37.2
		11	340	13	51	571	56	54			1096
13	Aliwal North	0.05	15.6	0.50	4.24	19.1	0.96	0.44	20.5	20.7	41.2
		2	360	7	85	678	46	27			1205
1	Florisbad	0.20	34.8	0.58	4.64	38.0	1.35	0.67	40.2	40.2	80.4
		8	800	7	93	1350	65	41			2364

*Table arranged in increasing order of salinity. Analysis were done by the Chemical Laboratory of the Geological Survey of Botswana.

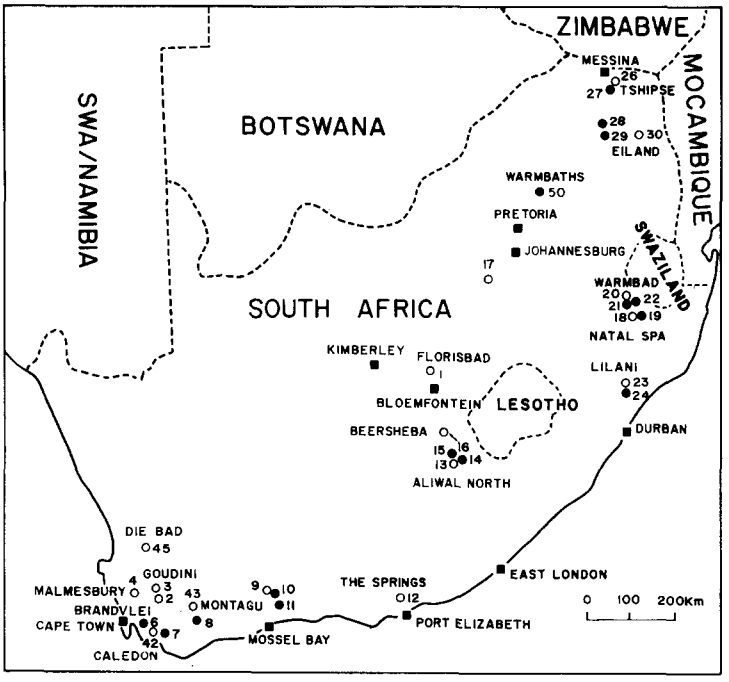

Fig. 1. Sample location map (○ = thermal springs; ● = rivers; numbers as in tables.)

(b) A fresher group, with 90—432 mg l^{-1} TDI, or 3—13 meq l^{-1} TDI. In this group no ions dominate specifically. To this group belong the remaining eleven thermal springs listed in Tables I—II.

Similar low-salinity thermal waters were observed in the igneous and metamorphic terrains of Swaziland (Mazor et al., 1974). There, six springs were found to contain 120—190 mg l^{-1} TDI, and only one spring, Sipofaneni, contained 400 mg l^{-1} TDI, predominantly NaCl. It has been suggested that the water in this last spring had some contact with Karoo sediments, exposed nearby. The NaCl-dominated Florisbad, Aliwal North and Tshipise water issue in Karoo sediments (Kent, 1969). The question of the salinity of the waters of Malmesbury and Eiland (Letaba), which are also NaCl dominated, is as yet unresolved.

STABLE HYDROGEN AND OXYGEN ISOTOPIC COMPOSITION

The stable hydrogen and oxygen isotopic values of the thermal springs are plotted along with an estimated mean rain line for southern Africa (I.A.E.A., 1981) being $\delta D = 6\delta^{18}O + 5$. The values scatter over a significant range (Table III; Fig. 2) but no geographical correlation is observed. This seems to rule out possible variations due to differences in the average isotopic composition of rains or dependence on the total rain amounts in

TABLE III

Isotopic data of thermal springs*

No.	Spring	Dominant ions	δD (‰)	$\delta^{18}O$ (‰)	Tritium (TU)	^{14}C (pmC)	$\delta^{13}C$ (‰)
26	Tshipise	Na—Cl, HCO_3	−34.1 ± 1.9	−6.17 ± 0.10	0.6 ± 0.3		
30	Eiland	Na—Cl	−18.5 ± 1.9	−4.86 ± 0.10	0.5 ± 0.3		
20	Warmbad	Na—HCO_3	−16.8 ± 1.9	−3.85 ± 0.10			
18	Natal Spa	Na—HCO_3, Cl	−18.5 ± 1.9	−2.95 ± 0.09			
23	Lilani	Na—SO_4, Cl, HCO_3	−20.0 ± 1.4	−4.15 ± 0.10			
1	Florisbad	Na—Cl	−36.5 ± 1.4	−6.82 ± 0.15	0.3 ± 0.3		
16	Beersheba	Na—HCO_3	−37.8 ± 1.9	−5.09 ± 0.09	1.1 ± 0.4		
13	Aliwal North	Na—Cl	−31.3 ± 1.9	−5.96 ± 0.09	1.3 ± 0.4		
12	The Springs	Mg, Na—Cl	−14.9 ± 1.9	−4.88 ± 0.12	0.5 ± 0.3		
9	Olifants	Mg, Na, Ca—Cl, HCO_3	−35.3 ± 1.9	−7.41 ± 0.12	0.3 ± 0.3		
43	Montagu Baths			−7.07		49.1 ± 0.6	−21.3 ± 0.2
42	Caledon			−6.17	0.8 ± 0.3	47.2 ± 0.6	−21.6 ± 0.2
2, 40	Brandvlei	Mg, Ca, Na—Cl, HCO_3, SO_4	−30.9 ± 1.4	−6.14 ± 0.15	0.5 ± 0.2	70.7 ± 1.4	−18.9 ± 0.2
3, 41	Goudini	Mg, Ca—SO_4, HCO_3, Cl	−21.1 ± 1.4	−4.78 ± 0.15	1.1 ± 0.3	78.2 ± 0.7	−24.5 ± 0.2
4, 44	Malmesbury	Na—Cl	−18.3 ± 1.4	−4.18 ± 0.15	0.3 ± 0.2	30.6 ± 0.4	−16.6 ± 0.2
45	Die Bad			−4.19 ± 0.15	1.1 ± 0.3	70.7 ± 0.7	−20.0 ± 0.2
50	Warmbaths	Na—Cl, HCO_3	−28.9 ± 2.0	−5.9 ± 0.2	0.2 ± 0.2	8.6 ± 0.4	− 6.8 ± 0.2

*Arranged in a geographical order (Fig. 1).

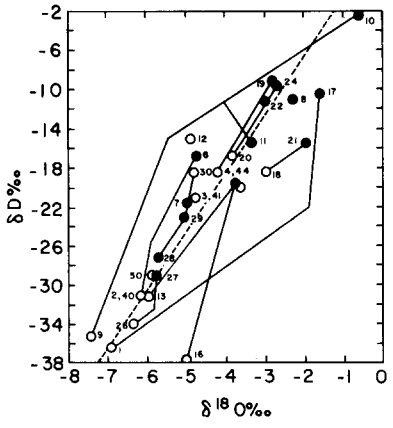

Fig. 2. Stable hydrogen and oxygen isotopic composition (○ = thermal springs; ● = rivers). The lines connect the values of thermal springs with those of the adjacent river (Tables IV and V; Fig. 1). The thermal springs are as a rule isotopically lighter than the adjacent rivers (*broken line* = estimated mean precipitation line: $\delta D = 6\delta^{18}O + 5$).

the various geographical provinces. The scatter in the values must reflect some other mechanisms.

Comparison of the stable hydrogen and oxygen isotopic composition of the sampled thermal springs with the adjacent river samples (Tables III and IV; Fig. 1) reveals that at the time of sampling the river waters were enriched in D and ^{18}O with respect to the adjacent thermal springs. This general trend is seen in Fig. 2 and is similar to the hot springs of Swaziland (Mazor et al., 1974). This observation indicates that the thermal springs are recharged either by direct (selective) rain infiltration without the effect of the averaging mechanism and evaporation of rivers, or were recharged during a different (colder?) climatic regime that could have had isotopically lighter rains. The few ^{14}C results at hand reveal no correlation with the hydrogen and oxygen isotopic composition as is seen in Table III. It does therefore not appear as though the springs were recharged under a climatic regime substantially different from the present.

The marked difference in the isotopic composition of thermal springs and the nearby rivers may be applied as an indication that the thermal waters issue with little or no intermixing with infiltrated river water. Examples are Lilani ($\delta D = -20.0‰$ and $\delta^{18}O = -4.1‰$) and the nearby river branch joining the Mvoti River ($-9.4‰$; $-2.75‰$) the Beersheba springs ($-37.8‰$; $-5.1‰$) and the adjacent section of the Orange River ($-19.6‰$; $-3.73‰$) and the Olifants Spring ($-30.3‰$; $-7.4‰$) and Olifants River ($-2.4‰$; $-0.62‰$) only 100 m away. These results are, of course, dependent on the time of sampling of the rivers.

Although the results in Fig. 2. scatter considerably from the estimated mean rain line, it appears to be random and no significant shift of $\delta^{18}O$ to higher values is observed. Therefore, in none of the thermal waters does a high temperature component ($> 150°C$) seem to be present.

TABLE IV

Isotopic data of river samples*

No.	River sample	Sampling date	δD (‰)	$\delta^{18}O$ (‰)
27	Mutamba, at Tshipise	03.1972	−29.0 ± 1.3	−5.67 ± 0.10
28	Middle Letaba, Soekmekaar—Tzaneen Road	03.1972	−26.3 ± 1.3	−5.77 ± 0.10
29	Letaba, at Tzaneen	03.1972	−23.0 ± 1.3	−5.06 ± 0.10
17	Vaal, route N-*1*, near Parys	12.1971	−10.5 ± 1.9	−1.68 ± 0.09
21	branch joining Pongola, upstream from Warmbad	12.1971	−15.7 ± 1.9	−1.94 ± 0.10
22	Pongola, N. of Paulpietersburg	12.1971	−10.9 ± 1.0	−3.00 ± 0.10
19	Bivane, upstream at Natal Spa	12.1971	− 9.2 ± 1.9	−2.86 ± 0.09
24	waterfall joining Mvoti, near Lilani	12.1971	− 9.4 ± 1.0	−2.74 ± 0.10
15	Caledon, N. of Aliwal North	12.1971		−5.50 ± 0.09
14	Orange, near Aliwal North	12.1971	−19.6 ± 1.9	−3.73 ± 0.09
11	Olifants, route N-*2*, S. of Oudtshoorn	12.1971	−15.5 ± 1.9	−3.43 ± 0.12
10	Olifants, 100 m upstream from spring	12.1971	− 2.4 ± 1.9	−0.62 ± 0.12
8	Bree, route N-*2*, at Swellendam	12.1971	−10.9 ± 1.4	−2.31 ± 0.12
7	Palmiet, route N-*2*, ear Elgin	12.1971	−21.6 ± 1.4	−5.02 ± 0.12
6	Diepgat, route N-*2*, near Somerset West.	12.1971	−16.7 ± 1.4	−4.27 ± 0.15

* Table arranged in geographical order.

^{14}C AND TRITIUM CONTENTS

Because of the possibility, at the time of measurement, of environmental contamination all tritium results below 1 TU*[1] should be regarded as effectively 0. All the samples analysed can therefore be taken as essentially tritium-free, with those just above 1 TU taken to be at the limit of detectability. Admixture of recent water (with at least several TU) is therefore small in all cases. The generally low alkalinity of river water implies that the effect on the ^{14}C contents of the springs is negligible.

The initial concentration of ^{14}C at recharge for the different hydrothermal systems is not known. In all measured cases, except Warmbaths, the $\delta^{13}C$-values are low ($< -16‰$) and within the range of biogenic carbon. It can therefore be assumed with some certainty that the initial ^{14}C concentrations in these cases might have been as high as 80—90 pmC*[2] and that no significant exchange with ^{14}C-free aquifer materials has taken place.

Brandvlei, Goudini and Die Bad contain ^{14}C at 71—78 pmC. These subrecent values suggest fairly short turnover times. The large discharge of Brandvlei (11,000 m^3 day^{-1}; Kent, 1969) supports this conclusion in one instance.

Montagu Baths, Caledon and Malmesbury contain only 30—49 pmC, suggesting turnover times of several thousands of years. Warmbaths produces water of surprisingly great apparent radiocarbon age (~ 19,000 yr. B.P.) and much higher $\delta^{13}C$, which sets it apart from the Cape springs for which carbon isotope data are available.

No correlation is observed between the spring temperatures and their radiocarbon contents.

THE DISSOLVED ATMOSPHERIC NOBLE GASES

The noble gases were collected and mass spectrometrically analyzed by techniques described by Mazor (1977). The analytical errors for He and Ne are estimated to be ± 8%, whereas for Ar, He and Xe the error is ± 5%. For the isotopic ratio of $^{40}Ar/^{36}Ar$ the error is ± 2% and a similar error is estimated for the ratios of the common isotopes of Ne, Kr and Xe. The following trends are observed.

(a) The results of duplicate and triplicate samples collected at the same springs are in good agreement (Table V).

(b) The relative abundances are close to those in air-saturated water between the limits of 17° and 40°C (Fig. 3).

(c) The isotopic ratios of the major isotopes of Ne, Ar (except for a few cases of radiogenic enrichment — Table V), Kr and Xe were found to be identical to the atmospheric ratios, within the limits of the analytical accuracy.

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*[1] Tritium units 1 TU $\equiv [^3H]/[^1H] = 10^{-18}$.

*[2] Per cent modern carbon: % of ^{14}C activity of atmospheric CO_2 before 1850.

Points (a)—(c) suggest that the waters studied are of meteoric origin.

(d) The representative values of the Ar, Kr and Xe concentrations in Table V were first corrected for the estimated mean elevation of the most likely intake areas and normalised to mean sea level (Mazor, 1977). The elevations and resulting correction factors are given in Table VI. These were then used to read off intake, or recharge, temperatures from air-saturation curves (cf. Mazor et al., 1974; Mazor and Verhagen, 1976). This should give the temperature at which the recharging water infiltrated (Table V). Such deduction is based on a number of assumptions, e.g. that water equilibrated with air prior its entrance into the ground; that it was kept as a closed system in the aquifer and no losses or gains occurred prior to or during sampling (Mazor, 1977). The results in Table VI reveal the following:

(1) In nine out of the eleven cases the temperatures deduced from the Ar, Kr and Xe concentrations agree to within ± 2° to ± 5°C, suggesting small gas losses. In the other two cases, the average deviation is ± 9°C, which suggests significant gas losses.

The deduced temperatures range from 15° to 39°C most of them being "reasonable" rain intake temperatures.

(2) The springs located in the winter rainfall area of the Western Cape (Montague, Caledon, Brandvlei, Goudini and Malmesbury) give a mean value of the calculated average temperatures (Table VI) of 20 ± 4°C. Those in the rest of the country (Tshipise, Eiland, Warmbaths, Natal Spa and Lilani) give a mean temperature of 30 ± 4°C. Although its temperature places Die Bad into the second category, it has not been included in either of the groups; geographically it lies in a borderline area between summer and winter rainfall regimes. In addition, the noble gas sampling conditions were doubtful (see Table V).

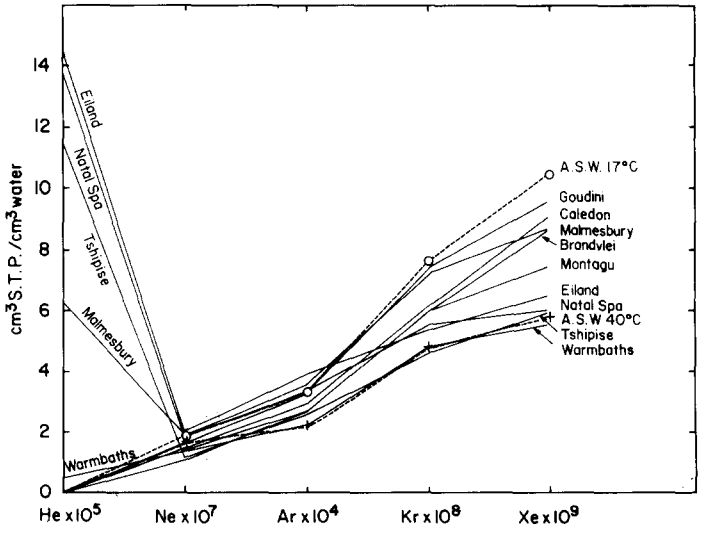

Fig. 3. Dissolved noble-gas patterns. ASW 17°C (○) and 40°C (+) — values for air-saturated water at 17° and 40°C.

TABLE V

Noble gases; 10^{-8} cm^3 STP per cm^3 water

Run	No.	Source	Temp. (°C)	He	Ne	Ar	Kr	Xe	$\frac{(^{40}Ar/^{36}Ar)_{samp}}{(^{40}Ar/^{36}Ar)_{atm}}$	$^{40}Ar_{rad}$	$(^4He/^{40}Ar)_{rad}$
264	*26*	Tshipise	58	9,970	11.1	27,100	3.54	0.47	1.13		
270				11,700							
278				6,770	13.5	26.500	5.68	0.72	1.06		
		rep. value*1		11,700	12.3	26.800	4.61	0.60	1.10*2	2,680	4.36
268	*30*	Eiland	39	14,500	22.0	38,600	4.75	0.55	1.25		
280				10,500	20.8	42,000	6.02	0.76	1.33		
		rep. value*1		14,500	21.4	40,300	5.39	0.66	1.29*2	11,690	1.24
320	*50*	Warmbaths	50	540	14.9	24,600	4.78	0.49	0.98		
331				440	14.4	23,100	5.01	0.62	0.96		
		rep. value*1		540	14.7	23,385	4.90	0.56	0.97		
248	*18*	Natal spa	37	14,100	20.1	34.500	5.54	0.62	1.05		
250				6,860	18.8	34.900	5.61	0.59	1.06		
		rep. value*1		14,100	19.5	34,700	5.58	0.61	1.06*2	2,080	6.78
251	*23*	Lilani	40	3,540	16.9	31,000	5.32	0.56	1.03*2	930	3.81
328	*43*	Montagu	42	40	15.3	28.100	6.36	0.77	0.93		
326		Baths		100							
314				46	16.4	31,900	5.66	0.72	0.93		
		rep. value*1		100	15.9	30,000	6.01	0.75	0.93		
330	*42*	Caledon	49	56	11.7	27,500	6.20	1.04	0.97		
325				59	10.9	30,400	7.01	0.94	0.97		
312				51	11.8	26,000	5.41	0.78	1.01		
		rep. value*1		59	11.5	27,970	6.21	0.92	0.98		

311	*40*	Brandvlei	61	41	13.6	28,700	6.07	0.85	0.96
321				28	16.6	27,800	6.04	0.63	0.95
323				33	14.6	26,800	6.02	0.82	0.97
		rep. value*1		41	14.9	27,770	6.04	0.77	0.96
316	*41*	Goudini	37	60	16.6	33,100	7.22	0.93	0.96
324				39	17.7	34,300	7.68	1.01	0.98
		rep. value*1		60	17.2	33,700	7.45	0.97	0.97
246	*44*	Malmesbury	31	3,550	18.9	36,200	7.03	0.88	0.99
317	*44*			6,330					
322	*44*			1,870	20.2	36,500	7.59	0.86	0.97
		rep. value*1		6,330	19.6	36,350	7.31	0.87	0.98
332	*45*	Die Bad*3	43	8	13.0	21,000	4.96	0.73	
327				21	11.7	26,600	5.98	0.81	0.99
319				10	13.9	24,300	5.26	0.71	0.94
		rep. value*1		21	12.9	23,970	5.40	0.75	0.97

*1 Representative value — maximum helium value (assuming minimal diffusion losses) and average values for the other noble gases.
*2 Values over 1.02 were regarded as analytically significant to calculate $^{40}Ar_{rad}$.
*3 Doubtful sampling conditions, re-equilibration might have occurred and could explain the low He values.

TABLE VI

Noble-gas-deduced intake temperatures*

	Spring Temp. (°C)	Mean intake elevation (m a.m.s.l.)	Correction factor	Deduced intake temperature (°C)			Average temperature (°C)	^{14}C (pmC)
				Ar	Kr	Xe		
Tshipise	58	800	1.10	32	37	35	35 ± 3	
Eiland	39	800	1.10	20	29	30	26 ± 6	
Warmbaths	50	1,200	1.15	30	32	37	33 ± 4	
Natal Spa	37	800	1.10	14	27	34	25 ± 10	
Lilani	40	600	1.08	18	30	39	29 ± 10	
Montagu Baths	42	500	1.07	19	24	27	23 ± 4	49
Caledon	49	400	1.05	24	24	19	22 ± 3	47
Brandvlei	61	1,000	1.13	20	22	23	22 ± 2	71
Goudini	37	800	1.10	12	16	17	15 ± 3	78
Malmesbury	31	250	1.03	12	18	22	17 ± 5	31
Die Bad	43	600	1.08	34	30	27	30 ± 4	71

* Table arranged in geographical order

The marked difference in the mean intake temperatures in non-overlapping groups can be explained by the different seasonality of the rainfall regimes, where the rain falls respectively in the hottest and coolest months of the year.

The absolute values seem somewhat high when compared to present-day mean seasonal surface temperatures. These are 22—24°C for the interior in summer and 12—14°C for the Western Cape in winter. The discrepancy may be partially explained by the gas losses discussed under (1). Another factor may be the recharge process. As the infiltrating rain water will undergo its final equilibration with air in the surface layers of the soil (aerated zone), it can be expected that during summer rain storms the equilibration temperature will, on the average, be higher than the mean temperatures; in the winter rainfall areas the lower air temperatures will be moderated in the soil by thermal inertia and biological activity,

The calculated mean intake temperatures therefore appear to reasonably reflect differences in climatic, and in this case also geographic, factors.

(2) No correlation with the ^{14}C values is observable. The variations within the deduced intake groups therefore cannot be explained by a climate—time dependence.

(3) Temperatures calculated from the Ar, Kr and Xe values for Brandvlei and Goudini produced good internal agreement. Yet, these springs, in close proximity to each other, gave considerably different temperatures: 22 ± 2°C for Brandvlei and 15 ± 3°C for Goudini. This could indicate a difference in intake histories, as is suggested also by the differences in the δD- and $\delta^{18}O$-values — (— 30.9 and — 6.14‰, respectively) for Brandvlei and (— 21.1 and — 4.78‰, respectively) for Goudini.

THE DISSOLVED RADIOGENIC NOBLE GASES

Helium occurs in air-saturated water with a maximum concentration of $5 \cdot 10^{-8}$ cm^3 S.T.P. per cm^3 water. In Tshipise, Eiland, Natal Spa, Lilani and Malmesbury, the helium content is over three orders of magnitude higher, and two orders of magnitude for Warmbaths. Such helium enrichments are common in thermal springs (Mazor, 1977) and were found also in Swaziland (Mazor et al., 1974), Zimbabwe (Rhodesia) (Mazor and Verhagen, 1976) and in South West Africa/Namibia (Verhagen and Mazor, 1983). The excess helium is attributed to flushing of radiogenic helium, from the decay of uranium and thorium, which occur in common rocks in the ppm range.

The helium content in Montagu Baths, Caledon, Brandvlei, Goudini and Die Bad is surprisingly low for thermal springs.

No correlation between the helium content of the waters and their observed temperature is found. There is no clear correlation with the ^{14}C values, nor with the salt contents. Although these springs all issue in Table Mountain sandstone, with relatively low uranium and thorium concentrations the observed differences in helium contents covering three orders of magnitude cannot be related to this fact alone.

The low helium content of one of the springs, i.e. Brandvlei, might be related to the enormous discharge of this spring, which dilutes the available helium from the rocks, as well as to a rather low residence time.

The ratio of $^{40}Ar/^{36}Ar$ was observed in a number of springs to be larger than the atmospheric value, measured in each mass spectrometric run with respect to an atmospheric standard. The excess ^{40}Ar in these cases is attributed to radiogenic argon, formed in the decay of ^{40}K in the aquifer rocks. The amount of excess radiogenic argon was calculated by multiplying the total argon content by the factor:

$$\left[\frac{(^{40}Ar/^{36}Ar)_{sample}}{(^{40}Ar/^{36}Ar)_{atmospheric}} - 1\right]$$

and is given in Table V.

The ratios of ($^4He/^{40}Ar$) radiogenic (last column, Table V) vary in the range of 1—7, which is a narrow range considering that the involved radiogenic isotopes originate from parent-isotopes of two different element groups, uranium and thorium on one side and potassium on the other. Values of the same range were observed for Swaziland (Mazor et al., 1974) and for Zimbabwe (Rhodesia) (Mazor and Verhagen, 1976). These narrow ranges seem to indicate that the radiogenic helium and argon originate from common aquifer rocks in which the (U + Th)/K ratios vary over a narrow range (Zartman et al., 1961), in contrast to uranium ores in which this ratio is higher by several orders of magnitude.

CONCLUSIONS

All the thermal waters studied are of meteoric origin. Their temperatures, salinities and stable oxygen and hydrogen isotopic compositions show no correlation with radiocarbon age. The waters issuing in Table Mountain sandstone have low radiogenic helium concentrations, which, however, can not be related to the low U and Th concentrations of the aquifer material alone. Intake temperatures, calculated from the dissolved noble-gas concentrations, lie in the range of "reasonable" values. These temperatures, furthermore, fall into two distinct groups. The lower values are all encountered in the winter rainfall region of South Africa and are explained as reflecting the lower seasonal temperatures during rain water recharge as compared to the rest of the country.

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Discussion

[2]

DISSOLVED IONS, STABLE AND RADIOACTIVE ISOTOPES AND NOBLE GASES IN THERMAL WATERS OF SOUTH AFRICA — A COMMENT

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In their recent contribution Mazor and Verhagen (1983) report data for the concentrations of atmospheric noble gases dissolved in thermal spring waters in the summer rainfall and winter rainfall districts of South Africa. The temperatures at which the groundwater feeding these springs was originally recharged are calculated from these data, and yielded 30 ± 4°C for the summer rainfall areas, and 20 ± 4°C for the winter rainfall areas. Mazor and Verhagen (1983) explained the marked difference in these temperatures by:

> "the different seasonality of the rainfall regimes, where the rain falls respectively in the hottest and coolest months of the year".

A similar explanation was also proposed for the relatively high (21—31°C) recharge temperatures derived from gas data for thermal spring waters in the summer rainfall districts of other parts of southern Africa (Swaziland, in Mazor et al., 1974; Zimbabwe, in Mazor and Verhagen, 1976).

This *seasonal* explanation is in contrast to that proposed in a number of studies of non-thermal groundwater where the gas concentrations are believed to reflect *mean annual* temperatures (Andrews and Lee, 1979; Herzberg and Mazor, 1979; Heaton and Vogel, 1981). The distinction between seasonal and mean annual temperatures is important — it would have a profound effect on the interpretation of gas-derived recharge temperatures which, when combined with the ^{14}C age of groundwater, provide a very promising tool for palaeotemperature investigations. Mazor and Verhagen's (1983) "seasonal" interpretation needs careful consideration.

RECHARGE TEMPERATURES OF SOUTH AFRICAN THERMAL GROUNDWATER

The authors noted that their calculated recharge temperatures (30 ± 4°C and 20 ± 4°C) were high even when compared with present-day seasonal temperatures, and suggested that soil temperatures were of greater relevance, since:

> "the infiltrating rain water will undergo its final equilibration in the *surface* layers of the soil (aerated zone)" (my emphasis).

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TABLE I

Air and soil temperatures (°C) compared with Mazor and Verhagen's (1983) derived recharge temperatures

	Thermal springs recharge temperature*1	Mean air temperature*2		Mean soil temperature at 60 cm under bare earth*2,*3	
		annual	seasonal	annual	seasonal
Summer rain districts	30 ± 4	20 ± 2	22 ± 2	24 ± 2	27 ± 2
Winter rain districts	20 ± 4	17 ± 1	13 ± 1	20 ± 2	16 ± 2

*1 From data in Mazor and Verhagen (1983).
*2 From data of S.A.W.B. (1971, 1981) for stations at Riversdale, D.F. Malan, Elsenburg, Bien Donné, Robertson, Makatini, Towoomba, Pietersburg, Phalaborwa and Mara. Seasonal temperatures of October—March, or April—September for summer and winter rain districts, respectively.
*3 Soil temperatures under bare earth probably higher than under natural vegetation (cf. Table II).

TABLE II

Comparison of mean soil temperatures (°C) at 60 cm under bare earth and under adjacent grass plot at the Roodeplaat Horticultural Research Station (summer rain district), from data in Schulze (1965)

Under bare earth		Under grass	
annual	seasonal	annual	seasonal
23.4	27.5	19.8	23.2

Air and soil temperature data for stations close to the areas sampled by Mazor and Verhagen (1983) are shown in Table I, and compared with their calculated recharge temperatures.

It must be emphasized that the available soil temperature data shown in Table I are based on measurements under patches of bare earth and are probably higher than those prevailing under a natural vegetation cover, which are of more relevance to this comparison. This is illustrated by comparative data for temperatures measured under bare soil and under grass at the Roodeplaat station in Table II. The soil temperature data shown in Table I for 60-cm depth (the depth at which diurnal variations become negligible) are therefore considered to be maximum values; the long-term mean temperatures under natural vegetation would presumably be much closer to the mean annual air temperatures.

On this basis Mazor and Verhagen's (1983) calculated recharge temperatures of 30 ± 4°C for thermal springs in the summer rainfall districts are high even when compared with the mean summer seasonal temperatures at 60-cm depth in the soil. During the summer rainfall period at the Roodeplaat station (Table II) temperatures of 30°C or more are generally found only during the daytime at depths of less than 30 cm under bare soil, and at depths of less than 5 cm under grass (Schulze, 1965). In the winter rainfall district Mazor and Verhagen's (1983) calculated recharge temperatures are much higher than the winter rainfall seasonal temperatures, and show a closer correspondence to mean annual temperatures (Table I).

It would therefore appear that Mazor and Verhagen's (1983) data for thermal waters in the summer rainfall districts of South Africa would only support a seasonal effect if the recharge water underwent final equilibration with the atmosphere at *very* shallow depth during the daytime of the summer rainfall period. Their temperatures for the winter rainfall district show greater support for a mean effect.

RECHARGE TEMPERATURES OF NON-THERMAL GROUNDWATER

The data for thermal water in the summer rainfall district of South Africa are in fact at variance with our own, published data for non-thermal groundwater in this area (Heaton and Vogel, 1981). These are shown, with additional data, in Table III. Although the recharge temperatures were derived only from measurements of dissolved N_2 and Ar, which are not as suitable as Kr and Xe (used by Mazor and Verhagen, 1983), we are confident that meaningful temperatures are indicated in Table III (Heaton, 1981; Heaton and Vogel, 1981; Heaton et al., 1983).

The figures are based on groundwater samples with relatively young ^{14}C ages and suggest recharge temperatures of typically 18 ± 3°C. These temperatures, considerably lower than those derived from the thermal spring samples of Mazor and Verhagen (1983), show a close correspondence to present-day mean annual air temperatures, and not the high summer rainfall season temperatures. Groundwater from two areas in the winter rainfall district also shows this correspondence (Table III).

WHAT TEMPERATURES DO THE DISSOLVED GASES RECORD?

The temperatures recorded by dissolved atmospheric gases should represent those prevailing when the water is last in contact with the atmosphere. This would be at the base of the unsaturated zone, i.e. close to the water table, which in South Africa is usually several metres to tens of metres below the surface. At these depths seasonal temperature fluctuations are greatly reduced and, moreover, may occur *out of phase* with

TABLE III

Recharge temperatures (°C) based on data for non-thermal groundwater in summer and winter rainfall districts of South Africa*1

	Area*2		Recharge temperature*3	Mean annual air temperature*4
Summer rain district	Thabazimbi	(8)	21 ± 4	22
	Springbok Flats*5	(6)	20 ± 1	19
		(7)	15 ± 2	19
	Transvaal dolomites	(16)	19 ± 2	15—18
	Pretoria series	(10)	15 ± 3	16—19
	Venterstad	(13)	16 ± 2*6	16
Winter rain district	Cape Flats	(5)	17 ± 2	18
	Lamberts Bay	(9)	19 ± 2*6	18

*1 Data for five of the areas are from Heaton and Vogel (1981).
*2 Locations: Springbok Flats area is ~100 km north of Pretoria; Lamberts Bay area is ~200 km north of Cape Town; other areas are shown in fig. 1 of Heaton and Vogel (1981). Numbers in parentheses indicate the total number of samples (i.e. boreholes) analysed.
*3 Mean ± 1σ.
*4 From data for nearest meteorological station (S.A.W.B., 1981).
*5 Data for six boreholes in a basalt outcrop area, and seven boreholes in a sandstone outcrop area.
*6 Excludes temperature derived from one "outlier" sample.

seasonal fluctuations in surface temperatures (Schulze, 1965). In addition, the slow rate at which the recharge water penetrates the unsaturated zone (cf. Vogel et al., 1974; Verhagen et al., 1979) would tend to cause an "averaging out" of any temperature fluctuations which do occur. Under these circumstances one must expect the temperatures recorded by dissolved gases to represent a mean, non-seasonal temperature at the water table which may be similar to the mean annual air temperature (Heaton and Vogel, 1981). This expectation is supported by data for non-thermal groundwater in South Africa (Table III), England (Andrews and Lee, 1979) and Israel (Herzberg and Mazor, 1979) and possibly, it is suggested here, by the data for thermal waters in the winter rainfall area of South Africa.

It is therefore difficult to explain the high recharge temperatures calculated for thermal waters in the summer rainfall areas of South Africa (Mazor and Verhagen, 1983), Swaziland (Mazor et al., 1974) and Zimbabwe (Mazor and Verhagen, 1976) in terms of the seasonal effect proposed by these authors — unless special recharge conditions are implied.

Such conditions may occur if the water table is very shallow in the recharge area. In the classic study by Sugisaki (1961), for example, seasonally induced variations in gas concentrations were demonstrated in groundwater from an aquifer directly recharged by river water. In the studies on thermal waters in the summer rainfall districts of southern Africa,

however, hydrogen and oxygen isotope data were specifically used to suggest that the springs were not derived from river recharge (Mazor et al., 1974; Mazor and Verhagen, 1976, 1983).

Mazor has emphasized in a number of papers that thermal water presents special problems when sampled — the high water temperatures will tend to promote the loss of gas, and this will lead to the estimation of too-high recharge temperatures. This possibility was noted in the study of thermal waters in southern Africa, but the effects were generally considered to be small (Mazor et al., 1974; Mazor and Verhagen, 1983). *Unless a special recharge mechanism can be proposed*, however, gas loss during sampling would be the easiest way of explaining the high calculated recharge temperatures. If this does occur then the qualitative results could still be used for indicating a meteoric origin for thermal waters — one of the main conclusions of the earlier work. But it is doubtful that the results could be used in conjunction with discussions on the seasonality of the rainfall.

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[2]

DISSOLVED IONS, STABLE AND RADIOACTIVE ISOTOPES AND NOBLE GASES IN THERMAL WATERS OF SOUTH AFRICA — REPLY

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T.H.E. Heaton's (1984) comments are welcome as they raise important questions on the mechanisms of groundwater recharge, their effect on the dissolved gas contents of groundwaters and the groundwater uptake temperatures that can be derived.

VARIABILITY IN WATER INTAKE MECHANISM

Noble gas hydrology is in its infancy. Yet, several modes of recharge have already been recognised. The references cited by Heaton (1984) include the following modes of recharge:

(a) Infiltration through a homogeneous "sponge-like" aerated zone, in which recharging water is retarded, allowing it to assume average annual temperature. This is often reflected in the concentrations of atmospheric noble gases (cf. Herzberg and Mazor, 1979).

(b) Recharge through karstic conduits in which excess air is syphoned into the water, as reflected by excess atmospheric noble gases with the pattern of Ne > Ar > Kr > Xe (Herzberg and Mazor, 1979; Mazor et al., 1983).

(c) Recharge in non-karstic regions also producing excess air explained by entrapment of air bubbles by infiltrating water (Heaton and Vogel, 1981).

(d) Seasonal input of winter and summer rains, indicated by fluctuations in the atmospheric noble gases in shallow wells (Sugisaki, 1961).

(e) Ancient recharge during climatic regimes different from those prevailing. This is born out by atmospheric noble gas concentrations that are systematically different from the concentrations in recent groundwater in the same region. The palaeo-recharge is inferred from the age (via ^{14}C) and supported by deuterium and ^{18}O data (cf. Andrews and Lee, 1979).

Hence, when interpreting noble gas data in groundwater, the local mode of recharge has to be established rather than assumed. In the case of all the thermal springs quoted in our paper, the most likely recharge areas lie in mountainous terrain, with minimal soil cover, providing rapid and direct conduits for the recharging water through joints and fractures in the exposed

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rock surfaces. Runoff concentration can produce close to saturated conditions from the surface downwards during recharge events.

Thick soil covers, such as described in two of the references cited by Heaton (1984) (Vogel et al., 1974; Verhagen et al., 1979) would certainly *not* apply to the thermal springs discussed in our study, but would be more appropriately applicable to some of the phreatic waters cited by Heaton (1984) in his table III, leading to equilibration temperatures closer to the mean annual value.

Dissolved gas measurements on springs and artesian systems can of course be of considerable importance to palaeoclimatic studies as radiocarbon measurements may give reasonable residence times in such cases. However, as stated above, clear reference has to be made to the *actual* recharge mechanism (cf. Heaton, 1981, on the Uitenhage artesian aquifer) so that seasonally produced signals can be accounted for before long-term changes in mean annual temperature are inferred from dissolved gas data.

EVALUATION OF GAS LOSSES

The possibility of gas losses, or gains, by re-equilibration prior to sampling is a constant threat to noble gas studies in groundwaters. The likelihood of their occurrence has to be discussed in each case. The noble gas concentrations in the studied thermal waters of South Africa revealed two geographical–climatic groups:

(1) Springs located in the Western Cape (Montague, Caledon, Brandvlei, Goudini and Malmesbury) with noble gas intake temperatures of 15—23°C, with an average of 20 ± 4°C.

(2) Springs in the interior (Tshipise, Eiland, Warmbaths, Natal Spa and Lilani) with noble gas intake temperatures of 25—35°C, with an average of 30 ± 4°C.

This grouping corresponds to the figures given by Heaton 1984 in his table I for the mean *seasonal* soil temperatures at 60 cm under bare earth for the summer and winter rainfall areas of South Africa. The scatter in the individual figures of the two sets of data overlap. The actual mean seasonal soil temperatures may be somewhat lower due to the presence of vegetation, which on rock exposures in mountainous terrain, however, would be somewhat discontinuous. As we do point out the somewhat high *absolute* values derived from the observed gas concentrations may be due to small gas losses as well as possibly by some equilibration before sampling.

However, the observed noble gas-derived *relative* temperatures or grouping, which is clearly regional, cannot be explained by these arguments, which would lead at most to a random scatter. The distinctly different summer and winter rainfall regimes of the two regions and the nature of the probable recharge area leads to the seasonal, rather than average annual, interpretation of the noble gas data. Further research in this environment and elsewhere, possibly producing competing mechanisms, is clearly necessary to settle the question.

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